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# 15<sup>th</sup> INTERNATIONAL PLANSEE SEMINAR **2001**

# Powder Metallurgical High Performance Materials

# Proceedings Volume 3: General Topics

32/50

Editors: Günter Kneringer, Peter Rödhammer and Heiko Wildner



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# Preface

On the eve of the 15th Plansee Seminar we look back on half a century of this conference series founded by Professor Paul Schwarzkopf in 1951. The Proceedings of these Seminars form an impressive chronicle of the continued progress in the understanding of refractory metals and cemented carbides and in their manufacture and application. There the ingenuity and assiduous work of thousands of scientists and engineers striving for progress in the field of powder metallurgy is documented in more than 2000 contributions covering some 30 000 pages.

As we enter the new millennium the basic needs of the markets we are serving remain the same: improved material properties and designs translating into improved product performance and reliability. In view of ever shorter product life cycles, however, the pressure on material scientists and engineers to introduce these new products at reduced time-to-market and with improved benefit/cost ratio is continuously mounting.

Since 1951 the means to meet these demands have greatly improved: novel equipment with improved process control, faster computers for simulation as well as for data acquisition and reduction, analytical tools with undreamed-of accuracy; all coupled with the shrinkage of distances brought about by the revolution in global communication.

The 15<sup>th</sup> Plansee Seminar was convened under the general theme "*Powder*" *Metallurgical High Performance Materials*". Under this broadened perspective the Seminar will strive to look beyond the refractory metals and cemented carbides, which remain at its focus, to novel classes of materials, such as intermetallic compounds, with potential for high temperature applications.

It is with great pleasure that I welcome you in the name of Plansee Holding AG here in Reutte/Tyrol and extend to you my sincere wishes for a fruitful, inspiring seminar. Thank you in advance for your personal contribution to making the 15<sup>th</sup> Plansee Seminar a successful, memorable event.

Reutte, May 2001

For the Executive Board

Dr. Michael Schwarzkopf

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### Coated Metal Powder, Sintering Behaviour and Application in alternative Forming Processes

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Summary:

Coated powders can be produced by methods, which are commonly used for surface coating of metals and non-metals. The advantages of coated powders are excellent sintering behaviour, uniformity of combination, and exactness of the part dimensions and uniformity of properties of the sintered components. The special geometrical relationships in such powders especially the great interface between the combined materials enhance the densification. The outstanding sintering properties favours coated powders for processes, which start with low green density (slurry, direct consolidation) and need high densification rates to reach the sufficient density of the final components. In most cases liquid phase sintering takes place and the shape stability is an important fact. For other purposes if fast densification is needed for instance by particle repacking (laser sintering) the coated powders seems best suited.

## Keywords:

Coating of particles, iron powder, forming processes, laser sintering, slurry casting, sintering behaviour, liquid phase sintering, particle rearrangement

## 1. Introduction

In the field of PM processing a number of new forming methods have recently been developed, that can be referred to as Direct Consolidation Techniques. The common principle is the shaping of components by transforming a powder suspension into rigidity without powder compaction (plastic deformation of particles) or removal of solvent. The forming takes place by locking the powder dispersion in a homogenous state and no segregation effects are allowed. This gives the advantage of good material homogeneity

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that should promote control of the shrinkage during sintering and, hence, control of the ultimate dimensions of the components.

In the case of laser sintering a loose powder is transformed into rigidity by selective lightening of small areas with a laser beam and locking the particle contacts by local sintering steps.

In the traditional PM processing route normally no or only little shrinkage is obtained because the powder is pressed close to final density. Forming by alternative techniques requires powder loading in the forming step corresponding to relative densities of 50-60% on volume basis. In order to achieve good material properties significant shrinkage sintering must therefore follow to arrive a suitable final sintered density. In most cases (excluded MIM with fine powders) the required shrinkage during sintering can than only be obtained by means of liquid phase sintering.

The powder characteristics (size, shape, chemical homogeneity, surface chemistry) and the packing situation have a significant influence on the result of the sintering process. The starting powder can be a mixture of elemental powders of different chemical composition. During sintering one of the powder constituents melts and spreads throughout the remaining solid phase. At places of the molten powder particles pores are remaining and lower the final density. The volume fraction of liquid is critical as it sets the relative contribution of the different sintering stages (solution, particle repacking, solution-reprecepitation) and thus controls shape retention of the components in relation to volume shrinkage. Not only the amount of liquid is important but also the distribution and the place of the origin of the melt affect the densification mechanism during sintering.

The application of coated powder particles produces a strong geometrical effect relating the sintering process. The regular distribution of the components and the large interface area between them favouring sintering and homogenisation. For that reason some examples should be discussed in view of the sintering behaviour of such powders.

## 2. Coating of powders

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The majority of methods commonly used for surface coating of metals and non-metals can be chosen as coating process for powders too ( table 1). The choice of the suitable coating method depends mainly on whether metallic or non-metallic base powder particles are present and which material combinations are desired

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Туре	Method	Comment
	Milling	
Mechanically	Mechanic-fusion	Combination of densification, shear, friction
	Hybridisation	Shear-, friction demand
	Paste of fine particles	Spraying method
	Cementation	Difference of standard electrode potential
Chemically	Separation from solutions with reducing agent	<u>reducing agent:</u> Formaldehyde, Boron hydride, Hypophosphite, <u>Basic powder:</u> metal, non- metal
	Substitution (contact method)	powerful planetary mills
	CVD-method	Decomposition of CI-compounds, carbonyls, org. metal compounds
Electrolysis	galvanic coating	special cathodes
Physically PVD, sputtering		Weight rate of flow is good, cost of installation !

### Table 1: Coating methods for metal powders [1]

It is possible to produce compound powders with one or more layers on the particle or powders with partly inserting of sintering enhancer into the coating can be obtained. Examples of coated powders are shown in figure 1. The fundamental problem of all the methods is to make sure that the particles are desagglomerated, which is more important with decreasing particle size. In the range of 1µm particle diameter or smaller relatively high shearing demand must effect on the powder to create individual particles. In most cases this process takes place easier in aqueous solutions than in the gaseous medium. For that reason the coating in aqueous solutions was chosen for the investigations.

Varying the process parameters can modify the coating properties; for instance the interparticle friction and the compactibility can be influenced significantly.

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Figure 1: Microstructure of coated powder particles, a - iron powder with Ni layer, b – Fe-Carbonyl particle with Ni-layer, c – iron powder with Cu - Ni - Cu -laver

## 3. General aspects of coated-powder-sintering

The production of PM allovs starts in most cases from the mixture of the elemental powders, time to time from pre-alloyed powder and seldom from coated powder. In comparison of these alloying techniques considerable differences of the geometrical arrangement of the alloy components exist in view of the starting situation of sintering.

The mixture of two components (A and B) exhibits 3 types of particle contacts (A-A, B-B, A-B), a small interface area, a strong concentration gradient at A-B-contacts exists and demixing tendency is given, whereas in the coated powder only one contact type is given, nearly the contact region between the coat and core of the particle a strong concentration gradient exists and a maximum interface area (identical with the powder surface) is realised. Additional advantages of coated powder are the homogeneous distribution of the second element in the base powder and no demixing phenomena. In the case of pre-alloved powder a homogeneous distribution of elements is achieved but the driving force relating the geometrical constitution of components is non-active.

Commonly two types of microstructure in the sintered state can be obtained:

- The powder mixture forms two penetrating 3D-sceletons. One skeleton is formed by the solid solution around places of particles of the alloving elements and the other one is formed by the unalloyed particles of the basic powder.
- Coated powder particles show more or less homogeneous microstructure (time depending) with higher density or in the non-metallic /metallic combination the type of metal matrix composite.

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The sintering behaviour of coated powders is considerable different from that of a powder mixture of the same composition. In the case of thin layers the concentration gradient is influencing the shrinkage in a strong manner. In case of faster diffusion of the coating element into the core particle a higher vacancy concentration in the coat occurs which is enhancing the mass transport into the contact region. If the diffusivity of the core particle element is higher than the increased vacancy concentration will be obtained under the coating layer. The distance to the neck is greater and for that reason an effect on the sintering intensity is not evident. A melting of the coating material during sintering produces liquid films in every sintering contact which enhances the particle rearrangement uniform in the whole volume and the other mechanisms of liquid phase sintering.

The sintering investigations were carried out in a dilatometer or in a tube furnace mostly under hydrogen atmosphere. In some cases a mixture and a coated powder of the same composition are compared.

The basic relationships of the sintering process are to be shown in the case of the iron-nickel-system as example (Carbonyl-iron powder as core particles). The Ni-coat was obtained by cementation reaction.



Figure 2: Shrinkage of Carbonyl-Fe-Ni-samples (Ni-coated, Fe-Ni-mixture) compared with unalloyed Carbonyl-iron

The results of the dilatometer-investigations are given in fig. 2. The Ni -coated powder shows in the beginning of the heating period little more shrinkage in comparison with uncoated iron powder as a result of the higher defect

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concentration in the Ni-coat. With increasing temperature (>500°C) swelling occurs because the diffusion of Ni into iron is faster than vice versa.

From 1000°C the shrinkage rises because the accelerated diffusion of Ni is decreasing the thickness of the coat and the higher defect concentration nearly the interface Fe-Ni enhance the mass transport into the particle contacts. The Fe-Ni mixture shrinks not so much as the pure iron; the heterodiffusion causes swelling of the iron skeleton.

Producing the Ni-coat by the reduction method in Ni-salt solutions with phosphides as reductants the reaction generates free P, which is inserted into the coat. Such layers are amorphous, nano- or microcrystalline as a function of the extent of super saturation of the Ni with P influenced by the process parameters [2]. The sintering of iron particles with Ni-P compound coatings is characterised by higher shrinkage from the beginning because the layers are metastable and effect densification by transition of the structure (amorphous-crystalline) and a first liquid phase at about 550°C. With increasing temperature the melt remains exist because the diffusion of Ni and P into the iron produces additional liquid phase in the range 850°-1000°C (Fig 3).



Figure 3: Shrinkage of Carbonyl-iron samples coated with Ni (solid phase sintering) and Ni/P (liquid phase sintering)

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# 4. Forming methods and starting conditions for the sintering process

In the common PM route the component density after the compaction step is in comparison to the apparent density of the powder strongly increased as a result of the plastic deformation of the particles. No or a little shrinkage is obtained.

The alternative methods create components in the range of the apparent density of the starting powder after the forming step. In the case of MIM feedstock the solid loading is relatively high because a pressure is used to realise the perfect mould filling despite of the increased viscosity of the feedstock. The Direct Consolidation Techniques are working with a powder different consolidation suspension which solidifies at mechanisms (polymerisation, polycondensation, freezing and others). To realise a suitable mould filling the solid loading of the suspensions (low viscosity) is in the range up to 50 vol.-%. In other cases the solid loading is relatively low because a fixed volume portion must be water as basis for the solidification reaction after the forming step. This means that in the frame of the Direct Consolidation Techniques the tap density of the powder is not exceeded and the sintering process must generate high shrinkage values to create nearly full dens parts with regarding properties. Mostly the alternative forming methods are applied for larger components and small series and from a cost point of view the use of fine powder with high solid state sintering activity is not justified every time. Therefore the raw material is restricted to be coarse powder of similar size as used in die pressing. For that reason in most cases the required shrinkage during sintering can only be obtained by means of liquid phase sintering.

Extreme conditions exist in the case of the selective laser sintering. It is a tool less technology, which is producing solid freeform objects directly from a graphical computer description of the object. A computer model of the part is created and appropriately sliced to provide data layer wise to the laser and scanner. A uniform thin layer of powder is deposited (thickness: 50-200µm). The first layer of the object is traced with a laser coupled to the computer-controlled scanning system. The laser beam rasters the powder bed surface and raises the temperature of the powder it contacts, binding the loose powder. At the end of the first laser scan a second layer of loose powder is deposited and the process is repeated. The powder sintered in the second layer binds to itself and the material constituting the first layer. The process is repeated and by altering the shape of each scan layer a part of arbitrary shape may be produced. In comparison to the common sintering the duration

of the laser beam at any powder particle is very short, typically in the order of < 20 ms. the mass transport by diffusion is too slowly. The liquid phase sintering is the only possible process to produce shrinkage mainly by the primary particle rearrangement process [3]. The starting density is in this case the apparent density of the powder too. The powder is tailored to get a relatively high fill density (50-60% of the theoretical density of the material) and excellent flow properties (spherical particles).

## 5. Sintering conditions and coated powder particles

### 5.1. Shaping from powder suspensions

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The sintering process starts with parts of relatively low density and during the process a high densification and debindering must be realised. Homogenous shrinkage is needed to guarantee shape stability of the sintered components. On the other hand the high shrinkage sintering requires the presence of liquid phase but the amount must be limited in such a way that an optimum shrinkage without shape distortion is enabled. The coated powder particles represent the geometrical advantage that in every particle contact liquid occurs if the melting point of the coat is lower than that of the core material. The particle rearrangement can take place as the relatively quick densification step if the coat-melting temperature is reached. A decreasing melt content in the solid particle powder is increasing the viscosity  $\eta_{\rm sl}$  which is related phenomenologically to the viscosity of the liquid phase  $\eta_0$  in the absence of any solid and the relative solid content  $\Phi$  [4] :

$$\eta_{sl} = \eta_0 \left[ 1 - \left( \frac{\Phi}{\Phi_m} \right) \right]^{-2}$$
(1)

Where  $\Phi_m$  is a critical volume fraction above which the mixture has infinite viscosity. In comparison to the powder mixture the content of solid phase can be higher in coated particles as estimation has shown ( $\Phi_m = 0.87$ )

(Fig. 4). The particle shape influences the particle sliding. Irregular particles must have some more liquid than spherical ones.

It is very important to make sure that the shape stability of the parts is given.

It could be shown [5] that there are clear links between micro structural parameters and distortion behaviour. Quantitative micro structural data will be needed to numerically define the conditions that give distortions. Systems with limited inter-solubility give less grain growth and have relatively high dihedral angles consequently they have improved structural rigidity. The dihedral angle governs other micro structural parameters including contiguity, connectivity and the coordination number.



Figure 4: Influence of volume fraction of solid on the relative viscosity of the solid-liquid-mixture for particle mixture and coated particles (spherical and irregular shape). The numbers at the curves are the assuming mean coordination numbers of the particles in the powder bed.

In the case of Ni- (P)-coated atomised iron powder (Höganäs ASC100) the core particles are irregular and coarse. The powder was chosen to create components by a method of DCT. The starting powder is shown in fig. 5. The coating thickness was monitored to yield an alloy with 13 wt-% Ni and 1,4 wt-% P. The aqueous powder suspension was loaded with 47,6 vol.-% powder. The formed component started the sintering process with nearly 50% porosity. The sintering behaviour is characterised by the dilatometer curve in fig. 6. In the temperature range 950° – 980°C liquid phase occurs and particle repacking takes place and than solution-reprecepitation creates further

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shrinkage with particle shape accommodation. The sintering density reaches more than 95% of the theoretical density. The form stability is given



Figure 5: Micrograph of coated ASC100 particles with 14 wt-% Ni and 1,4 wt-% P



Figure 6.: Shrinkage behaviour of a DCT- formed component from coated iron powder

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Figure 7: Micrograph of sintered ASC 100 iron powder coated with Ni-P relating fig. 5

because rigid bonds between the particles are formed resulting in even greater structural rigidity. Other criteria may be necessary to fully explain this rigidity, because the dihedral angle is low in this case (fig. 7) and as first between the entire particles contacts melt occurs.

#### 5.2. Laser Sintering

In the case of laser sintering only the liquid phase sintering produces the needed high shrinkage during a very short duration mainly by primary particle rearrangement. Starting from the powder mixture with two components the lower melting powder creates liquid phase, which must distribute by capillary forces between the solid particles. This relatively time consuming process is followed by particle rearrangement of the solid particles between them melt is penetrated. It could be shown that the melt is spread over a small volume around the place of the molten particle, which remains as a pore. It means that the particle rearrangement occurs uncompleted. The result is mostly an insufficient densification and a poor bonding with the previous layer. The use of coated particles means that at any particle contact a sufficient amount of liquid phase is obtained if a lower melting layer on the particle exist.

As previous discussed, the viscosity of the solid-liquid-mixture (equ. 1) determines the shrinkage of a volume element and the so-called tendency for balling effected by the surface energy of the melt. An increasing solid particle

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content is increasing the viscosity. By adjustment of the volume fraction of the high melting phase it becomes possible to induce binding without balling. On the condition that only the viscous flow and particle repacking are working the sintering of coated particles was analysed for idealised conditions (equal-sized spherical particles) using finite-element method [6]. The sintering rate is determined by the liquid flow in the channel between the spheres. Starting from a particle packing of the relative density of 60% TD the normalised time  $\tau$ , which is necessary to result a certain density, can be estimated.

$$\tau = \left(\frac{3}{4}\pi\right)^3 \frac{\tau\gamma}{\eta\left(\frac{D}{2}+d\right)}$$
(2)

 $\eta$  - viscosity of the melt,  $\gamma$  - surface tension of the melt, D – radius of the core particles, d – layer thickness

With the corresponding values for copper melt (Cu-coating on the core particles) the total densification time  $\tau$  results in the range of  $\mu$ s to ms without consideration of the heating period. It can be assumed that the conditions are corresponding to the circumstances of laser sintering. Figure 8 show the predicted change in relative density of a packing of coated particles as a function of time. The amount of melt influences the sintering density after particle repacking, the balling tendency is determined by the surface tension of the melt. In the case of copper melt the surface tension is high and balling takes place. The behaviour can be changed by alloying elements, which are lowering the melting point and cause an overheating of the melt with decreasing of the viscosity. Some elements are lowering the surface tension for instance: Zn, Cd, Sn, Pb, Bi, Sb, S with increasing effect.

The sintering behaviour of a loose powder bed was tested in such a way that a small crucible with a constant mass of powder (0,15 g) was pushed from the cold region into the hot region of a furnace (1300°C, Ar-atmosphere).

There it was remained for some seconds and than pushed back into the cold region. The shrinkage of some Cu-coated iron powder samples is shown in fig. 9. The samples are reaching the melting point of Cu after 17 s. The whole amount of Cu acts as liquid phase and the particle rearrangement occurs in a very short time. Because the core particles are irregular the amount of melt influences the shrinkage of the powder bed. The effect of Sn and P (lowering

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Figure 8.: Relative sintering density of a packing of equal sized spherical coated particles with different layer thickness d

the melting point) is not so strong relating the particle repacking because the melt occurs gradually as Sn and P are reacting with the Cu-layer. The shrinkage is higher with the same amount of melt.

Relating the sintering behaviour the mechanical properties of the sintered components show interesting values as result of the high density and time depending uniformity of the microstructure. In some cases the remaining volume content of the partly brittle liquid phase (i.e. Fe-Ni-P) can lower the elongation. In such cases it is necessary to optimise the sintering duration and the content of P for instance. Some values in table 2 are given.

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Figure 9: Linear change of length of loose powder arrays after short duration in the heating zone of the furnace (x-axis: duration in the furnace / corresponding temperature); core particles: water atomised iron powder, av. particle size: 50 µm

Table 2: Mechanical	properties of	sintered to	est bars	from coated	carbonyl iron
powder					-

Coating (wt-%)	UTS (MPa)	Elongation (%)	Sint. duration (min)
Uncoated	200	5	20
3 Cu	350	20	20
2 Ni ; 0,8 P	500	7	20
1,4 Ni ; 0,03 B	430	9	60
2 Mo, 1 Ni ; 0,3 P	460	15	60

## 6. Conclusion

The coating of powder particles can be realised with methods, which are commonly known for metallic and non-metallic components. The result is powders without demixing tendency, good compaction properties and excellent sintering behaviour. The results of the sintering process are nearly

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dense parts with uniformly microstructure. Particularly in the case of liquid phase sintering a strong uniformly shrinkage and relating densification with shape-stability of the components can be obtained. The powders are suitable for such technologies with relatively low density of the parts after the forming step (direct consolidation techniques) and the aim to get high densities after the sintering process ore for short time sintering (Laser sintering), because the particle repacking process is enhanced by the geometrical effect (at every particle contact liquid is present and particle sliding occurs in all volume elements). The properties of the sintered parts are a function of the degree of homogenisation (sintering duration) and the brittleness of the remaining volume content of the liquid phase in some cases.

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### SHS Composites-A New Emerging Family of Advanced Composites

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### Summary:

Self-propagating High-temperature Synthesis as an advanced synthesizing technology is being paid more and more attention due to its unique advantages: energy saving, simple equipment, high purity and costeffectiveness etc. A series of SHS technology is being developed for making of both CMC and MMC of a wide range of material systems.

The unique non-equilibrium and self-propagating features of the SHS powder generate interest in research both on theoretical aspects including thermodynamics, reaction mechanism, combustion theory and structural macro-kinetics of SHS enabling synthesis hundreds of ceramics, and composites in porosity, bulk, coating and laminated forms. The paper reviews the research and the development work on SHS for making advanced composites contributed by the authors.

Keywords: SHS, composites, functionally graded composite

### 1. Introduction

In 1967, Marzhanov and Borovinskaya[1] discovered the phenomena of selfpropagating high-temperature synthesis (SHS) while studying the combustion of Ti-B cylindrical compacts. The term SHS is now being used to describe a process in which initial reactants when ignited transform into products spontaneously due to the exothermic heat of the reaction and the selfpropagating of combustion wave. The SHS process offers self-generation of the energy required for the process in contrast to the high energy consumption of conventional processes for producing refractory compounds.

The unique non-equilibrium and self-propagating features of the SHS process generate interest in research both on theoretical aspects including thermodynamics, reaction mechanism, combustion theory and structural macro-kinetics of SHS and material processing aspects in developing numerous processes of SHS enabling synthesizing hundreds of ceramics, and composites in porous, bulk, coating and laminated forms.

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More and more composites are being used in industry. The traditional processes for fabricating composite materials can be generally divided as follows: Firstly, synthesizing all the powders needed separately, secondly, mixing the composites together, then, sintering these mixture under suitable conditions, at last, sintered products were obtained with or without post-treatment after sintering. It is obvious that some problems exist in these process such as: prolonged process cycle, high energy consumption, difficulty in making uniform distribution of phases, phases boundary pollution etc. Insitu SHS can fabricate composite powders and/or materials in one or two steps by controlling the ratio of reactants and adjusting the combustion of the initial reactants. Compared with the traditional process, in-situ SHS consumption, uniform distribution phases, no contamination at the phase boundaries, good sinterability etc.

This paper outlines research and development work on SHS for making composites in Laboratory of Special Ceramics and Powder Metallurgy (LSCPM), University of Science and Technology Beijing (USTB). The following three types of SHS composites have been developed in LSCPM, USTB of China.

# 2. In-situ multi-phase ceramic composites through SHS of gas-solid system in combination with hot-pressing

Multi-phase ceramic composites  $Si_3N_4$ -Ti(CN)-SiC and  $Si_3N_4$ -Si<sub>2</sub> $N_2O_2$ -TiN was successfully synthesized with SHS of Si+TiC+ $N_2$  and Si+TiO<sub>2</sub>+ $N_2$  systems respectively following with hot-pressing.The compositions of green compacts used for Si-TiC- $N_2$  system were Si/Si<sub>3</sub> $N_4$ /TiC=3:1:1, 3:1:2.6, and 5:1:5(in weight proportion), which were named as ST31, ST32 and ST5 respectively.

The compositions of green compacts used for Si-TiO<sub>2</sub>-N<sub>2</sub> system were  $Si/Si_3N_4/TiO_2 = 3:1:0.6, 2:1:0.4, 1:1:0.2, and 2:3:0.4, which were named as S31, S21, S11 and S23 respectively.$ 

The compacts were put into a SHS reaction chamber which was filled to different nitrogen pressures .The compacts were ignited by passing 20A electrical current to the tungsten coil, which was placed above the compact. The combustion temperatures were recorded by a W-Re3/W-Re25 thermocouple connected with a computer.

After crushed and milled the SHS product to powders and sieved –200 mesh,  $Al_2O_3$  and  $Y_2O_3$  were added as sintering additive and mixed powder were compacted and hot-pressed to  $\Phi$ 40×10 mm at 1800°C for 1h under pressure of 25MPa.

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Powder compacts ST31, ST32, and ST5 could be ignited at a nitrogen pressure higher than 2 MPa. All the products consist of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ - Si<sub>3</sub>N<sub>4</sub>, Ti(C,N) and  $\beta$ -SiC, besides, there exists a small amount of Ti<sub>5</sub>Si<sub>4</sub> phase and residual Si in the SHS product from sample ST5.

In contrast to the effect of Si<sub>2</sub>N<sub>4</sub> addition in reactant mixture as an "inert" diluent for SHS. TiC acts as an "active" diluent, which not only plays the role of diluent, but also takes part in the chemical reactions of the reactant system during SHS. The addition of TiC to Si-N<sub>2</sub> system leads to the formation of  $TiC_{1,v}N_v$  in SHS products. According to the calculated parameters from X-ray diffraction results, and assuming that the as-synthesized Ti(C, N) was an ideal solid solution, the composition of the  $Ti(C_{1,x}N_{y})$  can be determined with Vegard's law as TC<sub>0.36</sub>N<sub>0.64</sub>. According to the calculated thermodynamic diagram of Si-TiC-N<sub>2</sub> system at 2123K, the stability boundaries favor the stable coexistence of  $Si_3N_4$ +TiC<sub>1,2</sub>N<sub>2</sub>+C under the present experimental conditions. The carbon atoms react with  $Si_3N_4$  or Si and therefore, the final product contains Si<sub>3</sub>N<sub>4</sub>+TiC<sub>0.36</sub>N<sub>0.64</sub>+SiC, which was consistent with the calculated thermodynamic stability diagram as shown in Fig1.

For SHS of the Si-TiO<sub>2</sub>-N<sub>2</sub> system, it is found that all the specimens can be ignited in nitrogen pressure range of 1 to 10MPa. All the SHS products are composed of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, Si<sub>2</sub>N<sub>2</sub>O, TiN, with or without residual Si. The relative contents of these phases in specimens S31, S21, S11, and S23 are shown in Fig3. It is noted that with the increase of the amount of  $Si_3N_4$  in the powder compacts, the conversion degree of Si to  $Si_3N_4$  increased dramatically. Besides, as the ratio of Si/Si<sub>3</sub>N<sub>4</sub> was higher than 1, the relative content of  $\alpha$ - $Si_3N_4$  in SHS product decreased with the increase of the amount of  $Si_3N_4$ diluent in green powder compact, while the content of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> increased. For all the specimens, the relative content of  $Si_2N_2O$  remained almost no change.



Fig.1 Calculated thermodynamic stability diagram for the Si-TiC-N<sub>2</sub> system at 2123 K

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Fig.2 Calculated thermodynamic stability diagram for the Si-TiO<sub>2</sub>-N<sub>2</sub> system at (a)1773K, and (b)1873K



Fig.3 The amount of different phases in the SHS products in dependence on Si/Si<sub>3</sub>N4 (wt.%) in reactants



Fig. 4 SEM of hot-pressed specimen Si<sub>3</sub>N<sub>4</sub>-Ti(CN)-SiC composites

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Complete nitridation of Si and TiO<sub>2</sub> was achieved as the ratio of Si/Si<sub>2</sub>N<sub>4</sub> reached 2/3 in specimen S23. The as-synthesized product was composed of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, Si<sub>3</sub>N<sub>2</sub>O and TiN. The amount of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> was higher than that of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. The maximum combustion temperature for S23 is 1773K, which is 100K lower than that of S11, favoring the existence of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> phase. The high amount of Si<sub>2</sub>N<sub>4</sub> diluent in S23 is effective in preventing the extensive melting of constituents. The experimental results are consistent with the calculated stability diagram as is shown in Fig2. Similar with TiC in Si-TiC-N<sub>2</sub> system,  $TiO_2$  in Si-TiO<sub>2</sub>-N<sub>2</sub> system not only acted as a diluent, but also participated in the reaction during SHS.

Good combination of mechanical properties has been achieved in hot-pressed specimens. With the as-synthesized Si<sub>3</sub>N<sub>4</sub>/Ti(C,N)/SiC composite powders as starting powders and Al<sub>2</sub>O<sub>3</sub> as sintering additives. The bending strength is 800 MPa, while the fracture toughness is 9.5 MPa•m<sup>1/2</sup>, the hardness is HRA 93-94. The micrography of hot pressed specimen of SHS Si<sub>3</sub>N<sub>4</sub>-Ti(CN)-SiC composite is shown in Fig. 4.

### 3. In-situ developed ceramic-intermetallic composites through SHS with simultaneous densification

Generally high porous compacts were produced through SHS of gas-solid system, as a good gas permeability in the burning sample for infiltration combustion is required to realize high degree of conversion, simultaneous. SHS and densification during SHS of gas-solid system were much more difficult than that of solid-solid system. Yet a new AIN-based composite AIN-ZrN-Al<sub>2</sub>Zr was successfully synthesized through simultaneous SHS and densification after systematic investigation of SHS of AI-Zr-N system.

In the present investigation, ZrN instead of AIN was used as diluent for the combustion of Al powders in nitrogen. For the 20wt% AI-ZrN system, the XRD patterns of the SHS products synthesized at 1, 5 and 10MPa nitrogen pressure are shown in Fig. 5. The diffraction peak of AIN increase while that of Al<sub>3</sub>Zr decrease with the increase of nitrogen pressure. It is found that the addition of ZrN took the role of dilution effectively, besides, the more the amount of ZrN added the lower the intensities of Al diffraction peaks of the SHS products were. It is speculated that the coagulation of Al melts and subsequent formation of "welding pools" can be prevented in certain degree, hence the local nitrogen availability for the unreacted AI in the combustion front can be improved; another reason for the high degree of nitridation comes from the reaction between AI and ZrN i.e.  $3AI+ZrN \rightarrow AI_3Zr+1/2N_2$ , therefore,

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with the increase of ZrN addition to Al powders, the Al<sub>3</sub>Zr phase formed, meanwhile nitrogen atoms were released at high temperature and these certainly increase the conversion of Al to AlN.

The measured relative density for specimen Al+50wt%ZrN combusted at 5MPa nitrogen pressure is about 91%, and the typical SEM morphology of this specimen is shown in Fig 6. Larger AlN grains and relatively small ZrN particles coexist with some Al<sub>3</sub>Zr in the grain boundaries which is characterized by EDS analysis, where Al:Zr=3:1(atm%). The melting temperature of Al<sub>3</sub>Zr is 1580 °C, which is far lower than the measured combustion temperature. Therefore the newly formed Al<sub>3</sub>Zr exists in the specimen in liquid form at high temperature, which is capable of penetrating to the grain boundaries driven bycapillary force, contributing to the densification of the as synthesized products.



Fig.5 XRD patterns of the SHS products (AI-ZrN 20wt%) synthesized at 1, 5 and 10Mpa nitrogen pressure

# 4. Bi-layered and functionally graded composites (FGC) with SHS or SHS/pseudo-HIP technology in one step

Bi-layered, functionally graded composites, cement composites, or ceramiccermet composites can be made with SHS/pseudo-HIP in one step. Typical examples were (a)  $TiB_2+TiN+x\%Me(x=0-40wt\%)$  based on SHS reaction  $2BN+3Ti \rightarrow TiB_2+2TiN$  or (b)  $TiB_2+x\%Me(x=0-60wt\%)$  based on the reaction  $Ti+B+Me \rightarrow TiB_2+Me$ . The effects of the type, the content of the metal (Cu, Ni) on the combustion feature as well as the wave propagating rate through the 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3

bi-layered powder compacts of (Ti - 2B - 60 wt% Cu) / 3 (Ti - 2BN - xNi) and (Ti - 2B - 60 wt% Cu) / (3Ti - 2BN - xNi) (x=0-40wt%) were investigated. Powder compacts were uniaxially powder stacked by hand in a mold, Ar gas>1 MPa was used as protection gas. Electric ignition was carried out with tungsten wire. The combustion process was recorded with video camera. The recorded video was computed and edited by computer. The location of the combustion wave along the propagating direction at different time was measured and calculated for determining the feature and velocity of the combustion wave.



#### Fig.6 SEM image of the AIN/ZrN/AI3Zr and EDS results of the grain boundary phase

Single-layered specimens	Compacting pressure (Mpa)	Wave velocity (mm/s)	Memo
3Ti-2BN	60	4.96	
3Ti-2BN-10wt%Cu	60	4.43	
3Ti-2BN-20wt%Cu	60	2.17	
3Ti-2BN-40wt%Cu	60		Combustion wave cannot propagate
Ti-2B-60wt%Cu	60	18.52	
3Ti-2BN-10wt%Ni	60	4.96	
3Ti-2BN-20wt%Ni	60.	3.83	······································
3Ti-2BN-40wt%Ni	60		Combustion wave cannot propagate
Ti-2B-60wt%Ni	60	28.35	

Table 1. Combustion wave velocity in single-layered specimen

Table1 shows the combustion wave velocity in single-layered specimen. It is noticed that the combustion wave cannot propagate in single-layered specimen (3Ti-2BN-40wt%Cu) and (3Ti-2BN-40wt%Ni).

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For bi-layered powder compacts with compositions listed in Table1, the effects of Cu, Ni content on the combustion wave propagating were shown in Fig.7.

In Fig.7(a), the measured combustion wave velocity in (Ti-2B-60wt%Cu) layer and (3Ti-2BN) layer was 22mm/s, 9mm/s respectively. The combustion wave velocity in (3Ti-2BN) was nearly doubled compared with that in single-layered specimen. There were effects of the combustion heat released from the layer (Ti-2B-60wt%Cu) on the combustion behavior of the neighboring layer (3Ti-2BN-xwt%Cu) preheating and ignition. The preheating accelerated the propagating velocity of combustion wave perpendicular to the layered phase. The overlapping of the perpendicular wave and parallel wave makes the wave appear as arc-shape.

The combustion wave velocity in (Ti-2B-60wt%Ni) layer was much faster than in (3Ti -2BN -60wt%Ni) layer, that leads to a step-shape combustion wave.

On the basis of the investigation on the combustion wave propagation features, some bi-layered, multi-layered composites and FGC of  $TiB_2+TiN+xMe$  system have been made directly with SHS. An interesting phenomenon is noticed that no deformation or densification emerged during and after SHS of (Ti-BN-xMe) system, while elastic deformation occurred in SHS (Ti-B-xMe) system.

In most cases, it was necessary to densify the SHS specimens just after SHS with pseudo HP technology. The green compact was embedded in sand, which served both as heat insulation and medium for transmitting pressure. After ignition and completing SHS, a pressure of >30 MPa was loaded on the specimen and makes it densified.Fig.8 shows SEM micrograph of a symmetrically compositional graded Ti+BN+NiAI FGM. It is well known, high thermal expansion coefficient of central region consisting of higher content of metals creates residual compressive stresses in surface region with no metallic content that offers improvement in both of strength and toughness.



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#### (a)(Ti-2B-60wt%Cu)/(3Ti-2BN); (b) (Ti-2B-60wt%Ni)/(3Ti-2BN) (c)(Ti-2B-60wt%Cu)/(3Ti-2BN-10wt%Cu); (d)(Ti-2B-60wt%Ni)/(3Ti-2BN-10wt%Ni) Fig.7 Combustion wave front location vs combustion time



Fig. 8 SEM of Ti+BN+NiAI (5-30 wt%, from surface to center) FGM

### 5. Conclusion

Three kinds of SHS composites with examples were being developed in LSCPM. USTB of China. According to the feature of different material systems. SHS with or without post-densification can be selected to make a wide range of composites including particulate reinforced composites, bi-layered composites, multi-phase composites and symmetrically compositionalfunctionally graded composites. Further investigations on properties of various kinds of SHS composites are being carried out.

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# THE INFLUENCE OF WORKING WAYS ON THE MICROSTRUCTURE AND PERFORMANCE OF Mo BAR

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#### SUMMARY:

A new Mo bar rolling process, step-by-step rolling, is introduced in this paper. Compared with the rolling processes before, such as the rejection forging and the pass rolling, a new process can acquire the bars with better microstructure and mechanical performance. like homogeneous microstructure, thin and long grains, obviously promoted plasticity, which can overcome the difficulties in the following mechanical working.

#### **KEYWORDS:**

Mo bar, step-by-step rolling mill, microstructure, mechanical performance

#### 1. Introduction

Mo bar is widely used in many fields, such as glass melting furnace, rare metal electrolysis, electrical parts, electrical light source and so on, because of its good heat conducting property, good electricity conducting property and heat resistance property. The normal process of the Mo bar is: powder compacting, sintering, then forging or rolling. This process has been used for tens of years in Northwest Institute for Nonferrous Metal Research. The existing problems of products produced by this process are low plasticity, high brittleness and bad mechanical working performance, such as broking bits from screw, trip, bad degree of finish, big burr and so on. It is due to the inhomogeneous microstructure of the Mo bar and the coarse grains from improper mechanical working process. So, it is necessary to develop and

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research a new working process. This paper introduces a new process of producing Mo bar, which is very useful to remove the mentioned defects of Mo bar.

#### **1. Process and Working Principle**

In order to solve the pressing working problems of the hard deformed metal bar, suck as W, Mo, Ti and Zr bar, a CULM175 step-by-step rolling machine was imported. The figure below is its working principle scheme.



Fig1. The working principle scheme

The rollers have four fan-shaped sectors, which are evenly distributed in the circle shaped supporting stand, the angle between two sectors is 90 degree. Each roller has one of fourth curved surface, and four rollers constitute a full curved surface. Activated by motor, the connecting rods pull the supporting gate to move to and from, so the rollers open and close periodically when they move with the supporting stand. When the rollers open, the bar feeding device feeds the bar one time, and when the rollers close, the bar is rolled one time. And then, the bar turning device turns the bar once, the bar feeding device feeds the bar again. This case goes round and round, and the bar is step-by-step rolled. This type deforming process has greater advantage than die forging and pass rolling. The first advantage is four direction pressing without tension stress for the bar material, so the rolling mill is very suitable for the brittle and hard deforming materials. The second is the big reduction per pass to get the same deformation for surface zone and core zone, so the microstructure is homogeneous, the grains are thin and long, and the various mechanical performances can be improved.

#### 2. Research Process

The experimental material is sintered Mo bars of  $\Phi$  50×500mm. The Mo bars are rejection forged, pass rolled and step-by-step rolled, respectively. The heating temperature and heating time are as same as the normal producing process. The product size is  $\Phi$  50×L. The bars were heated 5 times for the rejection forging process, 2 times for the pass rolling process, only 1 time for the step-by-step rolling process, the working rate after each heating is 20-30%, 45-55% and above 75% for the three processes, respectively.

To detect if there are macro defects, such as surface reeding, surface separating and cracks, three kinds of samples were first made for a macro inspection. Then density measurement, microstructure inspection, grain size measurement and mechanical test were performed, so we can determine the reasonability and advantage of the step-by-step rolling process.

In order to show the influence of the large working rate deformation on the microstructure homogenization, as comparison, the small working rate step-by-step rolling experiment is done, i.e., from  $\Phi 50 \times 500$  to  $\Phi 45 \times L$ , working rate is 19%. The microstructure of Mo bar was observed in the condition of deforming surface zone and without deforming for core zone to show the performance difference between surface zone and core zone after the tension test, and to deliver the theoretical proof of improvement of the material mechanical performance by the step-by-step rolling process.

#### 3. Experiment Results and Discussion

Mo bars were made by the pass rolling, rejection forging and step-by-step rolling. The density measurement, microstructure analysis and

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mechanical performance test were made. The results are as below:

The microstructure is showed in figure 2-5. There is small difference between core zone and surface zone for forced Mo bar. They all have coarse deforming microstructure, the axis ratio is about 1.5-2. The grains in surface zone are thinner than those in core zone; The difference between core zone and surface zone for pass rolled Mo bar is great. The surface zone has coarse deforming microstructure; and core zone has thin and small deforming microstructure; The axis ratio is about 2-3; The microstructure in the surface zone and core zone for step-by-step rolled Mo bar is completely same, they are both thin and small working microstructure, the axis ratio is about 4-5.

The microstructure for the step-by-step rolled Mo bar by small deformation is similar to that of original sintered Mo bar. The results of density measurement and mechanical performance are shown in table 1. There is no difference among the samples made by the three kinds of working ways respectively, and they all reach the theoretical density. So, the three working ways all can compact the sintered Mo bar effectively. The difference of



a- Cross section of core zone



c-Cross section of surface zone



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b-Vertical section of core zone



d-Vertical section of surface zone

Fig 2. Step-by-step rolled Mo bar microstructure(200x)



a-Cross section of core zone



c-Cross section of surface zone



b-Vertical section of core zone



d-Vertical section of surface zone

Fig 3. Forged Mo bar microstructure(200x)



c-Cross section of surface zone

b-Vertical section of core zone

d-Vertical section of surface zone

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Fig 4. Pass rolled Mo bar microstructure(200x)



a-Cross section of core zone



c-Cross section of surface zone



Vertical section of core zone



d-Vertical section of surface zone

Fig 5. Small deform	med step-by-step	rolled Mo bar	microstructure (	(200x)
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			Tension	test	
Sample status		σь	σ 0.2	δ (%)	density
Step-by- step	Largely deformed samples	745	6.83	16.0	10.2
rolled samples	Small deformed samples	474			-
For	rged samples	698	663	2.0	10.2
Pass	rolled samples	592	583	3.0	10.2

Table1	The mechanical	performance	comparison	of samples	made by	different
	working ways					

mechanical performance is very obvious, especially the specific elongation, which stands for material plasticity. The specific elongation of largely deformed step-by-step rolled Mo bar is 5-8 times higher than that of the other two kinds of bars. So the advantages of step-by-step rolling process is obvious.

The following is the theoretical analysis of the results of three kinds working process:

The first is the forged Mo bar. It's microstructure is decided by the following process: forged from  $\Phi$  50 to  $\Phi$  25, normally heated for 5 times, and decreased 5mm in diameter every pass. Because the pass working rate is low, the grain deformation centralized in the surface zone. There is almost no deformation in core zone. Every time the bar is heated, the temperature is above the recrystallization temperature, so the stretched grains caused by deformation are recrystallized to equi-axed grains. The final microstructure is the final pass created working deforming microstructure, and it is coarse and short, nearly equi-axed. The difference between core zone and surface zone is small because the final reduction larger than those before, and the deformation can penetrate to the core zone. The coarse and short microstructure makes Mo bar has low intensity and bad plasticity.

The second is the pass rolled Mo bar, rolled from  $\Phi$ 50 to  $\Phi$ 25, normally 2 passes are needed. In the first heating, the  $30 \times 30$  rectangle bar is made. in the second heating, the circle bar is made. 3-4 passes are needed in each time of heating. The reduction per pass is small, the deformation centralized in surface zone, and there is almost no deformation in core zone, so in surface zone is thin and small, and the grains in core zone are coarse. As the forging process, during the second heating, the recrystallization happens, and the microstructure changes into equi-axed grains. The final microstructure is stretched grains. Because the reduction is larger than forging process, the grains are a little bit thinner, longer than that of forged Mo bar. The specific elongation is better than that of forged Mo bar.

The last is step-by-step rolling process: rolled from  $\Phi$  50 to  $\Phi$  25, only one heating and pass is needed. The deforming rate reaches 75%, and the lengthening coefficient is 4. The high deforming rate lets the deformation penetrating to the core zone, so the microstructure in the core zone and surface zone is same. No second heating, so no recrystallization, the working microstructure is reserved, and finally the thin and long deforming microstructure is acquired. Due to this kind of microstructure, the Mo bar has high intensity and good specific elongation. The problems existed in following mechanical working processes is solved from the beginning.

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The microstructure of Mo bar at a low deforming rate is still the equi-axed grain. No stretched grain of working state is formed, so the mechanical performance is bad and the specific elongation can not be measured. From the opposite side, we proved that high working rate is the effective way to promote the mechanical performance of Mo bar.

#### 4. Conclusion

The conclusions below are drawn from the comparison of the step-by-step rolling process, forging process and pass rolling process:

- (1) The microstructure of forged and pass rolled Mo bar is coarse grains and inhomogeneous, so the mechanical performance is bad.
- (2) Because the high deforming rate and four direction pressing, the deformation of the surface zone and core zone of the step-by-step rolled Mo bar is uniform, and thin and long grains of working state are acquired. The mechanical performance, especially the specific elongation is promoted largely, so the problems exist in the following working can be solved.
- (3) High deforming rate is the effective way to improve microstructure and to promote mechanical performance for the step-by-step rolling process.



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# Cyclic behavior of Ta at low temperatures under low stresses and strain rates

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#### Summary

The cyclic stress-strain response of recrystallized technically pure Ta was investigated in the stress range well below the technical flow stress, for temperatures between 173 K and 423 K, at loading rates between 0.042 MPa/s and 4.2 MPa/s with resulting plastic strains between  $<1x10^{-5}$  up to  $1x10^{-2}$ . Cyclic hardening-softening curves were recorded in multiple step tests. Cyclic stress strain curves exhibit straight portions associated with microplastic, transition range and macroplastic deformation mechanisms. The microstructure of the deformed specimens was characterized by SEM and TEM techniques which revealed typical dislocation arrangements related to plastic strain amplitudes and test temperatures. A mechanism of the microstrain deformation of Ta is proposed.

#### Keywords

Ta, cyclic loading, low temperatures, low stresses, low strain rates, cyclic stress-strain curves, microstrain, deformation mechanisms, dislocations, SEM, TEM

#### 1. Introduction

The bcc transition metals of the Va and VIa group of the periodic system, e.g. Nb, Ta, Mo, and W, are characterized by high melting points and high strength at elevated temperatures. Due to their outstanding properties these metals are used to fabricate components for high temperature service conditions. The specific physical and chemical properties of some of these

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metals, in particular Ta, led to the use in the chemical industry, for medical implants and electronic device fabrication involving service conditions at low temperatures for which the mechanical properties have not been evaluated in sufficient detail. Investigations of these properties under static and dynamic loading in the range of low temperatures, low strain rates and low stresses are therefore not only of scientific but also of increasing technical interest.



Figure 1: Temperature dependence of the flow stress (plastic strain  $1x10^{-5}$ ) of recrystallized Ta, monotonic loading, total strain rate  $2x10^{-5}/s$ ; T<sub>K</sub> is the so-called knee temperature (see text)

It is known that the deformation response of bcc metals in the low temperature range strongly depends on temperature and strain. Below a characteristic "knee" temperature (1), initially assumed to be near 0.2 of the absolute melting temperature, the flow stress increases markedly with decreasing temperature, as shown by the experimental data in Fig. 1. Detailed studies have shown that the knee-temperature  $T_K$  is specific for each bcc metal and in addition dependent on the strain rate (2,3). The deformation mechanisms of bcc metals at low temperatures have been treated extensively in the literature (4-6). The essential findings are that below  $T_K$  the edge dislocations show a higher mobility than screw dislocations while above  $T_K$  the mobility of both types of dislocations becomes comparable. Investigations of the dependence of the deformation behavior of bcc metals

under quasi-static loading and sensitive strain measurements revealed persistent strains to exist already at stresses considerably below the technical flow stress, a phenomenon termed microplasticity (7). The microplastic deformation is attributed to the exclusive movement of edge dislocations. Microplasticity effects under monotonic loading have been described e.g. for single and polycrystalline Fe (8), Mo (9) and Ta (10). Relatively little information is available with respect to the effects of strain rate and temperature on the cyclic stress-strain response. Cyclic stress strain curves for single crystals of Nb (11), Mo (12), W (13) and Fe (14) have been published, mostly determined for high strain rates and high plastic strains. Only recently data on the cyclic stress strain response of Mo polycrystals for small cyclic plastic strain ranges (15) and polycrystals of Ta for low temperatures and small loading rates (16-18) have been reported.

#### 2. Experimental details

The specimen material consisted of technically pure Ta (melting point 3270 K, density 16.6 g/cm<sup>3</sup>), produced under tightly controlled powder metallurgical procedures. The specimens were machined from swaged rods of 5 mm diameter with a flat gauge section (25 mm length, cross section 5 mm x 3 mm). After machining the specimen were recrystallized (1373 K/2h in vacuum <10<sup>-5</sup> mbar) resulting in a mean grain size of 50 µm, an ultimate tensile strenght of 300 MPa at a strain rate of  $1 \times 10^{-4}$ /s, an a hardness of HV5 = 190 (16). Chemical analysis of the specimens in the heat treated conditions indicated following trace impurities (mass ppm): 13 Fe, 125 Nb, 3 H, 6C. From tensile tests performed in earlier studies (16.18) the temperature dependence of the flow stress (related to a plastic strain of 1x10<sup>-5</sup> at a plastic strain rate of 2x10<sup>-5</sup> <sup>6</sup>) and the value of  $T_{K}$  were deduced. The experimental value of  $T_{K}$ =320 K is in good agreement with literature. In addition, from these tests the values and the temperature dependence of the elastic and the anelastic stress limits were obtained for recrystallized specimens and also for specimens after a small tensile predeformation to a plastic strain of 5x10<sup>-4</sup>. (the significant effect of small predeformations was already pointed out by Kossowsky (10)). The value of the anelastic stress limit (for the smallest detectable plastic microstrain of about  $5 \times 10^{-6}$ ) at the smallest achievable loading rate (0.042) MPa/s) was defined as the "intrinsic flow stress" (for Ta predeformed to a plastic strain of 5x10<sup>-4</sup> at 300 K corresponding to 60 MPa), Table 1.

Table 1: Temperature dependence of the anelastic stress limit (corresponding to a plastic strain of  $5 \times 10^{-6}$ ) of polycrystalline Ta, loading rate 0.042 MPa/s in tension, plastic strain rate approx.  $5 \times 10^{-6}$ /s

temperature	T/T <sub>K</sub>	recrystallized	predeformed to a plastic strain of 5x10 <sup>-4</sup>
T [K]		MPa	MPa
373	1.2	40	40
300	0.9	100	60
228	0.7	200	160
173	0.5	450	330

The cyclic deformation behavior was studied by push-pull loading in the stress range from near the anelastic stress limit to stresses slightly above the technical flow stress, at temperatures between 173 K and 373 K (0.5 T<sub>K</sub> and 1.2 T<sub>K</sub>). The cyclic tests were performed under load control (servohydraulic test system, computerized control and data acquisition, push-pull tests R =-1, triangular wave form) to simulate technical loading conditions and to achieve low strain rates required for the detection of microplastic effects. Since these tests were only extended to small plastic strains it may be assumed that the experiments correspond to a stress controlled test.

To investigate the cyclic stress-strain response multiple step tests (19) were employed, in which the stress amplitudes for a single specimen were increased by a certain incremental value after saturation of the plastic strain was reached at the preceding stress amplitude. The validity of such multiple step tests has been proven by comparing cyclic plastic strain values of both single step and multiple step tested specimens (18,20). The cyclic strain ranges at saturation were identical for both types of tests, as long as a critical value of plastic strain was not exceeded. This results confirmed that in the evaluated stress range the cyclic stress strain behavior can be determined by performing multiple step tests requiring only one specimen for each test temperature and loading rate. The effect of loading rates were revealed by testing specimens at a constant stress amplitude and varying loading rates, (decreased from 4.2 MPa/s in consecutive steps to 0.042 MPa/s and subsequently increased to the initial value).

The microstructure of the cyclically deformed specimens was investigated by SEM and TEM techniques. The SEM investigations by the electron channeling contrast imaging (ECCI) technique (21) supported by selected area channeling patterns (SACP) (22) were applied to reveal the global (mesoscopic) dislocation arrangements while by TEM techniques selected

specimens were examined to resolve individual dislocations. To achieve the high quality of the specimen surface required for the SEM-ECCI investigations the specimens were electropolished immediately prior to the SEM examination. For details of the preparation procedures see Ref. (18,21).

#### 3. Results and Discussion

#### 3.1 Cyclic loading tests:

The results of the multiple step tests at various test temperatures and for various loading rates were plotted as cyclic hardening-softening (CHS) curves. For low stress amplitudes a small amount of cyclic softening to a saturated plastic strain range was observed. At higher stress amplitudes and higher test temperatures an initial period of cyclic softening was followed by a slight hardening to a constant strain range. At 300 K the curves exhibited only cyclic softening as long as the plastic strain range remained below 1x10<sup>-3</sup> beyond which cyclic hardening occurred. The hardening effect decreased with decreasing temperature, at 173 K only cyclic softening without saturation of the cyclic plastic strain was found. At this low temperature it was not possible to apply stress amplitudes larger than 343 MPa due to buckling of the specimens.

The saturated plastic strain data were plotted as cyclic stress-strain (CSS) curves. In semi-logarithmic stress vs. saturated plastic strain diagrams it is possible to distinguish between up to three straight line segments with characteristic slopes. In Fig.2 the segments are numbered following the interpretation of Planell and Guiu (12) for Mo. Segment 2 is related to the microplastic stress-strain regime, the total amount of plastic strain is attributed to the movement of edge dislocations and kink pairs along screw dislocations. In segment 3 the decrease in slope is due to the gradual onset of thermally activated movement of screw dislocation, the amount of mobile screw dislocations increases with increasing stress and increasing temperature. Segment 4 corresponds to the macroplastic stress-strain regime, the increasing slope is related to the decrease of the mobility of screw dislocations because of dislocation interactions. The segment 1 observed by Planell and Guiu (12) cannot be revealed in our data because of experimental limitations (the tests could only be started at stress amplitudes near the anelastic stress limit).



- pile up at grain boundaries
- short bundles
- long bundles
  - long bundles and cell walls
  - three dimensional cells
- large cells
  - three dimensional cells, distinct cell walls

Figure 2: CSS curves of recrystallized Ta for various test temperatures, loading rate 0,42 MPa/s, numbers refer to deformation ranges, letters to dislocation arrangements observed by SEM and TEM

Lower test temperatures shift the CSS-curves to higher stress levels. For  $T < T_K$  increasing loading rates also shift the CSS-curves to higher stress amplitudes, more pronounced with decreasing temperature. The larger stress amplitudes required to achieve a given cyclic plastic strain for increasing loading rates can be explained by the decrease in the effective part of the loading interval (i.e. the extent of loading time during the fraction of the cycle above the intrinsic flow stress). An example of the change in cyclic plastic strain during a stepwise decreased and subsequently increased loading rate is shown by the portions of CSH curves in Fig.3. Decreasing the loading rate resulted in a marked increase in the cyclic plastic strain, however, during a subsequent increase of the loading rate the initial values were obtained, as long as a critical plastic strain of 5x10<sup>-4</sup> was not exceeded.



Figure 3:Effect of consecutive increase and decrease of loading rate on cyclic plastic strain of recrystallized Ta, stress amplitude 100 MPa, 300 K



Figure 4: Effect of loading rate on cyclic plastic strain during a single tension-compression cycle, stress amplitude 120 MPa, 300 K, maximum plastic strain rate approx. 3x10<sup>-6</sup>/s for loading rates of 0.042, 0.42 and 4.2 MPa/s

To obtain detailed information on the stress-strain relationship during one loading cycle the digitally stored data were plotted for selected loading cycles for various loading rates (for identical stress amplitudes) as function of the cycle time. The superimposed plots of the plastic strains in Fig.4 reveal that the major portion of the plastic strain and the maximum strain rate during the individual loading cycles is almost independent of the loading rate, but depends on the magnitude of the effective stress, i.e. the difference between the instantaneous stress and the intrinsic flow stress ( $\Delta\sigma = \sigma - \sigma_{ux}$ ). An evaluation of the test data shows that the major part of plastic straining occurs for all loading rates under the same maximum strain rate in almost the same fraction of the loading cycle before and after the maximum stress  $(\varepsilon_{tri} = t \cdot \varepsilon_{rit})$ . It is concluded that the amount of plastic strain is a function of the length of the effective stress interval. From diagrams as shown in Fig. 4 it is possible to estimate the plastic strain rates occurring during a loading cycle in stress controlled tests. The results show that under stress control the plastic strain rate is depending on the stress amplitude but not on the loading rate  $(\varepsilon_{pl} = f(\Delta \sigma))$ . It follows, that the plastic strain increases with decreasing loading rate  $(t = f(\sigma); \mathcal{E}_{t'} = t \cdot \mathcal{E}_{t'} = f(\sigma) \cdot f(\Delta \sigma))$ , however, the plastic strain rate for a given stress amplitude remains nearly constant. As a consequence the plastic strain rate in CSS-curves determined under stress control increases with increasing stress amplitude. This is in contrast to CSS-curves determined under strain control for which the strain rate is kept constant. In present investigation the plastic strain rates were found between 1x10<sup>-8</sup> and  $2x10^{-6}$  for the evaluated range of cyclic plastic strains.

#### 3.2 Microstructural examinations

The typical microstructure of a recrystallized Ta specimen is shown in Fig.5. The uniform contrast in individual grains reveals an almost strain-free grain structure, variations in contrast are related to differences in the crystallographic orientation. The TEM micrographs of recrystallized Ta show a surprisingly high density of inhomogeneously distributed dislocations, in particular near triple points. The average dislocation density amounts to  $10^{10}/\text{cm}^2$ , which is in agreement with literature data (23). A selection of typical REM and TEM micrographs of cyclically deformed specimens is shown in the following. In specimens deformed in the anelastic and microplastic stress-strain regimes, segment 2 in Fig.2, no significant differences to the recrystal-

lized microstructure can be detected. Obviously, in spite of measurable microplasticity no detectable dislocation displacement, multiplication or interaction could be observed taking into account the initially high dislocation density. The SEM-ECC micrographs of specimen cyclically deformed at 173 K up to small plastic strains, Region A in Fig.2, showed only weak contrast variations near grain boundaries indicating local strain concentrations. The SACPs of corresponding areas consisted a sharp lines typical for a strainfree matrix, minor bending of the lines are indicative of localized bending of crystal planes. In TEM micrographs of this specimen isolated short dislocation bundles and occasionally networks of straight dislocations between these bundles could be seen. The long straight dislocations were identified as screw type. The dislocations bundles with embedded dislocation loops, indicative of local multiple slip, consisted mainly of edge type dislocations. In specimens deformed at 223 K in the strain range of the onset of macroplastic deformation, Region C in Fig.2, short dislocation bundles could be observed in the SEM-ECC images, Fig.6. The bent SACP lines reveal the lattice distortion caused by the bundles. The TEM micrograph shows these bundles and the high density of straight dislocation segments and dislocation loops between these bundles, Fig.6. With increasing cyclic plastic strain the density of bundles increased, in some areas dense cell walls could be observed predominantly in the vicinity of grain boundary triple points. After cyclic deformation at 300 K up to the onset of macroplastic deformation, Region E in Fig.2, the microstructure consisted of straight dislocation bundles and dislocation cells, Fig. 7. The pronounced distortion of the SACP lines is due to increased lattice distortion. The TEM micrographs show dense dislocation bundles and a large number of dislocation loops, Fig.7. At the test temperature of 373 K a transition of the dislocation bundles into cell walls was observed, indicative of pronounced local plastic deformation with dislocation interactions.

The observed dislocation arrangements are indicated in Fig.2 by the letters A to G and summarized for the range of test temperatures for two levels of cyclic deformation in Table 2. It can be seen that after small levels of cyclic deformation at temperatures below  $T_K$  dislocation pile-ups and dislocation bundles with straight screw dislocations are formed, at temperatures near and above  $T_K$  dislocation cells are predominant.

Table 2: Effect of test temperature on dislocation arrangement after cyclic deformation of polycrystalline Ta to saturation of plastic strain, multiple step tests, loading rate 0.42 MPa/s

Temperature [K]	Т/Т <sub>К</sub>	deformed to cyclic plastic strain below 10 <sup>-3</sup>	deformed to cyclic plastic strain near 10 <sup>-2</sup>
173	0.5	pile-ups at grain boundaries, straight screw dislocations (A)	pile-ups at grain boundaries, straight screw dislocations (A)
223	0.7	short bundles (B)	numerous short and long bundles (C)
300	0.9	many long bundles, localized formation of rectangular cells (D)	large rectangular cells with dense cell walls (E)
373	1.2	large rectangular cells near triple points, dense cell walls, many dislocation tangles within cells (F)	large cells with pronounced orientation differences, high density of straight dislocations within cells (G)



Figure 5: REM-ECC and TEM micrographs of recrystallized Ta



Figure 6: REM-ECC and TEM micrographs of recrystallized Ta cyclically deformed in multiple step test at 223 K to plastic strain of 1x10<sup>-2</sup>, loading rate 0.42 MPa/s, dislocation arrangement correspond to "C" in Fig. 2



Figure 7: REM-ECC and TEM micrographs of recrystallized Ta cyclically deformed in multiple step test at 300 K to plastic strain of 5x10<sup>-3</sup>, loading rate 0.42 MPa/s, dislocation arrangement correspond to "E" in Fig. 2

#### 4. Summary and Conclusions

• Tensile tests at plastic strain rates of 2x10<sup>-6</sup> revealed for the Ta specimen material a  $T_K$  value of 320 K. From the values of the elastic and anelastic stress limits an intrinsic flow stress could be deduced (about 60 MPa at 300 K, for recrystallized Ta specimens after prolonged loading times at this stress or predeformed to a plastic strain of 5x10<sup>-4</sup>), below which no residual

plastic deformation occurs even for extended loading times and lowest loading rates.

- In stress controlled cyclic tests within the microstrain regime the plastic strain rate (between 10<sup>-8</sup>/s and 10<sup>-6</sup>/s) was found to depend on the stress amplitude with no effects of the loading rate. Multiple step tests resulted in similar values of plastic saturation strain as single step tests as long as a cyclic plastic strain of 1x10<sup>-3</sup> was not exceeded.
- The shape of CHS-curves is affected by test temperature, stress amplitude and loading rate. Saturation of the cyclic plastic strain was observed for low test temperatures and small stress amplitudes as long as the cyclic plastic strain did not exceed a value of 5x10<sup>-4</sup>. In semi-logarithmic plots the exhibited several straight-line segments which CSS-curves were interpreted in analogy to literature (12). An anelastic region (strain corresponds to bowing out or reversible motion of pinned edge dislocations (24)) could not be resolved for the Ta material because of experimental limitations (the cyclic tests were started at stresses corresponding to the anelastic stress limit). In the **microplastic region** the plastic strain is attributed to an increased movement of edge dislocations and kink pairs of screw dislocations, the magnitude of plastic strain depends on the time interval of loading and the difference between the actual stress and the intrinsic flow stress. In the **transition region** the plastic strain is a result of the gradual onset of local mobilization of screw dislocations, the contribution increasing with stress amplitude and test temperature. In the macroplastic region an extensive activation of screw dislocation takes place, cyclic hardening occurs due to the interaction of the mobilized screw dislocations. The tests revealed this macroplastic behavior to occur at cyclic stress amplitudes above the technical flow stress.
- The loading rate affects the CSS-curves significantly only for test temperatures below  $T_K$ . Decreasing temperatures and increasing loading rates shift the CSS-curves progressively to higher cyclic stresses. Decreasing loading rates result in increasing cyclic plastic microstrain, as a result of the increase of the effective loading time. The increase in plastic strain with decreasing loading rate is reversible as long as a critical value of plastic strain of  $5x10^{-4}$  is not exceeded. It could be shown that in stress controlled tests the plastic strain rate increases with increasing stress amplitude in contrast to strain controlled cyclic test.

- The microstructural investigations revealed in agreement with literature a high dislocation density and an inhomogeneous dislocation distribution in the recrystallized Ta material. Attempts to reduce the number of dislocation by annealing treatments resulted only in accelerated grain growth without appreciable decrease in dislocations density. an The dislocation arrangement in the cyclically deformed specimens are characteristic for test temperatures and the cyclic plastic strain ranges. At temperatures well below  $T_{\kappa}$ , for strains in the anelastic or microplastic regime, the dislocation arrangement appeared not to differ from that of the recrystallized material.
- The dislocation arrangement in specimens cyclically deformed in the microplastic and transition regimes is only dependent on the applied maximum cyclic plastic strain at saturation, but shows no relationship to the cumulative plastic strain. The straight dislocation lines between the dislocation bundles were identified in the TEM as screw dislocations.
- The onset of macroplastic deformation behavior occurs above a critical cyclic plastic strain of about  $5x10^{-4}$  independent of test temperature. Up to this strain the contribution of screw dislocations is considered negligible, the plastic strain should be caused exclusively by the movement of edge dislocations. For Ta it is interesting to note that localized movement of screw dislocations appears to contribute to the "microplastic" deformation, however, only minor interactions are taking place as shown by the small number of short dislocation bundles. Apparently, the observed transition strain of 5x10<sup>-4</sup> is the limit for Ta above which a sufficient number of pinned dislocation is mobilized, no multiplication of dislocations is required. Thus, the microstrain regime of Ta may not be solely related to microplastic deformation mechanisms (exclusive movement of edge dislocations) but may be interpreted as small macroplastic deformation due to mobilization of weakly pinned screw dislocations with insufficient loading time to reach higher strain values.
- The interpretation of the plastic microstrains in Ta as a small macroplastic deformation is supported by results of stress relaxation tests which show for recrystallized Ta under microstrain loading conditions high values of the activation volume (4000  $b^3$ ), high density of dislocations (2x10<sup>10</sup>) and a small mean free path of mobile dislocations (2 µm), (18, 25, 26).

 For practical applications the findings of this investigation appear of particular importance that in recrystallized Ta the dislocation density is high, the dislocations appear only weakly pinned, which may explain in combination with a high solubility of interstitial elements the high ductility at low temperatures. Even below room temperature relaxation of internal stresses to levels of the intrinsic flow stress takes place within hours. Plastic strains occur already at stresses far below the technical flow stress. This effect should be taken into account in storing and handling as well as in service applications of engineering products of recrystallized Ta.

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# Investigations on the Formability of a Tungsten Alloy by Use of Acoustic Emission Analysis

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## Summary:

The knowledge of the formability of metals for hot working processes is of great importance for process design and process optimisation. In this paper an experimental set up is presented to detect crack initiation and crack growth at high temperatures and high strain rates for a tungsten alloy.

The method used to examine initial cracking during compression tests by acoustic emission analysis was developed at the Institute of Metal Forming (IBF). During forming, upcoming acoustic waves, caused by material failure, are detected by piezoelectric sensors, recorded and analysed.

A sintered tungsten-alloy was investigated with respect to its formability. The samples were produced out of one powder blend, applying different sintering parameters to investigate their influence on the crack formation during hot forming operations.

For testing the material at high deformation temperatures the samples are heated up (max. temperatures now 1400°C) using a combined radiation and induction heating equipment. The samples are deformed with a servo-hydraulic machine in compression applying different strain rates up to 5 sec<sup>-1</sup>. The compression test under sticking-friction conditions induces tension stresses at the circumference of the samples and leads to cracking after a certain level of plastic deformation.

It is shown that this test method is practical to determine the formability limits of the tungsten alloy for the first passes of a hot working process (e.g. rolling or forging).

## Keywords:

Tungsten Alloy, Formabillity, Acoustic Emission Analysis, Metal Forming

# 1. Introduction:

Hot working of refractory metals has the aim to achieve the required mechanical properties, to eliminate the porosity remaining from the solid state sintering process and to get the desired geometrical shape. The first passes of deformation, like rolling or forging are often critical with respect to the formation of cracks, due to the presence of pores and a small strength of the grain boundaries. The occurrence of tensile stresses during this stage of deformation, specially at the surface of the workpiece, may responsible for reaching the local formability.

This is why knowledge of the formability of the sintered parts is an important criterion for the process design and the efficiency of a technical forming process. However, due to the complexity of the influences it is very difficult to determine this value for a real process.

This article will present a method, developed at the Institute of Metal Forming (IBF), to determine the formability of a material on the basis of basic tests (1). A representative method allowing significant statements on basic tests will be explained by determining the displacement to crack initiation by use of an acoustic emission (AE) analysis. Here, a record and analysis of high-frequency sound pulses, which are emitted from the cracking material, will be performed. With this method the formability of a sintered tungsten alloy was investigated with respect to its temperature, strain rate and sintering densities sensitivity.

## 2. Experimental Procedure:

The most precise forecast of crack initiation is a great advantage for technical processes. A better design of the process up to the limits of process safety and avoidance of waste during production can help to save any costs. In this respect, independent and uncomplicated tests are needed. Furthermore, simple evaluation methods must be available, so that the crack criteria discovered in the experiments can be transferred to other, technical relevant forming processes.

## 2.1. Material:

The investigated material is the tungsten alloy W-CeO<sub>2</sub> with 2 wt% CeO<sub>2</sub>. The common application of the material are electrodes for inert gas welding (TIG). The CeO<sub>2</sub> particles are fine dispersed in the W-matrix, the average size is approx. 3  $\mu$ m.

All samples were made of one powder blend. After pressing the slabs isostatically (diam. 22 mm and length 200 mm), the green parts were turned to achieve the same outer diameter for all samples. The green parts where sintered in different batches, applying various sintering parameters.



**Figure 1.** Used types of cylindrical cone sample 'C' and cylindrical 'Z' geometries.

Two axisymmetric samples geometries 'C' and 'Z' were produced of the sintered slabs (see **Figure 1**) for every sintering parameter. The samples were machined out of the sintered slabs without turning the outer face anymore (see also **Figure 1**). This guarantees, that the condition of the free surface, were the crack initiation is expected, is the same as for the real forming process (e.g. rolling or forging).

#### 2.2. Testing Method:

If the samples are compared in terms of their state of stress at the crack critical point with identical effective strains, the conical sample 'C' has higher circumferential tensile stress values than the cylinder sample 'Z' with at the same time identical strain values. The crack critical points are located at the circumference of the sample and the emerging stress/strain histories should be similar to that of a real forming process (e.g. the first passes of a rolling sequence, where the temperature is nearly constant, if the hoop direction of the sample is compared with the longitudinal direction of the slab in the hot rolling procedure). The compression tests have been performed on a servohydraulic compression machine of the company SCHENCK (**Figure 2**). This system consists of a maximum load of 630 kN and a maximum velocity of the working cylinder of 500 mm/s.



SCHENCK testing system



Servohydraulic testing system at IBF and test set up to perform Figure 2. compression tests at highest temperatures.

If the internal stresses in a crystal compound is exceeding locally during forming the certain stress limit there is a sudden change to a new state of equilibrium with lower potential energies. The potential energy emitted in this way is dissipated in form of elastic waves and could be detected in the surrounding as sound pulses.

The recording and analysing of the high-frequency acoustic waves is called acoustic emission analysis. Piezoelectric sensors are used to record the sound signals. Two R15 acoustic emission sensor heads with a resonant frequency of 125 kHz are mounted in the cooled area of the top upsetting tool outside of the furnace's hot zone. The weak sound signal is pre-amplified with a gain of 40dB, filtered to separate process-relevant and interfering frequencies and amplified again before put into the data aguisition of the PC (2). Here, a fixed threshold of 65dB was used to eliminate the high extraneous background signals from hydraulic, electrical and mechanical

noises. The values for load and displacement are also read into the AE analysis device PCI-DSP4 of the company PHYSICAL ACOUSTICS CORP.. With this, a correlation between the AE signals and the upsetting load and displacement is also possible.

The most effective testing technique used for the compression tests is described in the following. An electrically heated radiant furnace, surrounding the forming zone, was heated up to 800°C. The samples were placed on the upsetting plate, made of ceramics, which was constructed that way by diving the sample completely into an induction heating spool. This induction spool in the centre of the furnace heats up the samples to forming temperatures up to max. 1600°C. For achieving the correct test temperature a temperature control with use of thermocouples was performed at the beginning of each test serial. Here, thermocouples of type Ni-CrNi for temperatures up to 1200°C and type Pt-PtRh for temperatures above 1250°C were used. Finally the samples are compressed up to crack initiation while the ceramics upsetting plate was diving through the induction spool and upcoming AE events caused by material failure have been recorded.

#### 3. Results:

In a first stage of the investigations the reproducibility of predicting crack initiation with use of AE monitoring during compression testing was studied. The in the following mentioned experimental test conditions are normalised due to its relevance to industrial application. In Figure 3 the results of four tests with cylindrical samples of two sintered slabs of tungsten alloy is shown. The samples were compressed at a normalised temperature of '1' and with a constant strain rate of 0.1/s. The good reproducibility of the test is shown comparing the results of the first row (left figure and right figure) and the second row resp. Here, one could observe at the one hand no sudden drop in load caused by material failure. On the other hand a good correspondence of monitored AE events at crack initiation with the sample's height displacement is given. This is presented for different sintering parameters. Monitoring the AE signals by use of two piezoelectric sensors leads to a very good agreement with the detection of crack initiation. Here, the cumulated peak amplitude of incoming acoustic events is used. During the compression, AE events could be recognised at the beginning of testing due to contact of the sample to the upper die. With further compression, a small amount of acoustic events due to friction and extraneous background noises could be detected. Apart from this, the cumulated amplitude increases smoothly. As crack initiation and further formation of cracks occurs, the cumulated

amplitude rises dramatically. At the beginning of the increase, the displacement up to crack initiation could be located.



AE monitoring compression tests for two different sintering Figure 3. parameters.

Top: Tests with sintering parameter 1

Tests with sintering parameter 2 Bottom:

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The next step of investigations was to observe the effect of inductive heating on the temperature distribution inside of a cylindrical sample. Samples of one slab with a diameter of 16mm and a height of 16mm have been heated up within the above described test setup. A temperature of 1000°C at the radial surface of the sample was adjusted at the voltage regulator of the induction heating system. The temperature was controlled with the use of a Ni-CrNi thermocouple. With the same conditions the temperature development in the centre of the sample was recorded. After 5 minutes heating a stationary temperature field was achieved inside of the sample. At this time a temperature difference of 27.6°C between surface and the centre of the sample was observed (cf. Figure 4). The reason for this temperature difference is in the skin effect. The total magnetic field strength is a result of a primary magnetic field from the spool and secondary self inducted magnetic fields causes the eddy current. The skin effect describes this matter of fact that the current density exponentially decreases from the outer to the inner radius of a metallic cylindrical sample.



**Figure 4.** Effect of induction heating on the temperature development inside of the sample.

In AE testing the displacement to crack initiation was recorded during compression of samples with the above two geometries. The tests have been carried out at a normalised temperature of '1' and varying strain rates of 0.1/s,

1/s and 5/s. The displacements up to crack initiation were determined by analysing the upcoming AE events due to material failure during upsetting. A conclusion of this work, showing the specific height reduction up to crack initiation is given in Figure 5. The specific height reduction up to crack initiation is defined as

$$\varepsilon_{\text{h.crack}} = \left| \frac{\mathbf{h}_{1.\text{crack}} - \mathbf{h}_0}{\mathbf{h}_0} \right| \tag{1}$$

where  $h_0$  is defined as the initial height of the sample and  $h_{1 \text{ crack}}$  is the final height at the time of crack initiation.

In **Figure 5**, no significant influence of the strain rate on the material failure is visible. Obviously the conical geometry is more sensitive as the cylindrical geometry.



Figure 5 Effect of strain rate on formability of tungsten alloy W-CeO<sub>2</sub>

The influence of the temperature on the formability was as well investigated. Here, samples of each geometry have been deformed up to cracking at normalised temperatures of '0.8', '1' and '1.2'. The strain rate has been held constant during the tests at a value of 0.1/s. The displacements up to crack initiation have been obtained by analysing the upcoming AE events during material failure. The specific height reduction up to crack initiation are shown in **Figure 6**. Here, a significant drop in  $\varepsilon_{h, Crack}$  from could be noticed from normalised temperature '1' to '0.8'. Therefore, a loss in formability in the range of normalised temperatures between '0.8' and '1' could be propagated.



**Figure 6.** Effect of temperature on formability of tungsten alloy W-CeO<sub>2</sub>

The influence of the different sintering parameters on the formability was as well investigated. Here, samples of each geometry have been deformed up to cracking at a temperature of '1' with a strain rate of 0.1/s. The specific height reduction up to crack initiation is shown in **Figure 7**. In total 9 slabs with different sintering parameters have been produced. Both types of geometries have been tested. Because of a smaller contact area for geometry 'C' not every test produced detectable AE signals. Therefore the AE testing of geometry 'C' for the sintering variants is not completed at the moment.

In this case one can observe a significant influence of the sintering parameters on crack initiation for both types of sample geometries and the good reproducibility within one sintering parameter. A further result is the fact, that a sample which shows a high formability using geometry 'Z' does not necessarily lead to a good formability for geometry 'C' (see e.g. var. 5). This may be explained by the occurrence of different fracture modes during deformation. In the case of geometry 'C' the maximum principal stress is the hoop stress, whereas the crack opens parallel to the axial-direction and grows in radial direction. This hoop stress acts from the beginning of deformation on a high level, this explains the low strain to fracture in comparison to geometry 'Z'.

For the sample type 'Z' the tensile stress in hoop direction are very low (the level is dependent on the ratio  $h_0/d_0$  and the friction between the sample and the tool) at the beginning of deformation and increases with increasing height reduction. During the first stage of deformation the maximum stress

component is a shear stress acting under 45° to the axial direction, which explains the occurrence of cracks under this angle.

These results show clearly that the formability is a parameter which is very sensitive to the applied stress-strain-path. A decision which sample geometry should be used to make predictions for the real forming process, the stressstrain-path may be calculated via an FE-simulation and can compared with the stress-strain-history of the sample.

A more detail method is the construction of a so called 'stress limit curve', which is explained in (1). With this method more than two sample geometries are used to get the forming limit in the stress-strain space (e.g. equivalent stress versus equivalent plastic strain or maximum principal stress versus equivalent plastic strain).



Figure 7. Effect of sintering parameter on formability of tungsten alloy W-CeO<sub>2</sub>

#### 4. Concluding Remarks

- 1. Investigations on the formability of a sintered tungsten alloy has been done with use of acoustic emission analysis for detection of the crack initiation during compression tests.
- 2. A test set-up was developed to perform compression tests up to highest temperatures of 1600°C with using a combined radiation and induction heating equipment.

- 3. The good reproducibility of predicting the crack initiation with use of acoustic emission monitoring during upsetting was shown up.
- 4. The effects of temperature, strain rate and different sintering parameters on the formability was investigated with above mentioned testing technique. Here, no significant influence of strain rate on the formability could be observed. On the other side, influences of temperature and sintering parameters on the formability could have been extracted. Optimised production parameters could be derived with the information given by the analysed tests.
- 5. The next steps in research is to proof the formability at 1600°C, simulating the compression tests via FEM and developing a failure criterion based on crack hypotheses for tungsten alloy W-CeO<sub>2</sub> to predict the local formability in a hot working process (e.g. rolling or forging)

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# Simulation of Hot Forming Processes of Refractory Metals using Porous Metal Plasticity Models

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#### Summary

In this work two models for predicting the densification behavior of sintered refractory metals during hot working operations are presented. It is known from experiments and cell model calculations that the pore shape change has a significant influence on the densification behavior. Therefore this effect should be included in a continuum constitutive description. The first model presented is a phenomenological extension of the Gurson model, the second one is the model of Gologanu, Leblond & Devaux, which was implemented as a user material model into the Finite-Element-code ABAQUS. The numerical results are compared with the density distribution of a tapered disk made of pure molybdenum after the hot forming operation.

#### Keywords

Porous Metal Plasticity, FE-Simulation, Hot Forming

#### 1. Introduction

Hot working of refractory metals after the sintering procedure aims at achieving the desired shape and mechanical properties and to eliminate the porosity. Therefore understanding of the densification behavior of the porous metals during the hot forming operation is of great importance for process design and process optimization.

The presence of pores in sintered parts requires that pressure-dependent, dilatant constitutive laws are used to model hot forming operations on these materials. The porosity (or the relative density), is treated as an internal variable.

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In the past a large number of phenomenological as well as micromechanics based constitutive laws for porous materials were developed. The first phenomenological yield functions for porous media (Kuhn & Downey 1971, Shima & Oyane 1976) assume isotropic response at yielding even for finite plastic deformation. The only microstructural feature is the relative density. Some models originate from the continuum damage theory of ductile materials, the well-known Gurson model (Gurson 1977), extended by Tvergaard (1981), being one of them. Gurson's model assumes that the pore shape is spherical at the beginning as well as throughout plastic deformation, and therefore the mechanical behavior remains also isotropic. The material behavior of the matrix is assumed to be perfectly plastic. Isotropic constitutive laws for linear and nonlinear viscous materials were also developed and applied to hot isostatic pressing simulations (Duva & Hutchinson 1984).

More recently, Gologanu et al. (1993, 1994) generalized the Gurson model to include the evolution of the pore shape during plastic deformation. The pore aspect ratio is an internal variable, and the stress-strain response becomes anisotropic as the pores develop prolate or oblate shapes. An alternative approach based on a constitutive theory for particulate composites was proposed by Ponte Castañeda & Zaidman (1994).

In the present work two approaches of continuum-models describing the densification behavior of sintered refractory metals are presented. The first one is a modification of the Gurson model (referred as model 1), by introducing evolution equations for the parameters  $q_1$  and  $q_2$  proposed by Tvergaard, with the restriction that the influence of the pore shape change on densification is incorporated in a phenomenological manner (the model remains isotropic). The parameters of the evolution equations for  $q_1$  and  $q_2$ , are fitted to experimental results (uniaxial stress state) and axisymmetric unit cell calculations (stress states with arbitrary triaxialities). The advantage of this model is that different microstructural features which characterize the material (like the local distribution of the pores within the matrix or the effect of different pore sizes) can be taken into account in an overall manner. The disadvantage is that the model is applicable strictly only for proportional loading conditions (no change of triaxiality during plastic straining).

As a second approach, we have implemented the model of Gologanu et al. (1993, 1994) as a user defined material model in the FE-code ABAQUS (referred as model 2) (Andrieux et al. 2000).

The advantage of this model is that it describes the evolution of the pore shape and of the anisotropic material response consistently, based on reliable models for void growth and void deformation. Hence a much wider range of validity is expected than for model 1. For example, data measured in uniaxial
compression can be applied with greater confidence to forming operations where the stress triaxiality may be much higher. In its present form the model neglects possible rotations of the principal axes of the pores.

### 2. Experiments

Green compacts with different green densities were produced from pure molybdenum powder by applying different compaction pressures. All samples were sintered in one batch. The same temperature history implies that the grain size is the same in all samples, and only the relative density varies due to the different densities of the green parts. This means, that the mechanical behavior after sintering depend on the density only.

The sintered samples were tested in uniaxial compression at a temperature of 1000°C. One set of samples (diam. 5 mm and height 6 mm) were deformed up to a plastic strain of  $\varepsilon \approx 1$  to evaluate the stress-strain-behavior. The relative densities of this set ranges from  $D_0 = 0.917$  to 0.96. The samples of the second set (diam. 12 mm and height 14.4 mm) with initial relative densities of  $D_0 = 0.92$ , 0.94 and 0.96 are compressed to different heights, in order to measure the relative density after a certain amount of plastic strain with the Archimedes method. Details are described in Parteder et al. (1999). Additional compression tests on tapered disks for verification of both models are described in section 5.

### The Gurson model and its modification

Gurson's yield function was derived from an upper bound solution of the velocity field of a hollow sphere or a shell with an incompressible shell material. The flow potential  $\Phi$  has the form

$$\Phi = \frac{\sigma_e^2}{\sigma_M^2} + 2q_1 \cosh\left(\frac{3q_2\sigma_h}{2\sigma_M}\right) - \left[1 + q_3\left(1 - D\right)^2\right], \tag{1}$$

where  $\sigma_{M}$  denotes the matrix flow stress, D is the relative density defined as  $\varrho/\varrho_M$ , where  $\varrho$  is the density of the porous metal and  $\varrho_M$  is the density of the matrix material,  $\sigma_e$  is the equivalent stress of the porous continuum and  $\sigma_h$  is the hydrostatic stress.  $q_1$ ,  $q_2$  and  $q_3$  are the parameters proposed by Tvergaard. He suggested values of  $q_1 = 1.5$ ,  $q_2 = 1$  and  $q_3 = q_1^2$ . For all further calculations we also use the relation  $q_3 = q_1^2$ . Note that for  $q_1 = q_2 = q_3 = 1$  the

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original Gurson model is recovered and that for D = 1, which means that the material is fully dense, the Mises yield condition is gained.

The constitutive model is completed by the argument that normality of the matrix material implies normality of the porous continuum (Berg 1970)

$$d\varepsilon_{ij} = d\lambda \frac{\partial \Phi}{\partial \sigma_{ij}}.$$
 (2)

#### 3.1. Uniaxial stress state

As a first step the uniaxial stress state is investigated. The modification of Gurson's model is attained by considering the parameters  $q_1$  and  $q_2$  as internal variables representing the influence of the pore shape in a manner which is not explicitly specified. The evolution of  $q_1$  and  $q_2$  is linked to the equivalent plastic strain of the porous metal and the following equations are proposed

$$q_{1} = q_{1}^{0} \left( 1 + \frac{\varepsilon_{e}}{\overline{\varepsilon}_{1}} \right)^{n_{1}}, \quad q_{2} = q_{2}^{0} \left( 1 + \frac{\varepsilon_{e}}{\overline{\varepsilon}_{2}} \right)^{n_{2}},$$
(3)

where  $\varepsilon_e$  is the equivalent plastic strain of the porous material,  $q_1^0$  and  $q_2^0$  are the initial parameters for zero plastic strain,  $\overline{\epsilon}_1$ ,  $\overline{\epsilon}_2$ ,  $n_1$  and  $n_2$  are constants which will be determined by a best fit with the experimental results, see table 1 below.

For uniaxial compression the yield condition,  $\Phi$  = 0 , with  $\Phi$  from equation 1 gives the yield stress  $\sigma_v$  of the porous metal

$$\sigma_{y} = \sigma_{M} \frac{2\left[1 - q_{1}\left(1 - D\right)\right]}{\left[4 + q_{1}q_{2}^{2}\left(1 - D\right)\right]^{1/2}} \quad .$$
(4)

The evolution of the density is related to the volumetric strain increment, which is obtained from equation 2. For uniaxial compression it follows

$$dD = -\frac{3D q_1 q_2^2 (1-D)}{4 + q_1 q_2^2 (1-D)} d\varepsilon, \qquad (5)$$

where  $\varepsilon$  is the component of the plastic strain along the compressive axis. Equation 5, together with equation 3 is integrated numerically using computer algebra. This gives relations for the yield stress  $\sigma_y = \sigma_y(D, \varepsilon)$  and for the evolution of the density  $D = D(\varepsilon)$ . Figures 1 and 2 show the results of the



Figure 1. Yield stress of the porous metal versus relative density for different levels of plastic strain; experiments (uniaxial compression) compared with the modified Gurson model (model 1).



Figure 2. Density evolution in uniaxial compression for different initial densities; experiments compared with the modified Gurson model (model 1).

integration adjusted to the experimental results, and table 1 shows the values of the parameters resulting from the best fit.

$q_1^0 = 4.66$	$\overline{\epsilon}_1=0.1$	$n_1 = -0.75$
$q_2^0 = 0.45$	$\overline{\epsilon}_2=0.2$	n <sub>2</sub> = 1.25

Table 1. Parameters of equation 3 for the uniaxial stress state.

#### 3.2. Arbitrary compressive stress states

For arbitrary compressive stresses experimental data are hard to obtain. Instead, micromechanical cell model calculations are a suitable method to get reasonable results for characterizing the densification behavior of the porous metal. In our case simple axisymmetric cell models with symmetric boundary conditions were used (Parteder 2000).

Figure 3 shows the simplification of a porous solid, assuming a regular cubic pore arrangement and the approximation of a hexaedron with a cylinder. For a given triaxiality, which is defined as  $X = \sigma_h/\sigma_e$ , the ratio of the axial load  $\sigma_z$  and the radial component  $\sigma_r$  can be calculated as

$$\frac{\sigma_{r}}{\sigma_{z}} = \frac{3X+1}{3X-2} \rightarrow \text{"sphere to crack"},$$

$$\frac{\sigma_{z}}{\sigma_{r}} = \frac{3X+2}{1-3X} \rightarrow \text{"sphere to needle"}.$$
(6)

Note that for axisymmetric stress states we have to distinct between the evolution of oblate and prolate pore shapes. In the first case the full densified state is a penny shaped crack, starting from a spherical pore, the evolution is reffered as "sphere to crack". The prolate pore shapes evolve from "sphere to needle".

The densification characteristic of the cell can be computed from the displacement vector of the edge node of the cell. In order to fit the modified Gurson model to these cell model calculations the parameters  $q_1$  and  $q_2$  were assumed to depend on the stress triaxiality in addition to the dependence on the plastic strain specified in equation 3

$$\mathbf{q}_1 = \mathbf{q}_1(\boldsymbol{\varepsilon}_{\mathrm{e}}, \mathbf{X}), \quad \mathbf{q}_2 = \mathbf{q}_2(\boldsymbol{\varepsilon}_{\mathrm{e}}, \mathbf{X}). \tag{7}$$



Figure 3. Sketch of regular pore arrangement and the extraction of a axisymmetric unit cell.

The functional form of equation 7 is given in Parteder (2000). The above relation is only valid for proportional loading conditions, because it is assumed that the change of the triaxiality during loading will influence the pore shape evolution and therefore the density evolution.

Figure 5 below shows the density evolution for various triaxialities as predicted by cell models, by the modified Gurson model and by the Gologanu model.

#### 4. Gologanu model and its implementation as a user defined material model

The model of Gologanu et al. is a generalization of the Gurson model. In addition to the relative density D, which is the only state variable in the flow potential of the Gurson model, the model of Gologanu et al. contains a pore shape variable S as a second state variable. If a and b are the semi-axes of a spheroidal pore (a is the semi-axis in axial direction, b is the semi-axis in radial direction), S is defined as S = ln(a/b). Prolate pores have S > 0, oblate pores are characterized by S < 0, and spherical pores by S = 0.

The material model exhibits an evolving anisotropy depending on the orientation of the axes of the pore and on the value of S. The functional form of the flow potential is given as

$$\Phi = C \frac{\sigma_{e}^{*2}}{\sigma_{M}^{2}} + 2q_{1}^{*} (g+1)(g+1-D) \cosh\left(\frac{\kappa\sigma_{h}}{\sigma_{M}}\right) - (g+1)^{2} - q_{1}^{*2}(g+1-D)^{2}.$$
(8)

The parameters C,  $\kappa$ , and g are dependent on the pore shape parameter S and the relative density (g = 0 for prolate and spherical pores).  $\sigma_e^{-}$  is a modified equivalent stress, dependent on the internal variables. The Tvergaard parameter  $q_1^*$  in this case is also dependent on the the pore shape. The evolution of the pore shape is given by the relation

$$\dot{\mathbf{S}} = \mathbf{S}_{\mathbf{a}} \dot{\boldsymbol{\varepsilon}}_{z}' + \mathbf{S}_{\mathbf{b}} \dot{\boldsymbol{\varepsilon}}_{\mathbf{h}},$$

(9)

where the parameters  $S_a$  and  $S_b$  are functions on the stress triaxiality and the pore shape.  $\dot{\epsilon}_z$  is the deviatoric part of the plastic strain rate in direction of the axis a (axial or z-direction) and  $\dot{\epsilon}_h$  is the volumetric strain rate. The model of Gologanu et al. was coded in Fortran for arbitrary uniform straining histories (with no spatial dependence) and as a user subroutine for the FE-code ABAQUS/Explicit. Special care must be expended for spherical pores (when the pore shape parameter of the model is S = 0 and expressions of the form  $\infty - \infty$  occur), and for crack- or needle-like pores (when  $S = \pm \infty$ ). Euler forward integration is used throughout, including the yield condition, which is treated as  $d\Phi = 0$ . Concerns that the stress state could drift away from the yield surface, if only the incremental form of the yield condition is used, proved to be unnecessary. With the small time steps that are chosen by an explicit code the deviation from the yield surface usually remained smaller than 1% and is probably not larger than other inevitable inaccuracies of the time integration scheme.

Figure 4 shows the yield stress of the porous metal in dependence on the relative density for different levels of plastic strain. The results for the modified Gurson model (model 1) and the Gologanu model (model 2) are compared with the original Gurson model (model 1 gives the best coincidence with the experimental results). One can see the increasing drop of the yield stress predicted by model 2 due to the evolving anisotropy. Figure 5 shows the evolution of the density for two different stress triaxialities. For the uniaxial stress state all three models are in good agreement, except during the last stage of densification (during this stage model 1 - which represents the experimental results - shows a slower densification rate than the axisymmetric cell models and the Gologanu model). For the triaxiality X = -4/3 the Gologanu model gives the highest densification rate.



Figure 4. Yield stress of the porous metal versus relative density for different levels of plastic strain; original Gurson model (with  $q_1 = q_2 = 1$ ) compared with the modified Gurson model (model 1) and the Gologanu model (model 2).



Figure 5. Density evolution for different triaxialities; comparison between axisymmetric unit cell calculations, the modified Gurson model (model 1) and the Gologanu model (model 2).

### 5. Tapered disk compression

### 5.1. Forging experiments

In order to subject the two models presented in this paper to a critical test, tapered disk compression experiments were carried out. The initial specimen geometry is shown in figure 6. This test configuration provides a wide range of stress states: in the center of the disk high hydrostatic compressive stresses result in a rapid local densification, whereas tensile stresses at the outer parts lead to a decrease in relative density. Two disks of sintered molybdenum (initial density  $D_0 = 0.95$ ) were deformed with a screw-press. The first stroke reduced the specimen height to  $h_1 = 50 \text{ mm}$ , the second one to  $h_2 = 40 \text{ mm}$ . The temperature at the beginning of deformation was  $T = 1000^{\circ}\text{C}$ . Samples were cut from each disk after deformation to determine the local density distribution with the Archimedes method. The finite element mesh is depicted in figure 7 together with the contour plots of the experimental and numerical results for the density distribution.

### 5.2. Numerical results

An isothermal simulation was carried out using axisymmetric conditions with 4 node linear elements. The Coulomb friction factor was taken to be 0.05 between the disk and the rigid dies. This value was obtained from ring upsetting tests. The flow curves for various temperatures and strain rates were also obtained experimentally (Parteder 2000). The parameters of model 1 (equation 7) were defined by the option USER DEFINED FIELD in the ABAQUS input deck, for model 2 a UMAT was developed, as described above. In figure 7 the experimental results can be compared with the predictions of the two models and the original Gurson model (with constant parameters  $q_1 = 1.5$  and  $q_2 = 1$ ). On the left column the results for  $h_1 = 50$  mm (first stroke) are shown, on the right side results for  $h_2 = 40$  mm (second stroke) are depicted.

A comparison of the experimental results and the three models shows, that the modified Gurson model with parameters adjusted to results of hot upsetting tests and cell model calculations (model 1) gives the best consistency with the experiments. Especially in the center of the sample the predicted values are quite reasonable (the relative density in the center obtained from the experiment is  $\approx$  99.6 %, which is also predicted with model 1). This is not surprising since the triaxiality in the center of the sample

is about  $X \approx -0.4$ , which is close to uniaxial compression for which the parameters were fitted.



Figure 6. Sketch of the tapered disk sample with finite element mesh.

Also the Gologanu model (model 2) gives density distributions that are generally in good agreement with the experiments. However, the model predicts that the material is completely densified in the center of the sample. This overestimation can be explained looking at figure 5, where the densification in the last stage is more rapid compared with the experimental values. Contrary to the modified Gurson model the Gologanu model contains no adjustable parameters (except the hardening curve of the base material). On the other hand, the original Gurson model gives density distributions that are far less accurate.

Another comparison can be made with the model of Ponte Castañeda (Kailasam et al. 2000). In this case the same tapered disk sample was used and the first stroke was simulated, however with an initial density of  $D_0 = 0.85$ . In the center of the sample the same tendency as with Gologanu's model can be seen: the final density is overestimated compared to the experimental results.

In figure 8 the pore shape parameter S is plotted for the first stroke calculated with model 2 together with micrographs on four specific positions. In the center (point 1) a value of S = -6.73 is predicted, which means a very low pore aspect ratio and therefore an almost fully dense material. The micrograph



Figure 7. Density distribution for the first stroke (left side: A1 - D1) and for the second stroke (right side: A2 - D2). Comparison of the measured values (A1 and A2), the modified Gurson model (model 1: B1 and B2), the Gologanu model (model 2: C1 and C2) and the original Gurson model (with  $q_1 = 1.5$  and  $q_2 = 1$ ) (D1 and D2).

at this position shows little porosity, corresponding to the relative density in figure 7, A1 (experimental value). The aspect ratio calculated at the outer side (point 2) is approximately 1 and is in good accordance to the micrographical

observations. At point 3 a value of 0.51 and 0.59 at point 4 resp. is predicted. Also these values are in good coincidation with the micrographs.



Figure 8. Pore shape parameter S for the first stroke calculated with the Gologanu model (model 2), together with four optical micrographs.

### 6. Conclusion

The accuracy of predicted density distributions during forming processes of porous metals with closed porosity (up to levels of 10%) can be increased significantly by incorporating the pore shape evolution within the continuum model. Two possibilities were presented in this paper, the first one was a phenomenological modification of the Gurson model, the second one was the model of Gologanu et al. Both models lead to much better results for the

density distribution in a tapered disk sample in comparison with the original Gurson model.

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G. Schulz

# ULTRAFINE METAL POWDERS FOR HIGH TEMPERATURE APPLICATIONS MADE BY GAS ATOMIZATION

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### Summary

A new gas atomizing process disintegrating a stabilized thin melt film by a laminar gas flow at sonic velocity allows the direct production of bulk quantities of 10  $\mu$ m metal powders in a direct way, avoiding costly screening operations. Thus, large amounts of ultrafine metal powders for advanced applications like superalloys, nickel and iron aluminides, chromium and platinum group metal alloys can be made at very reasonable cost. Examples of powders and their applications like metal matrix composites, sputtering targets, thermal spraying and metal injection molding are given.

### Keywords

gas atomization, melt film, ultrafine powder, intermetallics, superalloys, NiAl, FeAl, rapid solidification

# 1. Introduction

Most metallic materials for structural or coating applications operated at high temperatures are made from powders as starting materials. Powder metallurgy offers (near) net shaping technologies for making parts, where conventional mechanical working cannot be used due to brittleness and high wear resistance of those materials. Thermal spraying is used to coat base metals with functional high performance layers.

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Gas atomizing in general is able to process any metal or alloy, if it can be molten. Standard processes give coarse metal powders with broad particle size distributions.

A new technology – the WIDEFLOW melt film gas atomizing process – produces fine and ultrafine metal powders with narrow particle size distributions required for near net shaping.

### 2. Melt film gas atomizing – the WIDEFLOW process

Is there a direct access to ultrafine powders in bulk quantities at reasonable costs? Productivity seems to be most cost effective, followed by specific gas consumption. To increase productivity, atomizing rate must be high, and this essentially requires a melt guidance tube exit with a large cross section. As it is known, a high specific transfer of kinetic energy form the gas to the metallic melt is necessary in order to obtain a powder of a high fineness. With round melt guidance tubes common in standard gas atomization, a large melt throughput and a high specific energy transfer cannot be realized at the same time.

WIDEFLOW's concept (pat. pend.) uses a linear melt nozzle which converts the metallic melt into a thin melt film. Melt throughput can be adjusted simply by increasing the length of the melt nozzle exit slit.

A melt film intrinsically has a large surface area interacting with the atomizing gas, much larger than a round melt stream. As the kinetic energy of the gas is transferred through that interface, a melt film can be disintegrated much more efficiently.

A WIDEFLOW atomizing system (see Fig. 1) is composed of two vessels operated at different pressure levels, a high pressure section "autoclave" 1 containing the melting and pouring system and a low pressure section "spraying tower" 2, separated by a linear de Laval gas nozzle 3. The pressure difference between the two vessels forces the gas to a laminar, accelerated flow through the gas nozzle. A linear melt nozzle 4 converts the melt 5 to a melt film 6 and feeds it into the accelerated laminar gas flow field of the linear deLaval gas nozzle. The film is perfectly stabilized by the gas flowing in parallel.

The atomizing gas accelerates to sonic velocity at the narrowest cross section of the deLaval nozzle, if the pressure ratio  $p_1/p_2$  exceeds the critical pressure ratio of the gas. Kinetic energy is transferred very efficiently to the large surface area deployed by the melt film. In the diverging part of the deLaval nozzle, the melt film is disintegrated into a tent-like spray plume of very small droplets **7** spherical in shape if an inert gas is used, because the melt surface tension minimizes the surface area of the particles. Using nitrogen or argon, mean particle diameters around 10 µm can be achieved with pressures of 2.0 to 2.5 MPa. Finally, the particles cool down and solidify rapidly to a spherical metal powder.



Figure 1. Simplified drawing of the WIDEFLOW linear melt film atomization nozzle system.

Powder particle size distribution is narrower than in conventional gas atomizing, because atomizing conditions are very well defined and constant. However, disintegration remains a statistical process, and its mechanism is far away from being completely understood. Process parameters like gas pressure, gas-to-metal ratio, density and surface tension of the melt, act in the same manner as they do in conventional gas atomization - but at finer particle sizes.

Melt nozzles with round orifices of small diameters are known to be prone to freezing. The WIDEFLOW linear melt nozzle indeed has also a small orifice width, but as the outer surface of the compact melt nozzle block is small in relation to the very high melt throughput, heat balance is kept much easier and the atomization runs pretty safe.

# 3. THE ATOMIZER

Fig. 2 shows a photo with a total view on the pilot plant atomizer. The horizontal cylinder in the first floor is the autoclave head, underneath there is the spraying tower. To the left, the big vertical vessel is a bag dust filter, and to the right there is a cyclone seperating the powder from the gas. Fig. 3 is a schematic plot of the pilot plant atomizer.



Figure 2. Photo of the WIDEFLOW atomizer, before commissioning of platforms, staircases, tubes and electric wiring.

The autoclave head has a front cover lid designed for fast removal. The lid has a weight of 3.500 kg and is held by 48 bolts with a diameter of 48 mm and a length of 350 mm each. The lid can be removed within less than 2 minutes, starting from depressurizing the autoclave. Two rails inside the autoclave carry a lorry with a tiltable melting crucible/induction coil package. After removing the lid cover, the rails can be extended outside the autoclave for exchanging the crucible package. A second lorry loaded with raw metal bars can be moved into the autoclave for an easy recharge of the melting crucible, which is tilted to 90° into the loading position.

The melt level inside the tundish is measured and kept constant by smoothly tilting the melting crucible. Driven by an electric motor connected to a gear unit outside the autoclave, the crucible is moved by a hollow shaft of 220 mm diameter, which carries inside leads for induction power and cooling water for the induction coil.



Figure 3. Schematic plot of the WIDEFLOW pilot plant atomizer.

The off-gas system is designed for a maximum pressure of 13 bars. Operating the off-gas system under overpressure is advantegeous, because cyclone and filter can be build much smaller and the cooling of the powder particles is much more efficient due to the higher gas density.

With much higher Weber numbers at higher gas densities, it can be expected that secondary atomization would grant an additional increase in powder fineness. Finally, the system is explosion proofed to allow the safe production of aluminum powder with oxygen doped atomizing gases, if the off-gas system is operated at ambient pressure. The autoclave head and the spraying tower are water-cooled vessels.

The WIDEFLOW nozzle system is mounted at the intersection of both vessels.

autoclave head max. pressure	2.6 MPa
off-gas system max. pressure	1.3 MPa
induction heating melting crucible	1000/2000 Hz switchable, 270 kW
melting crucible	volume 60 I, approx. 300 kg
1	stainless, tiltable, railed for easy
	exchange and charging
refractory materials	alumina, zirconia, graphite, clay-
	graphite, dolomite, depending on
	melt chemistry; special ceramics on
	request
Tundish	volume up to 8 I
max. atomizing gas throughput	2000 Nm <sup>3</sup> /h
nominal vacuum pump suction rate	400 Nm <sup>3</sup> /h
atomizing gases	N <sub>2</sub> , Ar, O <sub>2</sub> -doped inert gases; He on
	request
gas supply tanks storage capacity	13.700 Nm <sup>3</sup> N <sub>2</sub> ; 8.650 Nm <sup>3</sup> Ar
powder product materials	stainless, HSS, superalloys,
	intermetallics, copper, aluminum,
	magnesium alloys, precious metals,
	RE alloys

Table I. Main Characteristic Data of the WIDEFLOW Pilot Plant Atomizer

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Before each heat, the whole atomizer is evacuated by a large vacuum pump and flushed with the atomizing gas. Apart from two simple testing autoclaves, this pilot plant is the first of its kind and size. Many details were especially designed, and some details are highly innovative.



Figure 4. Particle size distribution 'as atomized' of MIM grade NiAl intermetallic powder 316 L, mean particle diameter  $d_{50}$  = 11 µm, atomized with 25 bars argon, atomizing rate 440 kg/h, specific gas consumption 4 kg Ar/kg NiAl powder.

#### 4. Rapid solidification:

Gas atomized metal powders solidify rapidly. The finer the particle size, the higher is the cooling velocity, as the surface to volume ratio increases. Up to very high temperatures, heat transfer from the small particles to the surrounding gas flow is dominated by convection. Thus, radiation can be neglected, and the cooling velocity can be approximated by

$$\frac{dT}{dt} = -\frac{6h(T_m - T_g)}{\rho \times c_{Pm} \times d_m}$$
(1)

with the droplet temperature  $T_m$ , the gas temperature  $T_g$ , the metal density  $\rho$ , the specific heat capacity of the metal  $c_{pm}$  and the droplet diameter  $d_m$ .

The convective heat transfer coefficient h strongly depends on the nature of the gas flow as well as the particle size, characterised by the Reynolds - number Re, the Prandtl - number Pr and the thermal conductivity of the gas k:

$$h = \frac{k}{d_m} \left( 2 + 0.6 \,\mathrm{Re}^{1/2} \,\mathrm{Pr}^{1/3} \right) \tag{2}$$

Despite the the velocities of the cooling particle and the atomizing gas are changing permanently, a simply assumption of the two extrema of the velocity difference between zero and sonic velocity allows an estimation of the expected range of cooling velocities, as Figure 5 shows. Metallographic determination of secondary dendrite arm spacings have shown cooling velocities of a similar magnitude.



Figure 5. Calculated cooling velocity for an aluminium particle in 0.1 MPa argon atmosphere

For a 10 µm particle, the cooling velocity is about 10<sup>6</sup> K/s in argon or nitrogen, and about 10 times higher in helium. The microstructures of the powder particles are within the nanometer scale, or are featureless, if the material is prone to amorphous solidification. Superior properties can be expected for such materials. Superplastic working requires ultrafine microstructures, too.

# 5. Applications

As high temperature applications often require property combinations which cannot be obtained by using simple metals or alloys, <u>metal matrix composites</u> (MMC's) are promising alternatives. If powder metallurgy is used as production route, powders of the components are blended. In order to obtain a homogeneous mixture and a uniform microstructure after sintering, it would

be advantageous to have powders of similar small size. The dispersed phase is quite often a nonmetallic material like an oxide, carbide, nitride, or silicide, which can be easily produced in small particle sizes. But the metallic matrix powder has quite often a particle size which much is more larger than the composite powder, as it is shown in the upper part of Figure 6. Thus, there is a strong demand for finer, gas atomized metal powders, which would allow more uniform composites (lower part of Figure 6) to be produced.

An example for MMC's recently published are TiC-Ni<sub>3</sub>Al cermets for diesel engine applications (1). Another application are dispersion-hardened platinum refractories for melt nozzles and furnace liners in the glass industry. Intermetallic NiAl powders are high-end binder matrix for diamond and tungsten carbide tools, replacing conventional but toxic and expensive cobalt powder. A special form of MMC's are functionally graded materials (FGM's), which provide a continuous change of the MMC composition from one end of the FGM layer or part to the opposite side.



Figure 6. Metal matrix composites require <u>fine</u> matrix powders

Near net shaping technologies like <u>metal injection molding</u> and <u>foil casting</u>, essentially requiring ultrafine metal powders and spherical powder particles for best results, are upcoming for high temperature applications. Examples are aircraft-engine combustion swirlers and automotive turbocharger wheels (2). Superalloys like F-75 CoCrMo alloys are under development for

MIM processing (3). Cermets can also successfully shaped by the MIM process. Foil casting of FeAl intermetallic powders (4) is a very promising process for the production of thin sheets.

Functional layers for high temperature applications can be coated on cheaper base materials by various <u>thermal spraying</u> processes, most of them using finer and finer powders as raw material. The powder is feeded into a flame which heats up the powder particles, melts down and accelerates them toward the base material, where the droplets splash and form the coating layer. As heating rates and particle acceleration are very sensitive to size, the particle size distribution is restricted within very narrow limits. However, the WIDEFLOW process produces raw powders with narrow particle size distributions, giving a high yield of thermal spraying powders. Popular materials used are MCrAIY, NiCr, Cr, selffluxing alloys and stellites. Without melting the powder, <u>kinetic spray coating</u> is a new way of cold welding particles to the surface, without destroying the particle microstructure. Fine powders are essential for this process, too.

Sputtering Targets are often combinations of metals of very different melting point, and thus powder techniques are often used for their manufacturing. The classic way is pressing and hipping, and thermal spraying is an alternative, which is also employed in reworking used targets. A homogeneous microstructure, which can be favorable achieved by using ultrafine powders, is essential for this application.

# 7. Acknowledgement

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# Spherical Rhenium Metal Powder

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# Summary

The development of a high-density, spherical rhenium powder (*SReP*) possessing excellent flow characteristics has enabled the use of advanced processing techniques for the manufacture of rhenium components. The techniques that were investigated were vacuum plasma spraying (VPS), direct-hot isostatic pressing (D-HIP), and various other traditional powder metallurgy processing methods of forming rhenium powder into near-net shaped components. The principal disadvantages of standard rhenium metal powder (RMP) for advanced consolidation applications include: poor flow characteristics; high oxygen content; and low and varying packing densities. *SReP* will lower costs, reduce processing times, and improve yields when manufacturing powder metallurgy rhenium components. The results of the powder characterization of spherical rhenium powder and the consolidation of the *SReP* are further discussed.

**Keywords:** Rhenium, spherical metal powder, powder metallurgy, vacuum plasma spray, hot isostatic pressing, laser additive manufacturing

# Introduction

Rhenium is one of the last naturally occurring elements to be found, and the discovery occurred in 1925 by Ida Tacke, Walter Noddak and Otto Berg. They named it after Germany's Rhine River. Only a few milligrams of rhenium were produced in 1927, and the first full gram in 1928. It was not until the 1960's that rhenium was produced in a full-scale manufacturing operation (1,2). Rhenium is a heavy transition metal with a melting point of 3453 K, and has the highest modulus of elasticity of all the refractory metals. It does not

form a carbide, even when exposed to methane and graphite at very high temperatures. Further, rhenium also possesses a high electrical resistance across a wide temperature range (2,3). Additionally, powder metallurgy rhenium has consistently provided high yield and ultimate tensile strengths at both ambient and elevated temperatures, while maintaining excellent ductility and exceptional creep qualities as well as the low-cycle fatigue properties required by demanding high-temperature applications (4,5,6,7).

Rhenium metal powder (RMP) is an irregularly shaped flaked powder with poor flow characteristics, and an oxygen concentration of 1000 ppm. The process of manufacturing hydrogen-reduced rhenium metal powder is described in reference 2. Rhenium Alloys, Inc. manufactures a powder metallurgical grade of rhenium that possesses a purity of 99.99%. The –200 mesh RMP has an average particle size of 3.5 um and an apparent density  $1.84 \text{ g/cm}^3$  with a tap density  $3.03 \text{ g/cm}^3$  (Figure 1) (7).

Due the inherent characteristics of rhenium metal powder (RMP), products made from rhenium have only been manufactured in a few basic forms to include: rod; bar; plate; sheet, foil and wire (Figure 2). To produce complex shapes, basic rhenium products are machined to specified dimensions and tolerances. A significant amount of scrap rhenium is created to produce a single complex component. Numerous attempts involving the use of RMP in advanced NNS techniques have met with very limited success (8,9), so a need has risen to exam other, more effective and more efficient means of manufacturing rhenium metal powder.





Figure 1: Rhenium metal powder

Figure 2: Rhenium products, plate, rod, sheet, foil and wire

The next step in rhenium near-net-shape (NNS) manufacturing techniques is to produce the components in large quantities at lower cost, with faster turn-

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around times, while using less material. This can be accomplished through the use of NNS techniques that include: vacuum plasma spraying (VPS); direct-hot isostatic pressing of powder (D-HIP); directed light fabrication (DLF); and metal injection molding (MIM). The enabling technology that promotes the usage of these extremely effective techniques will be the continued development of high density, low oxygen, spherical rhenium powders (*SReP*) in a wide range of particle sizes.

# Procedure:

To produce and develop spherical rhenium powders, Rhenium Alloys Inc. undertook an extensive, in-depth research program, partially funded by a Ballistic Missile Defense Organization (BMDO) Phase I Small Business Innovative Research (SBIR) program. The program's goal was to produce a spherical rhenium powder possessing low-oxygen content with less than 50 ppm. Additional required characteristics included a tap density of 12 g/cm<sup>3</sup> with an apparent density of 11 g/ cm<sup>3</sup>, and a flow rate of 4 second /50grams.

# **Rotating Electrode Process**

The BMDO Phase I goal for this project was to manufacture spherical rhenium powder (*SReP*) by the rotating electrode/plasma rotating electrode process/gas-assisted rotating electrode process (REP/PREP/GA REP)(10,11). This process utilizes a rhenium rod rotating at 15,000 rpm's in an atmosphere of argon, while a high-velocity plasma torch melts the rhenium into droplets. The GA-REP was investigated as a means to reduce the droplet size and can be described as a secondary atomization process (11). Typical particle size for the rotating electrode process is 200-600 micrometers, with bi-modal distribution (11).

To produce *SReP* by rotating electrode/plasma rotating electrode process (REP/PREP/GA-REP), Rhenium Alloys, Inc began with 96 Kg of 16 (30.5 mm), 7 (38 mm), and 4 (50 mm) rhenium rods. These rods were fed into the centrifugal atomizer through a collet and melted down to a length of 60 mm. To evaluate the particle sizes produced by different diameter rhenium rods the powder was individually collected by rod diameter size, and placed into separate containers.

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# **Plasma Atomized Process**

Through a self-funded program, Rhenium Alloys, Inc. created and developed the plasma atomization process (PA) to produce spherical rhenium powder *(SReP)*. During the initial phase of this program a fine particle size of less than 40 micrometers was produced, but a wide range of particle size, ranging from 5-80 micrometer, can also be produced with the PA process (11).

# Advance Consolidation Methods

Two (2) non-traditional methods of producing NNS rhenium objects were examined, as was the traditional die compaction method with the use of *SReP*. The first process investigated was that of vacuum plasma spraying (VPS). VPS is an excellent choice for metals that readily oxidize, and/or have high melting points. Under VPS conditions, the chamber is evacuated and then the chamber is back-filled with argon, or an argon/hydrogen mixture. Thus, by the use of a reducing atmosphere, the plasma will decrease the amount of oxygen present, and increase the heat transfer to the powder. Due to the high heat transfer of the VPS method, the powder is melted and at a high velocity contacts the substrate to form a splats structure that produced a dense coating.

The second method investigated was direct-hot isostatic pressing (D-HIP) (11). In this method, a high-temperature metal container capable of being formed into complex shapes is used as a containment vessel for the powder. The *SReP* can be poured directly into the HIP container. The container is then evacuated and sealed. After HIPing the can is removed from the rhenium part. The high-density and the low-oxygen content of the *SReP* will produces a high quality rhenium parts.

Traditional die-pressing was also examined to help increase our understanding of the properties of *SReP*. Several compactions were produced to examine particle interaction as well as particle size distribution in the compact, and further understand how these compaction parameters influences both the green and sintered densities of the compacts. Predictably, die-compactions of *SReP* were of particular interest, due to the enormous potential for highly complex, high-volume precision parts and components being manufactured by this method.

# Results

# **Rotating Electrode Process**

In all, a total of 96 kilograms of rhenium rods were used during the rotating electrode/plasma-rotating electrode process, and from this 56 Kg of SReP was collected, with the balance being melted rod end pieces, as seen in (figure 3). The desired goals of this phase of the project included; achieving an oxygen content of less than 50 ppm; a tap density of 12.5 g/cm<sup>3</sup> or greater; and the production of spherical rhenium powder particle possessing high flow characteristics. As shown in table 1, the tap, apparent densities and flow data are listed by specific particle sizes. In table 2, image analysis was used to determine particle size vs. the diameter of the starting rod, and as illustrated the larger the diameter of rod, the smaller the diameter of the SReP produced. For the rotating electrode process, the average sizes of particles are: 128 micrometer for the 50mm diameter rod: 161 micrometer for 38mm diameter; and 241 micrometer for the 30mm diameter. In addition, the majority of the SReP was in a 100 to 300 micrometer diameter range, with both the tap and apparent densities being very similar. This is typical for most spherical metal powders.



Figure 3: A melted rhenium rod 50 mm diameter from the Plasma rotating electrode process.



# Table 2: Image analysis of Rotating Electrode Processd SreP by rod diameter

Mesh	Micrometer	Tap Density g/cc	Apparent Density g/cc	Flow sec/50g
+50	300	13.111	12.782	6.244
-50 +100	300-150	13.532	12.4564	4.955
-100 +120	150-125	13.184	12.232	4.968
-120 +140	125-106	13.336	12.191	4.902
-140 +200	106-75	13.514	12.252	4.623
-200 +325	75-45	13.130	12.529	4.123
-325 +400	45-38	13.513	11.845	4.204
-400 +450	38-32	13.144	10.256	4.081
-450 +500	32-25	12.496	10.665	3.985
-500 +635	25-20	12.074	10.485	5.81
-635	-20	12.263	9.169	NF

### Table 1: Characterization of SReP by particle size

### **Plasma Atomized Process**

During the initial phases of the experimentation with plasma atomization of SReP, two experimental powders were produced, type A and type B.

The plasma-atomized spherical rhenium powder had a particle size of 37 micrometers  $\pm 17$  micrometers for type A (figure 4) and 25 micrometers  $\pm 8$  micrometers for type B (figure 5). The apparent density for type A was 10.27 g/cm<sup>3</sup> and for type B 10.37g/cm<sup>3</sup>. The tap density for type A was 11.60g/cm<sup>3</sup> and for type B 12.12 g/cm<sup>3</sup>. These densities are similar to the rotating electrode process illustrated in table 1. In addition, as illustrated in table 1, the smaller the size of the particle the more likely the flow characteristics are reduced. In contrast to the SReP, the traditional rhenium metal powder has an apparent density of 1.84 g/cm<sup>3</sup> and a tap density of 3.03 g/cm<sup>3</sup>, which is significantly less than the SReP.



Figure 4: Type A PA-SReP



Figure 5: Type B PA-SReP

### **Advance Consolidation Methods**

The first experiment conducted was to vacuum plasma spray (VPS) type A. *PA-SReP*. Several experiments were performed to optimize the VPS parameters, deposition rate and density of the rhenium coatings. As shown in figure 6, a flat coupon and a tube were VPS-ed to a maximum thickness of 5mm. In (figure 7) the microstructure of the VPS-ed PA-*SReP* is displayed.



Figure 6: VPS flat coupon and tube



The second experiment conducted involved the direct-hot isostatic press (D-HIP) of the B type *PA-SReP* into a19mm diameter rods. Hot isostatic pressing containers were filled with *SReP*, evacuated, and then sealed (figure 8). A density of 98% was achieved using the D-HIP process for the PA-*SReP*. As shown in (Figure 9), the microstructure of the direct hot isostatic pressed rod had a larger grain size and illustrated final sintering.



Figure 8: D-HIP container, filled and sealed with type B PA-SReP

Figure 9: Microstructure of D-HIP experiment with Type B PA-SReP

The vacuum plasma spraving and hot isostatic pressing of PA-SReP were performed at NASA Glenn Research Center, Cleveland, Ohio, in cooperation with the Great Lakes Industrial Technology Center under a NASA Space Act Agreement funded by Rhenium Alloys, Inc.

Additional experiments with the PA-SReP were performed utilizing traditional die pressing methods, with a two-way die. Several pellets were produced using type A and B powders. The small 20g pellets had an "as-pressed" density of 78% with a pre-sintered density of 85%. The microstructure of the pre-sintered pellet displayed in (figure 10) illustrates the deformation from die compaction of the spherical powder, and some necking of the powder particles after pre-sintering. Further, the sintered pellet achieved a density of 95.5%, with its microstructure showing intermediate sintering properties, as well as a fine grain size (figure 11).



Figure 10: microstructure of pre-sintered pellet



Figure 11: microstructure of sintered pellet

# Discussion

The experiments with REP/PREP/GA-REP produced SReP, but the yields were only 58% and the particle sizes, ranged from 100-300 micrometers in diameter. The size is too large for a majority of NNS applications. The REP-SReP particle size is too large for vacuum plasma spray applications because the residence time in the plasma will not be long enough to melt the large particle. If too large of a particle is used, the coating will either be extremely porous with non-melted powder particles or the powder particles will bounce off the substrate.

Typically, the particle size range for VPS is 10 to 50 micrometers, which is what the plasma atomization process provides, while direct-hot isostatic pressing can use small percentages of the REP *SReP* in bi-modal or multi-particle size blends with the smaller powder from the PA-*SReP*. Again, smaller particle sizes are preferred to produce a high-density (D-HIP) part, but to increase flow a small percentage of larger powder particles can be used.

The larger particle sizes produced by the REP/PREP/GA-REP are excellent for Directed Light Fabrication (9) and Laser Additive Manufacturing (12), which require a particle size of 100 to 300 micrometers. In these processes, a laser melts the rhenium powder to build up a 3-Dimensional rhenium part or component.

The *SReP* from the plasma atomization process is better suited for a majority of the applications for these types of advanced consolidation techniques. The overall cost of PAP-*SReP* is less than that of *SReP* made by the REP/PREP/GA-REP process, the *SRePs'* made by either process has excellent properties that include low oxygen content, high density and flow characteristic of 5 sec/50 grams of powder.

# Conclusion

The REP/PREP/GA-REP processes produce *SReP*, but presently the yields are too low to ensure a successful production environment and economy. Further, the REP-*SReP* has limited uses due to its larger particle sizes. The powder is being used in experiments involving Laser Additive Manufacturing (12), which requires a powder possessing high flow characteristic and particle size range of 100 to 300 micrometers. However, if these experiments prove to be successful, and it is found that the plasma atomization process can not provide powder particles of the sizes required for the and LAM methods, a more economical means of processing rotating electrode process should be developed.

Fortunately, the PA-SReP manufacturing method can be fine-tuned to provide the user with the ideal particle size for the unique and diverse material requirements and process specifications mandated by the various advanced consolidation techniques presently in use today. Further, PA-SReP presents an additional economic benefit in that it is the more effective, more efficient

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and much less costly method for the processing and production of *SReP*, far surpassing the levels achieved by the REP/PREP/GA-REP manufacturing technique.

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# ERZEUGUNG ULTRAFEINER PULVER UND HERSTELLUNG NANOSTRUKTURIERTER SCHICHTEN MIT DEM THERMISCHEN INDUKTIONSPLASMA

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# Summary

The Inductively Coupled Plasma (ICP) at atmospheric pressure is particularly suited for melting and evaporation of materials. The electrodeless ICP can be generated without limitation of the kind of plasma forming gases. Therefore, using an argon-oxygen gas mixture as sheath gas of the ICP nanoparticles can be processed by combustion of metal-organic liquid precursors injected in the hot plasma core. By this way, nanoparticles of alumina, titania and of a perovskite type oxide are produced. The powder particles are collected by an electrostatic filter. They are characterized by a log-normal size distribution with a median diameter of about 10 nm depending on the plasma parameters used. Interesting metastable phases and exactly doped, very pure materials can be obtained. Nanophase coatings synthesized by the ICP are made from the same precursor materials. For depositions, the plasma jet has to lbe supersonic. Impinging onto the substrate placed near the nozzle thin and dense coatings are obtained. The composition and the grain size of as-deposited coatings are analyzed by XRD.

# Keywords:

ultrafine particles, nanophase coatings, RF Inductively Coupled Plasma, thermal plasma processing, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Perovskite

# 1. Einleitung

Nanokristalline (nc-) Werkstoffe bestehen aus Kristallen mit einer Korngröße kleiner als 100 nm in wenigstens einer Dimension. Nanokristalline Werkstoffe werden gebildet aus Metallen, Keramiken, oder aus Kompositen mit kristallinen, quasikristallinen und/oder amorphen Phasen. Die Vorteile solcher nc -Werkstoffe sind hinreichend bekannt [1-3].

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Entsprechend ihrer chemischen Zusammensetzung, ihrer Form und Struktur werden die nc - Werkstoffe eingeteilt in:

(1) nanophasige Pulver,

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- (2) nanostrukturierte Schichten, wozu sowohl Einfach- oder Mehrfachschichten als auch Kompositschichten und Gradientenschichten zu zählen sind.
- (3) monolitische, nanostrukturierte Werkstoffe und
- (4) nanostrukturierte Komposite.

Nanopartikel oder ultrafeine Pulver, bei denen der Partikeldurchmesser meist gleich dem Korndurchmesser ist, zeichnen sich aus durch niedrige Sintertemperaturen, eine höhere Verdichtung (Verdichtung ist invers proportional der vierten Potenz der Partikelgröße [4]), weniger innere Fehlstellen (Poren), höhere Duktilität (durch Diffusionskriechen [5]), und durch optische oder katalytische Wirkungen (durch die große Oberfläche). Daher ist es nicht verwunderlich, dass sich in den letzten Jahren die Forschung verstärkt mit der Herstellung von Nanopulvern, speziell von keramischen Pulvern, beschäftigt hat.

Verschiedene Techniken werden zur Herstellung der Nanopartikel genutzt, seit Gleiter [1] die Inertgaskondensationsmethode erstmals angewendet hat. Dazu gehören neben der Abscheidung aus der Gasphase die naßchemischen Methoden sowie Verfahren aus dem flüssigen/geschmolzenen Zustand oder Feststoffverfahren. Zu Letzterem zählt das zeitaufwendige mechanische Mahlen. Die hiermit hergestellten Pulver sind durch die Mahlmedien teilweise verunreinigt. Für die Herstellung von Kompaktmaterial sind hohe Temperaturen weiterhin erforderlich. Das Verfahren ist auf die Herstellung von Pulvern beschränkt. Schichten können nicht hergestellt werden. Naßchemische verfahren, wie der Sol-Gel – Prozess, hydrothermische oder galvanische Prozesse erfordern eine Vielzahl von Prozess – Schritten, einbezogen die Vorbehandlung, Mischung, Filtration, Trocknung, Kalzinierung.u.a.

Gasphasenprozesse können dagegen sowohl für die Herstellung von Pulvern als auch für die Herstellung von Schichten genutzt werden. Unter den Gasphasenprozessen haben sich vor allem die Hochdruck – Plasma – Verfahren ausgezeichnet [5-7], womit eine viel höhere Erzeugungsrate erreicht werden kann (bis 100 Gramm pro Stunde [8]) als mit dem Vakuum-Inertgaskondensationsverfahren von Birringer [9] oder Chang [10] mit einigen wenigen Gramm pro Stunde.

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Unter den Hochdruck-Plasma-Prozessen ist speziell die Synthese mit dem Hochfrequenz (HF) – Induktionsplasma (IP) eine effektive Methode zur Erzeugung von Nanopartikeln und nanophasigen Schichten, weil

- das HF IP bei Atmosphärendruck sich auszeichnet durch ein großes Volumen, geringe Plasmageschwindigkeit und damit lange Aufenthaltszeiten des Precursors im Plasma.
- die Reaktanten axial in das Plasma mit Temperaturen von ca. 10 kK injiziert werden können, so dass sowohl feste als auch flüssige Precursoren verdampft werden können.
- das elektrodenlose HF IP nahezu frei von Verunreinigungen ist.
- es keine Begrenzung in Bezug auf die Verwendung von Gasart und Werkstoff gibt, bis auf die Ausnahme, dass sie verträglich mit dem Werkstoff der das Plasma einschließenden Rohre sind.
- hohe Quenchraten zu einer hohen Übersättigung oder Unterkühlung führen, die notwendig sind für die Erzeugung von Nanopulvern < 50 nm.</li>

Meist werden die Nanopartikel durch Verdampfung von festen Pulverpartikeln erzeugt, die durch wassergekühlte Förderlanzen direkt in das heiße HF-Plasma injiziert werden [11, 12], dort verdampfen und chemisch mit den das Plasma bildenden Gasen reagieren. Wenn Pulverpartikel als Ausgangsmaterial verwendet werden, sollte deren Größe 4 µm nicht übersteigen, um deren vollständige Verdampfung zu garantieren [13]. Flüssige Precursoren, wie SiCl<sub>4</sub> oder TiCl<sub>4</sub> für die Carbid-Synthese, sind vorzuheizen und zu verdampfen, bevor sie in das Plasma injiziert werden.

Eine vollständige Verdampfung bei Verwendung flüssiger organischer Precursoren ist relativ leicht möglich, wenn sie in feine Aerosole zerstäubt werden. Durch die homogene Verteilung des Precursors in der Lösung sind damit Entmischungsprozesse und Kornwachstum während der chemischen Reaktionen innerhalb des Plasma gering. Die unbedenkliche Verwendung nahezu aller Arten von Gasen im HF – Plasma ermöglicht die Synthese von oxidkeramischen Pulvern. Ein Überschuß von Sauerstoff im Plasma, injiziert zusammen mit Argon im Schutzgas, führt zu einer vollständigen Verbrennung (Oxidation) des Precursors. Über die auf diese Weise synthetisierten oxidkeramischen Aluminiumoxid, Titanoxid und Lanthan-Strontium-Manganat (Perowskit-Typ) - Nano-Pulver und Nano-Schichten und deren Charakterisierung mit XRD und REM wird nachfolgend berichtet. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

# 2. Versuchsanordnung und Versuchsparameter

## 2.1 für die Partikelsynthese

Der Hauptbestandteil der Versuchsanlage (Bild 1) ist das HF-Plasmatron (Bild 2), entwickelt an der TU Ilmenau [14]. Das Plasmatron ist aus konzentrischen Kieselglasrohren aufgebaut, wobei das Plasma durch ein wassergekühltes Kieselglasrohr eingeschlossen wird. In den Spalt zwischen diesem und dem Arbeitsgasrohr wird das Schutzgas tangential eingedüst. Es stabilisiert das Plasma und verhindert Ablagerungen auf dem das Plasma einschließenden Rohr. Das Arbeitsgas wird axial eingebracht. Die Düse am Ende des Plasmatrons besteht aus Bornitrid und dient der Quenchgaszufuhr.

Der wassergekühlte, dreiwindige Induktor mit einem äußeren Durchmesser von 80 mm wird gespeist von einem HF-Generator mit maximaler Anodenleistung von 60 kW mit einer Frequenz von 4,2 MHz.

Die metallorganischen Lösungen werden durch eine Zerstäuberförderlanze axial in das Plasma injiziert. Als Zerstäubergas wird Argon verwendet. Für die Herstellung der Nanopartikel wird reines Argon als Arbeitsgas und als Schutzgas verwendet. Letzterem wird Sauerstoff mit einem Überschuß als für die vollständige Verbrennung notwendigen Verhältnis zugemischt. Der Volumendurchsatz der jeweiligen Gase für einzelne Versuchsreihen ist in Tabelle 1 angegeben.

	Aluminiumoxid	Titanoxid	Perowskit
Versuchsnummer	19	37	34
Generatorleistung [kW]	22,4	19	19,6
Gasdurchsatz Arbeitsgas Argon [slpm]	15,4	16,3	16,3
Schutzgas Argon [slpm]	15,8	21	21
Sauerstoff [slpm]	16	16.3	16.3
Quenchgas Sauerstoff [slpm]	16,6		16,6
Zerstäubergas Argon[slpm]	4,9	5,4	5,0
Precursor-Förderrate [mlpm]	10,0	12,0	10,0
Precursor	Al-sec-	Ti(IV)-	La/Co/Mn/Sr-
	butoxid	isopropoxid	azetat
Lösung	Isopropanol	Isopropanol	wässrige
			Essigsäure

Tabelle 1: Verwendete Parameter für die Nanaopartikelsynthese

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Als Quenchgas wird Sauerstoff wegen der höheren Wärmeleitfähigkeit gegenüber Argon verwendet. Gleichzeitig wird damit die vollständige Verbrennung des Precursors abgesichert. Die Gasdurchsätze für das Quenchgas sind ebenfalls in Tabelle 1 angegeben.



Bild 1: Bild der Versuchsanlage mit Plasmastrahl vor der Filteröffnung

Bild 2: Verwendetes HF-Plasmatron

Für die Sammlung der Nanopartikel wird der aus der Düse in die Atmosphäre austretende Plasmastrahl in ein elektrostatisches Filter weitergeleitet, wie im Bild 1 zu sehen. Für das Filter wird eine koaxiale Elektrodenanordnung bei einer angelegten Spannung von  $U_B = 22kV$  verwendet, mit einem Draht als Hochspannungselektrode. Die Pulver werden im Feld aufgeladen und zur Außenwand des Filters transportiert, wo sie sich abscheiden. Das Rohr ist ca. 4 m lang. Dadurch ist garantiert, dass alle Pulverteilchen an der Rohrwand abgeschieden werden. 15' International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

# 2.2 für die Schichterzeugung

Das im Bild 2 gezeigte HF-Plasmatron wird auch für die Schichtherstellung verwendet, jedoch mit einer veränderten Düsengeometrie. Das Plasmatron wird an einen Reaktor angeflanscht. Durch eine Düse mit dem Innendurchmesser von 5 mm strömt das Plasma aus dem Plasmatron mit einem Druck von ca. 800 mbar in den Reaktor mit einem Druck von ca. 100 mbar. Durch die Druckdifferenz erreicht der durch die Düse ausstömende Plasmastrahl Überschallgeschwindigkeit (Bild 3).



Bild 3: Plasmastrahl im Reaktor (# 512) mit Titan-Isopropoxid



Bild 4: Substrat im Plasmastrahl (#512)

Durch die veränderten Druckbedingungen ergeben sich leicht geänderte Parameter für die Einstellung der Gasflüsse und damit der HF-Generator-Leistung gegenüber denen bei der Partikelsynthese, wie aus Tabelle 2 für zwei Versuchsreihen ersichtlich ist.

Der Precursor, injiziert wie im Punkt 2.1 beschrieben, wird im Plasma verdampft, ionisiert und reagiert dort unter Bildung von Oxiden. Bereits in der Düse kommt es zur Partikelbildung. Nur bei Überschallgeschwindigkeit und einer bestimmten Partikelgröße können die Pulver auf dem Substrat auftreffen und eine Schicht bilden. Da die Strahlgeschwindigkeit außerhalb der Düse durch die Expansion in den Reaktor stark abnimmt, muß das Substrat möglichst in einen geringen Abstand gebracht werden. (Bild 4).

Als Substrat wird Stahl oder Molybdän verwendet. Entsprechend den Gesetzen bei der Gasphasenabscheidung [15], [16] werden Substrattemperaturen eingestellt, die im Bereich des 0,3 - bis 0,5 - fachen der Schmelztemperatur des Schichtwerkstoffes liegen. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

	Titanoxid	Perowskit		
Versuchsnummer	537	556		
Generatorleistung [kW]	28,8	28,6		
Gasdurchsatz Arbeitsgas Argon [slpm]	2	2		
Schutzgas Argon [slpm]	36	36		
Sauerstoff [slpm]	10	10		
Quenchgas Sauerstoff [slpm]				
Zerstäubergas Argon[slpm]	1	1		
Precursor-Förderrate [mlpm]	2,0	2,0		
Beschichtungszeit	60 s	30 s		
Substrat-Temperatur	570°C	520°C		
Druck im Plasmatron	746 mbar	673		
Druck im Reaktor	131 mbar	126 mbar		

Tabelle 2: Parameter für die Schichterzeugung

Die Einstellung der Substrattemperatur erfolgt durch eine Basis-Wasserkühlung und zusätzlicher Regelmöglichkeit durch eine kombinierte Argon-Helium-Gaskühlung unmittelbar an der Substrat-Rückseite. Diese von Girshick [17] bereits für die Diamantsynthese verwendete und erprobte Anordnung wird für unsere Belange modifiziert. Das Prinzip ist im Bild 5 schematisch dargestellt. Dabei wird die um den Faktor 10 größere Wärmeleitung des Helium ausgenutzt. Durch geeignete Wahl des Werkstoffes von



Bild 5: Schema der Substrattemperatur - Regelung

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Zwischenschichten, die zwischen den Kupferträger und das Substrat, versehen mit Kühlkanälen, eingesetzt werden, kann prinzipiell jede gewünschte Substrattemperatur eingestellt und geregelt werden.

# 2.3 Werkstoffsynthese

Folgende chemische Reaktionen laufen im Gas ab:

 Titanoxid – Synthese  $TiO_2$  12 CO<sub>2</sub> + 14H<sub>2</sub>O  $Ti(OC_3H_7)_4 + 18O_2 \rightarrow$ 3 CO<sub>2</sub> +  $C_3H_7OH + 4\frac{1}{2}O_2 \rightarrow$  $4 H_2O$ • Aluminiumoxid – Synthese:  $2 \operatorname{Al}(\operatorname{OC}_4\operatorname{H}_9)_3 + 36 \operatorname{O}_2$  $AI_2O_3$  24  $CO_2$  + 27 H<sub>2</sub>O  $\rightarrow$ 3 CO<sub>2</sub> +  $C_3H_7OH + 4\frac{1}{2}O_2$  $4 H_2O$  $\rightarrow$  Perowskit – Synthese:  $(1-x) La(CH_3COO)_3 + x Sr(CH_3COO)_2 + (1-y) Co(CH_3COO)_2 +$  $y Mn(CH_3COO)_2 + (10,25-2x) O_2$  $\rightarrow$  $La_{1-x}Sr_{x}Co_{1-v}Mn_{v}O_{3-\delta} + (10-2x)CO_{2} + (7,5-1,5x)H_{2}O_{3-\delta}$ 

 $2 CO_2 + 2 H_2O$ CH<sub>3</sub>COOH +  $2 H_2 O \rightarrow$ 

#### 3. Ergebnisse der Partikelsynthese

Die im elektrostatischen Filter aufgefangenen Pulver werden für das Transmissionselektronenmikroskop (TEM) präpariert. Als Beispiel für die erhaltenen Pulver werden die Bilder von dem Perowskit-Typ (Bild 6) und von Titanoxid (Bild 7) gezeigt.

Wie zu erkennen, sind die Pulver mit Quenchgas kleiner. Die Verringerung des mittleren Partikel-Durchmessers beträgt 5 – 10 nm. Die Pulver zeigen nur eine geringe Neigung zur Agglomeration.

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Bild 6: TEM – Bilder von Perowskit – Pulverteilchen, links mit und rechts ohne Quenchgas synthetisiert



Bild 7: TEM – Bilder von Titanoxid – Pulverteilchen, links mit und rechts ohne Quenchgas synthetisiert

Aus den TEM-Bildern wird die Größenverteilung mit einer Klassifizierungsbreite  $\Delta$  = 5 nm ermittelt. Für die Versuchsparameter von Tabelle 1 sind die für die jeweiligen Versuchsnummern erhaltenen Verteilungen im Bild 8 dargestellt. 106

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Bild 8: Partikelgrößenverteilung für zwei Werkstoffe (mit Quenchgas)

Die Größenverteilung kann durch die Log-Normalverteilung (LNDF), die in die jeweiligen Diagramme eingezeichnet ist, mit einer Standardabweichung < 3 nachgebildet werden. Der aus der LNDF ermittelte mittlere Partikeldurchmesser ist in Tabelle 3 angegeben. Aus der L-N<sub>2</sub> – Adsorption wird die BET-Fläche bestimmt, aus der eine mittlere Korngröße ermittelt wird. Die daraus ermittelte Korngröße stimmt mit der aus den TEM-Bildern bestimmten überein, so dass der Korndurchmesser gleich dem Partikeldurchmesser gesetzt werden kann.

run #	Pulver	Modifikation	Größe [nm] (LNDF)	Größe [nm] (BET)	Fläche [m²/g] (BET)
19	Al <sub>2</sub> O <sub>3</sub>	$\gamma$ und $\delta$	$16 \sigma = 2.75$	27	57
37	TiO <sub>2</sub>	Anatas und Rutil(<10%)	13 σ = 2,5	18	88
34	Perowskit	La <sub>x</sub> Sr <sub>1-x</sub> Co <sub>y</sub> Mn <sub>1-y</sub> Oxid	10 σ = 1,85	14	85

Tabelle 3: Partikeldurchmesser einzelner Versuchsreihen

Die rasche Abkühlung durch das Quenchgas führt zu metastabilen Phasen in der Zusammensetzung der Nanopartikel, wie in Tabelle 3 vermerkt. So besteht das Titanoxid zu über 90 % aus Anatas, die thermodynamisch stabile Rutil-Phase ist nur mit einem Anteil kleiner 10% in den Titanoxidpulvern der verschiedenen Versuchsreihen enthalten.

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#### 4. Ergebnisse der Schichtabscheidung 4.1 Aufprall - Verhalten

Die Schichtbildung mit Partikeln kleiner 1  $\mu$ m ist stark abhängig davon, inwieweit die Partikel durch ihre Trägheit durch den *Bow Shock* hindurch auf das Substrat auftreffen oder den Strömungslinien folgen und umgelenkt werden, wie im Bild 11 schematisch dargestellt.



Bild 11: Partikelverhalten in der Schockschicht

Deshalb ist eine Mindestgröße der Partikel erforderlich, für die die Trägheitskraft größer ist als die Reibungskraft. Die dimensionslose *Stokes* – Zahl als Verhältnis dieser Kräfte ist ein Maß dafür, ob das Partikel die Schockschicht durchdringen kann oder umgelenkt wird. Die Stokes-Zahl in der Form

$$\mathbf{St} = \frac{\mathbf{L}_{stop}}{\mathbf{D}_{bow}} \tag{1}$$

mit L<sub>stop</sub> = Trägkeitsweg, D<sub>bow</sub> = Bow – Schock - Dicke

gibt an das Verhältnis des durch die Trägheit in der ursprünglichen Richtung der Strömung zurückgelegten Weges zu einer charakteristischen Länge bei Änderung der Strömungsbedingungen, die hier gleich der Dicke der Bow-Schock-Schicht gesetzt wird. Für **St** >> **1** überwiegen die Trägheitskräfte, das Partikel fliegt in der ursprünglichen Richtung weiter. Es kann mit einem Partikelaufprall und damit mit einer Deposition auf dem Substrat gerechnet werden. Für **St** << **1** folgen die Partikel strikt den Strömungslinien und werden folglich mit der Strömung umgelenkt und gelangen nicht bis zum Substrat.

Eine Abschätzung des Verhaltens der Partikel erfolgt in Analogie zum Verhalten von Aerosolen [18], [19] beim Auftreffen auf senkrecht zur Strömung

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gestellte Platten. Danach ergibt sich der Trägheitsweg aus der Partikelgeschwindigkeit  $v_p$  und der Relaxationszeit  $\tau$ , der Zeit, die ein Partikel benötigt, sich auf Änderungen der Strömungsbedingungen einzustellen:

$$St = \frac{v_p \cdot \tau}{D_{bow}}$$
(2)

mit 
$$\tau = \frac{\rho_{\mathbf{p}} \cdot \mathbf{d_{p}}^2 \cdot \mathbf{C_{slip}}}{18 \cdot \eta_{gas}}$$
 [18, Eq. 5-3] (3)

 $\rho_p$  – Partikeldichte, d<sub>p</sub> – Partikeldurchmesser,  $\eta_{gas}$  – Viskosität des Gases mit und mit

$$\mathbf{C}_{\mathsf{slip}} = 1 + \frac{1}{\mathbf{P} \cdot \mathbf{d}_{p}} \left( 15,60 + 7,00 \cdot \exp\left(-0,59 \,\mathbf{P} \cdot \mathbf{d}_{p}\right) \right)$$
(4)

dem Schlupf - Korrekturfaktor nach [18, Eq. 3-22], P - Druck

Mit dem Schlupfkorrekturfaktor C<sub>slip</sub> wird der Tatsache Rechnung getragen wird, dass Partikel kleiner 0,1 µm, abhängig vom Druck P und damit der mittleren freien Weglänge, nicht mehr so stark an die Strömung gekoppelt sind wie nach dem Stokes - Gesetz angenommen wird.

Ausgehend von diesen Gleichungen sollten alle Partikel mit einer Partikelgröße von

d<sub>n</sub> > 30 nm

auf dem Substrat auftreffen.

Sind diese Partikel einmal auf der Oberfläche des Substrates, haften sie trotz hoher Geschwindigkeit des Plasmastrahls [18], da die Adhäsionskräfte größer sind als die Strömungskräfte. Der Grund dafür ist, dass die Adhäsionskräfte, wie die van-der-Waalschen Kräfte, die elektrostatischen Kräfte und auch die Kräfte, die durch die Oberflächenspannung bedingt sind, nur proportional dem Partikeldurchmesser sind. Im Gegensatz dazu ist die Strömungskraft des Plasmastrahls - entsprechend der Bernoulli-Gleichung - dem Quadrat des Partikeldurchmessers proportional. Bei Pulvergrößen im Nanometerbereich überwiegen daher die Adhäsionskräfte, wie aus Tabelle 4 zu entnehmen. Für die Abschätzung wird ein Argonstrahl mit einer Geschwindigkeit von 1000 m/s bei einer Temperatur von 2000K angenommen.

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Tabelle 4: Kräfte auf ein Partikel am Substrat			
Durchmesser [nm]	Adhäsionskraft [N]	Plasmaströmung [N]	
100	10 <sup>-8</sup>	1x10 <sup>-9</sup>	
45	5x10 <sup>-9</sup>	2x10 <sup>-10</sup>	
10	10 <sup>-9</sup>	1x10 <sup>-11</sup>	

#### 4.2 Schichtherstellung

Mit dem im Bild 4 gezeigten Abstand Düse – Substrat von ca. 15 mm werden Pulverpartikel auf dem Substrat abgeschieden, aber es werden keine kompakten Schichten erzeugt, wie die Beispiele im Bild 12 zeigen.



Bild 12: REM-Aufnahme (links) und TEM-Aufnahme (rechts) des agglomerierten Pulvers

Sowohl für die REM – als auch für die TEM - Aufnahmen wird das nano-TiO<sub>2</sub>-Pulver mit Alkohol gemischt und mit einem Ultraschallzerstäuber auf ein Carbon-Gitter gesprüht. Aus den TEM-Aufnahmen kann die Größe der Primärpartikel mit 5 bis 50 nm abgeschätzt werden.

Aus XRD – Diagammen wird nach der bekannten Scherrer – Gleichung für die agglomerierten Pulver bei Titanoxid eine Korngröße von ca. 20nm ermittelt.

Um kompakte Schichten zu erhalten, darf der Abstand Düse – Substrat nicht größer als der halbe Durchmesser der Düsenöffnung gewählt werden. Ansonsten sind die Aufprallbedingungen für die Partikel nicht erfüllt. Der Ab-

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stand Düse - Substrat wird daher mit einer Entfernung von ca. 3mm so klein wie praktisch möglich eingestellt. Damit befindet sich das Substrat innerhalb des ersten Schock-Knotens, wo die Geschwindigkeitsabfall des Strahls noch gering ist. Unter diesen Bedingungen werden kompakte dünne, nanokristalline Schichten erhalten, wie an Hand der Bruchkanten im Bild 14 zu sehen ist.



Bild 14: Bruchkanten der erhaltenen Schichten

Die Schichtdicke sollte jedoch 25µm nicht übersteigen, um zu vermeiden, dass die inneren Spannungen zu groß werden, die Schichten reißen und abplatzen. Die Beschichtungszeit für die 25µm dicke Schicht liegt bei 30 s. Die beschichtete Fläche entspricht dem Düsendurchmesser. Für größere Flächen ist eine x-v-Bewegung des Substrates notwendig. Mit der vorhandenen Anlage konnten nur Spuren erzeugt werden.

Die aus XRD-Diagrammen ermittelte mittlere Korngröße der Schicht beträgt 42 nm. Das entspricht der nach dem Stokes-Kriterium ermittelten minimalen Größe von 32 nm für den Partikelaufprall. Die Korngröße ist doppelt so groß wie die auf dem Substrat aufgefangenen Pulveragglomerate und 4 mal größer als die im elektrostatischen Filter aufgefangenen Pulver.

Die Zusammensetzung im Fall von Titanoxid entspricht im Wesentlichen der Rutil-Phase. Nur ein geringer Anteil Anatas ist zu verzeichnen, da die Abkühlraten der Teilchen auf dem Substrat bei den verwendeten Substrattemperaturen im Bereich von 400 - 800 °C wesentlich geringer sind als bei der Pulverherstellung mit zusätzlichem Quenchgas.

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## 5. Schlußfolgerungen

Es konnte eindeutig gezeigt werden, dass das hier verwendete HF-Induktionsplasma sich hervorragend eignet für die Herstellung sowohl von Nanopulvern als auch von nanokristallinen Schichten. Die aus flüssigen Precursoren hergestellten Pulver hatten eine mittlere Korngröße von ca. 10nm. Die Kristallitgröße der Schichten lag mit 42nm nur unwesentlich über der Pulvergröße. Die XRD-Analysen ergeben für die TiO<sub>2</sub> - Schichten einen hohen Anteil an Rutil. Dagegen im Pulver überwiegt der Anatas-Anteil. Weitere Untersuchungen zur Mikrohärte, Haftfestigkeit und Rauheit der Schichten werden noch folgen.

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# PULVERBEHANDLUNG UND SPHÄROIDISIERUNG MIT DEM THERMISCHEN INDUKTIONSPLASMA

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### Summary:

Processing of advanced powder materials for the spraying industry is one of the most promising applications of the thermal RF inductively coupled plasma. By selecting the feedstock carefully and adjusting the RF plasma parameters, unique materials with high quality can be achieved. Powders injected in the hot plasma core emerge with modified shapes, morphology, crystal structure and chemical composition. Ceramic oxide powders such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub> are spheroidized with a high spheroidization rate. By using the RF induction plasma spheroidization rate at high feeding rates by densification of agglomerated powders consisting of di-tungsten carbide and monocarbide with a definite composition. This kind of ball-like powders is particularly suited for wear resistent applications.

### Keywords:

RF plasma, inductively coupled plasma, thermal plasma processing, spheroidizing,  $Al_2O_3$ ,  $SiO_2$ , WC-W<sub>2</sub>C,

# 1. Einleitung

Sphärische Pulver werden heute wegen ihrer großen Vorteile vielfach in der Praxis eingesetzt: Das Erreichen höherer Schüttdichten macht sie geeignet als Füllstoffe, z.B. für Fritten, Filter und poröse Keramik. Kugelige Hartmetallpulver zeigen bessere Verschleißeigenschaften als gebrochenes Material. In der Thermischen Spritztechnik werden sie verwendet wegen der besseren Rieselfähigkeit als spratzige bzw. gebrochene Pulver [1-4].

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Die Herstellung sphärischer Partikel erfolgt meist durch Schmelzenverdüsen, mit Gas oder Wasser, wobei die Kornfraktion stark variiert und ein Anteil an spratzigen Pulvern vorhanden ist [3]. Diese Pulver können in einem thermischen Plasma nachbehandelt und nahezu vollständig sphäroidisiert werden. Das thermische Plasma ist für diesen Prozess wegen seiner hohen Energiedichte besonders gut geeignet. Prinzipiell ist dies mit einem Gleichstrom-Plasmatron möglich [5]. Bereits in [6] wird jedoch darauf hingewiesen, dass das elektrodenlose Induktionsplasma Vorteile für die Pulverbehandlung bietet.

Folglich wird von den thermischen Plasmen vor allem das Hochfrequenz-Induktionplasma für die Pulverbehandlung eingesetzt, nicht nur wegen der Elektrodenfreiheit, sondern auch wegen seines großen Volumens, der geringen Strömungsgeschwindigkeit und der Möglichkeit, Pulver axial in das Plasma zu injizieren. Das große Plasmavolumen und die durch die Injektion und Strömung bedingten langen Pulveraufenthaltszeiten im heißen Plasmakern ermöglichen es, Pulverwerkstoffe auch mit hohem Schmelzpunkt und / oder relativ großem Durchmesser zu behandeln, zu verdichten und zu sphäroidisieren. Durch Wahl geeigneter Plasmaparameter, Einschuß- und Quenchbedingungen der Pulverteilchen können diese Pulvermodifizierungen mit chemischen Reaktionen und / oder Phasenumwandlungen ablaufen. So besteht die Möglichkeit, durch Verdampfen und anschließendes Quenchen [8] oder durch chemische Reaktion flüssiger Precursoren mit dem Arbeitsgas nanoskalige, sphärische Partikel im Plasma zu erzeugen [9],[10], gebrochene, spratzige oder aus Agglomeraten bestehendes Ausgangspulver zu kompakten Sphäroiden umzuschmelzen [7]. Nachfolgend wird über Ergebnisse der Sphärojdisjerung von verschiedenen oxidischen Pulvern (Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>) und der Herstellung von Wolframschmelzkarbid-Pulvern als Funktion der Arbeitsparameter berichtet. Mit Hilfe der optischen und der Elektronenmikroskopie wird die Morphologie bestimmt. Die Phasenzusammensetzung wird mit Hilfe der Röntgendiffraktometrie ermittelt.

#### 2. Experimentelle Anordnung

Der für die Pulverbehandlung verwendete Versuchsaufbau (Bild 1) besteht aus einem Pulverauffangbehälter, dem Reaktor, dem HF-Plasmatron, der Pulverförderlanze und dem Pulverfördergerät (MC-2, Medicoat AG, Mägenwil, CH), das unmittelbar oberhalb der Förderlanze positioniert ist. Das Schema des ver15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

wendeten Plasmatrons, entwickelt an der TU Ilmenau, ist ebenfalls im Bild 1 dargestellt.

Es besteht aus dem wassergekühlten, 6-windigen Induktor und konzentrisch angeordneten Rohren für das Hüllgas und das Arbeitsgas. Wie für TU Ilmenau HF-Plasmatrons üblich, werden Kieselglasrohre für beide Rohre verwendet, sowohl für das Hüllgas- als auch für das Arbeitsgasrohr. Die Pulverförderlanze steht bis zum Ende der ersten Induktorwindung zentrisch im Plasmatron und damit direkt im heißen Plasmakern. Das Pulver wird zusammen mit einem Trägergas injiziert. Durch den Flansch wird das Plasmatron mit dem Reaktor verbunden. Zusätzlich kann durch die Düse am Flansch Quenchgas injiziert werden. Das Plasmatron wird von einem HF-Generator mit maximaler Ausgangsleistung von 25 kW (IG 25/4000 der Fa. Hüttinger, Freiburg, ) bei einer Freuquenz von 3,5 MHz gespeist.



Bild 1: Experimentier-Anlage zur Pulvermodifizierung mit Schema des Plasmatrons

Pulverförderlanze

Arbeitsgæsrohr Induktor

Hülcasoh

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Es werden zwei verschiedene Größen des Plasmatrons verwendet. In Tabelle 1 sind die Standard-Parameter für beide Plasmatrons (Type Willi) angegeben.

Parameter	Plasmatron 1	Plasmatron 2
Induktordurchmesser	36 mm	47 mm
Generatorleistung	12 kW	20 kW
Arbeitsgasdurchsatz	6,5 NI/min	30 Nl/min
Hüllgasdurchsatz Argon	35 Nl/min	45 Nl/min
Hüllgasdurchsatz Stickstoff	0 – 6 Nl/min	0 - 6 NI/min
Trägergasdurchsatz Argon	2 sipm	2 slpm

Tabollo 1: Standard – Parameter für die verwondeten Plasmetrons

#### 3. Sphäroidisierung oxidischer Pulver

Die Sphäroidisierung von oxidischen Pulvern erfolgt unter Atmosphärendruck mit Plasmatron 1, nur mit Pulverauffangbehälter, ohne Reaktor. Die chemische Zusammensetzung wird beim Umschmelzen bei atmosphärischen Bedingungen nicht geändert. Aluminiumoxid-Pulver, das für das thermische Spritzen verwendet wird, ist fast ausschließlich gebrochener Korund. Dieses Pulver ist das Ausgangspulver für die Sphäroidisierung. Neben der thermodynamisch stabilen  $\alpha$  - Phase des Korund besitzt Aluminiumoxid noch mehrere metastabile Phasen (Bild 2), die sich bei der Plasmabehandlung durch unterschiedliche Abkühlraten infolge der schnelleren Gitterdiffusion der Sauerstoffionen gegenüber den Aluminiumionen bilden können.

Die Phasenumwandlungen sind bei allen herkömmlichen Spritzverfahren durch die rasche Abkühlung der Partikel beim Aufprall auf das Substrat nicht zu umgehen [11-13], ausgenommen das Induktionsplasmaspritzen bei Atmosphärendruck [15], [16]. Wie die Tabelle 2 zeigt, sind Phasenumwandlungen mit Eigenschaftsänderungen verbunden [14]. Deshalb wird beim konventionellen Thermischen Spritzen zur Stabilisation dieser Phasen eine zweite Komponente mitgespritzt, z.B. TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> u.a. [12].

Lange Aufenthaltszeiten des Pulvers im Plasma des HF-Plasmatrons ermöglichen die Sphäroidisierung relativ großer Pulverteilchen verglichen mit anderen Verfahren. Damit sind die Abkühlraten geringer, so dass sich die  $\alpha$ -Phase bilden 15° International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

kann und die Entstehung metastabiler Phasen unterbleibt. Dies wird durch Röntgendiffraktometrie (XRD) für alle sphäroidisierten Al<sub>2</sub>O<sub>3</sub>-Pulver bestätigt.



#### Bild 2: Bedeutung der Abkühlgeschwindigkeit für die Entstehung unterschiedlicher Kristallmodifikationen bei Aluminiumoxid

	Einheit	Alpha	Delta	Gamma	Schmelze
Struktur	-	trigonal	tetragonal	kubisch	-
Dichte	kg/m <sup>3</sup>	4000	3800	3600	2900
spezifische Wärme	J/kg K	1363	1402	1425	1888
Schmelztemperatur	K	2327	2308	2289	
Schmelzwärme	kJ/kg	1090	915	770	
Linearer kinetischer	mm/s K	2,47	2,11	1,80	
Koeffizient				1	

Tabelle 2: Eigenschaften von Al<sub>2</sub>O<sub>3</sub> – Phasen

Der Sphäroidisierungsgrad - gemittelt aus 5 Zählungen - wird bestimmt aus dem Verhältnis der Anzahl der sphärischen Teilchen zur Gesamtzahl der Teilchen in einem Flächenelement, wie im Bild 3b. Bild 3a zeigt die Morphologie des Ausgangspulvers.

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Bild 3: Al<sub>2</sub>O<sub>3</sub>-Pulver vor (a) und nach (b) der Plasmabehandlung, (c) REM-Aufnahme von (b)

Der ermittelte Sphäroidisierungsgrad als Funktion der Förderrate für Aluminiumoxid mit Plasmatron1 ist im Bild 4 gezeigt. Wie erwartet, sinkt bei konstanten Plasmaparametern mit zunehmendem Pulverdurchsatz die Sphäroidisierungsrate. Die Pulver kühlen das Plasma zunehmend ab, so dass seine Energie nicht mehr zum Schmelzen der Pulver ausreicht, bekannt als loading effect (z.B.[17]).





Mit Erhöhung des Volumenstromes des Trägergases und damit auch der Pulvergeschwindigkeit und somit der Reduzierung der Aufenthaltsdauer der Pulver im Plasma nimmt der Sphäroidisierungsgrad deutlich ab. Bei einem dreifachen Gasdurchsatzes des Trägergas wird nur noch ein Sphäroidisierungsgrad von 35% erhalten.

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Außerdem beeinflußt die Korngröße die Flugbahn der Pulverpartikel durch das Plasma. Kleinere Partikel folgen den Strömungslinien mehr, die größeren fliegen auf Grund ihrer Trägheit in der ursprünglichen Injektionsrichtung weiter. So ergeben sich unterschiedliche Oberflächenmorphologien der Partikel infolge unterschiedlicher Aufheiz- und Abkühlbedingungen, wie im Bild 3c zu sehen ist. Die dendritische Struktur bildet sich bei langsamem Abkühlen aus, während sich glatte Strukturen durch rasche Abkühlung bilden. Die relativ großen Pulverpartikel kühlen sich langsam ab. Durch die dendritische Struktur können jedoch das Fließverhalten und u. U. die Benetzungsfähigkeit des Pulvers beeinträchtigt werden.

Eine Vergrößerung der aktiven Oberfläche zur Sensibilisierung, wie beispielsweise für das **Spezialglas** - Pulver in Bild 5, kann durch eine Sphäroidisierung von großen Pulverkörnungen, im vorliegenden Fall 45 µm, mit einer gleichzeitigen Co - Verdampfung von kleinen (<2 µm) Pulvern im HF-Induktionsplasma erreicht werden. Das verdampfte Material kondensiert an den Pulvern und vergrößert so die Oberfläche.



Bild 5: Sphäroidisierung mit Co-Verdampfung von Spezialglas-Pulver

Der Sphäroidiserungsgrad für **Yttrium-stabilisiertes Zirkonoxid (YSZ)** liegt bei Verwendung gleicher Plasmaparameter niedriger als beim Aluminiumoxid (Bild 6). Wegen des höheren Schmelzpunktes und der niedrigeren Wärmeleitfähigkeit benötigen diese Pulver längere Aufenthaltszeiten im Plasma, um ausreichend aufgeschmolzen zu werden.

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Bild 6: Sphäroidisierungsgrad für YSZ – Pulver mit den Parametern für Plasmatron 1 als Funktion der Förderrate mit der Korngröße als Parameter

Bei konstanten Plasmaparametern ergibt sich für jedes Pulver eine optimale Korngröße, mit der die höchsten Sphäroidisierungsraten (Anzahl sphärischer Teilchen pro Zeiteinheit) erreicht werden. Im Fall YSZ ist es die Fraktion von 80 –100 µm. Nachteilig beim Plasmabehandeln von YSZ ist, bedingt durch die physikalischen Eigenschaften, wie die geringe Wärmeleitfähigkeit und die Anlagerung von Gasatomen/-ionen während des Durchganges durch das Plasma, das Auftreten von Hohlkugeln (Bild 7c). Beim Plasmaspritzen solcher Pulver ist mit einem erhöhten Porengehalt zu rechnen.



Bild 7: Sphäroidisierung von YSZ, (a) Ausgangspupver, (b) sphäroidisiertes Pulver, (c) Querschliff

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#### 4. Herstellung von kugeligem Wolframschmelzkarbid – Pulver 4.1 Ausgangswerkstoffe

Wolframkarbid gehört zu der Gruppe der Hartmetalle. Aus dem ursprünglich kubisch-raumzentrierten Wolfram-Gitter wird durch Besetzung der Oktaederlücken bei der Einlagerung der Kohlenstoffatome bei Wolfram-Monokarbid (WC) die einfache hexagonale Packung und bei dem Di-Wolframkarbid (W<sub>2</sub>C) die hexagonal dichteste Packung (Bild 8):



Bild 8: Wolframkarbid-Gitter, links: WC, rechts: W2C

Beide Verbindungen sind thermodynamisch stabil. Das W<sub>2</sub>C existiert in der  $\alpha$ -, $\beta$ und  $\gamma$ -Phase.  $\alpha$ -WC<sub>1-x</sub> ist kubisch flächenzentriert und hat einen großen Homogenitätsbereich. Dagegen existiert das WC nur bei einer Kohlenstoffkonzentration von 6,16 Gew.% (= 50At%). Von technischem Interesse ist besonders das **Wolfram-Schmelzkarbid (WSC)**, das aus einem Gemisch von W<sub>2</sub>C und WC mit einer Kohlenstoffkonzentration von 3,8 – 4,3 Gew.% besteht, wobei das härtere W<sub>2</sub>C in die weichere WC-Matrix eingebettet ist. Kugeliges WSC – Pulver verbessert die bekannt guten Eigenschaften des Hartmetalls gegen Verschleiß im Vergleich zum spratzigen Schmelzkarbidpulver beträchtlich.

Die zur Zeit bekannten Herstellungstechnologien liefern noch keine zufriedenstellenden Ergebnisse in dem gewünschten Korngrößenbereich (40 - 150 µm). Die Verwendung des HF-Induktionsplasmas erweist sich auch hierfür von großem Vorteil [7],[18]. Bei dem Induktionsplasma (ICP) - Prozess für die Herstellung von kugeligem WSC wird ein sprühgetrocknetes Ausgangsmaterial verwendet, das im Plasma chemisch reagiert und verdichtet wird. Das Ausgangsmaterial, bestehend aus W und WC mit einer Korngröße von 2 µm, wird zusammen mit dem Binder sprühgetrocknet und agglomeriert. Der Hohlraumanteil

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beträgt ca. 50%. Der geringe Zusammenhalt durch den Binder erschwert die Förderung des Pulvers bis in das Plasma. Für den Plasmabehandlungsprozess wird eine Pulvergröße von -125 µm +100 µm verwendet (Bild 9).



Bild 9: Rohpulver aus verschiedenen Chargen

#### 4.2 Herstellungsprozess

Das Plasmatron wird für diese Versuche durch Änderung der geometrischen Abmessungen modifiziert, so dass mit einem höheren Leistungseintrag die Pulverförderrate auf ca. 2,5 kg/h erhöht wird, um den industriellen Forderungen





Bild 10: Pulverdurchgang durch das ICP

Bild 11: Sphärisches WSC

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besser zu entsprechen. Mit den in Tabelle 1 angegebenen Parametern für Plasmatron 2 kann ein Sphäroidisierungsgrad für WSC-Partikel von größer 90% garantiert werden. Dies entspricht einer Sphäroidiserungsrate von ca. 2,2 kg/h.

Bei dem Prozess muß darauf geachtet werden, dass die Pulverinjektionslanze zentriert ist und das Pulver sich zentral durch das Plasma bewegt. Durch die Verwendung von Kieselglas-Rohren kann der Pulverdurchgang kontrolliert werden, wie Bild 10 zeigt.

Die Ermittlung des Sphäroidiserungsgrades mit dem Lichtmiskroskop ist bei dem WSC-Pulver einfacher als bei oxidischen Pulvern, weil die sphärischen WSC-Pulver glänzen (Bild 11), im Gegensatz zu dem Rohpulver (Bild 9). Der Glanz beweist den metallischen Charakter des WSC.

Der hohe Shäroidisierungsgrad wird durch die Rasterelektronenmikroskop (REM) – Aufnahme im Bild 12, links, sichtbar. Bei höherer Vergrößerung wird die ausgezeichnete Kugelform deutlich. Bei noch höherer Vergrößerung (Bild 13) ist aus der Oberflächenmorphologie zu erkennen, wie die einzelnen



Bild 12: REM-Aufnahmen von plasmabehandeltem Wolframschmelzkarbid (links: Vergrößerung 180x, rechts: Vergrößerung 320x)

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Wolframschmelzkarbid-Phasen miteinander verschmolzen sind. Der Querschliff (Kupferschliff) im Bild 14 zeigt das gewünschte Gefüge im Inneren des Partikels nach dem Polieren und Ätzen mit einer 1/1-Lösung von K<sub>3</sub>[Fe(CN)<sub>6</sub>] / KOH, jeweils 20% ig. Die feinfiedrige Struktur des W<sub>2</sub>C liegt fein verteilt im Partikel vor. Freier Kohlenstoff ist nicht zu erkennen und kann auch nicht nachgewiesen



Bild 13: REM - Aufnahmen plasmabehandelter Wolframschmelzkarbidpulver (Vergößerung: 900x)

werden. Der Kohlenstoffgehalt der Pulver liegt durchweg im erwarteten Bereich von 3,8 – 4,3 Gew.%, gemessen mit einem Gerät der Firma LECO. Die Mikrohärte der Pulver liegt stets über einem Wert von 3500 HV 0,1. Bei allen untersuchten Pulvern konnte keine Abhängigkeit von den Prozess-Parametern festgestellt werden.

Die Zusammensetzung der Pulver wird mit Hilfe der Röntgenbeugung (XRD) (CuK $\alpha_1$ -Strahlung, Fa. Siemens) analysiert. Das Ergebnis unterschiedlicher Versuchsreihen ist im Bild 15 dargestellt. Es ist ersichtlich, dass das freie Wolfram des Ausgangsmaterials vollständig mit dem Kohlenstoff reagiert und umgesetzt wird. Im plasmabehandelten Pulver sind nur karbidische Phasen nachweisbar. Unerwünschten Phasen von Oxiden oder Nitriden können nicht nachgewiesen werden.

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Bild 14: Draufsicht und Querschliff eines einzelnen WSC - Partikels



Bild 15: XRD-Diagramme von 6 Versuchsreihen

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In einem ersten Testversuch werden die Pulver mittels Hochgeschwindigkeitsflammspritzen (HVOF) mit einer selbstfließenden NiCrBSi-Legierung verspritzt. Bei diesem Spritzprozess treffen die Pulver mit hoher Geschwindigkeit (ca. 400 m/s) auf das Werkstück auf. Die Hartmetallpulver werden in der Flamme nicht aufgeschmolzen, nur das Matrix-Material wird aufgeschmolzen, in das das Hartmetallpulver eingebettet wird. Wie im Bild 16 im Querschliff zu sehen, sind die Pulver unverändert in der Matrix vorhanden.



Bild 16: HVOF-Spritzschicht von NiCr-Legierung und Wolframschmelzkarbid

Die sphärische Form der Hartmetallpartikel, die in der zähen Matrix gut verankert ist, garantiert einen hohen Verschleißschutz. Sie unterliegt weniger der Gefahr, bei abrasiver Beanspruchung aus der Matrix herausgerissen zu werden als die spratzige Form, so dass die Schutzwirkung der Schicht längere Zeit erhalten bleibt.

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#### 5. Schlußfolgerungen

Das HF-Induktionsplasma zeichnet sich u.a. aus durch Elektrodenfreiheit, ein großes Volumen und die Verwendbarkeit fast aller Gase und Pulverwerkstoffe. Letztere werden axial injiziert und besitzen dadurch eine lange Aufenthaltszeit im Plasmakern mit Temperaturen von über 8000K. Dadurch können Pulver mit Durchmessern über 80 µm auch von hochschmelzenden Stoffen im HF-Induktionsplasma behandelt, shpäroidisiert und / oder verdichtet werden.

Oxidische Pulver lassen sich bei atmosphärischen Bedingungen sphäroidisieren. Das erfordert einen geringeren Aufwand an zusätzlichen Anlagen.

Partikel, die sensibel gegenüber Sauerstoff sind, werden unter Schutzgas oder Inertgas im Reaktor plasmabehandelt. Damit wird bei der Wolframschmelzkarbid-Pulverherstellung der Kohlenstoffabbrand minimiert. So kann bei optimalen Bedingungen der Plasma- und Pulverförderparameter kugeliges Wolframschmelzkarbid in der gewünschten Qualität hergestellt werden.

Die Ergebnisse zeigen, dass die sphäroidisierten Wolframschmelzkarbid-Pulver gut verspritzt werden können. Dies eröffnet ein weites Anwendungsfeld für diese, mit dem HF-Induktionsplasma behandelten Pulver.

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# Mechanisms of the Hydrogen Reduction of Molybdenum Oxides

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### Summary:

The two stages of the hydrogen reduction of MoO<sub>3</sub> to Mo were investigated in a thermal balance under well defined reaction conditions. Starting with different grain and agglomerate sizes for both stages, the influence of a set of parameters (temperature, local partial pressure of H<sub>2</sub>O, gas flow, etc.) on the reaction progress and the final result were studied in detail. Depending on the set of parameters used, different reaction mechanisms like pseudomorphic transformation or chemical vapour transport (CVT) were observed. Taking into account that grains and agglomerates deviate from a spherical shape and a definite grain size, the extent of reaction is well described by standard theoretical gas-solid-reaction models such as the shrinking core model (SCM) or the crackling core model (CCM). Thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area measurements (BET-method) and laser diffraction were used for these studies.

Under all conditions, the first stage shows a reaction path  $MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$  via chemical vapour transport (CVT). The reaction extent follows the crackling core model (Park/Levenspiel,(1)). Depending on the local partial pressure of H<sub>2</sub>O during reduction, the formed  $Mo_4O_{11}$  and  $MoO_2$  exhibit different size distributions and shapes of the grains.

The extent of reaction of the second stage develops according to the shrinking core model (Yagi/Kunii, (2)). Depending on the local dew point, two different reaction paths can occur: Pseudomorphic transformation at low dew points and transformation via chemical vapour transport at high dew points.

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This paper is an extract from the Ph.D. thesis of W.V. Schulmeyer "Mechanismen der Wasserstoffreduktion von Molybdänoxiden", 1998, Darmstadt University of Technology, Institute of Material Science, Department of Chemical Analytics, FRG. It therefore focuses on a phenomenological description of the most important results.

# Keywords:

Molybdenum oxides, hydrogen reduction, gas-solid-reactions, pseudomorphic transformation, chemical vapour transport and grain size distribution

# 1 Introduction

Starting from molybdenum-containing ores, the hydrogen reduction of molybdenum trioxide to molybdenum is the last step in producing molybdenum powders. Properties of the resulting powder like average grain size, specific surface area and purity (in particular final content of oxygen) are determined by this step.

Therefore, a detailed understanding of the reduction mechanisms is of great interest, especially with regard to two points of view:

- Scientific literature offers only little information about real mechanisms during the reduction of molybdenum oxides. Although the system Mo-O is known sufficiently well concerning the occurring oxides, there exist only vague suggestions on the mechanisms during reduction, like pseudomorphic transformation or chemical vapour transport.
- 2.) Producing molybdenum on an industrial scale steadily demands for improvements on quality and cost-saving (e.g.: energy consumption, resources, process control) during production. On the other hand, a profound knowledge of the mechanisms offers to understand the influence of employed raw materials (MoO<sub>3</sub>) on the manufacturing process.

# 2 Experimental

## 2.1 XRD-Analysis

XRD-analysis was performed in a diffractometer "SIEMENS D-5000", using a "Theta-2-Theta" positioning of x-ray source, sample and detector.

In order to obtain reference standards for phase analysis, the four components  $MoO_3/Mo_4O_{11}/MoO_2/Mo$  were blended to 34 different proportions of mixture. By analyzing these 34 blends, the respective concentration ratios were computed by means of a multiple regression procedure.

## 2.2 Particle characterization

Particle size distribution measurements were performed with a lasergranulometer "CILAS-850" consisting of a He/Ne-Laser light source, a pumping system for circulation of the water suspended sample and a photodiode array as analysing unit. The particle size distribution is computed by analysing the Fraunhofer diffraction pattern of the particles.

Four levels of deagglomeration were applied during sample preparation: maximum deagglomeration leads to the actual "grain size" distribution, minimum deagglomeration (no deagglomeration) results in the "agglomerate size" distribution.

Measurements of specific surface areas of powder samples were carried out by the BET-method.

# 2.3 TGA-Analysis

Thermo gravimetric analyses were performed in a thermo balance system, type "CAHN TG-717", consisting of: a furnace including temperature control, balance, gas module facility for defined gas atmospheres (type of gas, gas flow, dew point) in a reaction tube ( $AI_2O_3$  ceramic tube), a Pt sample holder (Pt-cups, Pt crucibles) and devices for data collection and data processing.

### 2.4 Mo-Oxides

For the first reduction stage  $MoO_3$ -powders originating from two suppliers were used, cf. Table 1:

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Sample name	Mean grain size [µm] (max. deagglomeration)
MoO <sub>3</sub> -Climax	0,4
MoO <sub>3</sub> -Molymet	4,4

Table 1: Source and mean grain size of MoO<sub>3</sub>.

For the second stage, two  $MoO_2$  powders of different grain size were prepared in PLANSEE's first production stage:

Sample name	Mean grain size [µm] (max. deagglomeration)
MoO <sub>2</sub> -Molymet	2
MoO <sub>2</sub> -Standard	11

Table 2: Mean grain size of MoO<sub>2</sub>.

In order to obtain different agglomerate sizes for all of the above powders, 8 agglomerate fractions of each powder were prepared by careful sieving.

# 2.5 Experimental methods

### 2.5.1 Isothermal reduction

For all reduction experiments the oxides were heated up to the desired reaction temperature with a heating rate of 50 K/min in an Ar-atmosphere. After an equilibration time of 20 minutes to stabilize sample temperature, the reaction was started by switching to  $H_2$  gas. To stop the reaction, the gas atmosphere was switched back to Ar gas with a subsequent cool down of the sample.

In order to avoid exothermal and powder bed depth effects, the sample mass was partly reduced to a minimum of 20 mg per run. Additionally, a flat cup of platinum was used as sample holder, resulting in a bed depth of less than 1 mm. For the investigation of powder bed effects a cylindrical Pt-crucible was used, exhibiting an effective bed height of 1,4 cm.

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### 2.5.2 Dew point of reduction atmosphere

The dew point of H<sub>2</sub> was varied from  $\tau = -40^{\circ}$ C (H<sub>2</sub>-cartriges of LINDE) to 5°C <  $\tau < 25^{\circ}$ C. This was accomplished by leading the cartridge H<sub>2</sub> through a temperature controlled bubbler system. Because of condensation inside the TGA-System, the dew point was limited to 25°C. To achieve higher dew points in one experiment, the cylindrical Pt-crucible was covered by a tungsten foil. This way any gas stream was kept away from interacting with the powder thus all the reaction water formed was increasing the dew point.

# 3 Gas-solid-reaction models

### 3.1 The shrinking core model, SCM

The shrinking core model by Yagi/Kunii describes a shrinking core of educt, surrounded by a growing layer of product (cf. to fig. 1) during the reaction of a solid particle with gas.



Fig. 1: Schematic drawing of the shrinking core model.

The rate determining step consists of either the chemical reaction at the interface product/educt (reaction controlled) or the diffusion through a layer of the product (diffusion controlled).

The plot of the extent of the reaction X versus the relative reaction time  $t/\tau$  ( $\tau$  = time for complete transformation of a particle) is shown in figure 2 for both versions.
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Fig. 2: Extent of the reaction, X, versus the relative reaction time  $t/\tau$  for the shrinking core model: a) reaction controlled, b) diffusion controlled.

According to the "classical" theory of the SCM, the transformation of grains follows via a pseudomorphic transformation. In principle, there are two mechanisms for grain transformation:

- 1. <u>Mechanism of Pseudomorphic Transformation</u>: During the reaction, the reaction interface moves from the grain surface to the core of the grain. The shape of the product remains close to the educt one causing pseudomorphism. Typically, the product shows pores and pore channels.
- <u>Mechanism of Chemical Vapour Transport</u>: The decomposition of the educt is followed by forming an intermediate gaseous transport phase. This transport phase is deposited on a nucleus of the product. This way, the grain morphology of the product is generated completely new. The grain size distribution of the product is determined by the

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conditions of deposition (heterogenous/homogenous nucleation, nucleus growth) from the gas phase. The schematic of a CVT-transformation is shown in figure 3.



Fig. 3: Schematic drawing of a CVT-transformation. S<sub>1</sub>: educt (solid), TP<sub>1</sub>: transport phase (gaseous), S<sub>2</sub>: product (solid).

#### 3.2 The crackling core model, CCM

The crackling core model was introduced by Park and Levenspiel<sup>2</sup> and assumes the educt particle to be initially non porous. The transformation takes place in two steps: In step one the reaction gas forces the educt particle to develop a system of cracks and fissures from the surface to the centre, resulting in a grainy material which is then easily penetrated by the reaction gas. The grains of the now porous layer subsequently react via the shrinking core model (reaction controlled/diffusion controlled) to the final product:



In case of a chemical reaction in step 1 an intermediate product "I" is obtained with an intermediate reaction extent  $\alpha_I$ , with regard to the stoichiometry of the overall reaction:

$$\begin{pmatrix} S_{1,nonporous} \\ (\alpha = 0) \end{pmatrix} \xrightarrow{+gas} \begin{pmatrix} I_{grainy} \\ \alpha = \alpha_I \end{pmatrix} \xrightarrow{+gas} \begin{pmatrix} S_{2,porous} \\ \alpha = 1 \end{pmatrix}$$
(eq. 1)

An example is the reduction of  $Fe_3O_4$  to Fe by CO:

$$\begin{pmatrix} Fe_3O_4\\ (\alpha=0) \end{pmatrix} \xrightarrow{+CO} \begin{pmatrix} FeO\\ \alpha=\alpha_1=0,25 \end{pmatrix} \xrightarrow{+CO} \begin{pmatrix} Fe\\ \alpha=1 \end{pmatrix}$$
(eq. 2)

The overall time  $\tau_{tot}$  for the complete reaction of the educt consists of time  $\tau_{c}$ for the crackling front to arrive at the grain in the very centre of the pellet plus the time  $\tau_a$  to transform this last grain:

#### Fehler! Es ist nicht möglich, durch die Bearbeitung von Feldfunktionen Objekte zu erstellen. (eq. 3)

The ratio of  $\tau_c$  and  $\tau_g$  is defined as:

$$\omega = \frac{\tau_c}{\varsigma_c + \tau_g} = \frac{\tau_c}{\tau_{tot}}$$
(eq. 4)

The rather complex mathematical evolution of the CCM ultimately yields eight versions or reaction paths. Each one of these versions is characterized by the key parameters  $\omega$  and  $\alpha_1$ . Fig. 4 illustrates this by showing the extent of the reaction  $\alpha$  versus the relative reaction time t/ $\tau_{tot}$  for a reaction controlled grain transformation and an intermediate extent of this reaction with  $\alpha_1 = 0.5$ .



Fig. 4: Reaction extent  $\alpha$  of educt pellet versus the relative reaction time t/ $\tau_{tot}$  for a reaction controlled transformation of grain,  $\alpha_1$ =0,5.

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## 4 Results for the first reduction stage $MoO_3 \rightarrow MoO_2$

#### 4.1 TG-analysis



Fig. 5: TG reduction curves for various agglomerate sizes for thefirst stage  $MoO_3 \rightarrow MoO_2$ . Fraction F0 at far left, fraction F7 at far right. Set of parameters:  $MoO_3$ -Molymet, mean grain size d= 4,2 µm, Pt flat cup, T = 500 °C, weighed-in mass 20 mg,  $H_2 = 8 \text{ l/h}$ ,  $\tau(H_2) = 5^{\circ}C$ .

For varying sets of parameters (grain size, agglomerate size, reduction temperature,  $H_2$  dew point), s-shaped curves of the extent of the reaction have been observed. Figure 5 demonstrates the influence of agglomerate size on the reduction time.

#### 4.2 XRD-analysis

An oxide phase sequence of  $MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$  was observed by interrupting the reduction at various reaction times with subsequent XRD-analysis of the sample for any given set of parameters and without exception, cf. table 3.

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Reduction Time	MoO <sub>3</sub> [wt.%]	Mo <sub>4</sub> O <sub>11</sub> [wt.%]	MoO2 [wt.%]	Mo [wt.%]
5 min	85	7	8	
30 min	25	42	33	-
51 min	_	50	50	-
72 min	_	19	81	-
98 min	-	1	99	
24 h		-	99	1

Table 3: Phase contents at various reduction times. Experimental parameters:  $MoO_3$ Molymet, Pt flat cup, T = 550 °C, powder mass 100 mg, H<sub>2</sub> = 8l/h,  $\tau$ (H<sub>2</sub>) = 10°C.

#### 4.3 SEM-inspection



Fig. 6: Various states of reduction of a partly reduced  $MoO_3$ -Climax sample. a) initial  $MoO_3$  nonporous; b)  $Mo_4O_{11}$  porous growing on shrinking core of  $MoO_3$ ; c)  $Mo_4O_{11}$ , porous; d) area of magnification of figure 7.

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Based on the results of TGA and XRD, SEM was used to search for seeds of nucleation and growth of new phases. Therefore, reduction was interrupted at different states of progress and the powders were examined by SEM to understand spatial and chronological evolutions during the reduction. Some results are shown in the figures 6 to 8.



Fig. 7: Left: magnification of fig. 6, showing  $Mo_4O_{11}$  on a shrinking core of  $MoO_3$ -Climax (centre). Right:  $Mo_4O_{11}$  nucleus on the surface of a  $MoO_3$ -Climax agglomerate.



Fig. 8: Left: nucleation of  $MoO_2$  in a grain of  $Mo_4O_{11}$ . Right: growth of plateletshaped crystals of  $MoO_2$  on a  $Mo_4O_{11}$  agglomerate.

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4.4 Reaction mechanism of the first stage of reduction of MoO<sub>3</sub> to MoO<sub>2</sub> The first stage follows the two step version of the crackling core model:

$$\begin{array}{c} MoQ_{3,nonporoutagglomeral} & \xrightarrow{+112} & Mo_4O_{11}, grainyagglomeral} & \xrightarrow{-112} & MoQ_{2}, grainyagglomeral} \\ (\alpha = 0) & \alpha_1 = 0, 25 & \alpha = 1 \\ \end{array}, \quad (eq. 5) \end{array}$$

 $\alpha$  relates to removal of oxygen. Without exception, the transformation steps take place via a CVT route by generation of a gaseous transport phase:

$$MoO_3 \xrightarrow{k_1} TP_1(g) \xrightarrow{k_2} Mo_4O_{11} \xrightarrow{k_3} TP_2(g) \xrightarrow{k_4} MoO_2$$
 (eq. 6)

At otherwise constant conditions (temperature, educt habit) high dew points lower the reaction velocity and stabilize gas phases (longer transport range). Independent of MoO<sub>3</sub> agglomerate and grain size and the desired reduction temperature, Mo<sub>4</sub>O<sub>11</sub> and MoO<sub>2</sub> exhibit a constant habit of grains. Mo<sub>4</sub>O<sub>11</sub>grains are interconnected by massive bridges and building agglomerates of a "cauliflower" morphology. During transformation of MoO<sub>3</sub> to Mo<sub>4</sub>O<sub>11</sub> these cauliflower agglomerates grow towards the centre of the initial MoO<sub>3</sub> agglomerate.

The next step is the nucleation of  $MoO_2$  on the surface of  $Mo_4O_{11}$ -grains and a consecutive grain growth into the volume of MoO<sub>2</sub>. Resulting MoO<sub>2</sub>-grains exhibit a platelet habitus with a height h of 0,1-0,2 µm and diameter d of 1-2 µm.

Every transformation to the next oxide phase is oriented from the surface to the centre of the agglomerate. Depending on the extent of reaction and conditions of reduction, several oxide phases can coexist, showing a multilayer structure like onion skins. The habit of applomerate formation and therefore agglomerate size is kept during the first stage of reduction.

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## 5 Results of the second stage of reduction from MoO<sub>2</sub> to Mo

#### 5.1 XRD-analysis

As expected, no intermediate oxides occurred during the reduction of  $\mbox{MoO}_2$  to  $\mbox{Mo}.$ 

#### 5.2 TG-analysis

The main focus of TG-analysis of the second stage was to create extreme local dew points in order to proof the assumed mechanisms of pseudomorphic- and CVT-transformation. The experimental procedure is elucidated in table 4 and figure 9.

conditions of reduction:	for an extremely low dew point	For an extremely high dew point
principle:	little reaction water by	"self created" atmosphere
 	minimum sample mass +	of high dew point by large
	fast diffusion of	sample mass + impeded
	dry atmosphere	diffusion of H <sub>2</sub> O
sample	MoO <sub>2</sub> -Molymet F1	MoO <sub>2</sub> -Molymet
	d = (32-45)µm	d = (1-200)µm
applied sample mass [mg]	20	2500
sample carrier	flat Pt-cup	Al <sub>2</sub> O <sub>3</sub> crucible
powder arrangement	few particles, loosely spread out on cup	powder bed, densified and covered by W-foil
reduction temperature [°C]	1100	1100
Flow of H <sub>2</sub> [I/h]	8	8
dew point of H <sub>2</sub> at entry [°C]	-40	+20
off-diffusion of H <sub>2</sub> O	easy	strongly inhibited
reduction time	40s (100 wt.% Mo)	49 min (96 wt.%.Mo)
		300 min (100 wt.% Mo)

table 4: Experimental parameters for a reduction under extreme dew points.

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Fig. 9: Schematic of sample arrangement to create extreme dew points: a) for an extremely low dew point, b) for an extremely high dew point.

#### 5.3 SEM-inspection

Starting with different grain sizes and grain shapes,  $MoO_2$  was reduced to Mo under conditions of extreme dew points according to 5.2. The following sequence of SEM-micrographs proves the existence of the assumed reaction routes: pseudomorphic and CVT transformation. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3



Fig. 10: Pseudomorphic reduction of  $MoO_2$  under extremely low dew points. Left:  $MoO_2$ -Standard, sieve fraction F7 (355-500) µm, consisting of porous agglomerates built by  $MoO_2$ -platelets. Right: Surface of F7 agglomerate after complete reduction to Mo. Grains were transformed via the pseudomorphic route, showing the same platelet shape as the initial  $MoO_2$ -platelets. Mo-platelets shown here exhibit pyrophoric behaviour.



Fig. 11: Reduction of  $MoO_2$ -standard, sieve fraction (32-45)  $\mu$ m via the pseudomorphic route. Left: Initial compact grains of  $MoO_2$  (compactness of grains generated by "in situ" sintering of platelets due to overheated reduction during the first stage). Right: Close up of grain surface after complete reduction to Mo. The grain shows pore channels. Surface cracks and craters result from stress by tension due to a volume decrease during oxygen removal.

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Fig. 12: Reduction of MoO<sub>2</sub>-standard sieve fraction F7 (355-500) µm via the CVT route under an extremely high dew point. Left: surface of agglomerate after complete reduction to Mo, showing the change from  $MoO_2$ -flakes to octahedral/spherical grains. Right: close up of Mo derived by the CVT-route in a powder bed.



Fig. 13: Nucleation and grain growth of Mo via the CVT route. Left: nucleation (bright dots) and small grains of Mo on MoO<sub>2</sub>-platelets. Right: Intersection of a CVTbuilt Mo layer showing growth of a "skeleton" of Mo grains during the CVT-route. This CVT-layer was built in the centre on the upper side of the W-foil shown in figure 9.

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# 5.4 Reaction mechanism of the second stage of reduction of $MoO_2$ to Mo

Within the range of the investigated  $MoO_2$  agglomerate sizes d < 1 mm, no time-dependency for complete reduction was found. The diffusion velocity inside the porous structure of  $MoO_2$  agglomerates is sufficiently high to allow a description of kinetics by the shrinking core model.

Depending on the dew point of hydrogen two routes were observed for the transformation of grains:

#### a) Pseudomorphic transformation:

Up to a maximum adjustable dew point  $\tau(H2)$  of 20°C under the available experimental conditions a pure pseudomorphic transformation was observed. Therefore, the initial grain shape of MoO2 is kept. Mo powders reduced at extremely low dew points showed pyrophoric behaviour. Based on an increase in density during the transformation of MoO2 to Mo large grains experience tension stresses which lead to craterlike systems of cracks on the grain surface. The outer shape and size of grains and agglomerates are conserved. On a formal basis the pseudomorphic transformation follows the well known equation:

$$MoO_2 + 2H_2 \rightarrow Mo + 2H_2O$$
 (eq. 7)

#### b) CVT-transformation of grains.

By hindering H<sub>2</sub>O to diffuse out of the sample high local dew points were achieved (self created atmosphere). Due to this a pure CVT-transformation of the initial grains was observed ( $\tau$ (H2) > -40°C). On a formal basis the CVT-transformation follows the following scheme:

$$MoO_2 \xrightarrow{k_s} TP_3(g) \xrightarrow{k_b} Mo$$
 (eq. 8)

In contrast to the first stage of reduction, local dew points decisively influence the nucleation and the grain growth of the Mo-phase: Low dew points generate high numbers of nuclei and small grain sizes. High dew points generate low numbers of nuclei and large grain sizes. 15" International Plansee Seminar. Eds. G. Kneringer. P. Rödhammer and H. Wildner. Plansee Holding AG. Reutle (2001), Vol. 3

## 6 Conclusions

A detection of the observed transport phases was unfortunately impossible due to a restricted access to the reaction tube of the TGA under the conditions of reduction ( $H_2$ , temperatures of 400-1100°C). Therefore, only incomplete reaction equations were derived.

Because of a double transformation into gaseous transport phases (TP<sub>1</sub>, TP<sub>2</sub>) in the first reaction stage, the resulting grains of MoO<sub>2</sub> do not longer contain any information about the morphology and the grain size distribution of the initial MoO<sub>3</sub>, except for initial agglomerate size distribution. MoO<sub>2</sub> grain dimensions of  $(0,1-0,2) \times (1-2) \mu m$  were observed independent of reduction conditions in the first stage.

 $Mo_4O_{11}$  occurs as an intermediate phase during the first reduction stage under all conditions. Although  $Mo_4O_{11}$  constantly takes part in the mechanism of the first stage it is not a part of the respective existing literature (e.g.(3)).

Depending on the choice of the dew point in the second stage, one can produce a Mo-powder with nm-particle size via the pseudomorphic route. Routinely desired grain sizes in µm dimension can be obtained via the CVT route. For both routes the initial agglomerate habit is maintained.

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## QUANTITATIVE DESCRIPTION OF THE MICROSTRUCTURE OF SINTERED MATE RIALS

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#### Summary:

Sintered materials contain particles, grains and pores, interphase and grain boundaries. Depending on the details of the technological route they differ in the amount and the distribution of these elements. Such differences can be now analysed in a quantitative way using the methods of image analysis and stereology. In particular, these methods provide estimates of the number of microstructural elements of a given size (e.g. number of particles per unit volume), their shape (if applicable), and their spatial distribution. The paper describes methodology of these measurements, and how the results can be applied to optimise microstructure of sintered specimens.

#### Keywords:

Sintered materials, microstructure, quantitative description

#### 1. Introduction:

Sintering is an economic technology for a growing number of ceramic and metal parts (1). On the other hand, one of the significant drawbacks of sintered materials is their reduced plasticity. As the properties of materials depend strongly on their microstructure, their fracture toughness can be improved by microstructure design. This, in turn, requires proper methods for quantification of the microstructural elements of sintered materials.

The major elements of the microstructure of the sintered materials are:

- a) grains (G) and grain boundaries (GB);
- b) pores (P) and pore-solid boundaries (PSB);
- c) strengthening particles (SP) and interphase boundaries (IB).

Pores, grains and particles are 3-dimensional elements, while internal boundaries are 2-dimensional features, dispersed in volume of a material in

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question. The quantitative description of such elements requires methods of so called stereology (see for example (1,2)).

A description of the geometrical features of microstructural elements in general, consists of characterizing their: a) content; b) shape; c) size; d) spatial distribution (including location with respect to other elements).

The content of volumetric elements, e.g. strengthening particles and pores, can be characterized by their volume fractions,  $(V_V)_{SP}$  and  $(V_V)_P$  respectively. On the other hand, size of these elements is uniquely defined by their volume, V. As individual particles, grains and pores differ in volume, they form populations which can be described by volume distribution functions  $f(V)_{SP}$ ,  $f(V)_{MG}$  and  $f(V)_P$ , respectively, or  $f(V)_X$  in shorthand notation. In materials science applications such a description might be simplified to include information on mean properties and properties variability of these elements. The mean volume,  $E(V)_X$ , volume standard deviation,  $SD(V)_X$ , and coefficient of variation,  $CV(V)_X$ , can be used to characterize populations of these three dimensional elements. Volume fractions of 3-dimensional objects can be relatively easily estimated from the images of the microstructure revealed on sections of the materials from the following stereological relationship:

$$(\bigvee_{v})_{x} = (A_{A})_{x} \tag{1}$$

where  $(A_A)_X$  is the area fraction of the sections of elements of interest measured globally. On the other hand, the mean volume of such elements as particles grains and pores, E(V), can be estimated using either the classical Saltykov method and its modifications or modern stereological tools, such as the disector and point sampled intercepts. Detailed descriptions of these methods can be found in (1-3).

Based on the estimates of volume fractions and mean volume of 3-D one can calculate volumetric density of a given 3-D elements,  $N_v$ , from the following relationship:

$$N_V = (V_V)/E(V)$$
<sup>(2)</sup>

Various methods of measurements of particle density are discussed in (4).

A comprehensive description of the shape of particles, grains and pores usually requires systematic sectioning (serial sectioning) of the material. In a simplified way shape can also be described by shape factors which are determined from measurements carried out on sections. The following shape factors can be used to describe shape of particle, grain and pore sections:

p/d<sub>2</sub> - section perimeter to equivalent diameter ratio;

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 $d_{max}/d_2$  - section maximum chord to equivalent diameter.

The mean values of these two shape factors,  $E(p/d_2)$  and  $E(d_{max}/d_2)$  are sensitive measures of the local changes in the boundary curvature and elongation of grains, particles and pores (see for example (3)).

One of the important aspects of the spatial distribution of particles and pores in sintered materials is a potential tendency for their segregation/clustering. The clustering effect of the pores and/or particles can be described by cluster analysis (see (4)) or by the tessellation method (2,5). Alternatively, one can also use the covariance function (see (2,6)) to describe such clustering.

Grain, interphase and pore/matrix boundaries are 2-dimensional microstructural elements. Their content can be described in terms of the surface area per unit volume,  $(S_V)_{GB}$ ,  $(S_V)_{IB}$ , etc. In a general case, these parameters can be efficiently estimated using a method of vertical sectioning (see (2)). For a system of geometrically isotropic grains, particles and pores,  $(S_V)_X$  can be obtained using a grid of parallel test lines from the following relationship:

$$(S_v)_x = 2(P_L)_x$$
 (3)

where  $(P_L)_x$  is the number of intersections of the test lines with the boundaries of interest. Stereological relationships link this parameter with the mean length of an intercept through a system of elements bounded by the studied boundaries,  $E(\ell)$ , (mean intercept of particles, grains, pores). Simple geometrical arguments can be used to show that:

$$(S_v)_x = 2 \frac{(V_v)_x}{E(\ell)_x}$$
 (4)

where  $E(\ell)_X$  is the mean intercept length of the elements of interest and  $(V_V)_X$  is their volume fraction (see for example (1)).

In the past, stereological measurements were based on manual counting. Modern methods of microstructure characterization are supported by computer software. The aim of the present paper is to demonstrate how these methods can be used for characterizing microstructures of sintered materials and in turn their design. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3

### 2. Examples of microstructure quantification:

#### Characterization of particles in ceramic matrix composites

A characteristic image of the microstructure of SiC modified by carbon (7-9) is exemplified by Fig. 1. It can be noted that this microstructure reveals the following elements:

- (a)SiC matrix:
- (b)C particles;

(c) pores.



Fig. 1. A SEM image of section of the studied composite.

The volume fraction, shape, size and distribution of C particles have been studied using an automatic image analyzer with specially developed software. The initial images of the microstructure have been digitized and processed using the methods of image processing. The resulting images (shown in Fig.2) were used to measure geometrical features of the sections of individual particles. The mechanics of measurements is schematically explained in Fig.3. The data obtained from the measurements of the selected parameters can be directly used to model some of the properties of the sintered material, such as its density, strength, etc. Figure 4 shows, for example, plot of the SiC density against the content of C particles expressed as volumetric ratio and estimated via image analysis. The positions of the particle sections have been stored and analyzed from the point-of-view of possible tendencies for clustering among features of the same type and among features of different types. The existence of tendencies for clustering may have important implications to the improvement of the technology of mixing and sintering of such composites. It also influences resistance to cracking due to the interactions between fracture surface and C particles.

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Fig. 2. The images of the carbon particles (white) in SiC matrix with different carbon content.

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area (A), shape factors: p/d<sub>2</sub>; d<sub>max</sub>/d<sub>2</sub>





Fig.4. The density of the SiC sinter estimated via image analysis (dots) of the carbon contents and theoretical line based on volumetric ratio (the density of the pure SiC - 3.2g/cm<sup>3</sup> measured by hydrostatic method, the density of the carbon - 2.26 g/cm<sup>3</sup> from the data base)

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One of the methods used to describe quantitatively the clustering tendency is the covariance function, C(r).

The covariance function defines, for a given distance r, the probability, P=C(r), that two points at distance r apart, both hit the features of interest.

$$C(\mathbf{r}) = P[(\mathbf{x} \text{ hits a feature}) \land ((\mathbf{x} + \mathbf{r}) \text{ hits a feature})]$$
(5)

The examples of the covariance function for different types of structures are shown in Fig. 5a-c.



Fig.5. Plots of the covariance function for (a) random, (b) clustered and (c) periodic structures.

In case of random structure (Fig.5a) the covariance function drops rapidly to certain value, depending on the volume fraction of particles and remains close to it with only stochastic fluctuations. In the case of the clustered structure (Fig. 5b) the situation is quite similar, except that the initial decrease in less rapid than in the case of random structure. For the periodic structure (Fig.5c) covariance function measured in proper direction reflects well the periodic nature of analyzed sample.

For a homogeneous and isotropic system of features, the covariance depends only on the distance r and is independent of the position of the test points in space. For a random distribution of the particles C(r) does not depend on r (2,10,11,12). 15' International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

The results of the studies of the covariance are shown in Fig. 6. It has been found that the particles of carbon exhibit a tendency to clustering only for low level of carbon. This tendency is indicated by the position of the covariance function with respect to the reference curves:  $C(r)_{ref}=V_V^2$ , which are expected for a system with randomly distributed particles.



Fig. 6. Plot of the estimated values of the covariance function, C(r), for the studied samples. The respective reference lines (dashed) are computed for the measured value fractions of carbide particles

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#### Grain size in polycrystals

The flow stress of polycrystalline materials is known to be a function of the size of the grains. It has been postulated almost 50 years ago (13) that the flow stress of metals  $\sigma$  is a linear function of d<sup>-1/2</sup>:

$$\sigma = \sigma_0 + Kd^{-\frac{1}{2}}$$
 (6)

where d is a linear measure of the size of grains. Both the mean diameter,  $d_2$ , and the mean intercept length,  $\ell$ , have been used in the past to define the size of grains. It has been recently recognized that the latter parameter, the mean intercept length, is more appropriate measure of the grain size in this particular application. It should be noted, that  $\ell$  is inversely proportional to S<sub>V</sub>, where S<sub>V</sub> is the total area of grain boundaries in unit volume.  $(\ell = S_{y}^{-1})$ .

The models explaining equation 6 are based on the assumption that the grains have the same size and shape. Kurzydłowski (14) proposed taking into account the differences in size of individual grains. This model consideration, based on the assumption that a polycrystal can be described by a grain volume distribution function, f(V), leads to the following modified formula:

$$\sigma = \sigma_0 + K \exp [-a VAR (InV)] (S_V)^{1/2}$$
 (7)

where:

is the variance of the volume logarithm of grains; VAR(InV) а

is a numerical constant.

Since powder metallurgy gives the flexibility in shaping the grain size distribution functions, the importance of correction term in equation 7, -a VAR(InV), is expected to be relevant in particular in the case of sintered materials. In order to prove this point, polycrystalline specimens were produced using powder of 316L stainless steel (composition given in Table 1).

Element	С	Cr	Ni	Мо	Si	Mn	Cu	Р	S	Ν	0	Fe
Weight %	.022	16.9	11.1	2.11	.53	1.49	.19	.021	.005	.05	160 ppm	balance

Table 1 Chemical composition of the 316L powder used

Two types of powders with different mean particle size were mixed in different proportions to produce a series of specimens systematically differing in diversity in the size of grains.

The mixtures were used to sinter cylindrical specimens at 1100°C under the pressure of 70 MPa. Metallographic observations performed on the as-polished specimens revealed that the in all cases the porosity of material was lower

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than 2%. The polished specimens were later electrolytically etched to reveal the grain boundaries.

Systematic measurements of the grain sizes were performed on the specimens using a system for automatic image analysis. Methods of quantitative stereology have been used to obtain information about grain volume distribution (2). The results of the measurements confirmed that obtained polycrystals differed not only in the mean size of grains, but also in the normalized spread of the grain sizes, as indicated by the changes of values of coefficients of variation and standard deviations of volume logarithms.

Brinell hardness measurements were used to characterize the mechanical properties of the material. The hardness is known to reflect the value of the flow stress at a few percent plastic strain and to follow a Hall - Petch type equation (see for instance 15-18):

$$H = H_{o} + K_{H} d^{-\frac{1}{2}}$$
 (8)

The results of the measurements plotted in against the respective values of  $\ell^{1/2}$ are shown in Fig.7.



Fig.7. The hardness of the sinter as a function of the grain size

It is seen from the plot that the experimental points in general confirm Hall-Petch relationship as given by equation 8. If the data points are analyzed all together, the following values of  $H_o$  and  $K_H$  could be computed:

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#### $H_{o} = 107 [kG mm^{-2}]$ $K_{H} = 11.1 [kG mm^{-3/2}]$

However, upon a closer examination of the experimental points, it can be found that they systematically deviate from the lineal relationship predicted by equation **6** and **8**. In this situation it can be concluded that the material studied shows a systematic deviation from Hall - Petch relationship in its classical form. Moreover, it can be concluded that the experimental points deviate from the lineal relationship by the amount dependant on the variation in the normalized size of grains. This observation, in turn, rationalize the model proposed by Kurzydłowski (14), and the need for the use of term *-a VAR(InV)* in the analysis of grain size effect in sintered materials.

#### The effect of particle contiguity on toughness of tungsten heavy alloy

The typical tungsten heavy alloy (WHA) has a tungsten content between 90% and 98%. The alloys studied have been fabricated from powder mixtures by a liquid phase sintering at about 1450÷1500°C. After sintering the composite consists of a contiguous network of nearly spherical tungsten particles embedded in a Fe-Ni-W ductile matrix (Fig. 8).



Fig. 8 Typical micrograph of WHA studied

The mechanical properties of heavy alloys are primarily linked to the strength of W-matrix interface and the relative fraction of W-W interfaces, which are the weakest microstructural element of the alloy. Contiguity, parameter C, defined as the fraction of W-W interfacial area in total area of interfaces in a volume of an alloy, can be provided as structural parameter which may well correlate with mechanical properties. Values of C parameter can also be 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

correlated with other microstructural characteristics. Such a correlation is useful for property control and designing of WHA.

The images of the microstructure were digitised. Measurements of W-W interfaces were carried out using a concept of vertical sectioning and system of cycloid test lines (2,19). In order to calculate contiguity value, C, pairs of images were used: image A showing all W-matrix interfaces and image B with on W-W interfaces (or all interfaces).

The C values were counted using the following equation:

$$C = \frac{2N_{p_{w-w}}}{N_{p_{w-w}} + 2N_{p_{w-w}}} = \frac{2S_{V_{w-w}}}{S_{V_{w-w}} + 2S_{V_{w-w}}}$$
(9)

where:

 $N_{p_{w \text{-}w}}$  - number of W-W grain boundary interceptions with cycloid lines

 $N_{p_{w\text{-}w}}$  - number of W-matrix grain boundary interceptions with cycloid lines

 $\mathsf{S}_{\mathsf{V}_{\mathsf{ur},\mathsf{u}}}$  - surface area of W-W grain interfaces per unit volume

 $S_{V_{w,u}}$  - surface area of W-matrix interfaces per unit value

Data obtained from the image analyses, microhardness measurements and the impact tests are summarised in Table 2.

Table 2

Data obtained from the measurements of microstructural features, impact strength and microhardness

Specimens	E(d <sub>2</sub> )	S∨	С	Impact strength	Microhardness HV0,05	
	[µm]	1/mm		[J/cm <sup>2</sup> ]	grains	matrix
As-sintered	27,1	81,6	0,23	184	404	295
Swaged	16,5	115,8	0,36	72,5	478	351
Rolled	18,3	109,0	0,34	10	557	360
Hydroextruded	18,6	110	0,33	34	574	373

\* microstructural characteristic data was obtained from the longitudinal sections

A quantitative comparison of microstructures shows that particle size in all groups of cold worked samples is similar. As expected, the total tungsten grains surface area per unit volume is notably higher for samples with the small particle size, also contiguity is correlated with particle size (Fig. 9).

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Fig.9. Plot contiguity vs. grain size for WHA studied

There are four potential fracture paths, that can be defined for the WHA: through the matrix, across tungsten particles, along tungsten-tungsten interfaces and tungsten-matrix separation. The W-W boundaries are the easiest fracture path. The cracks at these boundaries were observed even in samples subjected to a small amount of cold working (before impact tests). Tungsten cleavage is observed at sufficiently high stresses, for which good W-M interfacial bonding is needed. The poor intergranular strength can be associated with an interface segregation or precipitation at the boundaries during sintering or during post sintering heat treatment. This reduces the load which can be carried out and reduces ductility of the material in a proportion depending on contiguity.

Results obtained from contiguity measurements give better insight to the fracture resistance of WHA. The contiguity varies in a broad range and is correlated with the tungsten particle size. For small particles (E(d)=16,5-18,7 $\mu$ m) C is relatively high (C = 0,28 - 0,38). For samples of large size (E(d)=23,0-29,4 $\mu$ m) C is smaller and have values in 0,20 - 0,28 range.

#### 3. Acknowledgements:

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## Oxygen Concentration and Defect Structure in Molybdenum and Tungsten

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#### Summary:

Oxygen concentration was directly determined in molybdenum and tungsten with a help of neutron-activation analysis for metals of usual commercial purity as well as for high-purity metals. It was found, that after special treatment (surface oxidation at relatively low temperature and annealing in a temperature range 800-1500°C) oxygen concentration depends strongly on subgrain or grain structure parameters. In a rolled refractory metals of commercial purity oxygen-defects interaction may cause significant delay of recrystallisation (more than 200°C). Comparison with high-purity metals illustrates the role of impurities was not the main and a big part of oxygen was bonded in molybdenum itself, but impurities effect basically the temperature level of recrystallisation. It was shown that oxygen concentration for recrystallized molybdenum is proportional to grain boundaries specific surface most likely for given compositions of impurities. Subsequent annealing in a hydrogen with low dew point was shown to be effective for to remove significant part of additional oxygen.

#### Keywords:

Molybdenum, tungsten, oxygen, recrystallisation, diffusion, grain boundaries, neutron-activation analysis

#### 1. Introduction:

It is a matter of a fact that oxygen concentration limits directly plasticity properties of tungsten, molybdenum and their alloys. Oxygen contamination is very "easy" in technology during hot and/or warm rolling, annealing in vacuum, noble gases atmospheres and even in hydrogen atmosphere with not sufficiently low dew point [1,2] especially whether surface of metal has oxide films or even spots of appreciable thickness.

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Unfortunately, experimental methods for determination of oxygen concentration are not always reliable. The neutron-activation method seems us to be the most reliable and it helps to determine separately the contributions of oxygen bonded on a surface and oxygen bonded in a bulk of material when it is possible to measure oxygen concentration twice: immediately after irradiation and after surface etching [1,2].

It was established [1,2] that in high purity and even in pure commercial molybdenum oxygen bonds during diffusion occurring simultaneously with recrystallisation in molybdenum itself mainly due its defect structure: subgrain and grain boundaries, particles of second phase were not detected with a help of electron microscopy of thin foils. Moreover, simple estimation of impurities capacity to bond oxygen in these cases had shown that these concentrations were evidently insufficient in comparison with defect structure capacity at 800-1200°C. For completely recrystallised structures oxygen concentration after saturation at 1200°C was shown to be directly proportional to absolute specific surface of grain boundary structure independently impurities concentration for relatively pure molybdenum or molybdenum alloy [2]. For temperatures above ~1200-1400°C oxygen solubility due to oxygen-defects interaction was shown to diminish significantly in comparison with oxygen solubility level in bulk material.

Concentration levels and rate of oxygen diffusion in refractory metals is important also for strengthening of molybdenum alloys by inside oxidation [3,4] processes due dispersed oxide particles formation.

This short communication is devoted to some unpublished results concerning oxygen solubility in tungsten and molybdenum in connection with structure particulars.

#### 2. Materials and experimental procedure

Molybdenum of commercial purity (in ppm): W- 50-100; Fe- 0.3-1; Si, Na- 1- 10; Cr, K- 3-10; Ca- 3-20; C, V- 10-40; N- 1-6; Mg-3-7; Al- 1-9; H, Zr -0.3.), after usual powder technology process. High purity double melted in vacuum molybdenum (C <10; W <20; Ni, Mn, As <30; O, Fe, Cu, Pb, Zn, Ta <1) and tungsten (C <10; Mo <50; Si <0.2; O <0.5; Ti, N, F, Hf<0.3, Al, Fe, Cr, Co, Ni<0.1) were used also.

Oxygen concentration was measured on tungsten disk samples ( $\emptyset$ 28, h=1.2-2.2 mm) with a help of neutron generator NG -150M («quick neutrons» with

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peak energy 14 Mev). For oxygen concentration determination nuclear reaction

$$^{16}O(n,p) \,^{16}N + \gamma(6.7 \text{ Mev})$$

was used.

Samples after surface oxidation were saturated by oxygen in vacuum chamber were pressure of  $MoO_2$  was a little higher than equilibrium pressure, [5], due to evaporation of additional quantity of  $MoO_3$ .

Reduction of samples with different initial oxygen concentration was carried out in hydrogen with dew point  $\leq -20^{\circ}$ C.

Structure of molybdenum sheets was studied on polished with diamond powder and pastes samples after electrochemically polished in sulphuric acid an subsequent etching in colouring reactive (water solution of  $H_2O_2$  and  $HNO_3$ , [6] Optical microscope «Neophot-32» was used.

#### 3. Experimental Results and Discussion

As it was established earlier, [1,2], oxygen can significantly change structure of deformed molybdenum after annealing in 900-1200°C interval. Typical zone of recrystallisation retardation (ZRR), [1,2] is shown on Fig.1 for 0.45 mm rolled molybdenum sheet cross section. Depth of ZRR usually does not exceed 0.5 mm. Whether somebody would like to restrict his control of recrystallisation structure only on samples prepared without cross sectioning the sheet, it would be possible to conclude wrongly that this sample is not recrystallised at all.

In a common investigation with colleague A.A. Snegirev (ISSP) it was established that after warm rolling tungsten of usual for powder metallurgy technology purity also may forms ZRR of about 20-40 mkm depth.

As it was shown earlier [1,2], local oxygen concentration in ZRR may be at least 1-2 orders higher than in the bulk of molybdenum. And provided ZRR is not eliminated by complete recrystallisation after consequent annealing at high temperatures, its role is not manifested in drastic fall of plasticity. On the contrary plasticity usually arises after formation of ZRR due to additional dislocation sources near samples surface and relatively high plasticity in samples completely recrystallised core, Fig.1,2. The main condition is not to receive completely recrystallised structure. In the last case fall of plasticity would be truly drastic in tests with surface stress concentrators.

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During ZRR formation additional oxygen bonds with defects remaining in deformed structure with negligible level of oxygen contamination in the bulk of material, [2] even after complete recrystallisation in the samples core. Sample with ZRR is alike composite material with different properties of its layers. Strengthening due ZRR formation without disperse particles in relatively pure metals is not big -  $\leq 10\%$  usually, but plasticity arises in comparison with deformed state significantly.



Fig.1 Cross section of 0.45 mm of powder technology molybdenum sheet along the rolling direction (horizontal) after vacuum annealing at 1200°C for 1 hour, x250. The edges of cross-sectioned samples are visible. Photo height corresponds to 220 mkm.



Fig.2 Typical microstructure of commercial purity powder technology molybdenum in zone of recrystallisation retarding, x15 000, [1]. Thin foil electron microscopy.

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The defects (dislocations, subgrain boundaries), Fig.2, concentrates near the surface and helps to realise plasticity in strengthened thereof layers near surface without cracking, usual to recrystrallised molybdenum. We have experience of artificial creation of ZRR as well as preventing of ZRR formation.

Depth of ZRR depends mainly on three factors: surface conditions, metals composition and degree of deformation.

Surface conditions includes two aspects: annealing atmosphere and surface oxide film thickness and homogeneity.

Composition of relatively pure molybdenum, and molybdenum alloys especially, is very important for time-temperature dependence of recrystallisation processes. ZRR may be formed in high purity molybdenum also, but optimal temperature interval of its formation is lower than for molybdenum of commercial purity. More alloyed compositions usually posses higher temperature level of recrystallisation and it helps to receive ZRR with relatively large depth.

Influence of deformation degree was studied on powder metallurgy molybdenum of commercial purity after cold rolling on four-high rolling mill.

Experiments were carried out on 1.5 mm thickness samples after cold rolling in two different initial states:

- after warm rolling down to 1.5 mm
- after warm rolling down to 1.5 mm, cold rolling down to 0.7 mm and complete recrystallisation at 0.7 mm thickness

Rolled samples were annealed for to ZRR formation at 1100°C for 2 hours. Used artificial oxidising before annealing has resulted in ZRR with relatively little dispersion in depth, Fig.3, [7]. Dispersion is shown with a help of «whiskers». For each sample depth was measured twice - under opposite rolling surfaces.

Deformation was estimated as

 $e=ln(t_0/t)$ 

where  $t_0$  is initial sheet thickness and t is thickness before annealing.

It is evident after results illustrated by Fig.3: <u>cold rolling deformation cause</u> <u>significant decreasing of ZRR depth</u>, seems to be almost stabilising after true deformation  $e\approx$ 1-1.5 and subsequent annealing for ZRR formation.

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The only one reason for such behaviour we suppose to be an evolution of samples microstructure during cold rolling: cell dimensions diminishes considerably with deformation, [8] and are almost stabilised after deformations close to above mentioned. Also defects aligns along rolling plane and rolling direction.. Thus the way across the sample for oxygen diffusion by cell and subgrain walls is increased with deformation by rolling and the defect structure capacity for oxygen bonding is increased also with deformation interfering to «quick» diffusion of oxygen in samples depth. It is not possible to propose guantitative model of this mechanism now, but this explanation seems us to be the most probable. It should be mentioned that at relatively low temperatures of annealing measured residual oxygen concentration was higher and defects concentration near surface was higher too. Dependence of ZRR depth on temperature is more complex: it has a maximum.



Fig. 3 Dependence of ZRR depth (in mkm) (zone of recrystallisation retardation) on «true» deformation e by cold rolling for molybdenum sheet of commercial purity. Circles corresponds to rolling from 1.5 mm without previous annealing, triangles - to rolling after complete recrystallisation annealing at 1100°C for 2 hours, [7].

ZRR may be eliminated by subsequent annealing in hydrogen with low dew point and oxygen concentration "returns" to an initial level.

Data concerning oxygen concentration in tungsten seems us to be even more fragmented, than for molybdenum. One of the possible reasons for such situation is caused by serious difficulties in samples ( $\emptyset$ 28, h=1.2-2.2 mm)

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preparation. It is very easy to damage relatively thin tungsten sample of high purity even during oxygen concentration measuring in appropriate device on NG-150 neutron generator.

We have chosen warm (~1100°C) rolled down to 1.5-2.0 mm and then turned on tungsten disk samples without cracks - all of them were with oxygen concentration  $\leq$ 1.0  $\pm$ 0.2 ppm. And oxygen seems to be distributed not in a narrow layer under surface - polishing and etching of 15-100 mkm from each surface changed not oxygen concentration significantly.

Samples with oxygen concentration about 1 ppm were treated in atmosphere of hydrogen with dew point  $\leq$ -20°C at 1530°C for 2 hours. After this procedure oxygen concentration diminished down significantly to 0.5 ±0.2 ppm value.

Rough estimation of oxygen diffusion coefficient D (cm<sup>2</sup>/sec) is possible for given diffusion length  $\lambda$ =0.0750 -0.10 cm, diffusion time  $\tau$ =7200 sec

## $\lambda \sim (\tau^* D)^{0.5}; D \sim \lambda^2 / \tau$

gives  $D\sim(0.8-1.4)*10^{-6}$  cm<sup>2</sup>/sec for 1530 °C. This coefficient is of the same order as it was estimated after extrapolation to 1530°C of oxygen diffusion, [9], in molybdenum data.

This experiment also allow us to estimate 2 hours time interval of sample saturation by oxygen as sufficiently big to achieve quasi uniform distribution of oxygen in a sample during annealing at 1430-1630°C temperatures and 2 hours duration of annealing.

After oxidation of rolled and previously etched samples surfaces they were saturated with oxygen as it was described above at 1420, 1530 and 1630°C during 2 hours annealing. It was established that these time-temperature conditions provided complete recrystallisation of tungsten of high purity samples.

Even for 1-2 mkm steps for etching there was not found any layer near surface with increased oxygen concentration. Possible reasons may be connected with relatively low density of defects in warm rolled tungsten after such annealing and relatively low concentration of oxygen bonded on these defects in comparison with molybdenum.

Only 1-2 samples of acceptable quality it was possible to receive for each temperature of annealing.

Increase of oxygen concentration in comparison with preliminary controlled in every such sample was:

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Temperature, °C	Number of samples	Increase of oxygen concentration, ppm
1420±10	1	0.3±0.2
1530±10	2	0.5±0.2
1620±10	2	3.8-5.3

It is seems to be interesting, that value of 0.5 ppm we have received for 1530°C experiments twice: after treating in hydrogen atmosphere of relatively «oversaturated» by oxygen tungsten (3 samples) and after oxidation of relatively pure from oxygen tungsten (2 samples). The measured concentration change corresponds to the same rate of oxygen diffusion at the same temperature and the same .diffusion coefficient.

#### 4. Conclusion

1. Depth of ZRR (zone of recrystallisation retardation) diminishes with degree of deformation during rolling. Possible role of oxygen diffusion in defect structure is discussed. Strengthening due ZRR formation without disperse particles in relatively pure metals is not big -  $\leq 10\%$  usually, but plasticity arises in comparison with deformed state significantly.

2. Diffusion coefficient of oxygen in tungsten at 1530°C may be estimated as  $D\sim(0.8-1.4)*10^{-6}$  cm<sup>2</sup>/sec both in experiments in hydrogen and oxygen containing atmosphere.

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# Thermal Processes Under Mechanical Treatment of Powders and their Role in their Structure and Properties Formation of Dispersed Systems

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### Summary:

The defect formation as well as thermal processes that occur in materials under mechanical treatment are of special interest for the specialists working with disperse media. So, after switching on the grinder, grinding - defect formation process is accompanied with heat release. In other words, the mechanical reactor becomes to work simultaneously as a heat reactor. The heat released is being spent for heating DM, grinder components and environment. This report deals with some possibilities of experimental EPR study of the role of annealing that the spiking and accumulating mechanothermal effects play in the formation of a defect structure of the powders under mechanical treatment (grinding, pressing). The interesting possibilities of the directed modification of powders defect structure by changing the mechanical treatment conditions are discussed.

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The defect forming as well as thermic (mechanothermic) processes which occur in the material under mechanical treatment (MT) are of special interest for the specialists working with disperse media (DM). The guestion is that both the initial DM and the resulting product are usually considered from the position of external temperatures identity (for example, room temperature). Nevertheless, the situation is far from unambiguous one. Indeed, at the initial stage DM. mechanical reactor (grinder) and environment are in the identical temperature condition. But after switching on the grinder, grinding - defect forming process is accompanied with heat release. In other words, mechanical reactor becomes to work simultaneously as a heat reactor. The heat released is being spent for heating DM, grinder components and environment. And only after switching off the grinder, the grinder - DM system is cooling down to room temperature. Making measurements in the reactor under operation is a difficult enough problem. So, we have to do with the «black box» situation when studying the processes which occur directly under mechanical treatment of disperse media. This report deals with some possibilities of experimental study the role that the mechanothermal effects play in forming the defective structure of the DM under mechanical treatment.

The main areas of heat release when loading (shock) may be zones of new surface forming, zones of dislocation development and displacement, zones of interparticle friction (i.e. defect forming zones), zones of friction of the reactor's working parts [1]. In the case of high rates of fracturing under adiabatic conditions, the expected upper temperature limit at the top of the opening crack may be obtained using the Q value (heat released an the result of irreversible plastic deformation dependent on the cracking resistance R:  $Q=0.6\div0.9R$ )

 $\Delta T=T-To=Q/(c\rho \cdot 2\delta),$ 

(1)

where c is the specific heat,  $\rho$  is the density,  $2\delta$  is the width of the destruction zone [2]. This estimation [3] shows that maximum temperatures achieved at cracking exceed significantly 1000 K.

According to [4], the temperature in a zone of dislocations moving with a rate  $\upsilon$  under mechanical stress  $\sigma$  results in a temperature rise given by

 $\Delta T \approx b \sigma \upsilon / 2 \pi K n ln(n \Lambda / \lambda)$  if  $\lambda << \Lambda, \Lambda = 2 \chi / \upsilon$  (2)

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where: b is the Burgers vector, K is thermal conductivity, n is a number of movable dislocations,  $\chi$  is the temperature conductivity,  $\lambda$  is the mean distance between dislocations. In [5] a rise of temperature up to 1000 K in the process of deforming has been reported.

When the particles constituting the disperse system, i.e. the particles being in contact with each other, are in movement, the work being done against friction forces is transformed into a heat which is released. It has been shown [5, 6] that during sliding friction the temperature of contact areas increases up to the melting point of one of the substances. A formula has been proposed for evaluating of local temperatures at the contact of the bodies in friction as follows:

 $\Delta T = \mu P v / 4a l 1 / (k_1 + k_2)$ 

(3)

where:  $\mu$  is the friction coefficient, P is the pressure at the contact surface, v is a sliding velocity, a is a radius of contact area, I is Joules equivalent,  $k_1$  and  $k_2$  are thermal conductivities of the bodies in friction. According to this relationship [5], momentary temperature jumps up to 1300K may occur during this process. The duration of such temperature pikes at the area of  $10^{-7}$  -  $10^{-9}$  m<sup>2</sup> is of the order of 10<sup>-4</sup> s.

The process of development of mechanothermic effects in grinders -activators is of a space-heterogeneous and interruptive character. So, we have to expect the manifestation of collectivised mechanothermic effects. In the case of a single micro-crack (dislocation zone) development, the shape of ultra-high temperature jump will depend on the thermal conductivity of the material (Fig.1a). Thus, it is hard to estimate its role in modifying the defect structure because the active zone dimension  $\delta$  is much less than the specimen dimension I. In the case of forming the destruction zone with high local density of micro-cracks, transformation of a number of short-time single ultra-high temperature jumps into the averaged «collectivised high-temperature jump» of the zone with significantly larger duration takes place (Fig. 1b). The shape of the hightemperature jump must depend on the destruction-deforming mechanism, on the local density of initiated defect states and on the dimension of the destruction zone, the character and heat conductivity of its environment.

In the case of long-time MT, certain time is needed for the working system to go to the thermodynamic equilibrium state with the environment. Naturally, the equilibrium temperature T<sub>ea</sub> in DM will depend on temperature condition, type of

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grinder, amount of material, and so on. The kinetic scheme of the development of thermal processes in DM under treatment accounting collective processes is proposed in Fig. 1c:



Fig. 1. Scheme of temperature kinetics by MT of a disperse system: a) formation of a single micro-crack; b) high local density of micro-cracks. Contributions from single micro-cracks are indicated by the dashed line; c) disperse system. Thin vertical lines correspond to the contributions from «collective high-temperature spikes».

Thus, the formed «primary» defect structure is subject to thermal impact both of its own local ultra-high-temperature and collectivised high-temperature jumps, and significantly prolonged influence of the averaged temperature of the DM itself. We may expect in this case that the mechanothermic effects in the formation of the resulting defect structure of the powders under treatment will be of an annealing nature. The annealing kinetics for every individual centre (defect) may be described by the equation of the following type:

 $dn/dt=-n^{\gamma}K(T)$ 

(4)

where n is the concentration of the defects of particular type,  $\gamma$  is the reaction order, K(T) is the rate of the reaction constant (often but not always K(T) =K<sub>o</sub>e<sup>-</sup>  $E^{/kT}$ ) [7]. The solution of this expression for the reaction of first order is as follows:

 $\ln(n_t/n_0) = -K(t)$ 

(5)

where  $n_0$  is the concentration of centres in the initial moment of the action.

Such an approach makes possible to model the experiment which will allow us to learn the character of defect formation under MT and the effect of hightemperature jump upon the developed defect structure. The necessary preconditions of the experiment must be: preserving of the destruction zone dimensions, modification of its environment by changing the thermal conductivity, and minimum contribution of the temperature impact of the DM itself. Such an experiment may be carried out in the grinding process of the modeled material particles, playing a role of destruction zones, in the surroundings of the particles from other materials having a different heat conductivity.

MT of ZnO, the ZnO-SnO<sub>2</sub> (57:43 %mas.) and ZnO-TiO<sub>2</sub> (45:55 % mas.) resulted in initiation of EPR-signals in ZnO from V<sup>-</sup> <sub>Zn</sub>:Zn<sup>0</sup> - center with  $g_{\perp}$ =2.0190 and  $g_{\parallel}$ < $g_{\perp}$  -signal I [8, 9]; from V<sup>-</sup><sub>Zn</sub> - center with  $g_{\perp}$  =2.0130 and g<sub>1</sub>=2.0140 - signal II [9, 10] (in the ZnO-TiO<sub>2</sub> specimens this signal was practically absent); and from  $(V_{2n})_2$  -center with  $g_1 = 2.0075$ ,  $g_2 = 2.0060$ ,  $g_3 =$ 2.0015 -signal III [8, 9] (Fig. 2). The intensity of EPR-signals I, II and III in ZnO in all three systems was proportional to t (time of their MT). Maximum initiating of EPR signals I, II and III is characteristic of specimens of the ZnO-SnO<sub>2</sub> system. One can see a good enough correlation between micro-strength of specimen components and the increment of signal III. It was also observed to a less extent for the signal I while such a correlation was not observed between intensities of the signal II.

Fig. 3 presents the changes of the signals intensity I, II, and III dependent on the anneling temperature  $T_{an}$ . It follows from this figure that up to a value of  $T_{an}$ 140 °C not significant changes were detected. Beginning from T<sub>an</sub> = 155°C, a decrease of signal II, small increases of the signal III were indicated, being the intensity of the signal I practically constant. Signal II practically disappeared after treatment at T<sub>an</sub> = 180°C and the registered EPR-spectrum was practically the same as the EPR-spectrum in the mechanically-treated specimens of the ZnO-TiO<sub>2</sub> system (see Fig. 2). A decrease in signal I (smoother than signal II) was observed at T<sub>an</sub> =170°C and it disappeared after thermal treatment at T<sub>an</sub>= 220°C. These data allows us to interpret the centres responsible for the signal III as the most stable formations and the centres responsible for signal II as the least stable ones.

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Fig.2. EPR-spectra initiated in ZnO by the mechanical treatment of  $ZnO-SnO_2$  (a), ZnO (b) and ZnO-TiO<sub>2</sub> (c) specimens.



Fig.3. Influence of annealing temperature on the intensities of EPR-signals I, II and III initiated in ZnO by MT (t=5 min) of *a*-specimens.

Using the intensities of signal III as the standard signal indicating the «level of detection» of the mechanically treated ZnO particles, we may analyse some interesting aspects of the signals I and II formation. We may see that the relative intensities  $I_i/I_{III}$  and  $I_{II}/I_{III}$  are maximum in the specimens for the system ZnO-SnO<sub>2</sub> ( $I_i/I_{III} \sim 0.3$  and  $I_{II}/I_{III} \sim 1$ ) which contains additives with maximum heat conductivity, medium for ZnO ( $I_i/I_{III} \sim 0.25$  and  $I_{II}/I_{III} \sim 0.2$ ) and minimum for specimens of the ZnO-TiO<sub>2</sub> system ( $I_i/I_{III} \sim 0.12$  and  $I_{II}/I_{III} \sim 0$ ), i.e. the system with the additives having the minimum heat conductivity.

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The gualitative changes of the EPR- signals depend on the heat conductivity of the additives and are similar to those in the spectra forming under heat treatment. This allows us to connect the first with the specificity of the development of the mechanothermal processes and with their «annealing» effect upon the formation of defect structure. High locality of zones of heat release may cause the chain-like process of heat transfer: micro-particle dispersion system - components of grinder-activator - outer space. The process of the establishment of Teg in the mechanothermically excited particle will depend on its dimensions, the heat locally released, the thermal conductivity of the components of the chain as well as on the temperature of the dispersion system.

The changes with time of the particle energy density may be calculated from the heat transfer equations for the problem without heat source [11]

$$q=Q/(4\pi\chi t)^{3/2} \exp(-r^2/4\chi t)$$
 (4)

where Q is the heat released when t=0 in the point r=0. The dispersion systems under consideration are the porous ones. According to [12] the temperature conductivity of porous formations may be described by the following expression:

$$\chi = \chi_{0} \left( 1 - \Theta_{S} \right)^{m-1} \left( 1 - \Theta \right)$$
(5)

where  $\chi_{o}$  is the temperature conductivity of a porousless material,  $\Theta_{s}$  is the relative part of free surface of contacting particles ( $\Theta_s = S_{\text{free}}/S_{\text{total}}$ ),  $\Theta$  is the porosity, m - depends on the state of dispersion system and usually lies within the range of 2-5. Thus, the temperature conductivity of porous formations may differ from the temperature conductivity of volume material by several orders of magnitude.

One can see that the duration of the thermal jump on the particle is inversely related to the temperature conductivity of its environment, i.e.  $\tau \sim 1/\chi$ . From this point of view, the least durable heat jump (with the least annealing effect) must occur for specimens of the ZnO-SnO<sub>2</sub> system and the most durable heat jump (with maximum annealing effect) - for specimens of the ZnO-TiO<sub>2</sub> system. We just observed such a situation.

The interesting possible applications of modifying of fine defective structure of dispersion systems by MT are noted.

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# EFFECT OF THE HIGH PRESSURE ON THE DENSIFICATION OF Nb-ATR POWDER COMPACTS

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#### Summary:

This work presents the results of the compacting behavior of Nb-ATR powder under high pressure. The powder was produced by the aluminothermic reduction of Nb<sub>2</sub>O<sub>5</sub>, followed by mechanical comminution (< 38  $\mu$ m). The samples were initially pressed in a cylindrical steel die of  $\phi$  = 7 mm at 500, 700 and 1,000 MPa, followed by high pressure of 2.0 - 6.0 GPa. The experiments of high pressure were carried out in a special hydraulic press of force 630 ton. using an HPHT toroidal type apparatus of concavity 13.5 mm. Emphasis is put on the correlation between the compact final density and the pressure used in the precompacting and high pressure. The results have shown that the compacts densification are strongly dependent on the applied precompacting and high pressure values.

#### Keywords:

Compacting, densification, high pressure, niobium-ATR powder

#### 1. Introduction:

The main technological characteristics of niobium are high melting point of 2468 °C, good acid corrosion and wear resistance, good fabricability, and stable oxide film with high relative dielectric constant (1). Their main applications are in chemical and metallurgical industry, medical field, superconductivity, and electronic devices (2,3). Niobium is mainly processed by powder metallurgy techniques.

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Some of the techniques of powder metallurgy usually employed for fabrication of niobium powder compacts of high density are rigid die pressing and cold isostatic pressing, followed by high vacuum sintering at high temperature(4). To obtain high densities it is necessary to use very high sintering temperatures, however, at considerable expenses. In addition, at high temperatures grain growth takes place intensely. An alternate approach that have been studied to achieve these high densities is the activated sintering(5).

The introduction of new techniques or perfecting of the recent techniques of powder compacting is of high technological interest. The compacting behavior of metallic powders in the conventional pressure range (10 - 800 MPa) have been intensity studied(6,7). In this work we investigated the densification of niobium-ATR powder under high pressure. The objective is to obtain compacts of high final density (near theoretical density) without external heating supply, eliminating sintering step.

#### 2. Experimental Procedure:

The niobium-ATR powder used in the work was produced by Faenquil-Demar (Lorena-SP). Initially the niobium-ATR electrode was obtained by aluminothermic reduction of the Nb<sub>2</sub>O<sub>5</sub> oxide (8). The niobium-ATR density of  $5.99 \text{ g/cm}^3$  was determined by picnometry.

The niobium-ATR powder was produced by mechanical comminution. The electrode was ground in a niobium-aluminum rammer (particle size range > 200 mesh) and subsequently ground in a ball mill. The cup and milling ball were made of niobium. The powder was than classified by sieving down to 400 mesh (< 38  $\mu$ m). The powder apparent density was of 1.79 g/cm<sup>3</sup>. The morphology of the powder particles was observed by scanning electron microscopy (Zeiss, DSM 962 model) opering at 15 kV. The present phase identifications were done by X-ray diffraction (Seifert, URD 65 model) using Cu-K $\alpha$  radiation.

Initially the niobium-ATR powder was submitted to the precompacting step by using a steel cylindrical die of 7 mm diameter at 500 MPa, 700 MPa and 1,000 MPa. After this procedure, the obtained compacts were pressed under high pressure. In the experiments of high pressure it was used an HPHT toroidal type apparatus with concavity of 13.5 mm to the generation of high pressure. This apparatus permits the accomplishment of compacting test in samples of 7mm diameter and 9 mm height. The necessary force to generate high pressure was applied on the HPHT apparatus using a special hydraulic press of 630 ton (Ryazantyashpressmash, D0138B model). The applied high

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Figure 2 - X- ray diffractogram of the niobium-ATR powder.

The results of the rigid die compacting of niobium-ATR powder are given in Table 1. An increase of the green density can be observed as the compacting pressure increased. However, the increase of the green density between 700 MPa and 1,000 MPa is very modest. At the end of this precompacting step the densified niobium-ATR powder is still far from high density stage. The values obtained represents only 76.8 - 80.6 % of the niobium-ATR theoretical density. An explanation for this may be the powders-ATR particles that are very hard and difficult to compact, which provokes density gradients(11). This indicates that a new increase of green density with increase of pressure is very difficult by using rigid die compacting.

Samples	Precompacting (MPa)	Green Density (g/cm³)	Relative Density (%)
A	500	4.60	76.8
В	700	4.77	79.6
С	1,000	4.83	80.6

## Table 1 - Results of rigid die compacting of niobium-ATR powder.

Table 2 shows the results of the compacting under high pressure. For most metal powders the compacting behavior during pressing has been evaluated by using plots of density after compaction versus pressure. As it can be observed the applied precompacting to the niobium-ATR powder positively influenced the final density (Fig. 3). Higher final densities are achieved under high pressure, where densification levels > 98 % are obtained in green compacts.

Samples	Precompacting (MPa)	High Pressure (GPa)	Final Density (g/cm³)	Relative Density (%)
A1	500	$2.00\pm0.05$	5.69	95.0
A2	500	$4.00\pm0.08$	5.72	95.6
A3	500	$6.00\pm0.10$	5.88	98.2
B1	700	$2.00 \pm 0.05$	5.57	93.0
B2	700	$4.00 \pm 0.08$	5.81	97.0
B3	700	$6.00 \pm 0.10$	5.25	87.7
C1	1,000	$2.00 \pm 0.05$	5.82	97.2
C2	1,000	$4.00 \pm 0.08$	5.87	98.0
C3	1,000	$6.00 \pm 0.10$	5.52	92.2

Table 2 - Results of high pressure compacting of niobium-ATR powder.

In the range of 500 - 2,000 MPa the densification rate is relatively high, and different mechanisms of powder consolidation act simultaneously during compacting. This mechanisms are: 1) plastic deformation localized at the contact points between grains, leading to work hardening; and 2) axial plastic

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deformation of each grain. Perhaps powder-ATR agglomerates fracture occurs. Already in the range between 2,000 MPa - 6,000 MPa the densification rate is low. In this range of pressure the predominant mechanism is the axial plastic deformation of the grains.

Also, probably cold welding between the grains occurs, which contributes to the development of higher final densities.



#### Figure 3 - Relative density versus logarithm of pressure for the niobium-ATR powder.

It should also be noted in Figure 3 that some important changes occurred in the final density, when high pressure above 4,000 MPa is applied. Reduction of the final density is observed. This can be explained because, under these conditions, densification occurs, and also the influence of the residual shear stress in each grain provoked by a new increase of axial plastic deformation. As a consequence it occurred the appearance of microcracks in the grains and also in the compacts transverse sections.

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From these results of high pressure it is suggested that the ideal value for precompacting is between 500 - 700 MPa. This fact is related to the major easiness of the conditions of compacting operation. On the other hand, the ideal value of high pressure is up to 4,000 MPa. Above of this value the compacting operation is very critical. It is observed decrease of the final density of the green compacts, as well as the appearance of structural defects in these pressed compacts.

#### 4. Conclusions:

The results presented allow the following conclusions to be drawn: the niobium-ATR powder had angular morphology, and is constituted by the phases Nb<sub>ss</sub>, σ-Nb<sub>2</sub>Al and NbAl<sub>3</sub>. The compacting of this powder in rigid die is very difficult as the objective is to obtain high density.

The application of precompacting followed by high pressure permitted to obtain high final densities, with densification levels > 98 %. Two different densification mechanisms govern the compacting under high pressure: 1) plastic deformation at the contact points between grains; and 2) axial plastic deformation of each grain. It was also verified that the high final densities obtained under high pressure are dependent on applied precompacting. In general, it is recommended a precompacting value between 500 - 700 MPa and a high pressure value up to 4,000 MPa.

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# CHARACTERISATION OF POWDERS

## UP TO DATE LAWS OF COMPRESSION

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#### Summary :

Many studies have been carried out in order to be able to describe the relationship d = f(P) of the compression phase of a powder in a more or less empirical fashion. Among the different laws, that of Heckel is the more frequently applied. The inconvenience of this, however, is that it does not bear witness to the behaviour of the powder at extremely low pressures. Two new laws are described hereinafter (a complement to Heckel's Law and a new model), in attempt to solve this problem. The outcome of these equations forms the basis of the identification of the analysed powder, and its statistical sample testing contributes to product quality control.

#### Key words :

Characterisation - Powders - Compressibility - Statistical process control

#### 1. Introduction :

Powder compression is a major part of powder metallurgy. This phase, which consists of a progressive reduction of porosity under the effect of a pressure field, brings complex phenomena into play.

Many studies (1-3) have been carried out in order to determine the equations which would allow to describe the density = f (pressure) in a more or less empirical fashion.

Thus, HECKEL's law, one of the more frequently used laws, describes the redensification of a compressed item in the field of plastic deformation of particles. The main inconvenience of this Law is its inability to define the behaviour of a powder at the lowest possible pressures, which are those used in industrial processes of compression. B. Cathala et al.

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This is the reason for which further research has been carried out on the basis of Heckel's Law in search of a new law to describe the relationship density = f (pressure) also for the lowest pressures.

#### 2. Heckel's Law and its complement at low pressures :

HECKEL suggests the following relationship :

with: P = Pressure

d = density measured for a given P
dth = theoretical density of the non-porous material
D = d / dth
A, K constants, characteristic of the powder in question

By plotting ln(1/(1-D)) = f(P), in the adapted pressure field (200 to 1000 MPa for W powders for example), we get a straight line, of which the ordinate at origin A and the slope K characterise the powder (or the mix of powders) in question. (see figure 1).

Fig 1. Heckel's Law – Determination of parameters A and K



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In order to have data which also describes the behaviour of powders at the lowest pressure fields, CIME BOCUZE carried out studies intending to demonstrate the fact that the deviation between Heckel's Law and the actual density measured is a linear function of In(P).

The suggested relationship is as follows:

Thus, Heckel's Law, and its complement at low pressures may be used to characterise metal powders or powder mixes. Parameters A, K, B and C would hence constitute the identification for the behaviour of the characterised powder under compression. Generally speaking:

- A and B are relative to the morphological and topological characteristics of the basic powder grains.

- K and C are representative of the energy to be dispersed to break the inter-crystalline bonds, mainly on agglomerate levels, and to plastically deform the inter-crystalline necks.

This compressibility test is used on a daily basis during powder acceptance inspection procedures before they are submitted to production lines.

For example, both table 1 and figure 2 specify the typical values of parameters A, K, B and C of Heckel's Law and its complement, for four different supply sources of tungsten 4-5  $\mu$ m fisher powders.

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# Tab 1. Parameters A, K ,B and C for different supply sources of tungsten 4-5 µm fisher powder

	Fiel	d 200 -	- 1000	MPa		Field 0	) – 200	MPa	
	in ( 1 / (1-D) = A + KP			In ( 1 / (1-D) = A + KP – (B + C In P)					
	A (* 100)		K (* 100 000)		B (* 100)		C (* 1000)		
	М	σ	М	σ	М	σ	М	σ	
Supplier 1	74	(2.0)	59	(2.0)	26	(2.0)	46	(3.0)	
Supplier 2	76	(3.0)	64	(1.0)	37	(2.0)	63	(3.5)	
Supplier 3	83	(2.0)	60	(0.5)	37	(2.0)	63	(4.0)	
Supplier 4	74	(1.5)	61	(1.5)	36	(2.0)	63	(4.5)	

- M:mean

σ : standard deviation





A\*100

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Thus, the following points are highlighted :

- <u>At low Pressure</u>: The "Supplier 1" powder differs from the other 3 due to its significantly weaker parameters B and C, to be linked with a lesser degree of agglomeration -aggregation owing to the characteristics of this supplier's production process.

- <u>At high Pressure</u>: The "Supplier 3" powder differs from the others due to its significantly higher parameter A. This is linked to a specific small grain/large grain size distribution favouring optimum packing at zero pressure.

- "Supplier 2" and "Supplier 4" powders, of which the morphologies are closely related, show very similar parameters A, K, B and C.

### 3. Relationship d = f(P) – new equation proposal :

Use of HECKEL's model and its complement at low pressures enables the characterisation and sample testing of the identification of compressed powders and powder mixes used in powder metallurgy.

The inconvenient aspect of this methodology is that two distinct mathematical models must be used in order to describe the behaviour of a powder throughout the entire pressure field in question.

Figure 3 shows experimental results d=f(P) for the 4 previously studied tungsten 4-5 µm powders.

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The curves obtained appear to be similar to "power law" curve results. It was therefore interesting to check whether it was possible to offer a model based on this principle which described the entire pressure field to be studied.

The new relationship offered is as follows:

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where: P = Pressure

d = density measured for a given P

dth = theoretical density of the non-porous material

do, K, n = constants characteristic of the powder in question

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This relationship was applied to previously studied tungsten 4-5 µm powders in order to determine the parameters; do, K and n specific to these powders (see table 2 and figure 4). The correlation coefficient ( $R^2 > 0.99$ ) suggests the adequacy of the empirical results to the law proposed.

Tungsten 4-5 µm powders Parameters; do, K and n of the law (d-do) / (dth/do) = K P<sup>n</sup> do Κ n Supplier 1 8.12 0.0186 0.491 7.37 Supplier 2 0.0340 0.415

Supplier 3	8.24	0.0326	0.417
Supplier 4	7.27	0.0345	0.411

Fig 4. Tungsten 4-5 µm powders – parameters; do and n



Tab 2.

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These results highlight the specific behaviour of the powders provided by each of the suppliers. In particular, they confirm the conclusions of the HECKEL test:

- Closely related behaviour of powders provided by suppliers 2 and 4.
- Specific behaviour of powders provided by suppliers 1 and 3.

Moreover, it was necessary to ensure the new model proposed could also describe the behaviour d = f(P) of a large spectrum of metal powders and powder mixes, and possibly even powders with an added organic binder.

Tests were therefore performed on the following samples:

- Submicronic tungsten (W) powders
- Molybdenum (Mo) powder
- Nickel (Ni) powders
- Silver (Ag) powders
- Mix of tungsten-nickel-iron (W-Ni-Fe) powders
- Granules of a mix of tungsten-nickel-copper (W-Ni-Cu) powders
- + organic binder

The results obtained are shown in table 3.

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Tab n°3.	parameters; do, K and n of the law	$(d-do) / (dth/do) = K P^{n}$
	for different types of powder	

	do	К	n	R <sup>2</sup> correlation coefficient
Non-milled submicronic W powder	3.94	0.0744	0.274	0.997
Milled submicronic W powder	6.63	0.0188	0.445	0.997
Mo powder	1.83	0.1033	0.288	0.999
Ni powder	3.17	0.024	0.51	0.998
Ag powder	1.52	0.1559	0.283	0.998
W-Ni-Fe mix	8.05	0.0196	0.487	0.999
W-Ni-Cu granules + organic binder	8.23	0.1861	0.22	0.991

This table shows that regardless of the type of powder or powder mix studied, the correlation coefficient obtained between the model and the experimental data is very high for the density-pressure field in question.

This new law may thus be used for the acquisition of the identification of a standard powder as well as for the sample testing of a given supplier by means of Statistical Process Control (SPC) type sample testing of this powder's parameters do, K and n.

To give an example, the sample testing of do and n for the tungsten  $4-5 \ \mu m$  powder provided by Supplier 4 is shown in figures 5 and 6.

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#### Fig 5. Supplier 4 – SPC sample testing of the do parameter



Fig 6. Supplier 4: SPC sample testing of the n parameter



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## 4. Conclusion :

Powder compression is a major part of powder metallurgy. It is therefore important to be able to acknowledge, or even model the behaviour of a powder or a mix of powders during this vital phase.

Among the different models offered, Heckel's Law is one of the more frequently used. It nevertheless shows the inconvenience of not being representative of powder behaviour for the lowest levels of pressure. This is why a complement to Heckel's Law at low pressures is suggested.

For each powder or powder mix, these two laws thus provide access to four parameters (A, K, B and C), which are characteristic of this powder mix. These 4 parameters form the basis of the powder's identification, and their sample testing may be used for quality control each time the powders are delivered.

It is, however, impractical to have to resort to two distinct laws in order to characterise a compressed sample for the entire pressure field to be studied. This is the reason for which a new model meeting this need has been suggested. The validity of this law was checked on a group of metal powders and powder mixes (which may have contained organic binders).

So, to describe the whole of the pressure field studied, it is thus possible to use only one model providing 3 parameters of the analysed sample's identification, of which the SPC would contribute to quality control procedures.

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# The Development of Processes of Pressing of Articles from Powders on the Bases of Metals, Ceramics and Graphite

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#### Summary:

In the article we offer technological circuits of dry isostatic pressing at the compression in sealed volume and sequential cyclical loading. We represent original process equipment and appropriate technological processes of pressure handling of materials of different properties and compression nature. The offered technologies are designed for the manufacture of a broad spector of articles: porous permeable, constructional, heat-resistant, tools etc on the bases of metals, ceramics and graphite. There are examples of producing of some powder articles and new compositional materials with given properties in manufactured products.

#### Keywords:

Dry isostatic pressing, powder, material under compressing, technological process, powder article

Pressing processis belong to the basic production phases of powder metallurgy and to great extand define properties and quality of ready articles.

The development of pressing processes of powder materials (PM) is being carried out in 3 directions (1):

- developing of theoretical bases;
- creation and research of new technological processes;
- improving of traditional models by creating new equipment and instruments.

In works (1-4) it is determined that the description of multifactor seal process of the irreversibly pressed mediums can be based on studying the contract interaction of the particles of the medium or using continuous ideas about its heological properties. The advantage of contact theories based on

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simulating of seal process is its relative simplicity of estimating energy-power parameters and density. At the same time the canonization of some positions has caused the refusal from the search of new schemes of strain. The coming of new models of pressing promoted moving from studying contact interaction of particles to the developing continuous idea. Independent development of both directions or using them together allows to get the most authentic picture of behavious of powder medium and the whole pressing, the seal of PM should be considered a deformation process of the bodies being pressed, whoes properties are defined not only by porousity but also by mechanical and structural characteristics of the medium.

Let's consider the model of the toughness of powder materials with the surface of loading as an ellipsoid, that shows the correlation of the component of an effort tensor with the density and mechanical and structural characteristics of the medium.

The surface of loading looks (3):

$$\frac{3p^2}{\psi^2} + \frac{2T^2}{\varphi^2} = 1 \quad , \tag{1}$$

where  $p = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$  – hydrostatic pressure;

$$T = \frac{1}{\sqrt{6}}\sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_1 - \sigma_3)^2} - \text{intensity of tangent efforts};$$

 $\psi$  and  $\varphi$  -- functions of mechanical and structural performances of squessed materials,

$$\Psi = 2\sqrt{3}\sigma_{\tau_o} \left(\frac{\upsilon}{\upsilon_o}\right)^m \ell n \frac{1-\upsilon_o}{1-\upsilon}, \qquad (2)$$

$$\varphi = \frac{2\sqrt{6} \,\ell n \left(\frac{1-\upsilon}{1-\upsilon}\right) \left(\frac{1}{\upsilon_o}\right) - (1+\xi)\sigma_{\tau_o}}{\sqrt{9\left(\frac{\upsilon}{\upsilon_o}\right)^{2m} - (1+2\xi)^2 \left(\frac{\upsilon}{\upsilon_o}\right)^{2\ell}}},\tag{3}$$

were  $\sigma_{T_{1}}$  -- yield point of the material of dust particles in the initial state;  $v_{o}$ and v -- initial and current relative density; m and I - indexes of hardening of the descrete material at hydrostatic seal and axial pressing accordingly;  $\xi$  -factor of side thrust, depending on the porousity and properties of the material of the powder (1).



Fig. 1. The geometrical image of the surface of fluctuation of compressed powder materials at various densities

Fig. 1 illustrates the geometrical image of the surface of fluctuation of compressed powder materials at various values of density. When density is close to the theoretical, the surface of loading looks like a streched ellipsoid. It passes into the Mises surface at  $v \rightarrow 1$ , when  $\sigma_{ii} \rightarrow \infty$ .

Considering together the term of toughness, equations of equilibrium and the associated law of current limiting conditions:  $\varepsilon_z = 0$ , we get the basic equation for calculating the pressing pressure:

$$\sigma_r = \rho = \sqrt{\frac{\psi^2 + \phi^2}{3}} \tag{4}$$

The development of the theoretical ideas about deformation processes in compressed powder mediums is necessary for developing new and improving present processes of pressing.

From the variety of powder articles we should select long-length articles and articles of complex shape, the necessity of which grows with the

technical progress. The length of the articles is characterized by the ratio of length *I* to the maximum transversal size b ( $1/b \ge 3$ ). The preference is usually given to rotating bodies as they are the mast technological in manufacturing and exploitation.

The radial scheme of pressing is optimum for producing long-length articles (pipes, rods, bodies of complex shape) (1). It's characterized by reducing cross-sectional area of the mandrel when powder compressing. With the excluding of the processes of rolling and extruding it is carried out by means of elastic deforming instrument in hydrostatics, hydrodynamic machines, devices for dry isostatic pressing (DIP). The radial powder compression by means of the elastic instrument ensures uniform compression of all volume and thus the elimination of local planes of strain density and conditions for violations of unity at the stages of pressing and consequent sintering, that guarantees the required quality of the product.

The most perspective mode of pressing is DIP, which ensures saving of material consumption and cost of the equipment, improving of the efficiency, safety and culture of production (1).

We distinguish 2 basic DIP varieties:

- DIP at seal of a powder in closed volume on a mandrel or matrix;
- Sequential DIP at seal of a powder in nonclosed volume on a mandrel or matrix with the use of reusable elastic reinforced envelopes.

The scheme of the most universal device realizing DIP at seal of a powder in closed volume on a mandrel is submitted on fig. 2. Basic elements of the device are: the case 1 and the elastic inset 2, located in the central hole of the case making hermetic annular gap.

Pressing of the powder 3 is carried out in the mould which consists of the forming rod of a mandrel 4 and the elastic envelope 5. The construction of the device is carried out in such a way that the axial movements and strains of the mould elements and strains of the elastic inset 2 are eliminated. The axial strains of mould elements and the pressed preform are also eliminated. The central hole of the elastic inset 2 forms the working chamber of the device, deforming overall dimensions of the used mould. The sizes and the shape of the pressed body are defined by the appropriate parameters of the mould. When creating high pressure in the working concavity of the device, the elastic inset 2 and the envelope 5 due to the theological properties of their material uniformly distribute the pressure to the outside surface of the compacted preform pressing it on the mandrel 4 along the whole length. After the pressure recite the preform with an article is extracted and the process is resumed. The advantage of the circuit is the closed hydraulic scheme of small volume and the isolation of the mould with a preform from the hydraulic fluid



Fig. 2. The scheme of press-block to DIP: 1 - case; 2 - elastic inset; 3 powder; 4 - mandrel; 5 - elastic envelope

by means of the elastic inset 2, that allows to eliminate the evacuation and capsulation of the mould at each cycle of the pressing, as it happens in case of hydrostatic pressing (5). When seal of pressing the air goes out through the clearances between the mandrel 4 and the envelope 5. Therefore the removal of pressure doesn't cause cracking of the body in the compressed air.

In fig. 3 there is the general view of the device for pressing powders of seal on a mandrel. The drive of supplementary movements is carried out preumatically from a standard preumoweb with norminal pressure 0,5 MPa. The overall dimensions of the used shape: diameter - 100 mm, length - 220 mm. The maximum dimensions of the obtained body: diameter -70 mm, length – 170 mm. The maximum working pressure is 150 MPa. The authors developed the devices for radiall-isostatic pressing permitting to get an article of length up to 600 mm with the maximum transversal size of 120 mm. The hydraulic and mechanical drive of supplementary migrations has been 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3



Fig. 3. The general view of the device for pressing the powder materials on a mandrel

produced. The possibility of the devices operating in semi-automatic regime has been considered.

DIP on mandrel has some limitations connected with the increase of metal consumption of the equipment (as the result of its cost) and power inputs on powder seal when pressing articles with transversal dimensions of more than 120 mm. For pressing such articles it's more expedient to use the sceme of pressing on a matrix.

Pressing on a matrix is used for producing hollow articles and because of the construction, the hole mustn't be less than 15 mm. In fig. 4 there is the scheme of the device for producing articles with viahole at a powder seal on a matrix (left-before pressing, right-during pressing).

The device contains the matrix 1 and the elastic puncheon 2 carried out as an envelope dressed on the rigid frame 3. The configuration of the rigid frame and the interior surface of the elastic envelop guarantec puncheon selfseal while creating liquid pressure in the system of channels 4.

The device works in the following way. The matrix 1 is installed on the base 5. The initial powder is put into the annular gap between the matrix 1 and the elastic puncheon 2. The fuse 6 is installed and then the device is

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Fig. 4 The scheme of the device for producing the powder articles with viahole at a seal on a matrix:
1 – matrix; 2 – elastic envelope; 3 – frame; 4 –system of channels; 5 – base; 6 – fuse; 7 – powder

closed by the frame (isn't shown). The hydraulic fluid is given to the central channel of the frame 3 from a hydraulic station of high pressure. The hydraulic liquid passes to the working concavity (the clearance between the frame 3 and the elastic envelope 2) through the system of channels and stretches the envelope. Being stretched the elastic envelope 2 transmits the liquid pressure to the powder, pressing it on the matrix in radial direction and in axial direction at the bottom of the article. Thus the volumetric scheme of the deforming condition of the powder preform (isostatic pressing) is created. The magnitude of the liquid pressure is defined by the type and condition of the pressed powder. After the pressure is reduced the puncheon restores its inisial size by the elastic force replacing the liquid from the working part of the device and getting out of contact with the pressing. Then we release the article from the frame, take off the matrix 1 with the pressing and the fuse 6

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off the base 5 and applying an axial force to the fuse 6 push out the pressing from the matrix 1. To facilitate pushing out of the pressing from the matrix 1 it's expedient to make the hole of matrix with a grade (conic). Then the process is repeated.

Fig. 5 shows the device for the isostatic pressing on a matrix. The device works in a semiautomatic regime. Passing to the production of articles of other dimensions and shapes in the limits: length-up to 150 mm, outside diameter-up to 150 mm, is carried out by substituting the elastic puncheon and the matrix with the appropriate.



Fig. 5. A view of the device for the radial (isostatic) pressing of powder materials at compacting on a matrix

It's to be noted, that real liquid and elastic media at pressures necessary for pressing powder materials possess compressibility (1), which causes increase of energy losses in the process of pressing and reduces its efficiency. For example for this reason at hydraulic pressing energy losses

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are 40-60%, depending on the volume of the media, transmitting pressure. Devices for DIP on a matrix being different in small volumes of transmitting media with other things equal, allow to reduce essentially energy losses reduce and to increase efficiency of pressing processes.

It's expedient to use the pressing processes at compacting on a mandrel and a matrix in the whole volume for articles no more than 100 mm long. The magnification of the length of compacts leads to the growth of the equipment dimensions. The development of the methods of the sequential pressing, when the process of compacting is carried out continuously or at cycles not in the whole volume of a preform allows to reduce considerably the equipment dimensions and to obtain lengthwise measured articles of required quality under certain conditions. More attractive seem to be the methods of pressing based on the use of deformable instruments, manufactured from high-elastic materials. Such an instrument, able to be deformed in the field of heavy elastic strains with father complete restoring of properties and geometry, ensures not only a large resource of service ability, but also high quality of



Fig. 6. The scheme of the device for realizing the sequentially cyclic compacting of the powder tubes: 1 – elastic reinforced envelope; 2 – article; 3 – liquid; 4 – powder; 5 – mandrel
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articles. At pressing in nonclosed volume the use of the elastic instrument often allows to realize the scheme of loading approaching isostatic pressing. To realize a continuity of pressing process the method of continuous sequentially cyclic compacting has been developed. Fig. 6 illustrates the scheme of the device for realizing it. An idiosyncrasy of the device is the absence of the interior elastic envelope and presence of the sole reinforced envelope 1, whose length doesn't define the length of obtained article 2. During radial swaging at creating working pressure in liquid 3 there takes place sequential compacting of pressed material on mandrel 5 (1).

The possibilities of dry isostatic pressing methods in sense of a variety of configurations of pressed powder articles are wide enough. Fig. 7 shows some aspects of powder articles compacted by dry isostatic pressing. Powder preforms from different materials can be pressed: metals, ceramics, polymers, graphite.



Fig. 7. A view of the articles, obtained by dry isostatic pressing

The complex technological process DIP of powder materials includes the following basic operations:

- preparing the burden;
- filling a powder into a mould;
- installing the mould with the powder into a pressing device;
- pressing preforms up to the required density;
- extracting the mould with the compact from the working chamber of the device;
- removal of the compact from the mandrel or extracting it from the matrix;

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- drying the preform, if there's a plasticizer in it;
- checking the properties of the compact.

The pressing pressure is selected individually for each article depending on its assignment (required density) and a powder material. Fig. 8 on the example of titanium powder and copper powder illustrates characteristic correlation between the density of powder compacts and pressing pressure. The calculations are carried out by formula (4), the points – are experimental data.



Fig. 8. The correlation between the density of powder article and pressing pressure:

1 – titanium powder; 2 – copper powder

The authors developed technological pressing processes of porous permeable articles from metal powders based on titanium, nickel, corrosionproof steel, aluminum, iron, and ceramic powders of oxides, carbides.

Porous permeable articles are used for filtrating liquids and gases at aeration processes, heat exchange, sorbing etc. Possessing high durability, thermal and chemical stability, they are processed rather easily. The isostatic pressing processes allow to produce multilayer articles from powders of different granulometric composition or from different materials, what in many cases improves operating performance of the articles (for example of filtering ones). Raising of the pressing pressure, which leads to the consequent increase of the compact density allows to get powder articles of constructional assignment.

Almost all pressed powder articles at the final stage of the manufacture are exposed to thermal processing to give them durability. In this connection the application of self-spreading high-temperature synthesis (SHS) processes is rather perspective, when sintering of an article takes place at the expense 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3

of the heat of a chemical exothermal reaction with simullaneous formation of valuable condensed products. A powder preform is pressed from mechanical mixture of components, called reagents, then a short thermal impulse initiates SHS, which is a process of combustion without the supply of energy from the outside and in many cases without the use of protective atmospheres. Products of such reactions are materials, based on carbides, borides, nitrides, silicides.

Due to the fact that isostatic pressing ensures high uniformity of density distribution all along the compact the designed techniques have proved their value in pressing powder materials with limited toughness, as in case of ceramic materials. For the first time the authors developed pressing techniques of test-tubes and pipes from rigid electrolytes, based on bismuth oxide, ceric oxide, lanthanum - strontium cobaltite etc., which are applied as electrochemical oxygen diaphragms of different types, current-conducting jaws of high-temperature fuel elements, elements of oxygen pumps. The application of radial pressing has allowed to get significant saving in the manufacture of piezoelectric articles, thanks to increasing the capacity factor of the materials and reducing a rough tolerance on machine processing more than 10 times. There is a positive experience of producing ceramic articles from aluminum oxide of a complicated configuration with screwed interior surface by radial pressing the articles, not needing machine processing at all. Dry isostatic pressing has ensured a possibility of compacting massive articles in the form of bars with uniform density distribution, made from zirconium oxide, which are used as account electrodes in making plasma covering.

The use of graphite heaters in modern devices for chemical analysis has put forward a task of their manufacture. The authors have found out, that the radial pressing with consequent calibration allows to produce qualitative graphite heaters, in particular, from thermally decomposed graphite. It's perspective to use isostatic pressing of porous graphite articles for their employment in the processes of potable water puritication.

The growing demand for the articles with strictly regulated porous structure requires development of new appropriate techniques and materials. The radial pressing of specially collected packages of grids, as the authors' research has shown, allows to produce ready porous articles, which, in some cases don't require subsequent sintering. In this case combinations of metals, polymers, textile materials in one article are possible what can change its onepating properties. Obtaining porous articles from metal and other filaments is practically possible at the radial (isostatic) deformation of windings. L. Boginsky et al.

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Thus dry isostatic pressing processes are used and are perspective for obtaining articles of different assignment from a wide circle of materials.

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# **Characteristics and Production of Compound Powder Articles**

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## Summary

Characteristics of production of compound powder articles have been studied. It is shown that parts made from powder can be joined when heating using the "growth" effect of pressed parts during sintering due to austenitecarbide alloy introduction into composition of the insent.

Joining of parts is very strong if the structure of the jouning zone is similar to that of the basic material. It is reached by formation of grains common to joined materials due to the boundary migration induced either by primary or secondary recrystallization. The production parameters, temperature, sintering time, amount of the introduced addition, are ascertained to affect the joining strength.

Properties of sintered materials based on iron are studied as affected by the process of complex thermodiffusion alloying. Mechanical properties, corrosion and scale resistance are determined in sintered articles with diffusion coatings. Saturation with chromium, nickel and silicon is shown to increase essentially mechanical-and-physical properties of sintered articles.

## Keywords

Composite products, sintering, thermal expansion,  $Me_7C_3$ ,  $Me_{23}C_6$ , austenite, diffusion

## I. Introduction

It has been shown in Refs. 1 and 2 that all parts of fuel atomizers can be produced from a powder steel with subsequent hardening of working surfaces. The use of traditional methods of powder metallurgy can considerably simplify the technology of production. However, the complex form of the atomizer (with steps in the direction of pressing, a conical projection, the central hole of variable section, eight radial holes) inconveniences manufacturing and increases the cost of the press mold, complicates the obtaining of billets with uniformity of density and of other 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

properties throughout the whole volume, which may reduce the reliability of the part.



To simplify the technology of productrion the authors of the present report made the atomizer composite consisting of two parts, the embracing one and the one being embraced (Fig.1) whose

Fig.1.Composite atomizer: a) the embracing part, b) the part being embraced, c) parts of the atomizer

joining occurred in the process of heating. The growth effect in the sintering of polycomponent mixtures was made use of (3) which initiates the development of plastic strain of the parts being joined. The reasoning in this case was as follows. The quality of joining in the solid state, when the moving forces of the process are represented by the temperature and pressure, is determined by the formation of a physical contact, the activation of the contacting surfaces and the volume interaction in the coalescence of the materials being joined (4). Thus, if in the sintering process a plastic strain of the materials is initiated, a rapid growth of the strength of the reactive zone should be observed (5, 6).

We have studied some specificities in the formation of joining when sintering some composite articles made of powders.

#### II. Experimental procedure

The specimens which had the shape of a cylindrical insert with o.d. = 20 mm and h= 10 mm embraced by a ring of the size o.d. = 25 mm, i.d. = 20 mm and h = 10 mm were made from the powder mixture containing 98% of Fe of the "PJ4M" type and 2% C of the "GK-2" type by pressing in a closed mold (P = 600mPa). The porosity of the compacts obtained was 19-20%. Prior to pressing 0.5-8% of an addition was introduced into the material for the insert, namely a powder (0.05-0.12 mm) of austenite-carbide alloy: 26.8% Cr, 3.4% 15° International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

Ni, 3.2% Si, 1.5% Mn, 2.8% C, Fe - being the rest. This addition has a higher coefficient of thermal linear expansion compared to the starting material. The structure of alloy particles is represented by the chromium carbides of the Me<sub>7</sub> C<sub>3</sub> and Me<sub>23</sub>C<sub>6</sub> types (H  $_{\mu}$  = 15000 mPa); there is present the carbide eutectics of the ledeburite type consisting of the solid solution (austenite) with the chromium carbides (H  $_{\mu}$  = 8000 mPa). The stability of the austenite in the temperature range in which there occurs elimination of the carbides is insured by the addition to the alloy of Ni, Mg as well as C and Cr distributed between the solid solution and the carbides. Preliminary studies have shown that an increase in the volume of the part being embraced is promoted by the diffusional interaction between the particles of the austenite carbide alloy and the main material due to the formation of an excess phase of the chromium carbides of the Me<sub>7</sub> C<sub>3</sub> and Me<sub>23</sub>C<sub>6</sub> type.

The parts pressed were assembled by setting with a clearance of 0.02-0.03 mm. The sintering was carried out in hydrogen medium at 800 -1100oC for 2-3 hours. The strength of the joining was determined by the measuring of the force needed for the pressing of insert out of the ring. For research purposes the methods of optical metallography and X-ray structural analysis were used.



The effect of the 2-hour long action of the sintering temperature on the strength of the joining was studied on samples containing 8% of additions. Fig. 2 shows that this strength depends essentially on temperature. For example, when it was raised to 1000oC the strength of joining increased up to 22-23 kN and the fracture during the testing occurred in the main material with

#### **III. Results and Discussion**

cracks and tear-outs in the area of joining. This higher strength at 1000oC compared to the sintering at 900oC is, apparently, associated with a higher level of the development of the volume interaction stage which includes the processes of recrystallization and stress relaxation. Such processes are thermally activated and develop more intensely with the increasing temperature. A certain contribution to a better physical contact at 1000°C is also made by the sintering processes whose role is also enhanced with the increasing temperature (7).

The kinetical curves representing increase in the strength of the joint of parts containing 4% of addition are shown in Fig. 3. The strength at 800-850°C increases insignificantly with the duration of sintering. At 900°C the strength of joint attains in 2 hours of sintering 5 kN, but in this case the fracture takes place in the area of joining. When sintering is done at 1000°C, the lengthening of time improves the quality of the joint quite considerably and following the two-hour heating the fracture occurs in the main material. When the sintering temperature attains 1100°C the strength of the joint is lowered somewhat and the fracture takes usually place in the zone of the joining. We also studied the effect of the quantity of the addition on the strength of



Fig.3.Kinetics of the increase of the joint strehth. Here and in Fig.4: 1 - 800, 2 - 900, 3-1000,  $4-1100^{\circ}$ C.

joint when sintering was performed during four hours. It was found (Fig. 4) that an increase in the quantity of addition to the insert material entailed greater strength of the joint. However, when over 6% of addition is introduced. it becomes necessary to increase sharply the pressing pressure required for obtaining the needed porosity. there appear micro- and macrocracks and the compacts lose their strength. The strength of the joint of composite

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samples obtained at the temperature of 1000°C to 10-15 kN.

Metallographic studies have shown that the joint of the sintered-powder parts has high strength in the case when the structure of the joining zone does not differ from that of the main material. This can be achieved by the formation of grains common to the materials to be joined (Fig. 5) resulting from the migration of boundaries accomplished by the initial recrystallization of the material and then by its overall recrystallization. It should be noted that the grain boundaries orientated along the initial contact plane are also formed as a result of a successive development of processes leading to physical contact, to activation of the contact planes and their adhesion and to the diffusional ordering of the contact zone.

The kinetic curve represents the dependence of the growth rate of a diffusional layer containing an excess phase of the  $Me_7 C_3$  and  $Me_{23}C_6$ 



carbides. Its aspect corresponds to the conventional ideas (8) on the development of the

- reaction zone which occurs with the
- participation of a solid
- phase (formation of nuclei, their growth, appearance of a layer of the solid reaction product etc.). But it should be noted that the incubation period is very short and cannot be detected on the curve. This means, apparently, that the formation of the nuclei of the chromium carbide phase, at least in

some portions of the surface, takes place at a rapid rate not limiting the overall process at the observed stages of the diffusional sintering. The greatest values of the reaction rate are probably achieved with very small exposures; subsequently, this rate is sharply reduced, and then it is very slowly decreasing with time. This conclusion has been confirmed by the data of an electron-microscopic study of early stages of the diffusion layer formation.

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The carbide nuclei appear first of all along the grain boundaries that have the



Fig. 5. Microstructure of the interface zone and the effect exerted thereon by technological parameters: a) sintering at 1000°C for 4 h, a 3% addition; b) sintering at 1100°C for 2 h, a 4% addition. Magnification: a) x 500; b) x 100 least thermodynamic stability. These tiny particles should, apparently, be regarded as the initial stable forms of the carbide phase which emerge in the process of diffusional saturation. The thickness of the carbide particles that appear upon saturation at the initial stages does not exceed several atomic layers and the spherical crystals being formed from them have an approximate diameter of  $(1-5)\bullet10^{-7}$  mm.

The generally regular spherical form of the carbide particles results, in all likelihood, from the high formation rates due to a sharp increase in the surface energy (9). Subsequently, owing to reaction diffusion, the number of the carbide inclusions is sharply increased and the moment of the complete fusion of the nuclei on the surface is attained already after one hour of saturation, which, approximately, corresponds to the appearance on the surface of a single layer of carbide. In this case in the section

perpendicular to the layer growth the carbides are small equiaxial grains with the diameter of  $(1-2) \cdot 10^{-6}$  mm, while in the section parallel to the layer growth a tooth-like structure is observed pointing to the direction of the growth. From

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the data obtained one may unambiguously conclude that the reaction of the formation on the surface of a diffusion layer occurs in the initial stages on the interface; the limiting point is, in fact, the reaction in the surface single-layer of the sample. Having covered the surface with a chromium-carbide layer the reaction passes into the diffusion region where its rate depends on the diffusion rate in solids.

After a four-hour long saturation the tiny crystals of the phase formed (carbides) have different sizes. Clearly, in this case in accordance with the general laws of thermodynamics the solid solution is characterized by irregular distribution of carbon, i.e. there is a higher concentration of carbon round the smaller particles and a lower concentration around the greater ones (9). The difference in concentration gives rise to a diffusional stream of carbon from the smaller carbides to greater ones, to the dissolution of the former and growth of the latter. Thus, the formation of a two-layer carbide zone is determined by the coalescence process, i.e. the dissociation of rom the carbide lattice into the matrix solution lattice, as well as by the diffusion of carbon ad the metallic atoms and the transition of the latter into the growing carbide particle.

The micro X-ray spectral study of the distribution of adition elements in the diffusion zone of the sample after a six-hour long exposure has shown that the content of chromium on the surface attains 50-51%. Nickel and, in large measure, silicon are displaced into the region of the  $\gamma$ -solid solution with additions, the content of nickel and silicon amounts in this zone to 1.2-1.5 and 0.7-1.0%, respectively. In the carbide zone about 0.2-0.3% of silicon were found.

It has been ascertained that the growth rate of the carbide particles slows down with time which means that the time factor does not much affect this growth. The increase in the heating temperature to 1100 - 1150°C does not substantially change the picture of the origin and growth of the diffusion layer, only its overall depth is changed.

From the results presented it follows that the most suitable material for producing the embracing part of the atomizer is the iron-graphite mixture (100%). On the other hand, the part being embraced should be manufactured from a material containing 97% of the iron-graphite mixture and 3% of the austenite-carbide alloy. It is preferable to sinter the parts at 1000°C for four hours which allows one to obtain joints requiring the force of pushing out of 13-15 kN.

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The above-described technological regimes were used when manufacturing the composite atomizers of the heating burners for steam boilers. The results of their practical testing were fully compatible with the existing technological requirements.

#### **IV. Conclusions**

1.Some specificities of production of powder-material parts have been considered. It has been shown that the joining of such parts can be performed in the process of heating making use the effect of the compact growth during sintering. The effect of "growth" which initiates plastic strain in the parts to be joined appears after introduction into the composition of the main material of the austenite-carbide alloy.

2.The dependence has been shown of the rate of the diffusion layer formation on the contact surface on the duration of the process. The effect of the chemical composition of the material on the formation of the diffusion layer has been noted. It has been ascertained that the surface carbide layer is formed because of diffusion of the :carbide" carbon into the outer-kinetical region. A layer of the (-solid solution with additions appears owing to the diffusion of the saturating elements to the interface carbide-initial matrix.
3.The effect of technological factors on the strength of cohision has been determined. The technological process of manufacturing composite powder material atomizers of heating burners has been developed.

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# Low Temperature Processing of Tungsten-Fibre High-Strength Composite

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#### Summary:

A tungsten nickel/iron compound with a high tungsten content up to over 90 percent by volume of tungsten and an ideal distribution of the nickel-iron multilayer-matrix avoiding tungsten - tungsten interfaces, has been processed without the use of any sintering process and thus resulted in avoiding temperatures of above 700°C during the entire manufacturing process. An electrochemical coating of coarse tungsten powder with alternating layers of nickel and iron and a forging process at temperatures not exceeding 650°C resulted in a high strength compound, which easily could be altered into a tungsten fibre compound with a fibre-length to fibre-diameter ratio of more than 10<sup>3</sup>. From the viewpoint of the metallurgist, easier handling systems are obtained when both a liquid phase and high temperatures with their risks for grain structures and grain boundaries are lacking.

#### Keywords:

MMC, fibre-composite, low temperature processing, tungsten-fibre, multilayermatrix, electroplating

#### 1. Introduction:

In the field of service applications of high density materials under high dynamic load, certain conditions do demand for an exceptional spectrum of materials properties, consisting of a combination of the utmost maxima of tensile strength, ductile behaviour, resistance against bending perpendicular to the axis of the component and a retarded failure behaviour on mechanical impact. Many attempts have been made throughout the world to meet such requirements, but, as in most technical fields, each time a certain standard

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seems to settle, new goals and the ultimate necessity to meet them come into sight. This is what we call technical progress. So, development continues.

One of the material concepts designed to meet the described requirements was tungsten heavy metals - consisting of tungsten powder, sintered with the aid of some four to ten weight percent of nickel and iron which formed the matrix material. As this material in the sintered condition actually does not meet these requirements, more or less sophisticated measures with an increasing tendency to better improve the material has been taken throughout the years. The actual state of the art is a very sophisticated sintered material with many different treatments following the sintering process which resulted in thermomechanically forged material with a minimum of both inner oxydation and of tungsten-tungsten interfaces between the grains of the material itself.

## 2. Fibre Reinforced Compounds

Another approach taken to reach the described goal was the transformation of the concept of fibre reinforced materials from the field of extremely lightweight construction materials to the field of tungsten heavy metals.

In order to increase the performance of materials in technical applications, high strength fibres are used to improve the behaviour of low strength materials.

In the field of polymer compounds this method is well established. Well known, not only to technical experts, is the fact that glass fibre and carbon fibre, in high strength applications, reinforced polymer compounds.

To transfer these benefits into the larger field of metallic materials, high strength fibres are used to reinforce metallic materials and their alloys (1). They are usually developed to serve as light-weight high-strength materials. Mostly they consist of ceramic fibres in a ductile matrix and are manufactured by casting, squeeze casting or extrusion. The fibres are intended to provide the high strength required. However, as the volume fraction is generally limited to about 40%, their contribution to the mechanical strength is not so pronounced.

To take advantage of the high strength level of the fibres without having to accept the disadvantages connected with high strength materials, such as brittleness and poor behaviour under dynamic loading, the fibre content should be raised and the matrix properties should be made adaptable to a wide range of characteristics.

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In order to meet these objectives and to prove the validity of the basic concept, a model material was designed and manufactured in the laboratory. It consisted of cold worked high strength tungsten wires with tensile strength levels of about 2000 MPa and a metal matrix material which was added by coating the wires by physical vapor deposition (2), or by electroplating (3). Then, the wires were bundled up and compacted by a thermomechanical treatment, <u>Fig.1</u>. This treatment consisted of a forging operation, which bonded the coatings by friction bonding and resulted in a dense microstructure, without pores or holes, <u>Fig. 2</u>. As the highest temperature applied was just above the beginning of recrystallisation of the matrix metal, no liquid phase occurred.



The fibre content was varied from 88 to 96 percent by volume without affecting the compaction process in a detrimental way. The tensile strength of the fibres could be stabilized at the high level of the starting material. Characterization of the compound by means of static and dynamic testing revealed the matrix to be the weakest link of the system. Ideally, the matrix material should have different properties in different areas relative to the fibre. Therefore, a matrix material comprising a gradient of mechanical properties should be desirable. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3

## 3. Multi-Layer Structured Matrix

The demand for a matrix material which allowed a gradient of material properties within the matrix itself could be achieved by an electrochemically deposited multi-layer matrix with alternating layers of different metals, <u>Fig.3</u>. Partial alloying by the diffusion process combined with thermomechanical compaction led to smoothing down abrupt changes of prerequisites within the transition zones of the directly neighboured layers. This is one of the important conditions in such a material to avoid high peaks of internal stress which would lead to early failure. By varying thickness and succession of two or three different types of coating metals and temperature and time of application, a widespread field of different characteristics of the matrix material could be produced (4).

As a result, wire / matrix-composites were obtained which exhibited high tensile strength, an excellent behaviour during dynamic bending and a retarded failure mode, showing cracks stopping at interfaces as it is known from wooden structures, <u>Fig.4</u>. Thus, the matrix layers serve as very effective crack stoppers (5).



250 : 1 etched (DIK) Fig. 3: electrodeposited multi-layer matrix with alternating layers of different metals



Fig. 4: fracture of wire/matrix composite resembling fracture of wooden structures

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#### 4. Elektroplated Metal Powders

A new coating process allows electroplating of metallic powders. The former coating process to obtain a metallic layer on the surface of metallic powder particles was done by electroless plating. Restriction to layers of nickel or copper electroless plating results in metal/non metal alloys with a remarkable amount of hard phases which are responsible for hardness and corrosion protection; but, they prevent the layers from being processed mechanically after the plating process. The mechanical process includes deformation of the material resulting in brittleness. The advantages of the electroplating process are both the possibility of a wide range of plating metals to be used and of applying different fabrication processes after plating, including mechanical deformation. Multi-layer coating systems could be achieved by the electroplating process (6), Fig.5 and 6.





Fig.6: Ni/Cu/Ni- layer on grains of CrNi-steel powder

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#### 5. In - Situ Formed Fibres

Using coarse metallic powders, the thermomechanical compaction process can easily be extended to reduce the diameter of the powder particles and to stretch the length of them, <u>Fig.7</u>. A length to diameter ratio of  $2x10^3$  was already achieved by using a forging process consisting of three steps, ratios of  $10^4$  to  $10^5$  should be within reach.

The main profit of the new process compared to the state of the art is manyfold:

avoiding high temperatures and herewith the danger of inner oxidation of the material during the manufacturing process,

each particle of the powder is covered with matrix material and remains so even during thermomechanical deformation, <u>Fig.8</u>. Thereby, in the resulting material no grain- or fibre-interface tungsten/tungsten exists,

easy handling and easy quality management during production, and



low production costs as compared to the state of the art.



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#### 6. Performance and Future Applications

As the new material, even in the laboratory-model wire-version, managed to egalize the performance of the "state of the art" tungsten heavy metal in most respects, the described fine-fibre-version sets a new base for future development in the field of tungsten heavy metals for exceptional service conditions not only limited to penetration purposes.

Multiple possibilities of combinations of matrix material and fibre or grain conditioning opens a widespread field for taylored materials wherever your application demands for contrary material properties.

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## IMPROVEMENTS IN THE DUCTILITY OF MOLYBDENUM WELDMENTS

## BY ALLOYING ADDITIONS OF Zr, B and C

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## Summary:

A significant improvement in the ductility of molybdenum weldments has been achieved through the addition of zirconium, aluminium, carbon and boron at the parts per million level. A ductility of 20% has been obtained in gastungsten arc weldments in 6.35-mm-thick plate. This improvement over molybdenum's traditional 3% ductility has been achieved by improving the normally low fracture stress of grain boundaries. Atom probe tomography has revealed beneficial segregation of zirconium, boron and carbon to and depletion of oxygen at the grain boundaries in the base metal and the heat affected zone.

## Keywords:

Molybdenum, refractory metals, ductility, grain boundary, segregation, atom probe tomography, microstructural characterization.

## 1. Introduction:

Molybdenum-based alloys possess a unique combination of physical properties including high strength at elevated temperatures, high thermal conductivity, low coefficient of thermal expansion, and excellent performance in neutron flux environments. Therefore, molybdenum alloys are potential candidates for applications in fusion and space power reactors and other high temperature environments. However, the low ductility of welds (typically 3%) has limited their applications. The lack of ductility has been especially apparent for welds made in thick material where triaxial constraint predominates. Bryhan has shown that controlled additions of substitutional

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and interstitial alloying elements can provide almost 20% elongation from gas-tungsten arc (GTA) welds in 6.35-mm-thick material (1).

## 2. Experimental:

The composition of the molybdenum alloy used in this investigation as determined by glow discharge mass spectrometry is given in Table 1. The alloy was vacuum arc-cast with a zirconium addition intended to getter the oxygen and nitrogen impurities together with parts per million additions of carbon and boron intended to strengthen the grain boundaries. The 4-pass welding process was performed on 0.25 inch (6.35mm) plate in a controlled atmosphere chamber where the oxygen, nitrogen and water vapor impurity levels were each less than 10wppm. The welding filler metal was molybdenum containing 20, 30 or 47 wt. % rhenium.

Table 1. Composition of the molybdenum alloy used in this study as determined by glow discharge mass spectrometry.

Element	wppm	appm
Zirconium	1500	1600
Carbon	12	96
Boron	6	53
Oxygen	42	250
Nitrogen	26	178
Iron	6	10
Silicon	3	10
Molybdenum	Balance	Balance

The grain structure of the alloys in the base material, weld region and heat affected zone was characterized by a combination of optical metallography and backscattered electron imaging in the scanning electron microscope (SEM). The fracture surface of a failed tensile specimen was also characterized by secondary electron imaging in the SEM.

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The distributions of the alloying additions in the microstructure of the base metal and the heat affected zone were characterized by a combination of field ion microscopy (FIM) and atom probe tomography (APT) (2). Atom probe tomography enables the elemental identities of the atoms and their positions to be determined with near atomic spatial resolution [~0.2 nm lateral and  $\sim 0.06$  nm depth (3)]. Microstructural characterizations were performed in the Oak Ridge National Laboratory (ORNL) energy-compensated atom probe and the ORNL energy-compensated three-dimensional atom probe (2). То eliminate the possibility of specimen contamination with carbon no prior examination or pre-selection of the field ion specimens in the transmission electron microscope was performed. Field ion images were recorded with the use of helium as the imaging gas and with a specimen temperature of 30-50K. Atom probe analyses were performed with a specimen temperature of 50K, a pulse repetition rate of 1500 Hz and a pulse fraction of 20% of the standing voltage.

## 3. Results and Discussion:

#### Mechanical Properties and Fractography

Tensile tests (1) were performed at room temperature at strain rates between 8.3 x 10<sup>-3</sup> and 12.5 x 10<sup>-6</sup> s<sup>-1</sup> in stroke control. The results are summarized in Table 2. Strain was measured over two weldment regions to measure strain localization: 25 mm centered over the weld and 8.5 mm over one heataffected zone. Tests were performed at a standard strain rate of 8.3 x 10<sup>-4</sup> s<sup>-1</sup> and also at faster and slower rates to determine the effect of strain rate. The maximum observed elongation, pertinent to typical engineering use, was 19.5%. Even at 8.3 x  $10^{-3}$  s<sup>-1</sup>, useful ductility (>10%) was apparent in the material welded with Mo-30 wt% Re filler alloy. The ductility of these weldments is apparent by the reduction in cross section that is visible in the optical micrograph shown in Fig. 1.

Fracture was found to occur in the heat-affected zone, as shown in optical micrographs in Figs. 1 and 2 and in the scanning electron micrograph in Fig. 3. The brighter contrast in the weld region of the backscattered electron image is due to the presence of rhenium from the filler material. Some porosity was observed in the weld region, particularly close to the edge of the weld next to the heat affected zone. The fracture mode was transgranular cleavage, as shown in Figs. 2a, 3 and 4. This observation is in contrast to the

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intergranular fracture typical of welds in commercial grade molybdenum alloys and indicates that the grain boundaries are not preferentially embrittled. This change of fracture mode suggests that the alloying additions increased the grain boundary fracture stress above the yield stress.



Fig. 1. Optical micrograph of a fractured tensile specimen a) top view and b) side view. Note the reduction in area in the base metal and heat affected zone.



Fig. 2. Optical micrographs of a) and c) heat affected zones and b) weld centerline showing the grain structure and the presence of cracks in the heat affected zone and some porosity in the weld region.

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Fig. 3. Backscattered electron micrograph of a crack in the heat affected zone (dark region on left hand side) and the weld (brighter region).



Fig. 4. Secondary electron micrograph of the fracture surface of the molybdenum tensile specimen showing the transgranular mode of failure.

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Table 2. Room temperature tensile test results for GTA-welded molybdenum alloy with three different Mo-Re filler alloys (1).

Filler metal	Strain	Range of elongation in		Yield	Ultimate
(wt. %)	rate in	gauge length, %		stress,	tensile stress,
	25mm,	25 mm	8.4 mm	MPa	MPa
	s <sup>-1</sup>				
Mo-20% Re	8.3x10 <sup>-4</sup>	8.2-15.2	10.4-14.0	428	524
i	8.3x10⁻⁵	11.0	6.0	392	470
Mo-30% Re	8.3x10⁻³	10.0-12.6	7.9-11.6	537	583
	8.3x10 <sup>-4</sup>	19.5	>15.01	481	544
	1.25x10 <sup>-6</sup>	22.6	>15.0 <sup>1</sup>	267	457
Mo-47% Re	1.25x10⁻ <sup>6</sup>	10-26	8->15.0 <sup>1</sup>	250	484

<sup>1</sup>15.0% maximum measurement with the extensometer.

## Microstructural Characterization

Extensive field evaporation studies of the matrix revealed no intragranular precipitates. The matrix compositions were measured in the threedimensional atom probe and were found to be consistent with the alloy composition (4). These matrix measurements together with the extensive field evaporation studies of the matrix indicate that no significant loss of the solute additions occurred due to precipitation of oxides, carbides or borides.

Field ion micrographs of grain boundaries in the base metal and the heat affected zones are shown in Fig. 5. In addition to the typical zone contrast exhibited by molybdenum alloys (2), both materials exhibited some bright spot decoration at the grain boundaries. These bright spots are indicative of solute segregation (2). Comparison of the predicted low temperature evaporation field of molybdenum (41 V nm<sup>-1</sup>) with the other solutes suggests that the bright spots (i.e., atoms that are more resistant to field evaporation) are boron (64 V nm<sup>-1</sup>) or carbon (103 V nm<sup>-1</sup>) atoms rather than zirconium (28 V nm<sup>-1</sup>) atoms (5). The level of segregation appeared to be significantly higher in the heat affected zone.

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Fig. 5. Field ion micrographs of grain boundaries in a) the base metal and b) the heat affected zone. Solute decoration is apparent at both grain boundaries.

The identity of the solute species responsible for these bright spots was determined by atom probe tomography (2). Atom maps of regions of specimens that contained grain boundaries in the base metal and the heat affected zone are shown in Fig. 6. In these atom maps, each sphere represents the position of an atom in the volume of analysis. The molybdenum atoms have been omitted for clarity. It is evident that significant segregation of zirconium, carbon and boron to the grain boundary has occurred in the base metal. In addition, the oxygen level at the grain boundary was significantly reduced from the matrix level. The boron segregation was found to be significantly more prevalent in the heat affected zone.

The Gibbsian interfacial excesses of the solutes at these grain boundaries were determined by selected volume analyses of the grain boundary and matrix regions (2). The results are given in Table 3. The boron excess at the grain boundary in the heat affected zone was two orders of magnitude higher than in the base metal, whereas the zirconium and carbon excesses were substantially less enriched. The oxygen level at the grain boundary in the

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heat affected zone was found to be very slightly enriched compared to the matrix whereas in the base metal, the oxygen level was significantly reduced. A previous imaging atom probe study of a grain boundary in molybdenum revealed significant enrichment of oxygen (6).



Fig. 6. Atom maps of grain boundaries in a) the base metal and b) the heat affected zone. The molybdenum atoms have been omitted for clarity. Each sphere represents a single atom.

Table 3. Gibbsian interface excesses of solute at the grain boundary in the base metal and heat affected zone. Errors are based on counting statistics of the number of atoms detected.

	Element	Gibbsian Interfacial Excess		
		Atoms m <sup>-2</sup>		
Ì		Base Metal	Heat Affected Zone	
	Zirconium	$7.6 \pm 0.6 \times 10^{17}$	$1.4 \pm 0.4 \times 10^{17}$	
	Carbon	$1.1 \pm 0.3 \times 10^{17}$	9.9 ± 9.9 x 10 <sup>15</sup>	
	Boron	$7.3 \pm 2.7 \times 10^{16}$	9.9 ± 0.2 x 10 <sup>18</sup>	
	Oxygen	-3.9 ± 0.6 x 10 <sup>16</sup>	1.1 ± 0.4 x 10 <sup>17</sup>	

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## 4. Conclusions:

These atom probe tomography results have demonstrated that there is reduced segregation of oxygen to the grain boundaries in this zirconium-, boron- and carbon-doped molybdenum alloy. The oxygen segregation may be inhibited due to the presence of zirconium, carbon and boron at the grain boundary. This change in segregation behavior correlates with an order-ofmagnitude increase in ductility and a change in the observed fracture mode from the intergranular failure observed in commercial molybdenum alloys to transgranular failure in this molybdenum alloy.

## 5. Acknowledgements:

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# The Effects of the Various Intermittent Annealing Temperatures on the Mechanical Properties of the 0, 45, and 90° Rolled Rhenium Samples.

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#### Summary

The objective of this study was to analyze the properties of Rhenium rolled along the 0°, 45°, and 90° directions. Density, microhardness, tensile strength, along with pore and grain structures, and crystallographic texture were analyzed. The study was divided into nine parts, a 10-12% reduction in thickness along the 0°, 45°, and 90° directions was applied between intermittent annealing temperatures. The annealing temperatures were: 1200°, 1650°, and 1800°C. The crystallographic texture of the processed samples was evaluated and correlated to the mechanical properties. The study showed that the density of all tested samples remained the same. The microhardness increased with thickness reduction for all annealing temperatures. In the 45° rolling mode, the work hardening rate was significantly lower than that of the 0° and 90° modes. Twinning was more evident as the percent reduction in thickness increased.

**Keywords:** 0°, 45°, and 90° rolling modes (directions), work hardening rates, crystallographic texture.

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## 1. Introduction

Rhenium is used in space and missile propulsion systems as a pure structural metal and a liner in conjunction with graphite or carbon-carbon structural materials [1]. Other applications include the use of rhenium in thrust chambers for satellite control and as structural material for the SP-100 Space Reactor. In the Sp-100 Space Reactor, rhenium is utilized as a chemical barrier between uranium nitride nuclear fuel and niobium alloy cladding [2]. Rhenium is also used in the thrust chamber for high performance liquid apogee/perigee or delta-V engine applications [3].

In previous work by Pupirov and Kapcherin [4] and Azahaza et al [5], microhardness anomalies of rhenium were observed. It was concluded that there are directions along which stresses necessary for deformation are at a minimum [4]. Es-Said and co-workers performed off-axis stretching and offaxis rolling on several anisotropic alloy systems including Al-Li [6-8] and Mg-Li [9]. The 45° direction exhibited the lowest mechanical strength in these alloys [6-9]. Teitz and Wilson [10] reported similar results for Tantulum. In more recent work Es-Said et al [11] evaluated the effects of the 45° rolling mode on the mechanical properties of rhenium. The ultimate tensile strength was increased considerably from 827.6 MPa (120 ksi) for non cold-rolled specimen to 2388 MPa (346.6 ksi) for the 82.9% reduced specimen. Despite the large reduction in thickness, a 3.3% elongation and partial recrystalization Carlen and Bryskin [12] summarized the work of several were retained. authors on the tensile properties of rhenium fabricated in different forms. It can be noted that a combination of 2388 MPa (346.6 ksi) and 3.3% elongation was never achieved in previous works [12].

The aim of the present work is to study the effects of rolling rhenium along the 0, 45, and 90° direction with respect to the original rolling direction. Three different temperatures were used for annealing in the three directions. These are 1200°C (1473 K), 1650°C (1923 K) and 1800°C (2073 K). The properties studied are tensile strength, density, microhardness, porosity, grain characteristics, and crystallographic texture.

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#### 2. Experimental

Rhenium bars compacted from high purity (99.99%) powder of 200 mesh size were provided by Rhenium Alloys Inc., Elyria, Ohio. The density measurements were carried out in accordance with ASTM B328 and microhardness measurements in accordance with ASTM E92-82. Mechanical strength testing was determined at room temperature at a constant crosshead speed (1.27 mm/minute) using a screw driven Instron machine.

#### 3. Thermomechanical Processing

Figure 1 summarizes the thermomechanical processing of the rhenium bars. Samples were reduced 10-12% reduction in thickness along the 0, 45, and 90° directions, Figure 2. Intermittent annealing was performed at 1200°C (1473 K), 1650°C (1923 K) and 1800°C (2073 K) for 30 minutes. Density, microhardness, porosity, grain structure, and preferred grain orientation (crystallographic texture) were evaluated.



Figure 1: Mode of Rolling: 0°, 45° and 90° Modes

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# 0°,45° and 90° Rolled Rhenium



Figure 2: Outline of the Thermomechanical Procedure

#### 4. Results

The density of the as-received samples was 99.97% theoretical density. The as-received samples of 2.54 mm (0.1") in thickness, Figure 2, had been rolled to 60% reduction in thickness. The as-received samples of 2.54 mm (0.1") in thickness were further rolled until 50 % reduction in thickness in the 0° and 90° directions and 80 % in the 45° direction.

The tensile strengths of the as-received samples in the 45° direction and for the samples rolled in the 45° direction until 50 % reduction in thickness were obtained and is shown in Table 1. The samples were annealed at 1200°, 1650° and 1800°C.

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Table 1: Tensile strength comparison for as-received and rolled 50% at 45°					
	AR	1200°C, Rolled	1650°C, Rolled	1800°C, Rolled	
		51.7%	47.19%	55.91%	
Yield	30	174.3	156.9	100	
Ultimate	125	180.4	163.1	132.5	
%	≈ 23	6.6	5.9	4.2	
Elongation					

There is a sharp increase in both yield and ultimate strengths for all annealing temperatures after approximately 50% reduction. The samples annealed at 1200°C (1473 K) had the highest increase in strength. The lower annealing temperature (1200°C) produces the highest strength due to lack of sufficient thermal energy for full recrystallization [12].

The density remained constant, within 1% of the theoretical density (21.04 g/cm<sup>3</sup>). The different annealing temperatures and rolling directions had little effect on the measured density, see for example Figure 3 for samples rolled at 45° mode and annealed at three different temperatures. This was probably due to the fact that the density of the as received samples was above 99% theoretical.



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## 4-1. Microhardness

The microhardness of all rolled samples at the three annealing temperatures increased as the percent reduction in thickness increased. This was true for all rolling directions, see for example Figure 4 for the variation in microhardness measurements at the three annealing temperatures. As expected, a lower intermittent annealing temperature resulted in a higher work hardening rate, [12,13]. For the 0°, 45°, and 90° rolling directions, the samples annealed at 1200°C had the highest work hardening rate, followed respectively by the 1650°C and 1800°C samples. Figures 5(a) through 5(c) show the effects of rolling at different angles with the same annealing temperature. The lowest work hardening rate was observed for the 45° rolling direction. This was true for the 1200°C, 1650°C, and 1800°C annealing temperatures. The 0° and 90° rolling directions had similar work hardening rates.



Figure 4: Microhardness Measurements vs % Reduction in Thickness (45° Rolling Mode)

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#### 4-2. Microstructure

Figure 6 shows micrographs at various stages of rolling for the 45° rolled samples, annealed at 1200°C. As percent reduction increased, a decrease in pore size and frequency was observed, which is in accord with the findings of other researchers, [12,14]. This was true for all rolling directions and annealing temperatures. Grain microstructure, 45° rolling direction at 1200°C, for samples rolled at 15% and 50% reduction in thickness respectively is shown in Figure 7. Twinning was more evident as percent reduction increased. This was true for all annealing temperatures and rolling directions, however it was more pronounced at lower temperatures. The deformation mechanism for Rhenium is twinning [14]. Rhenium is a HCP structure, which only contains three slip systems. Accordingly, when the crystal is strained the atoms can be displaced causing twins to develop.

The microstructure for the samples rolled in the 45° direction and annealed at 1800° C reveals the expected grain growth at elevated temperatures, Figure 8. It is worth noting that samples annealed at 1200°C rolled in the three different rolling modes (0°, 45°, and 90°) developed microcracks. These microcracks increased as the percent reduction in thickness increased.

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# Figure 6: Pore Pictures of As Received Samples and of Samples Rolled at the 45° Mode (1200°C).



Figure 7: Microstructure of As-Received Sample and of Samples Rolled in the 45° Rolling Mode (1200°C)



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# Figure 8: Microstructure of As-Received Sample and As-Rolled at 45° Rolling Mode (1800°)



AS RECEIVED



ROLLED 53.9%

#### 4-3. **Preliminary Results of Texture**

Specimens for texture analysis were machined at different stages from the thermomechanically processed samples. The specimens were mechanically polished and etched to remove any residual deformation layers. The rolling direction was used as the pole figure reference orientation. The crystallographic texture was evaluated using the x-ray diffraction technique on a Scintag x-ray diffractometer operating at 40 kV and 50 mA using CuK<sub> $\alpha$ </sub> radiation. The diffractometer was equipped with a curve monochromator. A number of incomplete pole figures were obtained using the reflection technique. The resulting data was analyzed using the popLA software package from which the Orientation Distribution Functions (ODFs) were calculated using the spherical harmonic approach. [15].

The texture data was analyzed using popLA. The results show that the asreceived sample showed the typical 30° tilt from the normal direction with a

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texture intensity of 7 times random, Figure 9. Annealing the samples at a temperature of 1200° C resulted in an increase in texture intensity of 10x random for the two levels of deformation (53% and 72%). The sample deformed to 74% did not show an increase in texture. An analysis of the micrographs shows signs of microcracks that may explain the lack of additional texture. Annealing at a temperature of 1650°C resulted in a much larger deformation texture (12x random) for a deformation of 50% and 16x random for a deformation of 73%. Such a large increase in the c-axis component maybe a result of grain growth.





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# 5. Conclusions

- 1. Since the as-received samples had over 99% theoretical density, the density of further rolled and annealed samples remained constant.
- 2. In the 45° rolling mode, the work hardening rate was significantly lower than that of the 0° and 90° modes.
- 3. Microhardness and twinning increased with increased percent reduction.
- 4. Microcracking was seen in the 1200°C samples rolled along the 45° direction. The cracks increased with further reduction in thickness.
- 5. The thermomechanical processing at 1650°C sharpened the deformation texture components.

### 6. Acknowledgements

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# POROUS MATERIALS WITH GRADIENT AND BIPOROUS STRUCTURE. METHODS OF THEIR PRODUCTION

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#### Summary:

We have worked out the technology of production porous powder materials (PPMs) of bronze, nickel, corrosion resistant steel and titanium powders with gradient and (or) biporous structure: vibrating forming of metal powders (including in electromagnetic field); layer-by-layer forming of metal powders with pore-maker while different proportion of the latter in the layer; forming of powder polymer layer on the preliminary sintered metal PPM surface.

We have worked out the technology of production biporous structure by the following methods: metal granules forming and sintering; forming and sintering of metal powder with granules (2-3 mm) and pores-forming powder (size of particles is 0,4 -0,63 mm).

The novelty is in creation of technological bases of pores sizes regulation from 5 mkm on one PPM surface to 120 mkm on the opposite PPM surface which thickness can be 2-6 mm. PPM porosity can be constant within 0.3-0.6 relative units. More effective are those PPM which pores sizes are changeable and also porosity (from 0,35 to 0,60) from one surface o the opposite one. Twolayer metal-polymer PPM have pores sizes of 20-40 mkm in polymer layer and porosity 0,4-0,5 and, correspondingly, in metal layer 80-100 mkm and 0,45-0,55. In biporous structures made of 2-3 mm metal granules the distance between granules is 300-600 mkm and in granules - 14-30 mkm. The integral porosity of such PPM is 0,55-0,70. The technology of forming and sintering metal powder with granules and pores-making powder (carbamide) enables to regulate the integral porosity within 0,7-0,8 and average pores sizes within 100-1000 mkm with average size of metal powder particles of 0.63-1.0 mm.

#### Keywords:

Powder, PPM, Stainless steel, Bronze, Titanium, Nickel, Porosity, Pore Size

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#### 1. Introduction:

Possibilities of production PPM by methods of conventional PM technologies are limited by a opposite directed dependency between basic operational; properties of PPMs and properties of their porous structure. Thus, for example, PPMs used as filtering elements should have high permeability and dirt capacity that increase together with pores sizes and porosity, on one hand, and high cleaning fineness that dependent in a convert way on the pores sizes. Analysis of methods of production PPMs with improved complex of operational properties, that are improved permeability and dirt capacity at a certain pores sizes, showed that the most perspective methods, enabling to produce asymmetrical porous structures according to material cross-section (1). In some cases it is necessary to produce PPMs with porosity within the range of 0.5-0.8 relative units and with pores sizes more than 500 mkm, that is not possible to do by conventional PM technologies.

# 2. Production of PPMs with Asymmetric Porous Structure by Vibrating Forming

Vibrating forming, based on powder particles size segregation when a mold with powder is under vibration with certain parameters, is one of the most effective ways of production PPM with asymmetric porous structure (2).

The investigations of particles behavior in a mold under vibration we have carried out enabled to get a functional interdependence between acceleration and frequency of mechanical vibrations that provide disperse size segregation of particles:

$$3,96 e^{0,0103 f} < a \le 8,78 e^{0,012 f}$$

where a - acceleration, m/sec<sup>2</sup>; f - frequency, Hz. In fig.1 there are 3 areas of the disperse mixture condition which depends on vibration parameters, borders between them are described by the dependencies mentioned before. Powder compaction takes place in area 1. In area 2 there is particles separation according to their size, despite of relation between the biggest and the smallest particles in a fill.

In area 3 there is an intensive chaotic mixing (vibrating boiling) of mixture of powders with different particles sizes.

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Figure 1. Condition of metal powders mixture depending on vibration parameters: 1 – vibrating compaction; 2 - segregation; 3 - vibrating boiling.

We should note a side effect, which increases quality of PPMs, produced by vibrating forming - increase of porous structure regularity and also uniformity of PPMs surface permeability. This enables to reduce PPM thickness (15 - 20%) at guaranteed service characteristics and, thus, reduce material consumption and cost of the final product.

In figures 2 - 4 there are photos of three types of PPM microstructure, that were produced by vibrating forming of poly-disperse mixtures of wide granulemetrical composition: with smoothly changing pores sizes - from bronze powder and nickel powder with superposition of the outer magnetic layer for additional pores and particles orientation; a double-layer biporous one from bronze powder.

In table 1 you can find results of comparison of PPMs characteristics with smoothly changing pores sizes, made of bronze powder by vibrating forming of poly-disperse mixture and by conventional sintering of free-filled powder of narrow fraction with the same average pores size (fine cleaning). Filters made of these PPMs were used for polymers melts filtering (polyethylentereftaletes) while production of electrotechnical and photographic films.





Figure 2. Microstructure of the PPM, Figure 3. Microstructure of the produced by vibro-forming from tin- PPM, produced by vibro-forming sulfur bronze powder, \*25.

from carbon nickel powder in a magnetic field, \*25.



Figure 4. Microstructure of a double-layer PPM, produced by vibrating forming from tin-sulfur bronze powder, \*25.

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#### Table 1. Properties of the bronze powder PPM

Properties of the PPM	conventional	vibrating
	technology	forming
Average pores size, mkm (µm)	20	20
Permeability coefficient, x10 <sup>13</sup> , m <sup>2</sup>	3.24	12.6
Dirt capacity (i.e. ratio between quantity of caught		
foreign particles and the filter volume), g/cm <sup>3</sup>	0.03	0.1

Thus, vibrating forming enabled to increase 3 times permeability and dirt capacity when producing filtering PPMs with asymmetrical porous structure in comparison with PPMs produced by a conventional technology and at the same time to save filtering fineness. And also it enabled to reduce 20 % thickness of the material saving its guality owing to higher structure regularity of the PPMs produced by vibrating forming.

# 2. Layer-by-layer Production of PPMs with Asymmetrical Porous Structure by Forming of Metal Powder with Different Content of a Poremaker in Each Layer

One of perspective methods to increase operational properties of PPMs is forming powders with a pore-maker. The pore-maker enables to increase parts porosity and, thus, their permeability. That's why investigation of the poremaker influence on the PPM properties allows not only to define optimal guantity of it for obtaining the necessary PPM properties but also will offer initial data for the optimal pores distribution to be calculated that will provide high operational characteristics.

As an object of investigations there was chosen a PPM of 12Cr18Ni10 corrosion-resistant steel and a pore-maker - CO(NH<sub>2</sub>)<sub>2</sub> carbamide powder.

Basing on investigations carried out earlier (3), the chosen powder particles size was 0.1-0.16 mm as this fraction enables to produce PPM with an average pores size of 20 mkm and this gives us an opportunity to compare this technology with vibrating forming developed earlier (2).

Influence of the pore-maker quantity on the pores size and porosity is shown in figures 5 and 6. As it is shown in the chart, addition of the pore-maker leads to increase of pores sizes and porosity, and these characteristics can be increased few times.

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Figure 5. Influence of compaction pressure and pore-maker concentration on porosity of the PPM of 12X18H10 steel powder with the particles size 0.1-0.16 mm.



Figure 6. Influence of compaction pressure and pore-maker concentration on the pores sizes of the PPM of 12X18H10 steel powder with the particles size 0.1-0.16 mm.

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From the point of view of optimal filtering characteristics, PPMs with asymmetrical porous structure used for cleaning liquids or gases which are characterized by presence of poly-disperse hard contaminants of low concentration should have lower porosity and smaller pores sizes in the flow direction. At the same time the regime works when a layer, placed on the outlet surface of the PPM, with zero pore-maker concentration and, therefore, with minimal porosity and pores sizes, provides the necessary filtering fineness; a layer, placed on the inlet surface of the PPM, with the maximal pore-maker concentration and, therefore, with maximal porosity and pores sizes separates the biggest particles. Porosity and pores sizes of intermediate PPM layers are easy to regulate by changing pore-maker concentration in them.

The achieved results of the investigations enabled to develop a technology of production PPM by the method of layer-by-layer forming. The technology consists of preparation of initial metal powder and a pore-maker powder, dosing layer compositions, mixing, layer-by-layer forming, compaction at pressure 85-95 MPa, preliminary sintering in dissociated ammonia at 300 °C during 30 minutes, vacuum sintering at 1250°C during 90 minutes.

In figure 7 you can see a photo of the microstructure of the PPM of 12Cr18Ni10 steel powder with particles size 0.1-0.16 mm, consisting of 5 layers with height of 4-6 average steel powder particles sizes with 0, 25, 30, 40 and 50% concentration of the pore-maker.

Filtering elements, produced by the layer-by-layer forming with the poremaker, with the microstructure mentioned above were used in units for drying and cleaning natural compressed gas at car gas-filling stations, where they have replaced analog filtering elements, produced by conventional technology, with a homogeneous pores structure of the same type of steel powder and with the same particles sizes. But the service life of the PPMs developed by our researchers was 6 times higher than conventional ones have.

# 3. Composite Metal-Polymer PMMs Production

An additional actor that increases effectiveness of using PPM for filtering multiphase environments is using not only their structural but also physicalchemical properties, such as water receptivity and water-repellency. For that we have developed a production technology of composite metal-polymer PPMs by the method of moulding of a porous blank made of metal powder, its sintering and spraying porous polymer layer when cooling on its surface.

In table 2 you can find results of comparison of PPMs made of titanium powder, PTFE and a composite powder based on titanium with porous PTFE

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layer. As it is seen from the table, the composite metal-polymer PPMs have higher operational properties than metal ones and also it is obvious that they also higher mechanical properties than polymer ones.



Figure 7. Microstructure of the PPM of 12Cr18Ni10 steel powder with the particles sizes 0.1-0.16 mm, <sup>x</sup>25.

In figure 8 you can see a PPM based on titanium powder with particles sizes 0.315-0.4 mm with a sprayed porous PTFE layer. Using of such PPMs in units for cleaning and drying air for painting automotive equipment enabled to reach a 99% water vapour cleaning (dew point - minus 4-5°C) when the bronze element used before enabled to reach only 53% of vapour cleaning, and a PTFE one - did not provide the necessary productivity of a compressor within a painting unit.

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### Table 2.

Characteristics of PPMs made of titanium powder, PTFE and composite PPMs (titanium-PTFE) used for drying and cleaning gases.

Characteristics	Titanium PPM	PTFE PPM	Compos- ite PPM
Average pores size, mkm (µm)	20-22	20-21	20-21
Permeability coefficient, x10 <sup>13</sup> , m <sup>2</sup>	230	310	419
Absolute filtration fineness, mkm (4m)	5	5	5
Outlet dew point, °C, not higher	+10	+4	-5
Fumes cleaning degree, %, not less	53	99,3	99,7



Figure 8. Microstructure of the composite PPM made of titanium and PTFE powders,  $^{\rm x}$  50.

# 4. Production of PPMs with a Biporous Structure

It is quite hard to produce pores with sizes of  $\geq$  1.0-1.2 mm by conventional PM technology (4). But for a number of applications (medical implants, mechanical dryers of technical gases and pneumatic systems, elements of flying vehicles) it is necessary to produce PPMs with such and even bigger pores sizes. Because of low specific weight, good bio-compatibility, optimal corre-

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spondence of physical-chemical and thermal-physical properties PPMs like these should be produced of technically pure titanium powder.

There are few well-known methods for increasing porosity in PPMs of titanium powder: injection of zinc stearate and sulfur molybdenum (5)as fillings; technical stearine (6,7). The other technology for increasing porosity of PPMs uses Kirkendale's effect - growth of a compacted part volume when sintering because of the non-equality of coefficients of hetero-diffusion and formation of intermetallic compositions when injection up to 6% aluminum and tin (8). But all these well-known processes enable to increase porosity of PPMs to 50-60% max practically not increasing pores sizes higher than 0.7-0.8 of the average size of the initial titanium powder particles. In the work (9) to produce titanium PPMs pores sizes significantly bigger than particles sizes we propose a porous blank preliminary formed of fine powder and sintered, and than milled. After sizing a PPM with pores of 100-150 mkm is formed while particles sizes of the initial powder are 5-10 mkm only. Also we should notice that in the work (9) there are negative results of attempts to used a volatilizing pore-maker ammonium bicarbonate - for increasing porosity and pores sizes, as the authors did not manage to prevent parts from cracking and distortion when sinterina.

In the work (10) there is a technology of production high-porous cell material by compaction of fine titanium powder (40-45 mkm) with granules of a volatilizing pore-maker - a spherical and granulated carbamide. We have investigated influence of heating (170 °C) and compaction type, with a filling and without it, on hydrogen, oxygen and nitrogen in a PPM that has porosity 75-80 % and pores sizes bigger than 1 mm.

We have reproduced this technology, but it has few characteristic features. Mixing fine titanium powder (40-63 mkm) with carbamide granules was carried out in a hand-mixer with additions of ethanol or acetone for cladding granules with metal powder particles. Mixture was compacted wet. Compacted parts were kept not less than 24 hours in room temperature to remove excess of liquid. Sintering was carried out in 2 steps: preliminary sintering was carried out at temperature of 950-1000 °C during 1 hour. Pressed blanks were kept at 200 °C to remove carbamide. The final sintering was carried out in vacuum at 1050-1100 °C during 1 hour. Properties of the produced PPMs of titanium powder corresponded to the ones described in the work (10). But the porous structure was less homogeneous, and the technology of mixing fine titanium powder with big carbamide granules was not perfect and did not provide absence of segregation.

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In this respect we have developed the second variant of production PPMs of titanium powder. We have used titanium powder with particles sizes of 630-100 mkm as an initial material, which is easy to mix with carbamide granules with sizes of 2.0-3.0 mm. After dry or wet (with ethanol or acetone) compaction it was enough to remove carbamide in argon at 200 °C. Sintering in vacuum is better to carry out at 1100-1150 °C during 90-120 minutes. The PPM structure in this case is also cell with an average pores sizes more than 1 mm (figure 9).



Figure 9. Photo of the titanium powder PPM microstructure with particles sizes 630-1000 mkm, ×10. Compaction pressure - 56 MPa. Carbamide concentration - 60 %.

In figure 10 you can see dependencies between porosity of titanium powder PPMs with particles sizes of 630-1000 mkm and compaction pressure and concentration of carbamide granules; and in figure 11 - dependencies between an average pores sizes of these PPMs and the same technological parameters. Pores sizes, because of their high values, were measured by a metallographic method.

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Figure 10. Dependencies between titanium powder PPM with particles sizes of 630-1000 mkm and compaction pressure and carbamide granules concentration Figure 11. Dependencies between average pores sizes of titanium powder PPM with particles sizes 630-1000 mkm and compaction pressure and carbamide granules concentration

The third variant of production PPMs is compaction and sintering granules of technically pure titanium with sizes 2000-3000 mkm. These granules are an intermediate product of which a powder is made by milling. In figure 12 you can see a photo of a structure of a PPM like this; and in figure 13 - dependencies between PPM pores porosity and sizes and compaction pressure.

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Compaction pressure, MPa

Figure 12. Photo of PPM microstructure made of titanium granules with sizes 2000-3000 mkm. Compaction pressure 56 MPa, ×10.

Figure 13. Dependencies between porosity and sizes of PPM pores and compaction pressure of titanium granules with particles sizes 2000-3000 mkm.

#### 5. Conclusion:

We have developed a technology of production gradient porous structure by the methods of: vibrating forming of bronze and nickel (incl. Vibrating forming in an electromagnetic field) powders; layer-by-layer forming of corrosionresistant steel powders with a pore-maker (carbamide) at different concentration of the latter in a separate layer; forming of porous polymer layer on the surface of a preliminary sintered metal PPM.

We have developed technology of production biporous structure by the methods of: forming and sintering titanium granules (particles sizes 2-3 mm); forming and sintering of titanium powder (particles sizes 0.4-0.63 mm) with granules (particles sizes 2-3 mm) and a pore-maker powder (0.4-0.63 mm).

The developed materials have higher operational properties than conventional ones and are used in filtering elements for filtering polymer melts; filters-wateroil separators for pneumatic systems; filtering elements of gyro-drive systems; filters of production medical preparations and foodstuffs; cleaning diesel fuel, separation of water vapor and oil aerosols out of gas flow; surgical implants.

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# Modelling of Sintering of Functionally Gradated Materials

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#### Summary:

The functionally gradated materials (FGMs) are distinguished from isotropic materials by gradients of composition, phase distribution, porosity, and related properties. For FGMs made by powder metallurgy, sintering control is one of the most important factors. In this study sintering process of FGMs is modelled and simulated with a computer. A new modelling approach was used to formulate equation systems and the model for sintering of gradated hard metals, coupled with heat transfer and grain growth. A FEM module was developed to simulate FGM sintering in conventional, microwave and hybrid conditions, to calculate density, stress and temperature distribution. Behaviour of gradated WC-Co hardmetal plate and cone specimens was simulated for various conditions, such as mean particle size, green density distribution and cobalt gradation parameter. The results show that the deformation behaviour and stress history of graded powder compacts during heating, sintering and cooling could be predicted for optimisation of sintering process.

#### Keywords:

Sintering, modelling, hard metals, gradated materials, FGM, FEM

#### 1. Introduction:

Powder metallurgy is one of major processing methods for fabrication of Functionally Graded (more correct, Gradated) Materials, or FGM (1-3). Combination of powders layout techniques gives a versatility of virtually any kind of component distribution in the volume of final article. However, for FGM consist of phases of too different properties (metal – ceramics, etc.), sintering is usually becoming a problem due to rather different sintering temperatures, shrinkage rates and resulting shrinkage non-uniformity as well as possible accumulation of stresses.

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Hence a special attention should be given to sintering behaviour of FGM, because of higher probability of appearance of bending or distortion of the sintered bodies, or cracks, due to the difference in shrinkage between the phases (1-5). Recently, the stress state and cracks in heterogeneous powder compacts induced by non-uniform shrinkage have been analysed. Finite element analysis for sintering process has been widely used to predict deformation behaviour during isothermal sintering of gradated compacts, including WC-Co hardmetals (3-7). It was underlined that compacts may exhibit different behaviour (elastic or visco-plastic) at different stages of sintering.

The deformation of the test piece and internal stress during entire cycle (heating, isothermal holding and cooling) are necessary to know for optimisation of the sintering and prevention of defects and undesired distortions, as mentioned above. In this work, the finite element analysis based on the thermal elasto-visco-plastic sintering model proposed by the authors (8,9) was carried out for sintering of functionally gradated hardmetals of simple (plate) and more complicated shape (cone). Gradated hardmetal plate and cone sintering was simulated with various parameters, like particle size, green density distribution and cobalt gradation parameter.

#### 2. Model for Sintering of FGM:

The behaviour of sintering gradated bodies is usually considered to be adequately represented by elasto-visco-plastic model (8,9). The basic feature of the generalised equation is that the deformation is divided into four different contributions: elastic, viscous, sintering shrinkage and thermal deformation (11). This model was applied for calculation of distribution of temperature, density, strains/strain rates and displacements, as well as normal and shear stresses:

$$\{d\sigma\} = [D^*] \{ \{d\varepsilon\} - [\eta]^{-1} \{\sigma\} dt - \{d\varepsilon^s\} - d\{\alpha T\} \}$$
(1)

where {d $\sigma$ }, {d $\epsilon$ } are stress and strain increment matrixes, [ $\eta$ ] is viscoplastic matrix, d{ $\alpha$ T} is thermal strain increment, {d $\epsilon$ <sup>s</sup>} is volumetric sintering strain increment, and [D<sup>\*</sup>] is a modified elastic compliance matrix (6,8,9,11).

The constitutive equation (1) is also coupled with the heat transfer. The latter is based on the energy balance and material parameters (thermal conductivity, specific heat and density). Here these parameters have been introduced as a function of temperature, cobalt volume fraction and porosity were 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

calculated using original micromechanical model (10). For the solid state sintering, the dominant mechanism of mass transport is assumed the grain boundary diffusion. The grain growth during sintering was described as

$$d^{3} = d_{0}^{3} + \int_{0}^{\tau} C_{1} T(\tau) \exp(\frac{C_{2}}{T(\tau)}) d\tau, \qquad (2)$$

where  $d_0$  is the initial average grain size,  $T(\tau)$  is the current temperature, and the constants  $C_1$ ,  $C_2$ , are obtained from experimental data (5,6,8,9).

#### 3. Sintering of Gradated WC-Co Plate and Cone:

For the stress and deformation analysis, a graded WC-Co plate and a cone with gradated outer layer was considered (Fig. 1). The plate of  $25 \times 31 \times 6$  mm was supposed to have with 6% Co at the top and 10%Co at the bottom. Cone specimen has 10% Co inside (core) and 6%Co on the rim.





Fig. 1. FEM mesh for simulation of sintering of FGM plate and cone specimens. Numbers show elements designations.

Cobalt concentration change across the thickness is governed by power law with the gradation parameter p (9,11):

$$%Co(z) = %Co(0) + (%Co(H) - %Co(0)) \cdot \left(\frac{z}{H}\right)^{p}$$
(3)

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where *H* is plate thickness, *z* - vertical coordinate and p = 0.5...2.5 (i.e. p = 1 means the linear function). Respective function for a cylinder takes form of:

$$%Co(r) = \begin{cases} %Co(0), & 0 \le r \le r_{core} \\ %Co(0) + (%Co(R) - %Co(0)) \cdot \left(\frac{r - r_{core}}{R - r_{core}}\right)^{P}, & r_{core} < r \le R \end{cases}$$
(4)

In these simulations, the program code was implemented into ABAQUS (Standard and CAE), where quadric elements have been chosen for the meshing for fully coupled displacement analysis (12). Heating and cooling rates have been chosen of 10 K/min and sintering was performed at 1573 K during 30 min. The same parameters (except cooling rate) have been also used previously in dilatometric experiments (8,9).

In the calculations, attention was directed on influence of other parameters (grain size, density) on final stress level and shape of the specimen. Impact of gradient function (p value) is discussed elsewhere (11,12).

#### 4. Results of simulation:

#### 4.1. Plate sintering:

In the first case, a flat plate design (Fig. 1) was chosen to get closer correspondence with other literature data (7). For the aspect ratio H/L = 0.2 ("large plate") and applied pressure of 630 MPa, the green density variation was reported to be between 0.60...0.65. In the 10% Co - 20% Co combination these differences were found to be 0.52...0.62 of theoretical density (7). Corich mixtures show higher green densities at higher pressures (>100 MPa), whereas at lower pressures mixtures with smaller Co content have higher green density. Thus, all cases shown below (Table 1) may be realised by adjusting particle size, cobalt content and compaction pressure. 15" International Plansee Seminar. Eds. G. Kneringer, P. Rödhammer and H. Wildner. Plansee Holding AG. Reutte (2001), Vol. 3

	%Co	∇%Co = const		
Layer #		Case 1	Case 2	Case 3
1 (top)	6	0.62	0.70	0.62
2	7.33	0.636	0.683	0.63
3	8	0.653	0.666	0.64
4	8.66	0.666	0.653	0.65
5	9.33	0.683	0.636	0.66
6 (bottom)	10	0.70	0.62	0.67

Table 1. Plate design (top	= 6%Co.	bottom = 10%Co	. linear	aradation
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Results of sintering simulation for these cases 1-3 are shown in Fig. 2. For these data, it is clearly seen that the green density distribution is necessary to know for the prediction of the final shape for correct shape estimations (also, the grain growth and real particle size/distribution are needed).



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Fig. 2. Final shape of three plates with the same cobalt gradient from 10 to 6% (in the direction "3", i.e. to the top) and different density gradients: case 1 (a), case 2 (b), and case 3 (c).

Elastic stresses appeared during cooling might be also important because bending of the plate at the sintering temperature may be opposite to that after cooling (i.e. similar to the phenomenon of thermal vibration of bimetallic beams).

No full analogy with bimetallic beams may be, however, applied because all shrinkage, shrinkage rate and thermal expansion are acting simultaneously. One may conclude that the green density variations among with particle size are very important parameters to control sintering and to obtain a compliant shrinkage in FGMs.

#### 4.2. Cylinder and cone sintering:

In the second simulation case, cylindrical specimen with a cone top part (as for punching tools) was chosen (Fig. 1). Radial and hoop stresses in this specimen "after sintering" (i.e. after isothermal soaking, but before cooling starts) are shown in Fig. 3. Here at the tip tensile radial and hoop stresses are being induced of order ~27 MPa. Compressive stresses (~15 ...17 MPa) appear in Co-rich underlay.

In respect to radial direction, these stresses are highest at the tip, but in respect to tangential direction (hoop stresses), they are the highest at the surface of cylinder (~35 MPa). This effect could be expected due to higher radial shrinkage of WC-10% Co, as also found by experiments (8,9,11). When cooling starts, some porosity in the material still exists, and final shrinkage happens together with thermal contraction of the material.

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Fig. 3. Radial (S11) and hoop (S33) stresses in the cone specimen after sintering (before cooling).

These differences in shrinkage rate and thermal expansion coefficients result in new stress distribution. In this case, after cooling to room temperature, Fig. 4, the tip, edges and surface should be under compression with stress level of 8...43 MPa. Tensile stresses appear the highest in the core and in the layer close to edges. These stresses are, however, much lower than WC-Co tensile or fatigue stress level (400...700 MPa according to literature data), so risk of cracking during and after sintering could be minimised.



Fig. 4. Radial (11) and hoop (33) stresses in the cone specimen after cooling.

Stress values are found to be strongly influenced by elastic module and thermal expansion dependencies of temperature. Little data are available for high-temperature properties of WC-Co materials and yet less for these made of new, submicron and nanopowders.

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In order to prevent bending and decrease residual stress level, further optimisation of the component parameters is necessary. This could be made using several ways like green shape adjustment, green density and/or particle size distribution, position of the specimen in the furnace, proper substrate selection, etc.

#### 5. Conclusions:

The behaviour of the graded compacts during heating, sintering and cooling can be simulated with FEM technique using developed thermal elasto-visco-plastic model. If compositional gradient (e.g. cobalt for the WC-Co FGM hardmetals) is only used, the final distortion and residual stresses of the sintered component may be significant.

For the WC-Co plate with both gradated cobalt and density gradients it was demonstrated that an optimal combination of these gradients exists, which may retain the flat shape of the plate after sintering.

The optimisation of FGM design should consider also additional gradients of such parameters like distribution of green density, particle size and possibly FGM green shape to minimise residual stresses incurred during entire sintering cycle.

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# Theoretical and Technological Fundamentals of Pressing Porous Powder Articles of the Complex Shape

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### Summary:

Intensification of technological processes, limited by the square of the surface of an active element porous powder field, is possible at the expense of magnification of the square of the surface of the latter by its addition. Thus the overall dimensions of such skew field are preserved.

The analytical dependence of the factor of magnification of the surface K on geometrical parameters of a powder article of the complex shape is obtained. The optimization of these parameters in view of technological limitations for the maximization of K is carried out.

The technique of calculating of the intense — deformed state of the powder skew field of the complex geometrical shape in the isostatic pressing is developed. The basic correlations permitting to calculate strain and deformation fields when pressing are gained.

The technique of dry isostatic pressing of the article of the complex shape and the corresponding deforming instrument are developed.

# Keywords:

Dry isostatic pressing, powder, complex shape, intense and deformed state, deforming instrument

Intensification of technological processes, limited by the square of the surface of an active element — porous powder skew field (processes of filtration, adsorption, catalysis), is possible at the expense of magnification of the square of the surface of the latter by its complicating. Thus the overall dimensions of the skew field are preserved.

There is a problem of choice of the optimal shape of an article, which at saving the adaptability of manufacturing ensures the maximum increase of

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the square of the surface without magnification of the overall dimensions of the article, that it is necessary to calculate the shape of the article, and then to develop the technique of the production of an article of this shape. Besides, for checking the possibility of preserving the quality parameters of the article (uniform density, uniform thickness the absence of flaws and cuts off) within the selected shape of the article and the technique of gaining the shape it is necessary to calculate fields of strain and deformation originating when pressing.

Let's consider the process of radial pressing of an article of the complex shape on a rigid frame (1). In fig. 1 the scheme diagram of radially-isostatic pressing along the whole length of an article isolating the mould with powder from the fluid is submitted. To the mould including rigid frame 1 and inner



Fig. 1. The scheme of radially-isostatic pressing of an article on the frame

elastic cover 3 filled with powder 2, the uniform pressure is applied. Thus the radial swaging of the powder 2 on the frame 1 along all its length is carried out. At such circuit (scheme) the longitudinal strain is restricted by rigid walls, and in most cases it is possible to neglect the exterior abrasion along these walls, i.e.  $\varepsilon_z = 0, u_z = 0, \tau_{xz} = 0, \tau_{yz} = 0$ . The shape of the frame defines the interior surface of the article, and the shape of the elastic cover — the outside.

Let's consider the problem of calculating the optimum shape and geometrical parameters of an article. We shall be limited by the class of articles, whose cross-section has a complicated shape, and the lengthwise shape and dimension of an article do not vary.

Let's stop on an article whose cut is shown in fig. 1, on the right (in the figure the article with the amount of edges equal to 4 is shown, but generally the amount of edges is not equal to 4). The given shape of an article seems to be preferable contrasted to the articles with an edge of a trapezoidal or

rectangular shape, as it allows to get the factor of magnification of a surface K more than 2 (K is equal to a ratio of the square of an article surface to the square of a surface of a pipe with the same critical dimensions) (2, 3, 4).

As the square of an article surface limits field-performance data, we shall consider an interior surface of an article, as it is smaller than the outside one. Therefore further calculations will be made with reference to the frame, uniquely reflecting an interior surface of an article at the given scheme of the pressing.

It is expedient to proceed to the square of a surface referred to the length of an article or, what is the same, to the perimeter.

The shape and the dimensions of such an article are defined by the following parameters (fig. 2):

- D (R) - diameter (radius) of an outside circle of a workpiece;

r — radius of a hole;

s — distance from the centre of a workpiece up to the centre of a hole;

- n amount of edges;
- --  $r_c$  radius of a fillet.



Fig. 2. The cut of the frame

Let's find an optimum correlation of the parameters, defining the structure and dimensions of an article, from the point of view of deriving the maximum surface magnification factor. In this case the technological limitations should be observed:

$$d_1 \geq d_m, \ d_2 \geq d_0, \tag{1}$$

(2)

(3)

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where  $d_m$  — minimum width of a half of the frame edge, which is selected from a condition of hardness and rigidity of the frame;  $d_0$  — minimum possible distance between the edges of the frame,  $d_0 = \delta_{0} + h_0$ ,  $\delta_0$  — width of an elastic cover,  $h_o$  — initial height of powder filling.

Let's get the function linking the square of the article surface with geometrical parameters, defining this square.

As a workpiece can be divided into n of identical parts, at an output of the formulae we shall consider only one segment of a workpiece (fig. 3).

Perimeter of the segment is defined by the expression:

 $L_{ABDE} = L_{AB} + L_{BD} + L_{DE}.$ 

Perimeter of the whole workpiece relative square:

 $L = 2n(L_{AB} + L_{BD} + L_{DE}).$ 

The figures AB, BD, DE represent arcs of circles of radius r, r<sub>c</sub>, R respectively. For definition of the length of an arc it is necessary to find an angle coming on this arc:

 $L_{AB} = r \alpha_{AB};$ 



Fig. 3. A segment of an article

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 $L_{BD} = r_c \alpha_{BD}$ 

(4)

 $L_{DE}=R \ \alpha_{DE}.$ 

Utilizing simple arithmetical transformations from a condition of contingence of a circle of a rounding with a circle of a hole and outside circle it is possible to find coordinates of basic points on a surface of a segment:

 $x_c$ ,  $y_c$  — coordinates of the centre of the rounding;

 $x_{o}$ ,  $y_{o}$  — coordinates of the centre of the hole;

 $x_{B}$ ,  $y_{B}$  — coordinates of the point B;

 $x_D$ ,  $y_D$  — coordinates of the point D.

Having defined the coordinates of the basic points, it is possible to find the angles of the arcs *AB*, *BD*, *DE*.

Having substituted the obtained results in expression 3 we receive the correction linking geometrical parameters of an article with the square of a surface.

In our case the geometrical limitations 1 for the considered shape (fig. 3) will look like:

$$d_1 = \operatorname{s} \, \sin\!\left(\frac{\pi}{n}\right) - r \ge d_m; \tag{5}$$

$$d_2 = y_c(s, r) - r \ge \frac{d_0}{2};$$
 (6)

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Extreme value of function 3 when observing limitations 5, 6 is found by standard methods, for example by the method of Lagrange (5), or by numerical methods (6, 7).

The computer program for calculating optimum parameters of an article (n, s, r) is developed from the point of view of maximizing the magnification factor of the surface. Input data for calculating are the following parameters:

- diameter of an outside circle of part D;
- r<sub>c</sub> radius of rounding;
- limitations d<sub>m</sub>, d<sub>0</sub>.

Fig. 4 shows the dependence of K on the amount of edges for the considered type of an article with parameters calculated with the help of this program, for the following input data: D = 63 mm,  $d_m = 18$  mm. As we see in the figure at the given input data the rate of the magnification of the surface is maximum when the amount of edges is equal 4. The modelling of articles with different diameters show that with the increase of the diameter of an article the rate of the magnification of the surface increases.

At the manufacture of powder articles of the complex shape the task of calculating of a deformation field and field of efforts originating in pressing of the preform is actual. Knowing the stress distribution of the pressing, it is possible to calculate the surface of the powder filling for preserving uniform density and uniform thickness of the article and to estimate the quality parameters of it. That is, it is necessary to define efforts ( $\sigma_x$ ,  $\sigma_y$ ,  $\sigma_z$ ),  $\tau_{xy}$ ,  $\tau_{xz}$ ,  $\tau_{yz}$ and migration  $(u_x, u_y, u_z)$  (or strain  $(\varepsilon_x, \varepsilon_y, \varepsilon_z)$ ) in each point of the pressing after the application of evenly distributed external pressure directed along the normal to the surface of the powder.

The complexity of calculating the intense - distorted state of a skew field of the complex shape is in the impossibility to simplify the defining equations (as it is done for the article as a rotating body (1).

In the further considerations we shall consider a powder field as isotropic cramped irreversibly deformable.

In the calculations we shall use the cartesian frame.

The components of the tensor of efforts in the cartesian frame satisfy the following equations:

1. Equations of equilibrium.

$$\begin{cases} \frac{\partial \sigma_x}{\partial x} + \frac{\partial \tau_{xy}}{\partial y} = 0, \\ \frac{\partial \sigma_y}{\partial y} + \frac{\partial \tau_{xy}}{\partial x} = 0. \end{cases}$$
(7)
2. Condition of toughness (1):

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$$\frac{3(p-p_{*})^{2}}{\psi^{2}}+2\frac{T^{2}}{\phi^{2}}=1,$$
(8)

where  $p = \frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$  — hydrostatic pressure; p. — parameter of displacement of the center of an ellipsoid along a hydrostatic axis which takes into account the distinctions in the pressing resistance to tension and compression;  $\psi$  and  $\phi$  — functions of mechanical performances of dabbed materials, and  $\psi = \psi(p) = \psi(p), \phi = \phi(p) = \phi(p)(1); T$  — intensity of tangents of efforts (voltages) (8).

For the complete exposition of the tension of a distorted field it is necessary to supplement the set of equations 7 with the correlation linking the components of the tensor of efforts ( $\sigma_z$ ,  $\sigma_x$ ,  $\sigma_y$ ).

The function of loading in view of the equation 8 will look the following:

$$f = \frac{3(p-p,)^2}{\psi^2} + 2\frac{T^2}{\phi^2} - 1.$$
 (9)

According to the associated law of current for such field we have (8):

$$d\varepsilon_{ij} = d\lambda \frac{\partial f}{\partial \sigma_{ij}},\tag{10}$$

where  $\lambda$  — a positive factor.

From the associated law of current, taking into account, that  $\varepsilon_z = 0$ , we receive:

$$d\varepsilon_z = d\lambda \frac{\partial f}{\partial \sigma_z} = 0 d\lambda \neq 0, \tag{11}$$

Let's substitute function of loading 9 in 10 and express  $\sigma_z$ :

$$\sigma_z = a(\sigma_r + \sigma_t) + bp., \tag{12}$$

where  $a = \frac{\psi^2 - \phi^2}{2\psi + \phi^2}, b = \frac{3\phi^2}{2\psi^2 + \phi^2}$ 

Substituting  $\sigma_z$  from 12 in the condition of toughness (8) we shall express  $\tau_{xy}$ :

$$\tau_{xy} = \pm \frac{1}{\sqrt{6}} \sqrt{\frac{\phi^2}{6}} \cdot \left\{ 1 - \frac{3}{\psi^2} \left[ \frac{(\sigma_x + \sigma_y)(a+1)}{3} + \left(\frac{b}{3} - 1\right)p \right]^2 \right\} - (\sigma_x - \sigma_y)^2 - \left[ a(\sigma_x + \sigma_y) + bp - \sigma_y \right]^2 \right\} - \left[ a(\sigma_x + \sigma_y) + bp - \sigma_y \right]^2.$$
(13)
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Let's designate through U a radicand in 13, that is  $\tau_{xy} = \pm \sqrt{\frac{U}{\kappa}}$ .

Having substituted  $\tau_{xv}$  in the equation of an equilibrium 6 we shall receive:

$$\frac{\partial \sigma_x}{\partial x} \pm \frac{1}{2} \sqrt{\frac{U}{6}} \left\{ -\frac{2\varphi^2 3}{6\psi^2} \left[ \frac{(\sigma_x + \sigma_y)(a+1)}{3} + \left(\frac{b}{3} - 1\right)p_{\star} \right] a + 1 \left( \frac{\partial \sigma_x}{\partial y} + \frac{\partial \sigma_y}{\partial y} \right) - 2(\sigma_x - \sigma_y)(\frac{\partial \sigma_x}{\partial y} - \frac{\partial \sigma_y}{\partial y}) - 2[a(\sigma_x + \sigma_y) + bp_{\star} - \sigma_x \left[ a \left( \frac{\partial \sigma_x}{\partial y} + \frac{\partial \sigma_y}{\partial y} \right) - \frac{\partial \sigma_x}{\partial y} \right] - (14) - 2[a(\sigma_x + \sigma_y) + bp_{\star} - \sigma_y \left[ a \left( \frac{\partial \sigma_x}{\partial y} + \frac{\partial \sigma_y}{\partial y} \right) - \frac{\partial \sigma_y}{\partial y} \right] \right\} = 0$$
  
The second equation is similar:

$$\frac{\partial \sigma_{y}}{\partial y} \pm \frac{1}{2} \sqrt{\frac{U}{6}} \left\{ -\frac{2\varphi^{2} 3}{6\psi^{2}} \left[ \frac{(\sigma_{x} + \sigma_{y})(a+1)}{3} + \left(\frac{b}{3} - 1\right)p_{\star} \right] a + 1 \left( \frac{\partial \sigma_{x}}{\partial x} + \frac{\partial \sigma_{y}}{\partial x} \right) - 2(\sigma_{x} - \sigma_{y})(\frac{\partial \sigma_{x}}{\partial x} - \frac{\partial \sigma_{y}}{\partial x}) - 2[a(\sigma_{x} + \sigma_{y}) + bp_{\star} - \sigma_{x} \left[ a \left( \frac{\partial \sigma_{x}}{\partial x} + \frac{\partial \sigma_{y}}{\partial x} \right) - \frac{\partial \sigma_{x}}{\partial x} \right] - (15) - 2[a(\sigma_{x} + \sigma_{y}) + bp_{\star} - \sigma_{y} \left[ a \left( \frac{\partial \sigma_{x}}{\partial x} + \frac{\partial \sigma_{y}}{\partial x} \right) - \frac{\partial \sigma_{y}}{\partial x} \right] = 0$$

Thus, we have received the set of equations 12, 14, 15, whose solution allows to define components of a tensor of efforts.

To receive the solution of the given set of equations is not easy, therefore it is expedient to use the numerical methods or software packages permitting to solve different partial equations, for example package Matlab or package FlexPDE.

For complete exposition of the articles during the pressing, it is necessary to find the link between the components of the tensor of efforts and the strains.

According to the associated law of current it is possible to write

$$d\varepsilon_{x} = d\lambda \frac{\partial f}{\partial \sigma_{x}}, \ d\varepsilon_{y} = d\lambda \frac{\partial f}{\partial \sigma_{y}}, \tag{16}$$

But, as  $\varepsilon_x \neq 0$  and  $\varepsilon_y \neq 0$ , the uncertain factor d $\lambda$  can't be eliminated.

As  $\varepsilon_{z} = 0$ , the condition of the mass preserve makes it possible to write the following correlation (10):

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$$\varepsilon_{x} + \varepsilon_{y} = \frac{\Delta V}{V_{0}} = \sqrt[b]{\frac{\rho}{\rho_{x\rho}}} [1 - v_{0}]$$
(17)

where b – parameter of seal;  $V_0$  — original density of a briquette;  $\Delta V$  — modification of volume;  $V_0$  — original volume of a dust (1).

Having taken a total differential from both parts, we shall receive:

$$d\varepsilon_{x} + d\varepsilon_{y} = \frac{\frac{1}{b} \sqrt[b]{\frac{p}{p_{xp}}} [1 - v_{0}]}{p} dp$$
(18)

$$p = \frac{\sigma_x + \sigma_y + \sigma_z}{3}$$
 by the account 16 and, we shall receive:

$$d\lambda \left[\frac{\partial f}{\partial \sigma_x} + \frac{\partial f}{\partial \sigma_y}\right] = \frac{\frac{1}{b} \sqrt[b]{\frac{p}{p_{\kappa p}}} [1 - v_0]}{p} \frac{\sigma_x + \sigma_y + \sigma_z}{3}$$
(19)
$$\frac{\frac{1}{b} \sqrt{\frac{p}{p_{\kappa p}}} [1 - v_0]}{p}$$

Let's designate  $\frac{\overline{p} \sqrt[p]{p_{\kappa p}}}{p} = M$  and, taking into account, that

 $d\sigma_z = 0$ , we receive:

$$d\lambda = \frac{M(d\sigma_x + d\sigma_y)}{3\left[\frac{\partial f}{\partial \sigma_x} + \frac{\partial f}{\partial \sigma_y}\right]}$$
(20)

$$d\varepsilon_{x} = \frac{\frac{\partial f}{\partial \sigma_{x}} M(d\sigma_{x} + d\sigma_{y})}{3\left[\frac{\partial f}{\partial \sigma_{x}} + \frac{\partial f}{\partial \sigma_{y}}\right]}$$
(21)

$$d\varepsilon_{y} = \frac{\frac{\partial f}{\partial \sigma_{y}} M(d\sigma_{x} + d\sigma_{y})}{3\left[\frac{\partial f}{\partial \sigma_{x}} + \frac{\partial f}{\partial \sigma_{y}}\right]}$$
(22)

$$\frac{\partial f}{\partial \sigma_x} = \frac{6\left(\frac{\sigma_x + \sigma_y + \sigma_z}{3} - \rho_{\star}\right)\frac{1}{3}}{\psi^2} + \frac{2(\sigma_x - \sigma_y) + 2(\sigma_x - \sigma_z)}{3\varphi^2}$$
(23)

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$$\frac{\partial f}{\partial \sigma_{v}} = \frac{2(p - p_{z})}{\psi^{2}} + \frac{2(\sigma_{v} - \sigma_{x}) + 2(\sigma_{v} - \sigma_{z})}{3\varphi^{2}}$$
(24)

$$\frac{\partial f}{\partial \sigma_x} + \frac{\partial f}{\partial \sigma_y} = \frac{4(p - p_{\perp})}{\psi^2} + \frac{2(\sigma_x + \sigma_y - 2\sigma_z)}{3\varphi^2}$$
(25)

Finally we shall receive:

$$d\varepsilon_{x} = \frac{M(d\sigma_{x} + d\sigma_{y})}{3\left[\frac{4(p-p_{*})}{\psi^{2}} + \frac{2(\sigma_{x} + \sigma_{y} - 2\sigma_{z})}{3\varphi^{2}}\right]} \left[\frac{2(p-p_{*})}{\psi^{2}} + \frac{2(\sigma_{x} - \sigma_{y}) + 2(\sigma_{x} - \sigma_{z})}{3\varphi^{2}}\right] (26)$$

$$d\varepsilon_{y} = \frac{M(d\sigma_{x} + d\sigma_{y})}{3\left[\frac{4(p - p_{*})}{\psi^{2}} + \frac{2(\sigma_{x} + \sigma_{y} - 2\sigma_{z})}{3\varphi^{2}}\right]} \left[\frac{2(p - p_{*})}{\psi^{2}} + \frac{2(\sigma_{y} - \sigma_{x}) + 2(\sigma_{y} - \sigma_{z})}{3\varphi^{2}}\right] (27)$$

The equations 26 and 27 reflect the link between efforts (voltages) and strains of parts in pressing.

These equations can be solved through integration by numerical methods.

The obtained equations allow to calculate stress distribution on the volume of the skew field. From the point of view of security preserving the quality, it is necessary to aspire to a random distribution of direct stresses and absence of tangents. Besides, it is necessary to select the material of frame so that its yield limit is much higher than the pressure on the interior surface of the article. The rate of the pressure on an exterior surface of the article defines the choice of the material of the cover and characterizes force parameters of the process of pressing.

The deformations on outside surface of the pressing are the input data for projection the elastic distorting instrument.

Alongside with the pressing of porous powder articles a perspective direction is the creation of permeable articles of the complex shape with the organized pore structure on the basis of metal (wire) and non-metal (polymeric and textile) filaments.

The technique of manufacturing permeable articles (workpieces) on the basis of metal and non-metal filaments is similar to the technique of manufacturing powder articles: forming of the preform of an article by filling a mould tool with host material; of the preform in conditions of radial loading; sintering of the obtained pressing. When this there is some difference in the process of filling the mould with host material.

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When using powder material the mould tool is filled by putting the powder into the concavity of the mould, and when using thread-like material – by winding wire or filaments round the forming element.

In fig. 5 there is the scheme of a mould tool (transversal section) for pressing permeable articles of the complex shape on the basis of metal and non-metal filaments.

The filaments are wound on the mobile edges of the element with the



- Fig. 5. The mould for pressing permeable articles of the complex shape on the basis of metal and non-metal filaments:
  - 1 a preform of an article (skew field of winding); 2 a form making element; 3 an elastic cover; 4 a cóntract

winding regeme, ensuring, in view of the following deformation of the field of winding, preserving of the preset performances of the article. The forming element with the wound up filaments is installed into the elastic cover and hermetically sealed. The assembled mould is put into the hydrostat, where high pressure is created. Under the external pressure the field of winding distorts in a radial direction, thus occurs its simultaneous thicking ensuring the final shaping of the structure of the article, and goffering achieved by copying by a skew field of winding the profile of the edges of the forming element and shaping of the corrugations. Then the pressure is removed, the mould is extracted from the hydrostat and undone and the forming element with the obtained shape is taken out. Further, if it is necessary to give the article additional hardness, the caking of the pressing is possible if nonmetallic filaments were not utilized as the fundamentals of the article.

The given technological process of manufacturing of permeable articles of the complex shape on the basis of wire and filaments allows to receive articles with any amount of corrugation of different shapes and sizes.

The number of the corrugations of a porous article, their shape and size define the degree of maturity of its surface, which is express by the ratio of the square of the developed surface of a porous field to the square of the cylindrical surface, circumscribed around the skew field, and is described by the factor of magnification of the surface.

We optimize geometrical parameters of articles of the complex shape because of technological limitations with the help of maximizing *K*.

The standard scheme of the device for the radial isostatic pressing of articles with the isolation of the mould from the hydraulic fluid is shown in fig. 6. The basic elements of the device are elastic liner 1, reinforced by steel elements 2, providing a possibility of mounting contracting elements, and case 3, the central hole of which with annular gap 7 has the elastic liner. The pressing of powder 6 is carried out in a mould consisting of a form making rod 4 and elastic cover 5. The construction of the device is made in such a way that the axial displacements and strains of elastic liner 2, are eliminated. The axial strains of the elements of the mould and of the pressed preform are eliminated too. More often the oil will be utilized as a hydraulic fluid. Dimensions and the shape of a pressed article are defined by the appropriate parameters of the mould. On creating high-pressure in a working cavity



Fig. 6. The scheme of the device for the radial isostatic pressing of articles with the isolation of the mould from the hydraulic fluid

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devices 7, elastic liner 2 and cover 5 at the expense of rheological behavior of the material they are made of uniformly redistribute pressure along the outside surface of preform, pressing it up the frame at full length. The preform being contracted, the air goes out through clearances. Among the advantages of the given scheme is the presence of the self-contained hydraulic scheme of small volume, the isolation of the mould with a preform from the hydraulic fluid by means of elastic liner 2, what allows to avoid vacuum creating and hermetizing of the mould at each cycle of pressing. Since the free exit of air from the cover is ensured, on removing the pressure there is no cracking of a contract under the operation of the compressed air.

The universality of the device is determined by a possibility of arbitrary substitution of the moulds with the appropriate geometrical parameters. The only requirements to such moulds is their correspondence to the device by critical dimensions.

To manufacture an article of the complex shape it's necessary to manufacture the appropriate mould. The aspect of an interior surface of the mould determines the aspect of an outside surface of an article. The example of the mould for pressing a powder article with a screw outside and interior surface is shown in fig 7.

Thus, it is possible to make the following conclusion: complicating the



Fig. 7. The mould for pressing a powder article with a screw outside and interior surface

Porous Powder Article shape allows to intensity technological processes, to reduce metal consumption of the used equipment. The given calculations can be utilised when optimizing geometrical parameters of porous articles of the complex shape, projecting elastic distorting instrument and technological processes of pressing.

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## Main Aspects of the Theory and Technology of Producing Permeable Materials with the Organized Porous Structure Through Deformation Processing

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## Summary:

The possibility of materials with organized porous structure, given size and pore allocation, deriving from wire is established by its regulated winding on mandrel, deformation in conditions of isostatic loading and consequent sintering (if necessary).

To determine power characteristics of the pressing technological process, the calculating of workpiece (in the form of winding skew) tensedeformation state is made. Studying regularities of deformation field changing during the plastic strain in consideration of winding skew fields initial structure allowed to define structural characteristics of finished articles.

The technology of producing permeable materials with organized porous structure is developed.

## Keywords:

Permeable materials, wire, winding skew fields, deformation

Producing materials with organized porous structure, given size and pore allocation is relevant for new engineering development in the field of liquid and gas dispersal, noise and flame extinction, when realizing catalytic and sorption processes. The possibility of such materials deriving from wire is established by its regulated winding on mandrel, deformation in conditions of isostatic loading and consequent sintering (if necessary).

The creation of porous materials assumes necessity of their structural performances study, the control with which to the greatest extent is carried out at the stage of wire winding.

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The winding of wire with diameter *d* (fig. 1) on mandrel is carried out at the angle  $\beta$  to a plane, perpendicular to mandrel axis, in strata *n*, ensuring a clearance *s* between two next unidirectional coils of a stratum.



Fig. 1. The scheme of working of the winding skew field by the winding of wire on mandrel

The structural performances (porosity, porosity, coefficient of serpiginous of pores, pore sizes, specific surface of pores) belong to geometrical class and can be defined analytically.

For porous skew fields of winding on the wire basis the following expression of porosity  $\Pi$  is obtained:

$$\Pi = 1 - \frac{\pi}{8} \cdot \left(1 + \frac{s}{d}\right)^{-1}.$$
(1)

For porous skew fields of winding on the wire basis the expression of porosity c looks like:

$$c = \left(1 + \frac{d}{s}\right)^{-1}.$$
 (2)

It is known, that for materials with the organized pore structure the coefficient of serpiginous of pores is  $\xi = \Pi / c$  (1). Then, in view of expressions 1 and 2 we have:

$$\xi = 1 + \left(1 - \frac{\pi}{8}\right) \cdot \frac{d}{s}.$$
(3)

For porous skew fields of winding on the wire basis specific surface of pores is  $S_V = 4 \cdot (1 - \Pi) / d$  (2). With the account 1 we shall receive:

$$S_V = \frac{\pi}{2 \cdot (d+s)}.$$
(4)

In fig. 2 the scheme of generatrix is figured at winding a porous skew field of a mesh, which shape generally looks like a rhomb, and stacking of wire in places of intersection of differently directed coils of one stratum.

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Fig. 2. The scheme of generatrix and stacking of wire

The maximal size of a pore is  $d_{\Pi}^{max}$  conditionally determined by the maximal size of a spherical particle (diameter  $d_q$  in a fig. 2, a), transiting through a pore, which is equal to a clearance *s*. The clearance magnitude between coils is determined by conditions of wire winding.

However, to receive a skew field of winding with uniform pore structure, it is necessary to take into account the following condition:  $s \ge s_{min}$ , where  $s_{min}$  — minimally possible magnitude of a clearance between coils, defined by displacement of unidirectional coils of one stratum in places of intersection differently directed coils. From a fig. 2, b, where  $BD = 2 \cdot d$ , and CD = d we can find that:  $BC = d + s \ge d \cdot \sqrt{3}$ . From here:  $s_{min} = d \cdot (\sqrt{3} - 1)$ . Thus, we have:

$$d_{\Pi}^{\max} \ge s_{\min} = d \cdot (\sqrt{3} - 1). \tag{5}$$

For wire porous materials the average size of a pore  $d_{\Pi}^{cp}$  characterizing efficiency of a filtration, is determined according to the formula (2):  $d_{\Pi}^{cp} = d \cdot \frac{\Pi}{1 - \Pi}$ . In view of expression 1 we shall receive:  $d_{\Pi}^{cp} = \frac{(8 - \pi) \cdot d + 8 \cdot s}{\pi}$ . (6)

These expressions describe structural performances of porous skew fields of winding and allow substantially to forecast properties of articles on the wire basis wire obtained by the method of deformation handling.

For definition of force performances of pressing process we shall calculate the intense-distorted condition of perform as a skew field of winding.

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The high enough regularity of contracts in skew fields of winding allows to reduce a task to exposition of interaction of wires in simple contact. namely, to interaction of two adjoining cylinders loaded with concentrated cramping force.

Let's consider a case, when two identical cylinders, which axes form some angle  $0^{\circ} < \phi < 90^{\circ}$  between themselves, are loaded with a point force P. The scheme of cylinders loading is submitted in a fig. 3. Applying the cramping force the cylinders are distorted, and originally the dot contingence passes in a touch on a platform of contact shaped of an ellipse (fig. 3, a).



Fig. 3. The scheme of cylinders loading: a) the arising of the platform of contact; b) dimensional epure of pressure restricted to a surface of the platform of contact

For research of gains and migrations in a place of contact it is necessary beforehand to consider the problem about the intense - distorted condition of cylinders in elastic area of deformation.

Let point force P distribute on a platform of an ellipse, which square is  $F = \pi \cdot a \cdot b$ , where a and b — the large and small semiaxis of an ellipse accordingly. Dimensional epure of pressure p is restricted to a surface of an ellipsoid (3) (fig. 3, b), where z is the ordinate of an ellipsoid in an arbitrary point N (x; y); c is the third semiaxis of an ellipsoid;  $p_{max}$  is maximal pressure (at the center of an ellipsoid).

The full load P is connected to pressure p in an arbitrary point of a platform of contact by an integral  $P = \int p \cdot dF$ , and the pressure p in this point 15" International Plansee Seminar. Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

is proportional to ordinate *z*:  $p = p_{max} \cdot \frac{z}{c}$ . Then we shall receive:  $P = \frac{p_{max}}{c} \int_{F} z \cdot dF$ . Here  $\int_{F} z \cdot dF = \frac{2}{3} \cdot \pi \cdot a \cdot b \cdot c$  — the volume of semi-

ellipsoid. From here we discover:

$$\rho_{max} = \frac{2}{3} \cdot \frac{P}{\pi \cdot a \cdot b}.$$
(7)

Let's define migrations at ellipsoidal distribution of pressure (fig. 4).



Fig. 4. The state of cylinders: a) before deformation; b) after deformation

Let's consider two points  $N_1$  and  $N_2$  (fig. 4, a) on a surface of cylinders in an intersecting plane *yz* being on distance  $\xi$  from the common normal, platform, carried out to the center of contact. Under the action of a point force *P* there is a strain of cylinders in the contact zone, and their axes will be pulled together on magnitude  $\delta$  (fig. 4, b):

 $\delta = w_1 + w_2 + z_1 + z_2, \tag{8}$ 

where  $w_1$  and  $w_2$  — elastic migrations of points  $N_1$  and  $N_2$  accordingly;  $(z_1 + z_2)$  — distance between points  $N_1$  and  $N_2$  up to a strain.

The distance between points  $N_1$  and  $N_2$  can be also noted through the surfaces of two skew fields equations in an environ of tangency point in this way O(3):

$$z_1 + z_2 = A \cdot x^2 + B \cdot y^2, \tag{9}$$

where A and B — parameters depending on a curvature of principal normal cuts of adjoining skew fields in point of tangency.

For two cylinders of identical radius *r* the parameters A and B look like:

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$$A = \frac{1}{2 \cdot r} \cdot (1 - \cos \varphi); \ B = \frac{1}{2 \cdot r} \cdot (1 + \cos \varphi); \ 2 \cdot (A + B) = \frac{2}{r}.$$
(10)

Considering expressions 8 and 9 in common, we shall receive:  $\delta - (A \cdot x^2 + B \cdot y^2) = w_1 + w_2.$ (11)

On the other hand, migration w of an arbitrary point N (x; y), located inside the ellipse with semiaxes a and b, in which loading P is distributed, can be defined according to the following formula (3):

$$w = \frac{1-\mu^2}{E} \cdot \frac{p_{max}}{a} \cdot \left[ a \cdot b \cdot K - \frac{b}{a} \cdot D \cdot x^2 - \frac{a}{b} \cdot (K-D) \cdot y^2 \right], \quad (12)$$

where  $\mu$  and E — coefficient of the Poisson and Yung modulus of the cylinder material; K and L - complete elliptic integrals of the first and second sort accordingly;  $D = \frac{1}{e^2} \cdot (K - L)$ ;  $e = \sqrt{1 - \left(\frac{b}{a}\right)^2}$  — a relative eccentricity of an ellipse.

Equating coefficients at  $x^2$ ,  $y^2$  and constant terms of the equations 11 and 12, and also utilizing relations 7 and 10, we shall receive the formulas for definition of:

1) large semiaxis a of an elliptic platform of contact:

$$a = 1,144 \cdot n_a \cdot \sqrt[3]{P \cdot r} \cdot \frac{1 - \mu^2}{E}, \text{ where } n_a = \sqrt[3]{\frac{4 \cdot D}{\pi \cdot (1 - \cos\varphi)}};$$
(13)

2) small semiaxis b of an elliptic platform of contact:

$$b = 1,144 \cdot n_b \cdot \sqrt[3]{P \cdot r \cdot \frac{1 - \mu^2}{E}}, \text{ where } n_b = \sqrt[3]{\frac{4 \cdot \sqrt{1 - e^2}}{\pi \cdot (1 + \cos \varphi)}} \cdot (K - D); \quad (14)$$

3) coming together of adjoining cylinders  $\delta$ :

$$\delta_{\kappa} = 1,311 \, n_{\delta} \cdot \sqrt[3]{\frac{P^2}{r} \cdot \left(\frac{1-\mu^2}{E}\right)^2}, \text{ where } n_{\delta} = K \cdot \sqrt[3]{\frac{2 \cdot (1-\cos\varphi)}{\pi^2} \cdot \frac{1}{D}}; \quad (15)$$

4) greatest pressure  $p_{max}$  on a platform of contact:

$$p_{max} = 0.364 \cdot n_p \cdot \sqrt[3]{\frac{P}{r^2} \cdot \left(\frac{E}{1-\mu^2}\right)^2}$$
, where  $n_p = \frac{1}{n_a \cdot n_b}$ . (16)

For convenient use of the obtained dependencies we made the table of coefficients  $n_a$ ,  $n_b$ ,  $n_\delta$ ,  $n_o$ , included to the calculated formulas composed, 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner. Plansee Holding AG. Reutte (2001), Vol. 3

depending on an angle  $\varphi$ . While compiling it the tables of complete elliptic integrals were used (4).

φ	n <sub>a</sub>	n <sub>b</sub>	n <sub>δ</sub>	n <sub>p</sub>
0°	-	-	-	-
10°	6,6317	0,3109	0,4279	0,4861
20*	3,8167	0,4122	0,6038	0,6358
30°	2,7328	0,4930	0,7262	0,7426
40°	2,1360	0,5673	0,8177	0,8254
50°	1,7545	0,6407	0,8870	0,8898
60°	1,4857	0,7171	0,9376	0,9386
70°	1,2855	0,8000	0,9726	0,9728
80°	1,1280	0,8928	0,9931	0,9931
90°	1,0000	1,0000	1,0000	1,0000

The table of coefficients  $n_a$ ,  $n_b$ ,  $n_\delta$ ,  $n_\rho$  depending on an angle  $\varphi$ 

In a case, when two identical cylinders with perpendicular axes  $\varphi = 90^{\circ}$  interact, we have a circular platform of contact. In this case, having used the table of coefficients  $n_a$ ,  $n_b$ ,  $n_\delta$ ,  $n_p$  and substituted appropriate values of coefficients depending on an angle  $\varphi$  into the formulas 13 - 16, we shall receive:

$$a=b=1,144\sqrt[3]{P\cdot r\cdot \frac{1-\mu^2}{E}}; \quad \delta_{\kappa}=1,311\sqrt[3]{\frac{P^2}{r}\cdot \left(\frac{1-\mu^2}{E}\right)^2}; \qquad p_{max}=0,364\sqrt[3]{\frac{P}{r^2}\cdot \left(\frac{E}{1-\mu^2}\right)^2}.$$

Let's define efforts at ellipsoidal distribution of pressure.

As the greatest pressure  $p_{max}$  operates at the center of an elliptic platform of contact, the greatest interest represents the tension research in points located on an axis *z*.

As the analysis of researches of adjoining skew fields tension (3), the most dangerous at an ellipsoidal platform of contact is the point laying on an axis *z* and having coordinate  $z = 0,31 \cdot a$  (a point *M* in a fig. 3, b). For this point the equivalent calculated effort  $\sigma_{3\kappa\sigma}$ , scaled on a hypothesis of the greatest efforts tangents (a hypothesis of a Treska – Saint-Venant) at a relation of semiaxes of a contact elliptic platform b/a = 0,5, is equal:  $\sigma_{3\kappa\sigma} = 0,65 \cdot p_{max}$ . Application of average efforts tangents hypothesis (the hypothesis Guber – Mises – Genki) gives rather close outcome. And,  $\sigma_{3\kappa\sigma}$  varies at other values of a ratio b/a a little. For example, for a circular

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platform of contact ( $\varphi = 90^\circ; b/a = 1$ ) the most dangerous point has coordinate  $z = 0.48 \cdot a$ , and the equivalent effort in this point calculated according to a hypothesis of a Treska – Saint-Venant, is equal:  $\sigma_{3\kappa\theta} = 0.62 \cdot p_{max}$ .

The analysis of these data shows, that the ratio  $\sigma_{_{3KB}} / p_{max}$  varies in rather narrow limits at a ratio modification b/a and depends on the shape of contact platform, and also on the application of this or that hypothesis for definition of equivalent efforts a little. This circumstance allows to do the further accounts immediately according to the magnitude of the greatest pressure  $p_{max}$  on a platform of contact.

For an elliptic platform of contact while two cylinders loading by a point force *P* according to a hypothesis of a Treska – Saint-Venant  $(\sigma_{3\kappa\sigma} = \sigma_1 - \sigma_3 = \sigma_{\tau})$  the condition of a toughness in view of the formula 16 accepts an aspect:

$$\sigma_{_{3KB}} = 0.65 \cdot p_{_{max}} = 0.237 \cdot n_{_{p}} \cdot \sqrt[3]{\frac{P}{r^{2}}} \cdot \left(\frac{E}{1 - \mu^{2}}\right)^{2} = \sigma_{_{T}}.$$
 (17)

From here we discover the gain of compression in a simple contact, at which the plastic deformation occurs:

$$P = \frac{75,12}{n_p^3} \cdot r^2 \cdot \left(\frac{1-\mu^2}{E}\right)^2 \cdot \sigma_T^3.$$
 (18)

Let's consider the problem about the intense – distorted condition of cylinders in plastic area of deformation, having used a method of variable parameters of elasticity (5).

The equations of toughness theory deformation, which is basic in many practical accounts (there is also theory of plastic flow, when the plastic deformation of metal assimilates to current of thick liquid), are possible to present as the equation of elasticity theory, if a coefficient of elasticity *E* and coefficient of Poisson  $\mu$  to replace in variable parameters of elasticity *E'* and  $\mu'$ . The formulas for their definition are known (5):

$$E' = E_c; \mu' = \frac{1}{2} - \frac{1 - 2 \cdot \mu}{2} \cdot \frac{E_c}{E},$$
(19)

where  $E_c = \frac{\sigma_0}{\varepsilon_0}$  — the intersecting module on the curve of deformation representing the customary glow iris of deformation at pure tension  $\sigma_0 = f(\varepsilon_0)$ .

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Thus, size of a bonding contact pad, magnitude of adjoining cylinders coming together, greatest pressure on the contact platform and maximal compression gain in plastic deformation simple contact are defined as follows:

$$a' = 1,144 \cdot n_a \cdot \sqrt[3]{P \cdot r \cdot \frac{1 - {\mu'}^2}{E'}};$$
(20)

$$b' = 1,144 \cdot n_b \cdot \sqrt[3]{P \cdot r \cdot \frac{1 - \mu^{/2}}{E'}};$$
(21)

$$\delta_{\kappa}' = 1,311 \cdot n_{\delta} \cdot \sqrt[3]{\frac{P^2}{r}} \cdot \left(\frac{1 - {\mu'}^2}{E'}\right)^2;$$
(22)

$$\rho_{max}' = 0,364 \cdot n_p \cdot \sqrt[3]{\frac{P}{r^2}} \cdot \left(\frac{E'}{1-\mu'^2}\right)^2;$$
(23)

$$P' = \frac{75,12}{n_p^3} \cdot r^2 \cdot \left(\frac{1 - {\mu'}^2}{E'}\right)^2 \cdot \sigma_T^3.$$
(24)

The possibility of the exact account contacts in winding skew field allows to proceed pass from efforts voltages and strains in simple contract to force and deformation characteristics of pressing process of the whole skew field.

Thus, in view of the amount of contracts in one stratum  $n_{\kappa}^{c}$  of a winding skew field and number of stratums *n*, the common gain of pressing will be equal:

$$P_{\kappa} = n_{\kappa}^{c} \cdot n \cdot \frac{75,12}{n_{p}^{3}} \cdot r^{2} \cdot \left(\frac{1 - \mu^{/2}}{E^{/}}\right)^{2} \cdot \sigma_{T}^{3}.$$
<sup>(25)</sup>

The wire in the wire material stratum can be considered as a multispan continuous-solid beam by a diameter *d* with distance between legs *l*, loaded in the middle of spans with forces *P* (a fig. 5). By virtue of a loading symmetry an absolute value of transversal force in spans of a girder (beam)  $Q = \frac{P}{2}$ , and maximal magnitude (on an absolute value) flexing of the moment in abutment cuts and in the middle of spans  $M = \frac{P \cdot l}{8}$ .

As distance between legs and diameter of a beam – are values of one order, and  $l \approx d$ , seems sensible to define the influence of effort tangents on

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Fig. 5. The scheme of loading of the multispan continuous-solid beam

magnitude on extreme safe bearing loads, at which plastic deformation occurs.

As the maximal value of transversal force and abutment moment take place in the same cuts, we shall calculate a value normal  $\sigma_{max} = \frac{M}{W_{\star}}$  and tangents  $\tau_{max} = \frac{4}{3} \cdot \frac{Q}{F}$  of efforts in these cuts, taking into account, that section modulus for round cut  $W_x = \frac{\pi \cdot d^3}{32}$ , and square of round cut  $F = \frac{d^2}{4}$ :

$$\sigma_{max} = \frac{4 \cdot P \cdot I}{\pi \cdot d^3}; \tag{26}$$

$$\tau_{max} = \frac{8 \cdot P}{3 \cdot \pi \cdot d^2} = 0.849 \cdot \frac{P}{d^2}, \qquad (27)$$

The relations 26 and 27 assume, that the maximal flexural stress in cut reach the magnitude of a yield point of a wire material, i.e.  $\sigma_{max} = \sigma_T$ . Then, carrying out a separate account on normal and tangent efforts, we discover limiting value of loading P in an elastic loading range. From expression 26 follows, that:

$$P_{max}^{(\sigma)} = \frac{\pi \cdot d^3}{4 \cdot I} \cdot \sigma_T = \frac{0.785}{\chi} \cdot d^2 \cdot \sigma_T, \qquad (28)$$

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where  $\chi = \frac{l}{d} > 1,7$  — a ratio of length of span between legs to a diameter of a

beam, that follows from expression 5.

It is known, that using toughness condition of a Treska – Saint-Venant  $\tau_T = \frac{\sigma_T}{2}$ , and toughness condition of Guber – Mises – Genki  $\tau_T = \frac{\sigma_T}{\sqrt{3}}$ . Last relation is more exact and used for the further accounts. Then, in view of expression 27:

$$P_{max}^{(\tau)} = \frac{3 \cdot \pi \cdot d^2}{8 \cdot \sqrt{3}} \cdot \sigma_T = 0,680 \cdot d^2 \cdot \sigma_T.$$
<sup>(29)</sup>

Thus, it is apparent that limiting safe bearing load, at which plastic deformation occurs, is load scaled on direct stresses. Therefore influence of tangents of efforts may not be taken into account.

Let's consider curving a beam in plastic area of deformation (fig. 6).



Fig. 6. The spreadance of the stress at the elastic and plastic curving

At permissible stress method account the carrying capacity of a girder is considered exhausted with occurrence of flow in extreme fibers (fig. 6, a). At the further magnification of loading the area of plastic deformations will be spreaded deep into cuts, and the elastic kernel will be reduced (fig. 6, b). In cut the so-called plastic joint is formed which differs from a theoretical joint (which does not perceive the moment) as it has an operating fixed moment  $M_{max}$  equal to the limiting moment of interior forces. The moment in a plastic joint determines by itself a carrying capacity a girder cut. For continuous-solid girders the formation of one plastic joint yet does not mean loss of carrying

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capacity. Thus, the statically indeterminable girders have a padding redundancy of hardness.

In our case in each span of a girder there exist three equally dangerous cuts, in which the plastic joints are simultaneously formed.

limiting moment of interior forces  $M_{max} = \sigma_T \cdot W_T$ . So. Her  $W_T = 2 \cdot S_{1x}$  — plastic section modulus of round cut;  $S_{1x} = F_1 \cdot y_c$  — the static moment of a half-disk concerning a neutral axis;  $F_1 = \frac{\pi \cdot d^2}{8}$  — square of a half-disk;  $y_c = \frac{2}{3} \cdot \frac{d}{\pi}$  — ordinate of a barycantre of a half-disk. Then:  $S_{1x} = \frac{d^3}{12}$ , and  $W_T = \frac{d^3}{6}$ . From here, the limiting flexing the moment in cut is equal:  $M_{max} = \sigma_T \cdot \frac{d^3}{6}$ . Besides  $M_{max} = \frac{P_{max} \cdot I}{8}$ . Thus, we shall receive:

$$\mathcal{P}_{max}^{\prime(T)} = \frac{4}{3} \cdot \frac{d^3}{l} \cdot \sigma_T = \frac{1,333}{x} \cdot d^2 \cdot \sigma_T.$$
(30)

The expression 30 for the greatest loading at plastic curving is fair at account without the account of hardening of wire material (fig. 6, c).

Let's consider plastic curving in view of hardening (fig. 6, d).

At curving in a plastic zone  $M_{max}$  determine from a condition that the plastic deformation of extreme filaments of a girder reach strength  $\sigma_B$  of a material.

The effort in an arbitrary fiber  $\sigma_{\nu}$  (see fig. 6, d) is equal:  $\sigma_y = \sigma_T + \frac{\sigma_B - \sigma_T}{d} \cdot 2 \cdot y$ . The magnitude of the cut limiting moment is equal:

$$M_{max} = \int_{F} \sigma_{y} \cdot y \cdot dF, \text{ where } dF = b_{y} \cdot dy = 2 \cdot \sqrt{\frac{d^{2}}{4} - y^{2}} \cdot dy. \text{ Then:}$$

$$M_{max} = 2 \cdot \int_{-d/2}^{d/2} \left[ \sigma_{T} + \frac{\sigma_{B} - \sigma_{T}}{d} \cdot 2 \cdot y \right] \cdot y \cdot \sqrt{\frac{d^{2}}{4} - y^{2}} \cdot dy = , \quad (31)$$

$$= \sigma_{T} \cdot \frac{d^{3}}{6} + (\sigma_{B} - \sigma_{T}) \cdot \frac{\pi \cdot d^{3}}{32} = \sigma_{T} \cdot W_{T} + (\sigma_{B} - \sigma_{T}) \cdot W_{x}$$

where  $W_{\tau}$  — plastic section modulus;

 $W_{\rm x}$  — axial section modulus.

Let's rewrite this expression:

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$$M_{\max} = \sigma_T \cdot W_T \cdot \left(1 + \frac{\sigma_B - \sigma_T}{\sigma_T} \cdot \frac{W_x}{W_T}\right).$$
(32)

As 
$$M_{\max} = \frac{P_{\max} \cdot I}{8}$$
, then:  
 $P_{\max}^{I(B)} = \frac{8}{I} \cdot \sigma_T \cdot W_T \cdot \left(1 + \frac{\sigma_B - \sigma_T}{\sigma_T} \cdot \frac{W_x}{W_T}\right).$  (33)

Let's define migration of force application point P on a Vereshchagin method (6). In our case (fig. 5) we have:

$$\delta_P = \frac{2}{E \cdot J_x} \cdot \left( \omega_{p1} \cdot y_{c1} - \omega_{p2} \cdot y_{c2} \right), \tag{34}$$

where  $J_x$  — a moment of round cut inertia,  $\omega_{P1} = \omega_{P2} = \frac{1}{2} \cdot \frac{l}{2} \cdot \frac{P \cdot l}{8}$  — squares cargo epures of flexings of the moments in span of a girder from an operation of point forces *P*;  $y_{c1} = \frac{2}{3} \cdot \frac{l}{4}$  and  $y_{c2} = \frac{1}{3} \cdot \frac{l}{4}$  — ordinate epures of the simple moments which are under barycentres of cargo epures.

In view of these relations from expression 34 it is discovered that:

$$\delta_P = \frac{P \cdot I^3}{192 \cdot E \cdot J_x},\tag{35}$$

Then, the radial strain of one stratum of winding at different loading stages in view of expressions 28, 30, 33 and  $J_x = \frac{\pi \cdot d^4}{64}$  is defined as follows.

1. At the moment of approach of fluctuation in wire material:

$$\delta_P = \frac{l^2}{12 \cdot d \cdot E} \cdot \sigma_T = 0,0833 \cdot \frac{l^2}{d \cdot E} \cdot \sigma_T.$$
(36)

2. In plastic loading area, assuming, that the plastic deformation envelopes all round cut of a wire:

$$\delta_P^{I(T)} = \frac{4 \cdot l^2}{9 \cdot \pi \cdot d \cdot E} \cdot \sigma_T = 0.1415 \cdot \frac{l^2}{d \cdot E} \cdot \sigma_T.$$
(37)

3. At plastic curving in view of material hardening:

$$\delta_P^{\prime(B)} = \frac{16 \cdot l^2}{25 \cdot \pi \cdot d \cdot E} \cdot \sigma_T = 0,2037 \cdot \frac{l^2}{d \cdot E} \cdot \sigma_T.$$
(38)

The summarized strain of one stratum of a skew field of winding in view of a contact strain at its radial pressing in plastic loading area is equal:

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$$\delta = \delta_{\kappa} + \delta_{P} = 1,311 \cdot n_{\delta} \cdot \sqrt[3]{\frac{P^{2}}{r} \cdot \left(\frac{1-\mu^{/2}}{E^{/}}\right)^{2}} + \frac{0,32 \cdot (d+s)^{2}}{\pi \cdot r \cdot E} \cdot \sigma_{T}.$$
 (39)

The study of modification regularities of deformation fields at plastic deformation in view of starting structure of a winding skew field has allowed to define ready workpiece structural performances.

The porosity  $\Pi'$  of workpieces on the basis of a wire obtained by a deformation handling method is defined by the following expression:

$$\Pi' = 1 - \frac{\pi}{8} \cdot \left[ \left( 1 + \frac{s}{d} \right) \cdot \left( 2 - \frac{\delta}{d} \right) \right]^{-1} \cdot \frac{D_0 + 2 \cdot n \cdot d}{D_0 + 2 \cdot n \cdot (2 \cdot d - \delta)}.$$
(40)

The expression of a porosity c' for such articles look like:

$$c' = \frac{s-d}{s+d}.\tag{41}$$

Serpiginousity coefficient  $\xi'$  is expressed as follows:

$$\xi' = \frac{s+d}{s-d} - \frac{\pi}{8} \cdot \left[ \left( \frac{s}{d} - 1 \right) \cdot \left( 2 - \frac{\delta}{d} \right) \right]^{-1} \cdot \frac{D_0 + 2 \cdot n \cdot d}{D_0 + 2 \cdot n \cdot (2 \cdot d - \delta)}.$$
 (42)

The specific surface of pores  $S'_V$  is equal:

$$S_V' = \frac{\pi}{2 \cdot (d+s)} \cdot \left(2 - \frac{\delta}{d}\right)^{-1} \cdot \frac{D_0 + 2 \cdot n \cdot d}{D_0 + 2 \cdot n \cdot (2 \cdot d - \delta)}.$$
(43)

The average size of a pore  $d_{II}^{cp}$  is discovered under the formula:

$$d_{\Pi}^{l cp} = \frac{8 \cdot (d+s)}{\pi} \cdot \left(2 - \frac{\delta}{d}\right) \cdot \left(\frac{D_0 + 2 \cdot n \cdot d}{D_0 + 2 \cdot n \cdot (2 \cdot d - \delta)}\right)^{-1} - d.$$
(44)

The deriving technique of porous materials with the organized pore structure is developed. Here is the description of the technique. Wire is cruciformly wound on mandrel with a condition of winding ensuring preset performances of an article, in view of consequent deformation of skew field of winding. The cruciform winding happens at a reciprocative transportation of wire concerning rotating mandrel in such a manner that the coil are stracked under some angle to a plane, perpendicular axis of mandrel. Wire winding is carried out before stacking of necessary amount of stratums, and for winding one stratum a required amount of passes in both directions is made, ensuring a fixed clearance between two next unidirectional coils of a stratum and, thus, shaping meshes of a winding skew field. Reeled-up wire mandrel is put in an elastic envelope. The assembled mold tool is put in a working concavity of installation for radial (isostatic) pressing, where high pressure is created. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner. Plansee Holding AG. Reutte (2001), Vol. 3

Under operation of pressure transmitted through an elastic envelope on a winding skew field it is hardened and ensures shaping of article final structure. Then pressure is removed and the shape is extracted from installation, dismantled and obtained pressing is removed from mandrel. Further, if it is necessary to collimate the article with padding hardness, the caking of pressing is possible.

In this work the authors explain the basic aspects of the theory and technique of deriving of permeable materials with the organized pore structure by deformation handling. Here the condition of winding skew field distorted at its deformation is under consideration. The gains and migrations in places of coil contract of wire and in spans between two next unidirectional coils are investigated. In view of primary structure of a skew field of winding and strains at its plastic deformation the structural performances of a ready article are defined. The technique of deriving of porous permeable materials is developed on the basis of a wire.

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## PM - Verfahren zur Herstellung metallischer Zellularwerkstoffe

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## Summary:

In this review the major processes about manufacturing of metals with cellular structure are described - based on powder metallurgy, chemical deposition and some other methods (without melting techniques). It can be shown that during the last decade many interesting innovations led to new production methods to design cellular materials. Some of them are used nowadays in the industry. Also characterisation and properties become more important and have therefore been carried out carefully, because of their strong influence on the function and applications of such materials.

## Keywords:

Powder Metallurgy, chemical deposition, metals, cellular structure, foam, production methods

## 1. Einleitung:

Vor über 40 Jahren begann man sich intensiver mit der Herstellung von Metallschäumen zu beschäftigen. Ein aufschlußreicher Überblick dieser Initiativen findet sich bei Davis (1). Ab den 90er Jahren erfolgt wieder eine neue Offensive, wobei sowohl verbesserte / neue Produktionswege gesucht werden als auch eine genaue, eingehendere Charakterisierung dieser Materialien vorgenommen wird.

Gegenstand dieses Beitrages ist in erster Linie eine überblicksmäßige Darstellung der pulvermetallurgischen und eine etwas detailiertere der chemischen Verfahrenstechniken zur Herstellung metallischer Zellular15° International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

werkstoffe. Sehr schöne Ergebnisse werden auch durch schmelzmetallurgische Methoden erzielt - auf diese wird hier jedoch nicht näher eingegangen (vgl. 1, 2, 3, 4).

Allen Materialien mit zellulärer Struktur - ob geschlossen- oder offenporig sind zwei auffallende Merkmale eigen: ihr geringes spezifische Gewicht und ihre verhältnismäßig große Oberfläche. Ihre Struktur und die daraus resultierenden Eigenschaften bestimmen die Funktion und die Anwendungen der porösen Metallwerkstoffe (1, 3, 5, 6).

Eine effektive Beschreibung der zellulären Werkstoffe kann z.B. durch die Bestimmung folgender Eigenschaften und Charakterisierungsmerkmale erfolgen:

- 1. relative Dichte
- 2. Energie- und Schallabsorption
- 3. Permeabilität (Filter)
- 4. Wärmetausch
- 5. Katalyse (chemische Industrie)
- 6. Kompressionsversuch (Festigkeit, Duktilität / Sprödigkeit, offen- oder geschlossenporig)
- 7. Metallographische, REM- und tomographische Untersuchungen (Morphologie, Porenverteilung etc.)

## 2. Methoden zur Herstellung metallischer Zellularmaterialien:

Abbildung 1 zeigt eine Zusammenfassung über die aus der Literatur bekannten Methoden zur Herstellung metallischer Stoffe mit zellulärer Struktur (ausgenommen sind die schmelzmetallurgischen Verfahren), die anschließend kurz beschrieben werden. 15" International Plansee Seminar. Eds. G. Kneringer, P. Rödhammer and H. Wildner. Plansee Holding AG. Reutte (2001), Vol. 3



Abb.1: Übersicht der Methoden zur Herstellung poröser Metallwerkstoffe

Eine exakte Zuordnung jedes Verfahrens in eine der oben genannten Gruppen ist nicht immer möglich, da manche Herstellungsprozesse in Kombinationen auftreten.

## **PM-Methoden:**

1. Treibmittelverfahren:

auch unter dem Namen IFAM / MEPURA-Prozeß bekannt; Metallpulver und Treibmittel werden gemischt, vorkompaktiert, kompaktiert und zu Halbzeug geformt (hohe Dichte), anschließend bis zum Schmelzpunkt des Metalls/Legierung erhitzt, wobei das Treibmittel zersetzt und die 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

Schaumstruktur während der anschließenden Abkühlung erhalten wird (7, 8, 9, 10, 11, 12, 13, 14).

Problematisch ist hier der beträchtliche Dichteunterschied Rand- Kernzone, wobei am Rand recht dichte Bereiche auftreten, sowie die nicht immer befriedigende Gleichmäßigkeit der Zellgröße. Der Einfluß des Oberflächen-/Volumsverhältnisses auf die Erwärmung ist zu berücksichtigen.



Abb.2a: Al Schäume mit unterschiedlicher Porengröße ( $\rho$  = 500 kg·m<sup>-3</sup>) (46)



Abb.2b: Struktur eines geschäumten Aluminiumteils (Al99.96 - 15mm) (47)

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#### 2. Platzhalterverfahren:

Aufgrund der doch recht unterschiedlichen Einbringung des Platzhalters, scheint es angebracht, das Verfahren zu unterteilen. Allen angeführten Methoden sind folgende Verfahrensschritte gleich:

Metall-/Legierungspulver und Platzhalter, verdichten oder lose in eine Form einbringen, entfernen des Platzhalters, sintern.

Platzhaltermethoden sind relativ größenunabhängig, doch können Probleme bei der Mischung/Entmischung auftreten, und die rückstandsfreie Entfernung des Platzhalters ist oft nicht leicht möglich.

a. Metall-/Legierungspulver und Platzhalter (z.B. Harnstoff, Ammoniumhydrogencarbonat) werden vermischt, verdichtet, thermische Austreibung des Platzhalters, sintern (4, 12, 15, 16, 17).

b. Metall-/Legierungspulver und ein Bindergemisch werden auf einen Platzhalter gesprüht und dieser derart beschichtet. Anschließend wird



Abb.3a: Gesinterte Formkörper aus 316L vor und nach dem Kompressionsversuch (48)

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Abb.3b: Schliffbild eines gesinterten Formkörpers aus 316L (48)

kompaktiert oder eine lose Pulverschüttung in Formen eingebracht, dann erfolgt die Entfernung des Platzhalters (pyrolytisch) und die entstandenen Hohlkugeln werden gesintert (6, 18, 19, 20).

c. Hohlfaserherstellung durch Co-Extrusion von plastifizierten Metallpulvern und Füllmaterial, letzteres wird entfernt und abschließend gesintert (22, 23).

#### 3. Imprägnierverfahren:

Ein Schlamm bestehend aus Flüssigkeit und Metallpulver wird von einem Kunststoffschwamm aufgesaugt, getrocknet, der Platzhalter thermisch entfernt und gesintert (1, 21).

#### 4. Einspritzen / Verdüsen:

a. Gleichzeitiges Einspritzen von Inertgas und Schlamm auf Metallpulver-Aceton-Basis, die entstandenen Hohlkugeln werden unter Wasserstoff reduziert und gesintert, gegebenenfalls wird in einer geeigneten Atmosphäre  $(CO/CO_2)$  karburiert (24).

b. Verdüsen einer Metallschmelze in Inertgasatmosphäre (25, 26, 27) bzw. reaktiver Atmosphäre (28, 29). Hierzu zählt z.B. die Luftverdüsung von Gußeisenschmelzen (RZ-Verfahren): eine aufgekohlte Eisenschmelze wird mit Druckluft verdüst und nimmt dabei Sauerstoff auf. Anschließend erfolgt

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eine Glühbehandlung, bei der das Eisenoxid durch den Kohlenstoff reduziert wird. Bei diesem Prozeß entsteht ein gewisser Anteil an hohlen Partikeln.

#### 5. Reaktionssintern:

Sinterung von Pulvermischungen z.B. Fe-Al, die während des Sinterns eine exotherme Reaktion sowie eine starke lineare Schwellung bis maximal 25% aufweisen. Dabei kann bis zu 50% Porosität auftreten (30).

Auch hier spielen upscaling-Effekte auf das Oberflächen-/Volumsverhältnis eine große Rolle.

#### 6. Schüttsintern:

a. Sintern loser (hohler) Pulver- oder Faserschüttungen (siehe auch Punkt 2b), ggf. Kompaktieren / Formen: Vibration, axial Pressen, CIPpen, Formen von Pulver - Bindergemischen bzw. Verarbeiten von Pasten (powder rolling für Bänder).

Ebenso werden auch Verbundstrukturen gesintert, das sind diverse Kombinationen wie grobe - feine Pulver, Pulver - Fasern etc.

Faserherstellung: neben aufwendigen Verfahren (Drahtziehen, Schneiden, Spanen) wird das Schmelzextraktionsverfahren eingesetzt; Erzeugung von Matten und Geweben (5, 6, 31, 32).

#### 7. HIPpen und spezielle Wärmebehandlung:

Ti-Legierungspulver wird geHIPpt, wobei gleichzeitig Argon eingeschlossen wird. Erst nach einer Wärmebehandlung (T>1000°C, druck- und zeitabhängig) tritt eine Porenvergröberung ein, wobei bis zu 40 Vol% Porosität auftritt.

Vor der Wärmebehandlung kann das geHIPpte Material durch Strangpressen oder Walzen geformt werden (33).

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## Chemische Beschichtungsmethoden:

Platzhalter werden auf unterschiedliche Arten beschichtet (elektrochemisch, chemisch, CVD, mit Suspensionen, PVD). Das Füllmaterial wird thermisch entfernt und der entstandene Metallschaum bzw. eine Hohlpartikelschüttung gesintert.

#### 1. (Elektro-) Chemische Methoden:

Der Platzhalter (Kunststoffpartikel oder -faser) wird elektrisch leitend gemacht und galvanisch beschichtet (Ni, Cu, Co, Fe) bzw. mehrmals beschichtet, wodurch eine Legierungsbildung ermöglicht wird. Das Füllmaterial wird pyrolytisch entfernt und die entstandene zelluläre Metallstruktur gesintert. Wirkt während der Beschichtung oder der Sinterung Druck- bzw. Zugbelastung ein, entstehen elliptoidische, wabenförmige oder "spindle-shaped" Strukturen (5, 34, 35).

Bei den galvanischen Methoden ist die Schichtdicke des abgeschiedenen Metalls im Schwamminneren bzw. am Rand unterschiedlich. Dies hängt von verschiedenen Faktoren ab: z.B. Höhe des Schwammes, Stromstärke oder Elektrolytbewegung. Deshalb wird eine gleichmäßige Beschichtung des Gutes erschwert.

Die hier angegebenen Verfahren aus der Literatur unterscheiden sich durch die Beschichtungsmethode des Platzhalters.

a. Ein Kunststoffschwamm wird durch Eintauchen in eine Ruß enthaltende Dispersion elektrisch leitend gemacht und im Anschluß daran galvanisch mit Ni beschichtet.

Besonderheit: Der Schaum wird unter Zugbelastung galvanisiert, wodurch "spindle-shaped cells" entstehen (34).

b. Ein PU-Schaum mit einer Stärke von z.B. 1,5 mm wird chemisch derart vorbehandelt, daß eventuell vorhandene Poren geöffnet werden ("uncapping"). Die elektrische Leitfähigkeit des Kunststoffes wird durch PVD erreicht (besputtern mit einem Metall). Die Verstärkung des metallischen Layers erfolgt durch Galvanisieren oder stromlose Beschichtung (35).

c. Kunststoffpartikel werden in einer Dispersion, die u.a. Kupfernitrat enthält, beschichtet. Durch eine chemische Reaktion werden Kupferverbindungen (Hydroxide, Karbonate) abgeschieden. Während der anschließenden

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Kalzination unter Luft oder N<sub>2</sub> wird der Kunststoff entfernt, wobei in Abhängigkeit vom verwendeten Gas submikrone Hohlkugeln (z.B. 0,63 µm) aus CuO oder Cu entstehen (36),

(Dispersion: Cu(NO<sub>3</sub>), Harnstoff, Poly-N-vinylpyrrolidon).

d. Das Metallpulver (z.B. Fe) wird mit einem edleren Metall (z.B. Cu) durch eine Zementationsreaktion beschichtet, unter gleichzeitiger Auflösung des unedleren Metalls. Abhängig vom Ausgangspulver entstehen Hohlkugeln unterschiedlicher Größe. Nach einer Wärmebehandlung besitzen diese eine ausreichende Festigkeit, um eine gute Handhabung oder weitere Verarbeitung (z.B. Verzinnung) ohne Probleme zu gewährleisten. Schließlich werden durch Schüttsintern Hohlkugelformkörper hergestellt (37).

Hier können auch feinzellige Körper hergestellt werden. Nachteilig ist die Beschränkung der Metallpaarung für die Zementationsreaktion.



Abb.4: Schliffbild eines gesinterten Formkörpers aus Cu10Sn-Bronze (a: ungeätzt, b: geätzt) e. Bei der Regenerierung von salzsauren Beizlösungen aus der Stahlindustrie werden nach dem LURGI-Verfahren in einem Wirbelbett, das 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

von heißer Luft durchströmt wird, die Eisenchloridlösung und Sauerstoff bei Temperaturen zwischen 850 - 880 °C zur Reaktion gebracht. Dabei entstehen - neben  $Fe_3O_4$ -Pulver - Eisenoxidhohlkugeln (38).

#### 2. CVD-Methoden:

Die Beschichtung eines zellulären Grundkörpers erfolgt durch Zersetzung einer Verbindung in der Gasphase (CVD). Nach dem Ausbrennen und Sintern entstehen hochporöse Schaumkörper (39, 40, 41, 42,).

a. Ein Gemisch aus Nickelcarbonyl und CO-Gas wird in eine Reaktionskammer geleitet, in der ein über Infrarotquellen beheiztes und an Spulen eingespanntes Kunststoffschaumband mit Ni - durch die Zersetzung von Ni(CO)<sub>4</sub> - beschichtet wird. Anschließend erfolgt der Transport des Bandes über die Spulen in den Sinterofen. Während der Sinterung zersetzt sich der Kunststoff und man erhält eine offenporige Ni-Struktur (unter der Bezeichnung INCOFOAM bekannt) (39, 40).

Verglichen mit den durch elektrochemische Methoden hergestellten zellularen Materialien werden sehr gleichmäßige Ni-Schichten abgeschieden, da der Kunststoffschaum - bei horizontaler Ausführung der Reaktionskammer - unterschiedlich erwärmt wird. Dieser Umstand wirkt sich unmittelbar günstig auf die Eigenschaften des Ni-Schaumes aus (mechanische Festigkeit, elektrische Leitfähigkeit).

b. Ein offenporiger Kohlenstoffschaum wird über einen CVD-Prozeß - durch die Zersetzung von TaCl<sub>5</sub> - mit Ta beschichtet (41, 42).

(Lit. 43 beschreibt die Herstellung des C-Schaumes - siehe unter "Sonstige Verfahren" Punkt 2).

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## Sonstige Verfahren:

### 1. Siebdruckverfahren (Direct-Typing-Process):

Mit einer speziell konstruierten 3D-Siebdruckmaschine werden angepastete Materialien (Metall, Keramik, Kunststoff) Schicht um Schicht aufgetragen und zu porösen Körpern bestimmter Hohlraum- und Kanalstruktur verarbeitet (44, 45).

Hier ist vor allem die Variabilität von Zellgröße und -form attraktiv und ebenso die große Flexibilität in der Wahl der Ausgangsmaterialien. Ob eine solche Produktion für größere Serien ökonomisch ist, läßt sich derzeit schwer abschätzen.

#### 2. Erhitzen eines imprägnierten PU-Schaumes:

Ein PU-Schaum wird mit Harz imprägniert und stufenweise bis auf 2000°C unter Schutzgas oder in reduzierender Atmosphäre erhitzt, bis ein glasartiger Kohlenstoffschaum entsteht.

Weitere Beschichtungen dieses C-Schaumes über CVD-Prozesse sind möglich, z.B. mit SiC, BN, W, Ta (43).

#### 3. PVD-Methode:

a. Auf ein Substrat wird ein Metall unter Inertgaspartialdruck besputtert. Das abgeschiedene Metall wird auf Schmelzpunkttemperatur erhitzt, wobei das eingeschlossene Gas expandiert und individuelle Zellen formt. Nach dem Abkühlen erhält man einen Körper mit geschlossenporiger Struktur (1).

b. Beschichtung eines Kunststoffplatzhalters durch besputtern mit einem Metall (siehe unter "(Elektro-)Chemische Methoden" Punkt 1b) (35).

## 3. Zusammenfassung:

In diesem Überblick finden sich die aus der Literatur bekannten auf Pulvermetallurgie, chemische Beschichtung und einige andere Methoden (außer Schmelzmetallurgie) basierende Prozesse, die sich mit der Herstellung von Metallen mit zellulärer Struktur auseinandersetzen.

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Innerhalb der letzten 10 Jahre haben viele interessante Innovationen zu neuen Produktionsmethoden der Herstellung metallischer Zellularwerkstoffe geführt und einige davon werden heute industriell genutzt.

Immer größere Bedeutung erhält die Erstellung von Eigenschaftsprofilen und Charakterisierung dieser Werkstoffe, weil diese einen entscheidenden Einfluß auf Funktion und Anwendung besitzen.

Welche Herstellungsmethoden sich letztlich durchsetzen werden, hängt sicherlich von verschiedenen Faktoren wie

- Preis- / Leistungsverhältnis
- relativ unkomplizierte und / oder gut zu beherrschende Prozeßführung
- Eigenschaften des Werkstoffes
- Einsatzgebiet

und dergleichen ab.

Derzeit scheinen die Al-Schäume der großtechnischen Umsetzung am nächsten zu sein, allerdings ist auch hier der Durchbruch noch nicht wirklich gelungen. Die aus einzelnen Hohlpartikeln, analog zu Sinterteilen, aufgebauten Zellularwerkstoffe könnten hier aufgrund der besseren Gleichmäßigkeit der Struktur eine ernsthafte Konkurrenz werden, sofern die Hohlpartikel ausreichend kostengünstig hergestellt werden können.

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# Production and Properties of Bronze Based Cellular Materials

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## Abstract:

For production of lightweight components, cellular materials offer attractive potential. Here, manufacturing of sintered bodies from bronze hollow spheres is described. The process starts with fabrication of hollow copper particles by cementation of Cu on iron particles. The still fragile Cu shells are consolidated by coating with Sn and subsequent gravity sintering. The resulting specimens exhibit a closed cell bronze structure with rather consistent morphology and cell wall thickness. The apparent density may range between 1.5 and 3.0 g.cm<sup>-3</sup> and can be controlled by variation of particle size and wall thickness. The mechanical behaviour of the structures esp. during compressive loading is described and related to the microstructural parameters.

## Keywords:

Powder Metallurgy, chemical deposition, metals, bronze, cellular structure, properties, production

## 1. Introduction:

Porous lightweight materials have found increasing interest for various applications. This is due to the fact that natural cellular structures such as wood or bone (1) offer very attractive strength-to-weight ratios. In particular lightweight Al foams which in principle have been known for decades (2) have been produced and are being tested for vibration damping, energy absorption, etc. (e.g. 3, 4). The standard manufacturing process here is

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consolidation of Al-TiH<sub>2</sub> powder mixes with foaming above the melting point. The materials thus generated are characterised by fairly thin walls between the cells and by density and cell size gradients from the surfaces to the interior.

Cellular structures with more regular structure might be accessible by using already hollow powder particles (e.g. 5, 6, 7) for lightweight structures with possibly thicker and better defined walls. The problem here is mostly the manufacturing - and processing - of the particles. More or less hollow powder particles are found e.g. in RZ powder (8, 9) in which however the reproducibility of the structure is prohibitively poor. Thin-walled hollow particles of different metals have been produced (e.g. 6, 10) which are however difficult to obtain in small diameters. The thin shell also makes them mechanically weak.

Thick-walled and thus stronger hollow particles might be of interest for less extremely lightweight but mechanically stronger components. It has been found that for moderate density PM structural parts, which contain almost exclusively interconnected porosity, the mechanical strength is almost exclusively determined by the geometry of the sintering contacts. With increasing porosity the cross section of the contacts decreases much faster than the relative density (11), and higher porosity results in a lower strength-to-weight ratio since the particle cores do not contribute to strength but are only dead weight.

This unsatisfactory behaviour might be remedied by making the powder particles themselves lighter without changing the geometry of the sintering contacts. Within this work, the manufacturing of hollow spheres for model investigations and the structure and some properties of gravity sintered specimens made from such powders are described.

## 2. Experimental:

#### Manufacturing of Cu hollow powder

Since considerable experience had been gained previously with powder coating by cementation (12, 13), deposition of copper on spherical Feparticles by cementation with subsequent dissolution of the remaining iron

was regarded attractive. Cementation of Cu on Fe is very fast and simply done and could be used in an industrial scale without larger difficulties. As starting materials, spherical Fe powders were produced from iron oxide obtained in pickling acid recovering plants following the fluidised bed line. This oxide was reduced in flowing hydrogen for 6 hrs at 800°C to result in similarly spherical iron powder (Fig.1). After screening the fraction between 710-500  $\mu$ m was used. Coating with copper was done by pouring the powder into a CuSO<sub>4</sub>-solution the Cu content of which was adjusted such as to result in the desired Cu content of the coated powder (taking into account the amount of Fe dissolved). The suspension was stirred carefully until the blue solution had been completely discoloured.

It was found that considerable amounts of copper could be deposited on the Fe particles; even complete replacement of Fe by Cu was possible. The deposited copper layers are apparently sufficiently porous to enable diffusion of the Fe ions from the Cu-Fe interface into the solution (see Fig.2a). Since Fe is dissolved inwards and Cu builds up outward, the cavity in the materials is approx. the size of the original Fe particle. If there would be a solid Cu shell, the ratio external to internal radius of the shell R/r could be approximated as about 1.26, i.e. the shell thickness is 0.26 r. Since the shell is however highly porous (which is necessary to remove the Fe<sup>2+</sup> generated) the external radius is larger and is not so clearly defined while the internal one can be clearly seen from the micrographs (Fig.2b).

Since the particles are very weak and difficult to handle, a strengthening treatment was regarded necessary. This was done by annealing at 800°C in  $H_2$  atmosphere which causes reduction of oxides and also some sintering within the shell (although the morphology is not significantly changed), resulting in mechanically more reliable particles that could be handled more safely (Fig.3).

Measurements of external and internal radius and wall thickness of a typical annealed Cu hollow sphere showed that R/r (= D/d = 752  $\mu$ m/590  $\mu$ m = ) is 1,27 (calculated value 1,26) and wall thickness is 78 $\mu$ m (calculated 0,26 r = 0,26 295  $\mu$ m = 76,7  $\mu$ m).

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Fig.1a: Fe from Fe<sub>2</sub>O<sub>3</sub>, SEM



Fig.1b: Fe from  $Fe_2O_3$  (cross section )

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Fig.2a: Cu hollow sphere, SEM



Fig.2b: Cu hollow sphere (cross section)

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Fig.3: Cu hollow sphere, annealed (800°C, 1h, H<sub>2</sub>)

Nevertheless, gravity sintering of these particles in ceramic moulds showed that very weak bonding was attained. Another disadvantage is the poor packing density attained even after careful tapping: the rough surfaces cause too much friction between the particles to give reasonable packing density of the spheres. Therefore, sintering activation as well as smoothening of the surfaces was regarded necessary (12).

### Production of bronze based hollow spheres and parts

Both results were expected to be obtained by liquid phase activation. This could most easily be done by introducing tin to the system, tin bronze of the type Cu-10%Sn being commonly used e.g. for gravity sintering of filters.

Addition of tin as fine powder with subsequent sintering was not successful since even distribution cannot be attained by admixing. Therefore, also here a coating process was selected. After heat treatment (Fig.8, 2<sup>nd</sup>.step) the Cu hollow spheres were tin coated in aqueous solution (Fig.8, 3<sup>nd</sup>.step). It showed that in a single step process, maximum Sn contents of 5 mass% can

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be introduced, the Sn layer apparently acting as a barrier against further deposition. If more Sn is to be added, an intermediate anneal at 700°C in H<sub>2</sub> has to be done to dissolve the deposited Sn; afterwards, a second deposition run is possible by which Sn contents >10% can be attained ((Fig.8, 2<sup>nd</sup>. and 3<sup>nd</sup>.step must be repeated). Materials Cu-5%Sn, Cu-10%Sn, and Cu-14%Sn were obtained with reproducible results (Fig.4).



Fig.4: Annealed Cu hollow sphere coated with 5% Sn

If the Sn coated powders are tapped into moulds and gravity sintered, cellular structures with sufficiently strong sintering contacts are attained (Fig.5, 6). Of course, the sintering temperature has to be carefully selected according to the Sn content; at too high temperatures, large amounts of liquid phase result in unwelcome densification (Fig.7).

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Fig.5a: Cu-10%Sn, 800°C, 3hrs, H<sub>2</sub>



Fig.5b: Cu-10%Sn, 800°C, 3hrs, H<sub>2</sub>

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Fig.6: Cu-5%Sn, 900°C, 3hrs, H<sub>2</sub>



Fig.7: Cu-14%Sn, 800°C, 3hrs, H<sub>2</sub>

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The procedures described above will be shown in the following process scheme (Fig.8):



Fig.8: Flow sheet for manufacturing bronze cellular materials

#### 3. Properties of bronze cellular structures:

Cylindrical samples with two compositions Cu-5%Sn and Cu10%Sn and a reference material (spherical bronze powder 89/11, fractions between 500-710 $\mu$ m, produced by NA) were tapped into ceramic moulds and gravity sintered in a pusher furnace for 3 hrs. in flowing H<sub>2</sub> at different temperatures, which depend on the composition.

The density of the bronze bodies was measured - with two different methods: Archimedes-principle or dimensional measurements - and the relative densities  $\rho_{rel}$  (=  $\rho_{sample}$  /  $\rho_{theoretical}$ ) were calculated. The results can be seen in Table 1. Naturally, the hollow sphere samples show lower density compared with that of the reference material. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

#### Table 1

Density of Cu-5%Sn, Cu-10%Sn and BZ89/11 sintered bodies, 3 hrs., H<sub>2</sub>

Sample	<b>ST</b> [°C]	Density [g/cm <sup>3</sup> ]	Density(theo) [g/cm³]	Density(rel)	Porosity %
Cu-5%Sn	900	2,06	8,86	0,23	77
Cu-10%Sn	800	1,82	8,76	0,21	79
BZ 89/11	800	5,97	8,76	0,68	32

Useful application of cellular materials requires more detailed information on their mechanical behaviour. These materials can be characterised by their low density and their large surface area. The large pore volume minimises the load-bearing cross section. So, cellular solids usually can not stand high tensile forces. Therefore deformation experiments are conducted in e.g. compression (14).

Compression-tests were performed with cylindrical Cu5%Sn- and Cu10%Snbodies (preparation described before) and the resulted compressive loaddeflection curves are shown in Fig.9. For static compressive tests an INSTRON universal tester was used, cross-head speed was 0,2mm/sec. It can be seen that the compressive stress-strain curves obtained from sintered bronze hollow spheres were smooth and there was no horizontal or significant flat plateau region.

There are several reasons or their combinations for such behaviour of stressstrain curves: higher relative densities of the samples, closed-cell character of the solids, ductile material of the cell walls etc. (14). 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001). Vol. 3



Fig.9: Compressive load-deflection curves for sintered bronze hollow spheres

To optimise the sintering condition for Cu10%Sn-bronze, the hollow spheres were tapped into moulds and gravity sintered in a pusher furnace for 1 hour in flowing hydrogen. The sintering temperature was varied and the density measured (Table 2). The results are shown in Fig.10: the density increases with higher sintering temperature, but there is a remarkable increase of density observed at 830°C.

#### Table 2

<b>ST</b> [°С]	750	770	790	800	810	820	830
Density [g/cm³]	1,54	1,61	1,68	1,83	1,87	1,94	3,02
Density(rel)	0,18	0,18	0,19	0,21	0,21	0,22	0,34
Porosity %	82,4	81,6	80,8	79,1	78,6	77,8	65,5

Density of sintered Cu10%Sn hollow spheres, 1hr, in H<sub>2</sub>, variation of ST



Fig.10: Density of sintered Cu10%Sn-bronze hollow spheres as a function of the sintering temperature

## 4. Conclusions:

- Hollow and near-spherical Cu and bronze powder particles can be produced by cementation of Cu on spherical Fe powders.
- As-cemented Cu particles have a very porous shell and are mechanically weak; heat treatment at 800°C in H<sub>2</sub> is helpful for giving sufficient strength to safely handle the powders although the surface remains rugged which results in very poor tap density and inhibits formation of sufficiently strong sintering contacts.
- Sn coating with subsequent sintering results in virtually dense and strong shells that are externally rather smooth. Gravity sintering yields quite strong structures at low weight, with sound sintering contacts.
- Sintering at too high temperatures results in unwelcome densification, at least partially destroying the cellular structure.

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- Gravity sintered bodies of bronze hollow spheres show significantly lower densities compared with that made of bronze powder (reference material).
- The compressive stress-strain curves obtained from samples of bronze with cellular structure are smooth and there is no significant flat plateau region.
- Such behaviour of stress-strain curves indicates higher relative density of the samples, closed-cell character of the solids, ductile material of the cell walls.
- Density of Cu-10%Sn cellular materials slightly increases with higher sintering temperatures, but there is a marked increase observed at 830°C.

### 5. Acknowledgement:

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# Sintering and Thermal Conductivity of AIN Based Ceramics Containing Refractory Compounds

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#### Summary:

Aluminum nitride based ceramics is a promising material for wear- and thermal resistant components. AIN matrix ceramics with dispersed hard materials was prepared by liquid-phase sintering using yttrium oxide  $Y_2O_3$  as a consolidation aid. Vanadium carbide VC, tungsten carbide WC, chromium carbide  $Cr_3C_2$ , tungsten boride WB and titanium nitride TiN were used to reinforce the AIN ceramics. The AIN + 10 wt % VC, AIN + 10 wt% WC, AIN + 10 wt%  $Cr_3C_2$ , AIN + 10 wt % WB and AIN + 25 wt % TiN composite powders were homogenized by planetary milling. The composite green compacts have been sintered at 1850 °C for 30 min in nitrogen to the relative density higher than 95 %. Thermal conductivity of the samples at room temperature was measured to be 78, 75, 80, 70 and 87 W/m·K, respectively.

#### Keywords:

AIN, matrix phase, Y<sub>2</sub>O<sub>3</sub>,VC, WC, Cr<sub>3</sub>C<sub>2</sub>, WB, TiN, thermal conductivity, hardness.

#### 1. Introduction:

Aluminum nitride is a promising material for functional and structural needs. During the last decade, electronics was the main field of application of AlN dielectric material with high thermal conductivity. To achieve high thermal conductivity values, liquid phase sintering for preparing AlN dense material is the common technological route. Yttrium oxide is used as a sintering aid (1). To improve mechanical properties, hard particles can be incorporated into AlN matrix phase (2-3). In the present work, previous technological experience in pressureless sintering is used to prepare the AlN base materials with the dispersed particles of hard refractory compounds.

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#### 2. Experimental procedures and results:

Commercial AIN powder (TU 6-09-110-75) from DZChR (Ukraine) and vttrium oxide powder (ITO-I OST 48-208-81) from KGOK (Kirghizstan) as a sintering activator were used. Commercially available vanadium carbide VC. tunasten carbide WC, chromium carbide Cr<sub>3</sub>C<sub>2</sub>, tungsten boride WB and titanium nitride TiN powders from DZChR (Donetzk, Ukraine) grade P were used as the hard particle additives. Dry milling of aluminum nitride and yttria were performed in vibration mill (M-10, ISM, Ukraine) for 3 hours. The powder to hard alloy milling ball (7 mm in diameter) ratio was 1 to 6. The vibrating ball mill has power density of 1 W/g. Gomogenised powder compositions were produced by dry milling and mixing as prepared AIN-Y<sub>2</sub>O<sub>3</sub> composition and one of the reinforcing additives with a planetary activator (APF, Gefest, Russia) for 5 min. The planetary activator has centrifugal acceleration of 60 g, power density of 100 W/g, and powder/balls weight ratio was 1/5. The composite powders were uniaxially pressed into samples (23 mm width, 23 mm length, 5 mm height) with a pressure of 95 MPa. The sintering of the green bodies have been conducted in vertical furnace with tungsten heaters (SShV-1,25/25-I1, Russia) in the atmosphere of nitrogen under the pressure of 0.12 MPa. The heating rate was 10 K min<sup>-1</sup>. the sintering temperature was 1850 °C, the sintering time at final temperature was 30 min. The Vickers hardness (PMT-3, LOMO, Russia) was measured by indentation at a 0.5 kg load (4.9 N). Thermal conductivity of ceramic samples was measured at room temperature by the pulse method with a device for measuring thermal conductivity coefficient of high-thermalconductive materials (IT3-MChTI, Russia).

The relative green density of the cold uniaxially pressed bodies was 32 %. The densities of the pressureless-sintered samples reached more than 95 % of the theoretical values (Table 1). The relative density of AlN base ceramics containing  $Cr_3C_2$  and WB particles is 96.0 %. The AlN base ceramics containing VC, WC and TiN are characterized by 98.0 %, 99.0 % and 97.0 % of theoretical density, respectively. The hardness and the thermal conductivities of all samples studied are listed in the Table 2. The hardness of the AlN-WC and AlN-TiN composites is 87.0 and 87.4 kg/mm<sup>2</sup>,

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		Relative
Composition	Density, g/cm <sup>3</sup>	density, %
AIN + 5 wt% $Y_2O_3$	3.26	99.5
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt % VC	3.28	98.0
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt% WC	3.53	99.0
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt% Cr <sub>3</sub> C <sub>2</sub>	3.25	96.0
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt % WB	3.37	96.0
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 25 wt % TiN	3.53	97.0

Table 1. Composition and density of the AIN base composites

respectively. The AIN-VC and AIN-TiN ceramic composites are characterized by the Vickers hardness 10.02 and 11.13 GPa, respectively.

Table 2. Hardness and thermal conductivity of the AIN base composites

		Vickers	Thermal
	Hardness,	hardness,	conductivity,
Composition	kg/mm <sup>2</sup>	<u> </u>	W/m·K
AIN + 5 wt% $Y_2O_3$	85.1	9. 5±1.12	137
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt % VC	85.9	10.02±1.44	78
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt% WC	87.0	9.66±1.14	75
AIN + 5 wt% $Y_2O_3$ + 10 wt% $Cr_3C_2$	86.0	7.57±1.22	80
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 10 wt % WB	85.8	8.34±1.08	70
AIN + 5 wt% Y <sub>2</sub> O <sub>3</sub> + 25 wt % TiN	87.4	11.13±1.19	87

The thermal conductivities of the AIN based composites are in the 75-87 W/m·K range. The AIN-Y<sub>2</sub>O<sub>3</sub>-TiN composite has the highest thermal conductivity of 87 W/m·K. This is 65 % of the thermal conductivity of TiN- free AIN base ceramics produced by the same sintering conditions (Y<sub>2</sub>O<sub>3</sub> content, time, temperature), which was measured to be 137 W/m·K. Nevertheless, this is 1.58 times higher value than the thermal conductivity of the hot-pressed yttria-free AIN + 25 wt % TiN composite (3). Still, SEM, strength and fracture toughness studies of as prepared AIN based composites are worth consideration.

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#### 3. Conclusions:

Composite materials based on AIN containing 10 wt % VC, 10 wt% WC, 10 wt% Cr<sub>3</sub>C<sub>2</sub>, 10 wt % WB and 25 wt % TiN and sintered at 1850 °C exhibit density higher than 95 %, and that permits to produce parts of various shapes by pressureless sintering. High values of thermal conductivity and hardness make possible to test at elevated temperatures the wear and chemical resistant parts made from the AIN base composites containing VC, WC, Cr<sub>3</sub>C<sub>2</sub>, WB and TiN.

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# Investigations of Various Methods for Production of Nanostructured AIN Ceramics

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#### Summary:

Sintering of coarse and nano-AIN powders in the temperature range from 1000 to 2000°C were investigated. The following questions are discussed: 1) high rate of AIN selfdensification due to small sizes of the powder particles and formation of aluminum oxynitride; 2) mechanisms of recrystallization grain growth at the different stages of sintering; 3) phase transformation würtzite - multilayer polytypes during recrystallization in AIN. Formation process of polycrystalline microstructure during sintering after shock-wave treatment of nano-AIN is also discussed. Formation of grains with the high density of dislocations takes place during sintering as-treated AIN powders.

#### Keywords:

Morphology, sintering, structure-properties relationship, shock-wave treatment.

#### 1. Introduction:

Ceramic materials have been intensively investigated and success has been achieved in this field during the last decades. Ceramics based on  $AI_2O_3$ ,  $ZrO_2$  and SiC have found wider application so far. In spite of some success in ceramic materials, they are still rather functional than structural materials. Investigation of structural and functional characteristics of ceramic materials will significantly extend their applications.

Presently, aluminum nitride (AIN) is not classified as a basic ceramic material, but an increasing interest in it is observed. It can be attributed first to wider possibilities of utilization. Excellent thermal conductivity with good dielectric properties, very good chemical resistance and thermal shock resistance, non-toxicity of AIN and its composites make them materials with good prospects for engineering applications (1, 2).

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Studies have been focused on AIN ceramics as a heat-dissipating substrate in microelectronics because of the high thermal conductivity of AIN and its thermal expansion coefficient, which is close to that of silicon. During the last decade thermal conductivity of AIN ceramics has been improved drastically (3-5).

Nano-AIN is a powder with good prospects for producing nano-materials. There are two problems in fabrication of materials from AIN nanopowders (50-500 nm). The first problem is connected with difficulties of compacting such powders by the techniques traditionally used, the second - with their high sintering activity, leading to a coarse grain structure in obtained materials. Sintering of porous compacts of such powder in nitrogen at 1700°C results in formation of 2-3 µm grains. The key to these problems lies with explosive consolidation (6) or powder shock-wave treatment (7).

In this paper results of studying sintering of AIN powders having different mean particle sizes and the influence of shock-wave treatment on the structure of ceramics are presented.

#### 2. Results and Discussion:

Commercial AIN was synthesized by direct nitriding of aluminum powder through heating in an atmosphere of nitrogen (Table 1). Nanopowders of AIN have been produced by a plasma chemical synthesis. Specific surface of Alnit-1 and Alnit-4 are 34-36 and 15-20 m<sup>2</sup>/g, respectively. The oxygen contents of nanopowders have been determined by chemical analysis and by neutron activation analysis (NAA). NAA analyzes not only chemically bonded oxygen inside a particle but also the oxygen chemically absorbed by the particle surface. The amount of chemically absorbed oxygen depends on the specific surface area of powders and duration and conditions of their storage. A specific surface area of commercial AIN powder equaled to 2.0 m<sup>2</sup>/g. A planetary activator and vibrating mill were used as milling equipment. The planetary activator has a centrifugal acceleration of 60 g and a specific power of 100 W/g. The vibrating ball mill has a power density of 1 W/g. Both devices have the milling volumes and balls made of steel; the powder/balls weight ratio during experiments was 1/5. The milling was dry. The surface area of the powders has been measured by the BET method. The measurements of grain size distribution have been conducted by sedimentation technique

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using a SK LASER MICRON SIZER. Sintering was carried out in a temperature range from 1000 to 2000°C in a furnace under a nitrogen pressure of 0.12 MPa. The samples of coarse powder sinter badly. They achieve their maximum density of 90 % at 1900°C. Sintering of nanopowder samples proceeds actively in the temperature range from 1200 to 1800°C. In this case the shrinkage reaches 28 % and after sintering the density approaches the theoretical density. The structural investigations of sintered samples were conducted with electron microscopy of thin foils and carbon replicas of fractures. The particles are single crystal, as demonstrated by dark field images. In the 1200-1400°C range of sintering temperatures disperse particles coagulate and concurrently polycrystalline aggregates of about 1000-1500 nm in size form. Up to 1600°C, the sizes of aggregates change slightly but inside them structural transformations take place. The particles lose their faceting, became round and coalesce with neighboring particles. This causes aggregates to transform into single crystal grains of 0.5-1.0 um in size. Oxygen, absorbed on the surface of the particles, forms oxynitride phase, which is localized at the boundaries of the particles. The thermal differential analysis demonstrates that the formation of oxynitride phase is followed by the thermal effect at 1560°C. According to the X-ray investigation the oxynitride content is 3-5 %. At the temperature above 1600°C the oxynitride layers dissolve in the grains of the matrix phase to form a solid solution of oxygen in aluminum nitride. Above 1700°C, the grains grow and stacking faults develop in the (0001) planes. At 1800 - 1900°C multilayer polytypes arise, from which grains of a plate-type form. The structure of multilayer polytypes was identified by the X-ray diffraction. These polytypes are intermediate between würtzite and sphalerite structures in the extent of hexagonal nature (9). The formation of polytypes, occuring under the conditions of isomorphic stratification of the solution of the würtzitic structure (2H AIN-O), causes the anomalous growth of the grains. In this case, the plate-form grains with an aspect ratio up to 20 may form. The effect of temperature and porosity on mechanical properties and a mechanism of failure in sintered AIN has been studied. Samples of various densities were produced by sintering the AIN powder of initial specific surface of 15  $m^2/q$  in the temperature range from 1600 to 1950 °C in nitrogen (Table 2). The samples of 5×5×35 mm were three-point bend tested at temperatures from 20 to 1800°C using tungsten and ceramic supports for loading (Fig. 1).

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	AI	Ν	0	С	Fe	Si	Са
Trade-mark	(%)	(%)	(%)	(%)	ppm	ppm	ppm
DZChR							
TU6-09-110-75	65.1	33.3	0.5	0.73	200	60	0
Institute for							
Inorganic							
Chemistry, Latvia							
Alnit-1	65.0	33.7	2.0	0.1	80	23	0
			3.5(NAA)				
Alnit-4	65.3	33.5	1.5	0.25	17	20	0
			2.5(NAA)				

#### Table 1. AIN powder characteristics

Table 2. Grain size of nano-AIN samples.

Sintering temperature, °C	Density, %	Grain size, μm
1600	56.8	0.5-1
1700	80	1-2
1800	94	2-3
1900	99	3-5
Hot-pressing 1800 °C	≈ 100	5-7



Fig. 1. Temperature dependence of fracture strength of AlN nanopowders sintered at 1600 (1), 1700 (2), 1800 (3), 1950 (4) and coarse AlN powder hotpressed at  $1800^{\circ}C$  (5).

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At room temperature, tests were carried out in air and at higher temperatures in nitrogen. At room temperature the strength of the sintered AIN rises rapidly with density. A material of low density reveals an entirely intercrystalline fracture. With the increase of density the portion of intercrystalline fractured samples decreases and the densest material fractures only in the transcrystalline way. At temperatures higher than 800°C, the strength of AIN drops sharply with the temperature rise. The higher dislocation density indicates the development of the plastic deformation process in the regions near boundaries (Fig. 2).



Fig. 2. TEM micrograph of AIN.

The idea to use hydrodynamic pressing appeared when a great number of large-diameter balls from AIN nanopowder had to be made. Hydrodynamic pressing is similar to hydrostatic one with respect to the method of pressure applying. A distinguishing feature of the former is that the pressure to be applied in the work cell (up to 1.2 - 2.0 GPa) is generated by the gases from explosive material. The shape of the ball is an ideal object to create a uniform compression. An AIN powder with a specific surface 19.5 m<sup>2</sup>/g was loaded in elastic rubber bags. 30 balls of 120 mm in diameter were compacted simultaneously. Optimal shock-wave treatment parameters were determined experimentally by changing the amount of explosive to obtain a crack-free material of isotropic density. Porosity of the as-formed spheres was equal to 30 %. The spheres were sintered at T =  $1200^{\circ}$ C and  $1850^{\circ}$ C in nitrogen; isothermal holding was 90 min. Porosity of samples, sintered at 1200°C was 12 %; sintered at 1850°C was less than 1 %. X-ray structural analysis and electron microscope investigations have been conducted for examination of the nano-AIN powder before and after the shock-wave treatment. The X-ray investigations have been conducted with DRON-3 apparatus using CuK $\alpha$ radiation with Ni filter. The results of the analysis are presented in Table 3. Initial grain size range from 10 to 500 nm. The samples sintered at 1200°C reveal the fragmentary structure of grains. Based on the dark field images the

grain sizes were found to be 1-2 nm, i.e. considerably smaller than initial ones. The microstructure of samples sintered at 1850°C differs greatly from the samples of low-temperature sintering.

Characteristics of AIN sample	Diffra	action pe (β)∈1	eaks hal 0 <sup>3</sup> rad	Lattice parameter		
	100	002	103	112	a, nm	c, nm
nontreated powder	4.45	4.65	6.4	6.3	0.3111	0.4980
after shock-wave						
treatment	5.9	6.0	7.7	7.4	0.3112	0.4975

Table 3. Effect of shock treatment of the nano-AIN powder samples

First of all, the coarse grains (from 1 to 3-4  $\mu$ m) are typical for the firstmentioned samples. The grain boundaries are well formed. A high density of dislocations is observed in all the grains. There are some regions in the grains or groups of grains with resolution of separate dislocations. But diffraction contrast having ripple image is observed in the greater part of grains. This is the evidence of dislocation density being greater than 10<sup>11</sup> cm<sup>-2</sup>. The grains are single crystals. Only rare grains possess fields disoriented at 2-3° due to non-uniformly distributed pile-ups of dislocations. There are layers composed of AlN multilayer polytypes in a large number of grains. Some increase of strength, hardness and fracture toughness is typical for shock-wave treated samples (Table 4). This fact can be explained by strengthening of the material not only owing to hardening grains with polytypes plates, but also due to the high density of dislocations in the grains.

Table 4. Effect of shock-wave treatment on the strength properties of sintered AIN samples.

nano-AIN powder	Properties					
used for samples	Hardness H GPa	Fracture	Bending strength σ			
		$K_{1c}$ , MPa $\cdot$ m <sup>-1/2</sup>	MPa (20 °C)			
nontreated	12.40-13.65	3.8-4.1	350-380			
after shock-wave						
treatment	16.80-17.50	4.7-4.9	400-470			

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#### 3. Conclusions:

Sintering of nano-AIN powder ends at about 200°C below that of the coarse AIN powder. While sintering, oxygen contained in the absorbed impurities is dissolved in AIN to form a substitutional solution. The vacancies, produced in aluminum sublattice in this case, promote the growing of AIN self-diffusion coefficient, which, in turn, induces intensive grain growth. The formation of polytypes, occuring under the conditions of isomorphic stratification of the solution of the würtzitic structure (2H AIN-O), causes anomalous growth of plate-like grains. Shock treatment of a nano-AIN powder leads to a high level of fragmentation of grains, their mean size being decreased by one order of magnitude and more. Sintering the shock-wave compacted bodies proceeds with relaxation process via plastic deformation. This is evidenced by a high density of dislocations in grains, formed during sintering.

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# PREPARATION AND PROPERTIES OF NANODISPERSE TRANSITION METALS CARBONITRIDES

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#### Summary:

Nanodisperse powders (NDP) of carbonitrides of IV-VI group transition metals (for example,  $TiC_xN_{1-x}$ ,  $NbC_xN_{1-x}$ ,  $Cr_3C_{1.6}N_{0.4}$ ), their hard alloys (for example,  $Ti_xNb_{1-x}C_yN_{1-y}$ ) and mixtures (for example,  $TiC_xN_{1-x}-Cr_3C_{1-6}N_{0-4}$ ) with the medium particle size of 50 - 200 nm have been prepared by the method of plasmachemical synthesis. Due to the dynamic conditions of synthesis (starting products evaporation or decomposition, mixing and condensation of the end product is lasting for some tenths of second) the products is formed in a form of NDP, mainly as a monocrystals with a great concentration of the crystallic lattice defects. This determined high chemical activity of these powders, including increased sintering rate and decreased sintering temperature. Some examples of use of such powders are given.

#### Keywords:

Nanodisperse powders, transition metals carbonitride, preparation, cermets

#### 1. Introduction:

Due to the development of new hard alloys, including non-tungsten materials, the interest is lasting on preparation methods of transition metal carbides. nitrides and their hard solutions - carbonitrides. It is necessary to develop new methods of their preparation to satisfy the increase of their use. One of such methods is the plasmachemical method allowing to obtain a nanodisperse product. This paper deals with the interaction of IV-VI group transition metals with high temperature nitrogen flow in a presence of carbon in order to obtain nanodisperse carbonitride powders.

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#### 2. Experimental:

#### 2.1. Investigations of nanodisperse powders

Nanodisperse carbonitride powders and their composites are prepared by evaporation of coarse commercially available powders of chemical elements and subsequent condensation of products in a radio frequency inductively coupled nitrogen plasma. The elaborated experimental apparatus (Fig. 1) consists of radio-frequency (5.28 MHz) oscillator with maximum power of 100 kW, quartz discharge tube with induction coil, raw powder and gas supply systems, water cooled stainless steel reactor and heat exchanger, and cloth filter for collecting of powder. The flow rate of the plasma-forming gas (nitrogen) is 6,9-8,0 m<sup>3</sup>/h and the feed rate of raw powders is 1,0-2,2 kg/h.



Figure 1. Schematic view of plasma apparatus.

The calculated fractions of raw powders of chemical elements are premixed and introduced into plasma tail through 4 or 8 tubes by carrier gas. Conditions of injection and particle size are determined by theoretical calculations and preliminary experiments. The complete evaporation of raw powders can be reached by varying the particle size and their injection rate, feeding rate, plasma velocity and temperature. The formation of products, their particle size, chemical and phase composition are controlled by introduction the cold nitrogen and hydrocarbon into reaction chamber. 15' International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG. Reutte (2001), Vol. 3

Titanium (purity 99,1 wt.%), niobium (98,6%) and chromium (99,2%) powders, gaseous hydrocarbons (methane, mixture from propane and butane and others) were used as raw materials. High purity nitrogen (99,99%) was used as a plasma-forming gas simultaneously used also as one of reaction components.

The chemical composition (Me, N, C and  $C_{free}$ ) and phase composition of synthesized powders were determined by conventional chemical and X-ray powders diffraction analysis. The size and shape of particles were stated by the transmission electron microscopy (TEM), particle size distribution by photon correlation spectroscopy (PCS) by apparatus Zetamaster S 5002 ZEM, specific surface area by the BET argon adsorption – desorption method.

It was experimentally stated that making synthesis in a great excess of nitrogen, it is possible to change chemical composition of the carbonitride phase in a wide range changing the ratio carbon/metal in a raw material (Fig. 2).



Figure 2. The dependence of chemical composition of reaction products on ratio C:Me for titanium (A), niobium (B) and chromium (C):  $1 - C_{fixed}$ ,  $2 - C_{free}$ , 3 - N.

It is known that titanium easily forms cubic phases – nitride, carbide and continuous raw of its hard solutions (carbonitrides) [1]. In a pure nitrogen plasma the nanodisperse nitride powder forms with the composition close to the stoichiometric –  $TiN_x$ , where x = 0.95 – 0.97. Carbonitride  $TiN_xC_y$  (x+y $\approx$  1)

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forms in plasma in a presence of hydrocarbons. It is possible to regulate the carbonitride composition in a range from  $TiC_{0,1}N_{0,9}$  to  $TiC_{0,6}N_{0,4}$  changing the amount of hydrocarbons or the ratio C : Me. The crystalline lattice parameter changes linearly with the change of chemical composition (Tab. 1).

If the expenditure of hydrocarbons is low, i.e., preparing carbonitrides with high nitrogen content, the reaction product consists only from this phase without the presence of free carbon. If the amount of fixed carbon increases above 4 - 5 wt.%, free carbon appears in the reaction product and its content increases with the increase of hydrocarbons. For example, at the C:Ti ration of 0,55 the content of free carbon in product is 2,9 wt.%, but the content of fixed carbon is of 8,6 - 9,2 wt.%. The following increase of hydrocarbon expenditure results in a rapid increase of free carbon without a significant increase of fixed carbon in carbonitride. This could be explained by a great affinity of titanium to nitrogen and by a great excess of nitrogen in a system.

Metal	Phase content	Chemical composition, wt.%				Formula of the cubic phase	Lattice para-
		Me	Ν	С	C <sub>free</sub>	1	meter,
1							a, A
Ti	TIN	77,2	21,8			TiN <sub>0.97</sub>	4,248
	Ti(C,N)	77,8	16,5	4,7	0,2	TiC <sub>0.29</sub> N <sub>0.74</sub>	4,265
1	Ti(C,N)	77,7	12,5	8,1	0,7	TiC <sub>0,41</sub> N <sub>0,56</sub>	4,276
	Ti(C,N)	74,6	9,8	9,7	5,2	TiC <sub>0.52</sub> N <sub>0,46</sub>	4,288
Nb	NbN, Nb <sub>2</sub> N	86,2	12,6			NbN <sub>0.96</sub>	
Ì	Nb(C,N)	87,0	10,8	1,0	0,1	NbC <sub>0.09</sub> N <sub>0.83</sub>	
	Nb(C,N)	86,3	6,4	5,4	1,0	NbC <sub>0,48</sub> N <sub>0,49</sub>	
	Nb(C,N)	84,3	2,9	8,6	3,2	NbC <sub>0,76</sub> N <sub>0,22</sub>	
Ti-Nb	(Ti,Nb)(C,N)	62,9/16,5	10,2	8,6	1,0	Ti <sub>0.83</sub> Nb <sub>0.12</sub> C <sub>0.48</sub> N <sub>0.50</sub>	
(75:25)							
Ti-Nb	(Ti,Nb)(C,N)	26,6/56,8	19,2	4,5	0,5	Ti <sub>0,48</sub> Nb <sub>0,52</sub> C <sub>0,32</sub> N <sub>0.66</sub>	
(20.70)	1						

**Table 1.** Phase and chemical composition of titanium and niobium carbonitrides

Metals of the V-th group differ from metals of the IV-th group and can form carbonitrides of cubic (NaCI-type) structure as well as hexagonal structures –  $Me_2(C,N)$ .

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If there are no hydrocarbons in system, niobium forms cubic nitride NbN with the admixtures of hexagonal  $Nb_2N$ . In the presence of hydrocarbons the hexagonal phase disappears and product consists of only the cubic phase – Nb(C,N). In comparison with the IV-th group metals, metals of the V-th group possess higher affinity to react with carbon, resulting in carbonitride with increased content of fixed carbon, even if the excess of nitrogen is high.

It is known from literature that metals of the VI-th group, especially chromium can form several compounds in system Me-C-N. Reacting with nitrogen, chromium forms a product consisting of free metal,  $Cr_2N$  and somewhat CrN. In the presence of hydrocarbons free metal has not been stated. If the ratio C:Cr increases, the nitrogen content in product increases at the beginning, and then decreases (Fig. 2). The carbon content grows. The carbon-containing phase is  $Cr_2(C,N)$ , whose exact chemical composition has not been stated, because of the presence of other phases in product. If the ratio C:Cr increases, the content of another carbonitride phase grows, this phase has been identified [2] as  $Cr_3C_{1,6}N_{0,4}$ .

The mechanism of IV-VI-th group carbonitride formation is the same and therefore a similar synthesis conditions could be used for simultaneous preparation of several carbonitrides. Introducing the mixture of two or more metal powders into the reaction zone under certain conditions it is possible to obtain complex IV-V-th group metal carbonitrides, or their mixtures with chromium carbonitrides, or VI-th and Fe-group metals. Practical experience shows that the presence of IV-th group metals (for example, Ti) facilitates the formation of the cubic phase both in the case of V-th group metals ( $\delta$ -Nb(C,N),  $\delta$ -Ta(C,N)) and VI-th group metals ( $\alpha$ -MoC) [3]. In the system of IV-V-th group metal carbonitrides we obtain their hard solutions (Me<sub>I</sub>,Me<sub>II</sub>)(C,N) instead of mixture of separate carbonitrides (Tab. 1).

All mentioned compounds have been prepared as NDP with the specific surface area in the range of  $10 - 60 \text{ m}^2/\text{g}$ . The particle size of the reaction product is of 10 - 500 nm, moreover, the main amount is of size in the range of 20 - 200 nm (Fig. 3,4), being in good agreement with the medium particle size which is calculated from the measurements of specific surface area. Particles of synthesized carbonitrides are mostly monocrystallic.

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**Figure 3.** Characteristic shape and particle size of Ti(C,N) (1) and  $Cr_3C_{1,6}N_{0,4}$  (2) powders.



**Figure 4.** Particle size distribution of Ti(C,N) (1) and  $Cr_3C_{1,6}N_{0,4}$  (2) powders.

High dispersity and concentration of structural defects is the reason of increased activity of plasma synthesis products: high surface of powders results in adsorption of oxygen and water vapor explaining increased content of oxygen (1, 2 - 2, 5 wt.%) during long lasting storing. The starting temperature of NDP oxidation is significantly lower than for powders of the standard dispersity - 240 - 350 °C. Increased activity reflects also during sintering of these powders – sintering temperatures are significantly lower (for TiCN the difference is  $400 - 800^\circ$ ) and sintering rate is higher.

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#### 2.2. The Ti(C,N)-Ni,Mo and (Ti,Nb)(C,N)-Fe,Ni,Cr,Mo system

One of the versions for preparation of finely grained cermets should be the combination of traditional industrial powders with NDP based on different temperatures of sintering [4]. Characteristics of investigated powders are given in Table 2 (coarse powders prepared by the kiln method).

Nominal chemical		Content of elements, wt.%					SSA* of	ES**
formula of carbonitrides	Ti	Nb	Ν	C <sub>tot.</sub>	$C_{\text{free}}$	0	particles, m²/g	μm
$\begin{array}{c} {\sf TiC}_{0.52}{\sf N}_{0.48}\\ {\sf TiC}_{0.45}{\sf N}_{0.55}\ ({\sf NDP})\\ {\sf Ti}_{0.77}{\sf Nb}_{0.23}{\sf C}_{0.5}{\sf N}_{0.5}\\ {\sf Ti}_{0.76}{\sf Nb}_{0.24}{\sf C}_{0.49}{\sf N}_{0.51}\\ ({\sf NDP})\end{array}$	79,0 77,8 52,0 50,0	- 29,5 30,0	10,6 12,0 9,3 9,4	10,0 8,6 8,1 7,6	0,1 0,3 0,7 0,4	0,2 1,2 0,4 2,6	0,33 19,3 0,015 26,5	3,6 0,06 70 0,04

Table E. Offerniour composition and dispersity of starting powder	Table 2. Chemical	composition	and dispersit	y of starting	powders
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\*Specific surface area, \*\* Effective size

Metal powders synthesised in plasma (Ni:  $O_2=1,3\%$ ; SSA=8,1m<sup>2</sup>/g; ES=0,08µm, Mo:  $O_2=3,5\%$ ; SSA=7,1m<sup>2</sup>/g; ES=0,08µm, Fe:  $O_2=3,3\%$ ; SSA=12,5m<sup>2</sup>/g; ES=0,06µm, Cr:  $O_2=2,2\%$ ; SSA=8,9m<sup>2</sup>/g; ES=0,09µm) and the corresponding industrial low dispersed (LDP) metal powders - Ni (SSA=0,07m<sup>2</sup>/g), Mo (SSA=0,15m<sup>2</sup>/g), Fe (SSA=0,26m<sup>2</sup>/g) and Cr (SSA=0,21m<sup>2</sup>/g) were used for preparation of cermets Ti(C,N)-Ni,Mo and (Ti,Nb)(C,N)-Fe,Ni,Cr,Mo.

Mixtures were prepared from the mentioned carbonitride powders, containing 0, 33, 66 and 100% of NDP. The mixtures of starting powders were vibratory milled for 40 h in inert dispersion medium (petrol) using hard alloy balls. During the milling process LDP becomes more disperse (SSA=2,5m<sup>2</sup>/g, ES=0,5µm for Ti(C,N) and SSA=1,0m<sup>2</sup>/g, ES= 1,0µm for (Ti,Nb)(C,N)), but the dispersity of NDP does not change. The mentioned powders were mixed with 2 wt.% of paraffin, samples were pressed under 150 MPa and sintered at 1400 - 1800 °C for 1 - 3 h isothermally in pure nitrogen. The cermet samples were prepared in a similar way and sintered isothermally for 1 h at 1450 - 1600 °C.

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After sintering the most fine-grained structure is characteristic for intermediate composites, i.e., mixtures of LDP with NDP (Fig. 5). Their structure after sintering can be described as follows: great crystals, regularly distributed between small crystals, the great crystals have somewhat larger dimensions, in comparison with medium dimensions of the LDP after vibromilling for 40 h [5].



**Figure 5.** Microstructure of titanium-niobium carbonitride ( $T_{sint}$ =1800°C,  $\tau$ =1h). A- 0% of NDP, B- 33% of NDP, C- 66% of NDP, D- 100% of NDP.

The properties of samples sintered at the optimal conditions (1700 °C, the holding time 1 h for Ti(C,N) and 1650 °C for (Ti,Nb)(C,N)) are summarized in Table 3. The best strength properties have the carbonitrides of intermediate composition - mixtures of LDP with NDP, but in the case of 100 % NDP these properties are somewhat higher than those for powder of low dispersity. The application of plasmachemical NDP at the mentioned conditions ensures the increase of toughness of carbonitrides approximately for 20- 30 %.

Materials in system  $TiC_{0,5}N_{0,5}$  - Ni,Mo (3:1) and  $Ti_{0,76}Nb_{0,24}C_{0,5}N_{0,5}$ -Fe,Ni,Cr,Mo are described on Table 4. The highest values of flexural strength, hardness and impact viscosity are for samples with the optimum NDP concentration in the hard phase 35 % and in the metal matrix - 50 %, but the optimal sintering temperature is 1520°C.

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	Content	P <sub>op</sub> ,	d, kg/m <sup>3</sup>	σ <sub>bend</sub> ,	Η <sub>μ</sub> ,	ρ, Ω·m	λ,	E,
	of NDP, %	%	x 10 <sup>-3</sup>	MPa	GPa	x 10 <sup>8</sup>	W/(m·°C)	GPa
A	0	1,6	5,0	450	21,7	48	17	447
	33	1,0	5,1	550	23,1	46	17	456
	66	1,2	5,1	600	22,0	45	15	459
	100	1,5	5,1	460	21,8	45	14	447
В	0	1,2	5,6	700	22,5	64	16	470
	33	0,8	5,6	900	22,9	54	15	503
	66	0,8	5,6	870	23,2	50	15	470
	100	0,8	5,6	750	23,8	49	14	450

Table 3.	Some physical and mechanical properties of titanium (A) and
	titanium- niobium (B) carbonitrides, sintered at 1700 °C and
	1650 °C, respectively, isothermal holding time 1h

P<sub>op.</sub>- opened porosity; d- density;  $\sigma_{bend^-}$  bend strength; H<sub>µ</sub>- micro hardness; ρ- specific electric resistivity;  $\lambda$ - thermal conductivity; E- Young's modulus.

Table 4. Some physical and mechanical properties of cermets  $TiC_{0,5}N_{0,5} - Ni,Mo$  (3:1) (C) and  $Ti_{0.76}Nb_{0,24}C_{0,5}N_{0,5}$ -Fe,Ni,Cr,Mo (D)

	Content of binding metal,vol%	P <sub>op</sub> , %	d, kg/m <sup>3</sup> x 10 <sup>-3</sup>	σ <sub>bend</sub> , MPa	HRA	A <sub>t</sub> , J/m <sup>2</sup> x 10 <sup>6</sup>	ρ, Ω·m x 10 <sup>8</sup>	λ, W/(m·°C)	E, GPa
С	16	0,30	6,25	1700	90	16	53	18	480
	20	0,40	6,30	1900	89	18	52	16	450
	30	0,50	6,40	2000	88	22	56	11	340
D	16	0,35	6,34	1800	91	18	64	15	410
	20	0,40	6,40	2100	90	20	61	12	390
	30	0,55	6,45	2200	89	23	47	7	350

 $P_{op,-}$  opened porosity; d- density;  $\sigma_{bend^-}$  bend strength; HRA- Rockwell's hardness;  $A_t$ - impact viscosity; p- specific electric resistivity;  $\lambda$ - thermal conductivity; E- Young's modulus.

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Evidently, the cutting performance of created alloys is determined not only by increase of the strength characteristics, but also by the structural factor: when NDP is applicated, a part of NDP of the hard phase are situated in metal matrix in a form of ultrafine grains, even as nanodisperse particles, i.e., in this case we have a hard alloy with dispersively strengthened metal matrix, possessing an increased wear resistance.

#### 2.3 The Cr<sub>3</sub>C<sub>1,6</sub>N<sub>0,4</sub>-Ni system

Chromium carbide is widely applicated in a wear-resistant and corrosionresistant hard alloys. However, possibilities of application of chromium nitrides and carbonitrides for these purposes as well as their properties are scantily explored. Because chromium nitrides and carbonitrides are of great importance in ensuring of hardness and corrosion resistance of nitrided and cyanided steels, they can serve as perspective compounds for creating and improvement of non-tungsten hard alloys. Preparation of finely disperse chromium carbonitride ensure new possibilities of their utilisation for creation of materials with high physico-mechanical and exploitation properties.

Powders of  $Cr_3C_{1,6}N_{0,4}$  and  $Cr_3C_{1,6}N_{0,4}$ - 20 wt.% Ni with the specific surface area of 10-12 m<sup>2</sup>/g and medium particle size of 100 - 200 nm were used for investigations. Samples were pressed under 100-200 MPa and sintered at the temperature range of 1250-1600 °C in the atmosphere of pure nitrogen (at 0,12 MPa) isothermally for 1 h. Sintering in nitrogen ensures stability of chemical and phase composition of carbonitride. Some properties of chromium carbonitride dependent on sintering temperature are given in Table 5.

T <sub>sint.</sub> , °C	ΔV, %	Density, g/cm <sup>3</sup>	HRA	HV, GPa	σ <sub>bend.</sub> , MPa
1350	6,6	5,09	80	6,5	130
1400	8,2	5,20	82	7,6	160
1450	13,7	5,46	85	9,6	230
1500	21,1	5,82	89	12,8	300
1550	21,6	6,07	92	16,5	310
1600	21,5	5,84	89	-	-

**Table 5.** Physico-mechanical characteristics of sintered chromium carbonitride $Cr_3C_{1,6}N_{0,4}$
The best combination of density, hardness and flexural strength of Cr<sub>3</sub>C<sub>1.6</sub>N<sub>0.4</sub> -20% Ni is obtained for alloy, sintered at 1350 °C. The composition of sinterina temperatures of alloy on the basis of chromium carbide with those from chromium carbonitride with equal content of nickel binder (20 wt.%) shows that optimal sintering temperature of alloy on the basis of chromium carbonitride is of  $30-80^{\circ}$  higher in comparison with those for alloy Cr<sub>3</sub>C<sub>2</sub>-20 wt.% Ni [6]. Higher sintering temperature of alloy on the basis of chromium carbonitride can be determined by decrease of wettability of hard component with liquid nickel. The increase of edge angle of wetting of chromium carbonitride with nickel is affirmed by data from [7].

Some properties of alloys on the basis of carbonitride and carbide of chromium with 20 wt.% of Ni additive are given in Table 6. It is visible from these data that hard alloy on the basis of chromium carbonitride (with somewhat lower density) exceeds in hardness and especially in flexural strength alloy on the basis of chromium carbide.

Alloy	Density, g/cm <sup>3</sup>	HRA	σ <sub>bend.</sub> , MPa
$Cr_{3}C_{1,6}N_{0,4} - 20\%$ Ni	6,5	85,0	890
$Cr_{3}C_{2}$ - 20% Ni	6,88	83,0	700

Table 6.	Some properties of alloys on the basis of chromium carbonitride
	and chromium carbide with 20 wt.% of Ni [6]

As it follows from Fig. 6, the break of pure chromium carbonitride, although have mixed trans- and inter-crystallite character, in it's structure a viscous fracture occupies considerable part, evidenced by great amount of holes and imprints of strong local deformations.

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Figure 6. Morphology of chromium carbonitride fracture surface.

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## Explosive Compaction of Nanocrystalline Alumina Powder.

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Nano ceramics have special properties: they are superhard, frictionless and have very fine pores. These special properties are shown only with grain sizes below 100 nanometers (nm). It is very difficult to retain this small grain size during conventional consolidation of powders and subsequent sinter processes. A key to solve this problem could be the explosive consolidation with shock pressures up to ~30 GPa.

Experiments with nano  $Al_2O_3$  – powder which was produced by the "exploding wire technique" with a mean crystallite size of ~60 nm showed that almost 100% of crystalline density is achievable by explosive consolidation.

By SEM – and XRD – analysis is found that phase transitions occur and as a result of high shock wave treatment lattice distortion in the material decreases and subgrain size increases.

## 1. INTRODUCTION

Nanocrystalline materials reveal extraordinary properties as

- improved mechanical strength and increased fracture toughness
- ability for plastic deformation
- new chemical physical properties e.g. for catalytic applications
- sintered corundum with pore sizes between 15 to 50 nm for membranes
- hard metal of tungsten carbide with grain sizes of 200 nm
- special glasses with modified optical properties by nanoscaled gold deposits

Because of high friction between the nanosized particles, compaction by axial pressing is limited to about 30%TD density. Conventional methods as:

uniaxial cold and hot pressing, isostatic cold and hot pressing (CIP & HIP)<sup>1</sup>

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are leading to densities of about 80%TD. Subsequent sintering can only achieve high density when strong grain growth is taken into account. Up to now one has reported the fabrication of high density bulk ceramics starting from nanocrystalline  $\gamma$ - Al<sub>2</sub>O<sub>3</sub>.

The consolidation by ultrahigh pressures, as developed during detonation of explosives<sup>2</sup>, therefore is a very interesting alternative to conventional methods. The purpose of this paper is to report the continuation of research which was reported previously <sup>1,3</sup>

### 2. PREPARATION OF THE NANO-CRYSTALLINE POWDER

The alumina powders used were produced by the "explosive wire technique" developed by R. Abrams <sup>4</sup> in the USA. This method was further developed by S. Kotov <sup>5</sup> to produce n-alumina and n-zirconia. In the frame of a joint project with Forschungszentrum Karlsruhe, this method was used to produce n-alumina. Aluminum wires were exploded by electric pulse power in an oxygen environment resulting in n- alumina, consisting mainly of gamma – with traces of theta Al<sub>2</sub>O<sub>3</sub>. The chemical analysis of this powder and its main physical properties are shown in Fig.1 together with a SEM picture.



Figure 1. Alumina Nano-particles & size distribution

### **3. PRECOMPACTION OF THE POWDER**

As already mentioned the compaction by axial pressing is limited by internal friction in the powder to 30%TD. In this state the pellets are very fragile and not suitable for further treatment. By cold isostatic pressing

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(CIP) at 750 MPa the density of the pellets (9 mm dia x 3 mm) could be increased to about 60%TD. These pellets were used for the explosive compaction as described in the following chapter. All the experiments were carried out without the use of any pressing additives.

### 4. EXPLOSIVE COMPACTION

Dynamic pressures were released by detonating explosives. The pellets of nano - alumina were filled as a stack of 45 mm length in stainless steel tubes (9x1 mm dia/thickness) closed by an lower and upper end plug and sealed under vacuum. For loading at pressures up to about 20 GPa these samples were surrounded by an uniform layer of a proper explosive. The detonation was initiated at the upper end and was propagating downward in axial direction. The amount and type of explosive determines the pressure and loading duration. For pressures > 20 GPa a setup was used with a driver tube concentrically surrounding the container. Upon collision of this

explosively accelerated tube collision pressures are obtained. The pressure was calculated from the velocity of the driver tube and the impedance of colliding materials. – The thicker the driving tube, the longer the duration of pressure.

Both parameters are decisive for uniform consolidation of the cylindrical sample over its cross section. Details for optimizing the explosive parameters see ref.2. Fig. 2 shows the arrangement for explosive compaction. Table.1 is summarizing the performed experiments.



Figure 2. Arrangement of explosive compaction

Best results of samples with a glassy (transparent) appearance are obtained at pressure of 8 GPa and higher. Further increase of pressure does not improve properties of compacts; the phenomenon of cracking in between the areas of transparent granules is becoming more pronounced at higher pressure. Also samples with highest hardness up to 1200 HV 0.1 are obtained at 8 GPa. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

### Table 1. Performed Explosive Compaction Experiments and Results

Sample	Green	Pres-	Duration of	Final	Micro-	Remarks
No.	Density	sure	Pressure	Density	hardness	
	[%]	[GPa]	[µsec]	[% TD]	HV 0.1	
EXPLO 2	58	5.6	10	88	370	milky appearance
EXPLO 3	58	8	8	99	900 -1200	glassy appearance cracks
EXPLO 4	58	9	8	99	750	glassy appearance cracks
EXPLO 5	42	17.5	1	99	570	grains separated by cracks
EXPLO 7	64	20	1	100	600	
EXPLO 9	60	33.7	0.8	80		central molten channel (cif Fig. 3)
EXPLO 12 C	61	80	0.6	57	400	totally molten
EXPLO 13	60	43	0.9	92		many cracks
EXPLO 14	60	32	1.0	100	800	dense grains cif Fig.5
EXPLO 15 A	60	46	0.9	89	1125	cracks
EXPLO 15 B	60	39	0.8	100	970	dense grains cif. Fig.6

At pressures exceeding 30 GPa local melting is very likely to occur. Sample #9, due to Mach–Stem Formation, reveals a central channel that was performed by molten material. Newly formed crystallites can be seen at the border (Fig.3): we see small cubes with a size of 10  $\mu$ m x 10  $\mu$ m that seem tumbling in the central hole. The cubes were formed from an alumina melt by cooling of the face centered  $\gamma$ -phase to room temperature. This proves that the melting point of alumina with 2054 °C was reached and the explosive charge being too high.



Figure 3. Picture of central hole of sample 9

By rapid cooling from the melt the energy rich cubic  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is formed (Ostwald's rule).

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Figs. 4 and 5 show a cross section of sample EXPLO 3 which was shot with 8 GPa. These figures demonstrate the glassy appearance of this specimen.





Figures 4 and 5. Radial cross section of sample EXPLO 3

### 5. X – RAY INVESTIGATIONS

The compaction of powders is associated with morphological and structural changes of matter<sup>2</sup>. This can be revealed by X-ray diffraction. X-ray line broadening investigations were carried out using a Siemens O 500 - diffractometer with Cu K  $\alpha$ -Radiation ( $\lambda$  = 154 pm). Diffraction patterns were made both from the starting material and samples of compacted n-Al<sub>2</sub>O<sub>3</sub>, as shown in Fig. 5. It is obvious that a transformation from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has occurred.



Figure 6. Diffraction patterns of  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> taken with Cu K $\alpha$ -Radiation before (a) and after (b) explosive compaction.

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The diffraction patterns were analyzed using the procedure of Hall– Williamson, which had been successfully applied for analyzing explosively compacted  $Al_2O_3$  - powders of different grain size<sup>6</sup>. The full width of halfmaximum of the X – ray diffraction peaks were determined and corrected for instrumental broadening. To determine lattice distortion and mean crystallite size, the following relationship exists:

$$\frac{\beta \cdot \cos \theta}{\lambda} = \frac{1}{\Lambda} + \frac{4 \, \mathrm{da}}{\mathrm{a}} \cdot \frac{\sin \theta}{\lambda}$$

with  $\beta$  = FWHM = full width at half maximum  $\lambda$  = X - ray wave length  $\Lambda$  = mean crystallite size da/a = lattice distortion  $\theta$  = diffraction angle

According to this equation a Hall-Williamson plot allows to determine the subgrain size and lattice distortion.



Figure 7. Hall–Williamson plot for determination of sub–grain size and lattice distortion of  $Al_2O_3$  before and after explosive compaction at 8 GPa (Shot EXPLO 3).

### 6. RESULTS AND DISCUSSION

The pressure-density relationship for the  $n-Al_2O_3$  for static compaction (uniaxial pressing & BELT) and explosive compaction are given in the upper part of Fig.8. The lower part of Fig. 8 represents the mean crystallite size and lattice distortion, as function of pressure. 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG. Reutte (2001), Vol. 3



Figure 8. Relative green density, crystallite size and lattice distortion as functions of compaction pressures.

From the upper part of Fig.8 it is obvious that the "explosive" pressure - density relationship is just a continuation of the "static" pressure - density relationship obtained by uniaxial and cold isostatic pressing (CIP). Also data of  $Chen^7$  nicely fit this relationship, whereas BELT type data are leading to lower densities than expected. Maximum density with n-Al<sub>2</sub>O<sub>3</sub> is obtained at 8 GPa.

It is well established that shock loading of crystalline alumna is leading to severe amounts of Lattice defects, represented by increase of lattice distortion and decrease of mean crystallite size with increasing shock pressure<sup>6</sup>.

With  $n-Al_2O_3$  exactly the opposite is the case. An originally determined lattice distortion in the  $n-Al_2O_3$  of 0.36% is decreasing down to 0.04% at a shock pressure of 8 GPa. The subgrain size is increasing from 16 nm to about 250 nm at 8 GPa shock pressure. One sample, which was loaded statically in the BELT – type pressure device at 5.7 GPa also shows a decrease in lattice distortion from 0.36% to 0.1%. So this decrease seems not to be characteristic of dynamic loading, but just of pressure itself and needs to be investigated further.

All structural changes, phase transition  $\gamma \rightarrow \alpha$ , lattice distortion decrease and subgrain increase happens in the pressure range up to 8 GPa. Whether

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a phase transition is prerequisite for obtaining full density is not yet clear. During explosive consolidation of  $Si_3N_4$ <sup>8</sup>, it was observed that full density could be obtained without substantial changes in X–ray line broadening and without phase changes. Other nanocrystalline materials including metal powders as well show decrease of X – ray line broadening with shock pressure<sup>9</sup>.

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## 3D-simulation of residual stresses in TBC plasma sprayed coating

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### Keywords:

# PLASMA SPRAYED COATING, RESIDUAL STRESSES, COMPUTER SIMULATION

### Introduction:

Thermal barrier coatings (TBC) are used in gas turbine technology in order to protect against overheating of the nickel alloy turbine blades. This coating allows to increase turbine inlet temperatures and improve their efficiency(see in (1,2)).

Plasma spraying processes are widely used since several years in thermal barrier coating technology. Although the plasma spraying process of TBC's is largely successful, a fundamental understanding of the processi parameters influencing the TBC microstructure and mechanical properties is necessary. But this investigation has received much less attention so they could lead to considerable advances in performance of plasma sprayed thermal barrier coatings. The main reason of this mate is difficulties in experimental investigation of high temperature and high velocity process . One of the most effective ways to accelerate the process optimization is the application of computer simulation for the modeling of plasma spraying, as shown in (3). This enables the achievement of a maximum of information about the investigated process by carrying out a minimum number of experiments.

The main problem of plasma spray TBC coatings is crack formation during the deposition process and coating cooling. The reasons for this are

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quenched and residual stresses in the coating-substrate system, and peculiarities of TBC coating properties shown in (1-5). The problem of deposition and solidification of plasma sprayed coatings has received little attention to date and remains one of the unintelligible parts of the process. A fundamental understanding of heat transfer in the coating-substrate system and particles deformation processes are, however, critical for the prediction of the microstructural characteristics of the deposited coatings, the understanding of the mechanisms involved in formation of thermal stresses and defects (cracks, debonding etc.).

Residual stress in plasma-sprayed coatings has been recognised as one of their most important properties. It can give rise to deformation of coated workpieces and delamination or cracking of the coating. In addition, various types of coating performance indicators, such as adhesion strength, resistance to thermal shock, life under thermal cycling and erosion resistance are strongly influenced by the nature of the residual stresses (5-8).

Many coating models have been developed. But the majority of them are devoted to mathematical description of macroscopic thermal stresses arising from thermal gradient or mismatches in thermal expansion between the coating and the substrate as it is shown in (5, 8-12). These models usually have a two steps calculation procedure: 1) the solution of the 1D or 2D heat transfer equation with constant boundary conditions using finite difference or finite element methods; 2) computation of thermal residual stresses resulting from temperature history and Hook's law.

The main assumption of this models is the elasticity of the material properties, i.e. the materials behave elastically in the period of heating and cooling, then final residual stress in the coating can simply be expressed as the sum of the stresses arising from differential thermal contraction. But practically, there are a number of stress relaxation processes which may reduce the stress in the splat and coating below its theoretical value (edge relaxation, through-thickness yielding, interfacial sliding, micro- and mackrocracking, creep, delamination etc). The key question concerns the degree to which these relaxation processes can reduce the calculated thermal stresses in practice.

It is necessary to mention, that these relaxation processes are not taken into account in most coating models. This simplification is the basic reason of unconformity of simulation results and experimental measurements of residual stresses.

Stresses can be classified based on the balanced values (I, II and III kind). There are all kinds of stresses presented in plasma spraying coatings,

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but the reasons for crack appearance are stresses of the I kind. Therefore, mostly stresses of this kind are considered in the majority of published experimental and theoretical works. In a first assumption the coating is considered as a continuous medium due to its low porosity. This simplificates sufficiently the problem and allows to carry out calculations in the borders of well designed theories of continuous environment (materials resistance theory, theory of elasticity, plasticity and creep ).

For the first time this approach was applied for residual stresses calculation of coatings in work (13) conformably to exploration of thermal stresses in a stripe. Afterwards this method was successfully applied for the determination of thermal residual stresses in coatings of different materials. In work (14) calculations of residual stresses have been done including coating growth and crystallization.

In works (9, 15) the attempt of the account of the residual stresses relaxation is made at the expense of plastic deformation. Therefore, the commercial finite element program ABAQUS is used to calculate residual stresses in the multylayer system. The metallic substrate and the interlayer are calculated according to ideal elastic and ideal plastic material laws. The von Mieses yield condition was used to describe plasticity effects. But, as ceramic coatings have different yield points for compressive and tensile loads, it is difficult to apply the von Misses law to describe plastic deformation in such materials.

A more complete model is offered in (16, 17). The following characteristics serve to define the coating: lamellae structures, quantity of oxide skins, porosity and composition. For lamellae structure formation statistical method and simply Madjesky model, described in (18), were used.

This approach promises a better understanding of mechanical and chemical processes of plasma spraying. But the applied simplified stressmodel (elastic) does not give real information about residual stresses, relaxation processes, microcracks formation.

On the base of the above analysis of already developed models it is possible to make the following conclusions:

1) The main assumption of the developed models is elasticity of materials properties, i.e. the materials behave elastically in the period of heating and cooling, final residual stress in the coating is expressed as the sum of the stresses and arises from differential thermal contraction.

2) The stress relaxation processes to caused by macro- and microcrack formation and creep are not taken into account in the most of the developed coating models. This simplification of models is the main reason for the 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG. Reutte (2001), Vol. 3

inconsistence between modelling results and experimental measurements of residual stresses.

3) The finite element method is suitable and widely used for numerical description of thermophysical and mechanical processes that occur during plasma spray coating formation.

## 1. Mathematical model of stress generating in plasma coating and its computer realization characteristics:

This work is devoted to the development of models for the simulation of stress formation in TBC-coating with the possibility to implement them into the FEM-MARC program.

More precise and adequate coating models can be developed with 3D finite element simulation by consideration of all relaxation processes. The most common finite element programs are MARC, NASTRAN, ANSYS (see (19, 20)).

The total statement of the thermoelastisity problem consists, as it is described in (21, 22), of the necessity to find out 16 coordinates functions of  $x_k$  and time t: 6 components of the stress tensor  $\sigma_{ij}$ , 6 components of the

strain tensor  $\mathcal{E}_{ij}$ , 3 components of the displacement tensor  $u_i$  and temperature T, satisfying 3 movement conditions

$$\sigma_{ij,j} + F_i = \rho i l_i. \tag{1}$$

 $(F_i - \text{volume forces}, \rho - \text{material density}, \rho u_i$  - inertia forces), 6 relations between stresses and strains

$$\sigma_{ij} = 2\mu\varepsilon_{ij} + [\lambda\varepsilon_{kk} - (3\lambda + 2\mu)\alpha_T\theta]\delta_{ij}$$
<sup>(2)</sup>

(where  $\lambda$  and  $\mu$  - Lame coefficients in case of isothermal deformation corresponding to defined temperature T = T<sub>0</sub>), 6 relations between strains and displacements

$$\varepsilon_{ij} = \varepsilon_{ji} = \frac{1}{2} \left( u_{i,j} + u_{j,i} \right) \tag{3}$$

balance of energy equation:  $\partial (\rho(T)C(T))$ 

$$\frac{(\rho(T)C(T)T)}{\partial t} + Q = div(\lambda(T)gradT)$$
(4)

(where  $\rho(T)$  – density, C(T) – material heat capacity, Q – internal heat sources/drains density) with fixed boundary and initial conditions.

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Initial conditions are usually given as distributions of displacement vector components  $u_i$ , velocities  $\dot{u}_i$  and temperatures T in the whole region V of the elastic body. Boundary conditions (BC) on the elastic body surface  $\Sigma$  consists of mechanical and thermal conditions. Mechanical BCs, similar to elasticity theory, are given either in displacements or in stresses. Thermal BCs write as

$$\lambda(T)\frac{\partial T}{\partial \vec{n}} = Q \tag{5}$$

where  $\frac{\partial T}{\partial n}$  - normal derivative, Q – heat flux. In this connection heat flux due to convection and radiation is considered by:

$$q = \sigma \varepsilon (T_s^4 + T_E^4) + \alpha (T_s - T_E)$$
(6)

with the emissivity  $\mathcal{E}$  of the surface, the heat transfer coefficient  $\alpha$  and the Stefan-Boltzmann-number  $\sigma$ =5.669·10<sup>-8</sup>W/(m<sup>2</sup>K<sup>4</sup>). T<sub>s</sub>, T<sub>E</sub> and T<sub>G</sub> are the temperatures of the surface, environment and plasma-gas.

The set of equations mentioned above describe non-linear thermoelasticity problems even under small strains due to non-linearity of heat transfer equation.

The finite element approximation of equation (4) is based on the Garlerkin version of the method of weighted residuals. As central differential equation for the temperature distribution can be introduced as:

$$C(T) \cdot T + K(T) \cdot T = Q$$
<sup>(7)</sup>

where T is the nodal temperature vector differentiated with respect to time,

$$\mathbf{C} = \int_{V^e} \rho c \mathbf{N} \cdot \mathbf{N}^{\mathrm{T}} dV^e$$
(8)

is the heat capacity matrix, N is the vector of shape functions and K is described as:

$$\mathbf{K} = \int_{V^{*}} \left( \lambda_{x} \frac{\partial \mathbf{N}}{\partial x} \cdot \frac{\partial \mathbf{N}^{T}}{\partial x} + \lambda_{y} \frac{\partial \mathbf{N}}{\partial y} \cdot \frac{\partial \mathbf{N}^{T}}{\partial y} + \lambda_{z} \frac{\partial \mathbf{N}}{\partial z} \cdot \frac{\partial \mathbf{N}^{T}}{\partial z} \right) dV$$
(9)

Q is the nodal heat flux vector due to heat flux through  $S^{e}$ :

$$Q = \int_{S^e} N \cdot q \, dS \tag{10}$$

As ceramic coating have different yield points for compressive and tensile load it is better to use the anisotropic yield function (of Hill) and stress

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### potential are assumed as (19):

$$\sigma = \frac{I}{2} \left[ a_{I} (\sigma_{y} - \sigma_{z})^{2} + a_{2} (\sigma_{z} - \sigma_{x})^{2} + a_{3} (\sigma_{x} - \sigma_{y})^{2} + 3a_{4} \tau_{zx}^{2} + 3a_{5} \tau_{yz}^{2} + 3a_{6} \tau_{xy}^{2} \right]^{I_{2}}$$
(11)

Ratios of actual to isotropic yield (in the preferred orientation) are defined in MARC for direct tension yielding, and in YRSHR for yield in a shear (the ration of actual shear yield to  $\sigma/\sqrt{3}$  isotropic shear yield).

For creep description there are several phenomenological theories. They examine a value v – time derivative of strain or deformation velocity. One of the most frequently used formulas for its calculation is:

$$v(\sigma) = B\sigma^n \tag{12}$$

Numbers n and B are determined experimentally (n is in range of 3 - 8 for various materials). The dependence is strongly nonlinear. The use of exponential dependence is more suitable:

$$\frac{e}{e_e} = \exp\left(\frac{\sigma}{\sigma_e}\right) , \qquad (13)$$

where  $e_e$  and  $\sigma_e$  are properly chosen constants. However, dependence (13) can not be used for small values of  $\sigma$  because it gives non-zero creep velocity when  $\sigma = 0$ .

The next question concerns the crack appearance and growth. Two problems are solved in crack mechanics. First – prediction of the location of crack initiation and its growth. The second problem stress relaxation due to cracking. Both problems must bee solved together.

Determination of the points where failure can occur in the coating, can be realised using specified failure criteria. In MARC the following criteria are possible: maximum stress (MX STRESS), maximum strain (MX STRAIN), maximum stress for orthotropic materials with identical tensile and compressive behaviour (HILL), Hoffman criterion (HOFFMAN), modified Hill criterion with considering unequal maximum stresses in tension and compression, Tsai-Wu failure criterion - a tensor polynomial criterion-, and user defined failure criteria (subroutine UFAL).

An analysis of these criteria shows, that the Hill criterion is most suitable for plasma coatings. According to this criterion at each integration points, MARC calculates: 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

$$\begin{cases} \left(\frac{1}{X_{t}} - \frac{1}{X_{c}}\right)\sigma_{1} + \left(\frac{1}{Y_{t}} - \frac{1}{Y_{c}}\right)\sigma_{2} + \frac{\sigma_{1}^{2}}{X_{t}X_{c}} + \\ \frac{\sigma_{2}^{2}}{Y_{t}Y_{c}} + \frac{\sigma_{12}^{2}}{S^{2}c} + \frac{\sigma_{1}\sigma_{2}}{X_{t}X_{c}} \end{cases}$$
(14)

where F- the failure index (normally, F=1.0),  $X_t$ ,  $X_c$  - the maximum allowable stresses in 1-direction in tension and compression,  $Y_t$ ,  $Y_c$  - the maximum allowable stresses in 2-direction in tension and compression, S - the maximum allowable shear stresses.

It permits to determine locations of crack initiation and direction of crack propagation, as crack developed perpendicular to the direction of the maximum principal stress.

For further evaluation of crack propagation nonlinear fracture mechanic models of MARC (J-INTEGRAL, LORENZI) have been used as described in (19).

The extended J-integral takes into account the effect of inertial and body forces, thermal and mechanical loading and initial strains. The expression for the extended J-integral is then transformed into a surface integral for straightforward evaluation of its value, by means of numerical integration techniques.

For plane solid bodies the J-integral can be calculated with the following equation:

$$J = -\int_{\Omega} \frac{1}{\Delta a} \frac{\partial \delta x_i}{\partial \delta x_j} \left( W \delta_{lj} - \sigma_{ij} \frac{\partial u_i}{\partial x_l} \right) dv - \int_{\Omega} \frac{\partial x_i}{\Delta a} \left( (f_i - \rho u_i) \frac{\partial u_i}{\partial x_i} - \sigma_{ij} \frac{\partial \varepsilon_{ij}^o}{\partial x_l} \right) dv - \int_{\Gamma_i} \frac{\partial x_i}{\Delta a} t_i \frac{\partial u_i}{\partial x_j} da$$

In this equation regions  $\Omega_1$  and  $\Omega_2$  have borders  $\Gamma_1$  and  $\Gamma_2$ 

respectively.  $\Omega = \Omega_1 + \Omega_2$ ;  $\delta x_1 = \Delta a$  for border  $\Gamma_1$  and  $\delta x_1 = 0$  for border  $\Gamma_2$ .

The CRACK DATA option was applied to predict crack initiation and simulate tension softening by plastic yielding and crushing. In this model the cracking option is accessed through the ISOTORPIC option. Normally for this model the following data must be specified: the critical cracking stress, the modulus of the linear strain softening, and the strain at which cracking occurs. It is the critical stress that must be defined at the minimum. It is the stress where cracking occurs in tension. This situation is preferable for plasma spray coating. The crushing strain governs the behaviour in 15° International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG, Reutte (2001), Vol. 3

compression. The softening modulus and shear retention factor defines the behaviour after cracking occurs for tension and compression loading, respectively. If tension softening is included, the stress in direction of the maximum stress does not decrease immediately to zero; instead the material softens continously until there is no stress across the crack.

On the base of the above analysis, the development of the following model of stress formation in coating-substrate system under plasma spraying is offered.

The substrate system is represented by a plate (strip) with width 2-3 times smaller than diameter of the plasma jet (120x20x2 mm (Fig.1). A coating with general thickness of 0,06 mm is placed regularly on the whole area of the substrate. The coating is sprayed in one or three passes. The plasma jet moves from the top to the bottom. Coating is  $ZrO_2 + 7\%Y_2O_3$ , substrate is Steel 0,45%C.



Fig.1. Simulated system, adapted to MARC realisation

The substrate has one fixed edge and the plasma jet moves lengthwise the strip in direction to this edge. The coating is separated along the length into finite segments, which are sequently activated, according to a movement of plasma jet.

The following stages of plasma spraying process are simulated: 1) consecutive deposition of coating layers with intermediate natural or forced cooling; 2) natural cooling of the coating-substrate system to room temperature. The coating temperature in the moment of deposition is assumed to be melting temperature. Before the beginning of the coating the substrate's temperature is assumed to be 300K.

Ab advantage of such kind of amodel is possibility of its experimental verification with so called "deflection cantilever strip" method discussed in (18).

### 2. Simulation results and their analysis:

The results of simulation are shown on Figs. 2 - 9.



Fig.2. Temperature distribution in a sprayed sample after 7 increments of calculation (activation of 2nd lamella)

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Fig. 3 Displacement of a sprayed sample at the end of spraying – activation of the last of the lamella (a - with cracking, b - without cracking).



Fig. 4. Displacement of a sprayed sample at the end of cooling (a – with cracking, b - without cracking)

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Fig.5. Normal stresses distribution in a sprayed sample after 187 increments (end of spraying – activation of the last lamella) with cracking.



Fig. 6. Normal stresses distribution in a sprayed sample at the end of cooling (a- with cracking, b - without).

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Fig.7. Dynamics of temperature variation on the top of the coating (node 813), in the interface (node 1041) and on the back side of substrate (node 1497)



Fig.8. Normal stress dynamics in various points in the thickness of the system (without cracking)

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Fig.9.Normal stress dynamics in various points in system height (with cracking)

The analysis of the heating dynamics and the temperature distribution (Figs. 2, 9) shows, that after activating of a lamella the coating temperature rapidly decreases whereas the substrate temperature increases. The maximum temperature gradient is located in the centre of the activated lamella. During spraying the temperature the front moves in the direction of the sample mount. The sprayed parts of the sample at the time of last loadcase activation are cooling down to temperature about 300K.

A general comparison of the sprayed sample displacement in Zdirection (Figs. 3, 4) shows that for the first model (without cracking) the displacement is 10 times higher than for the last model. That can be explained by residual stress relaxation in the last model due to plastic deformation and cracking, because this phenomena are taken into account in the last model. Comparative analysis of normal stress distribution after the end of spraying (Figs.5, 6) verifies this regularity. The level of residual stresses in the elastic model is about 10 times higher than in the cracking model. In the elastic model the bulk of sprayed sample is undergoing tension stresses, in the cracking model – reversed, compression tensions. The obtained results show (Figs. 5, 6, 8, 9), that tension stresses are relaxed due to coating delamination. Delaminations are distributed periodically on the sprayed sample, according to lamella activation.

This regularity can be explained by rapid contraction of an activated coating lamella with generation of tension stresses (maximum in interface)

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due to mismatch in expansion coefficient of coating and substrate materials. But there is a reason for this process in the computation procedure, too. Side by side placing lamellas (with reduced temperature) make hindered contraction in Y-direction for activating and heating lamella. It is one of the reasons for the increase of normal stresses in this place (see Fig. 9, 8) and their relaxation due to cracking and delamination). These reasons for cracking must be eliminated by improvement of model.

## 3. Conclusions:

- 1. Models for heat transfer and stress evaluation during plasma spray coating for MSC/MARC are developed. These models include the stress relaxation due to plastic deformation, creep and cracking.
- 2. The first results of simulation are shown:
  - computation of stressess in a coating-substrate system during plasma spraying incorporating stress relaxation due to plastic deformation, creep and cracking give values of sample displacement and stresses about 10 times lower than calculations with an elastic model. This is in accordance with physical phenomena of residual stress formation.
  - the stress relaxation due to cracking is introduced mainly in form of the coating delamination at the place of lamellas activation.
- 3. One of the ways of model improvment is an the elimination of cracking initiation due to the procedure of coating activation in the calculation procedure.

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## PRODUCTION OF PRESS MOULDS BY PLASMA SPRAY FORMING PROCESS

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## Summary:

Plasma spray forming process for production of press moulds which are used for manufacture of articles from plastics was developed. The press moulds were produced by plasma spraying of Cu-Al-Fe-alloy powder on surface of a master model. The master models were made from non-metallic materials with heat resistance below 70C (wood, gypsum etc). Double cooling system which provides for a control of surface model temperature and quenching conditions of sprayed material was designed. It made possible on the one hand to support model surface temperature below 70 C and on the other hand to provide for temperature conditions of martensite transformation in Cu-Al-system with a fixation of metastable ductile  $\alpha + \beta^1$  -phase. This allowed to decrease residual stresses in sprayed layer (up to 0,5-2,5 MPa), to increase microhardness of the coating material (up to 1200-1800 MPa) and its ductility ( $\sigma_{\rm B}$  =70-105 MPa,  $\delta$  =6-12 %). This plasma spray forming process makes possible to spray thick layers (5-20 mm and more) without their cracking and deformation. The process is used for a production of press moulds which are applied in shoes industry, for fabrication of toys, souvenirs etc.

## Keywords:

Plasma spray forming, press moulds, Cu-Al-Fe alloy, cooling system, residual stresses, mechanical properties, application.

## 1. Introduction

Traditional application of the thermal spraying technology is deposition of coatings on surfaces of parts and structures to protect them from wear and corrosion, as well as to restore dimensions after wear. Conditions of

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formation of a thermal spray coating are characterized by deformation and microadhesion of the sprav material particles heated and accelerated as a result of their interaction with a high-temperature gas jet. Impingement of the particles on the substrate surface induces pressure in the collision zone. which is conventionally subdivided into two components, i.e. pulse and impact pressure. The value of the pulse pressure can be estimated using a modified Zhukovsky's equation of water hammer, while that of the impact pressure can be estimated, assuming the state of the spray material having the form of a melt, using the Bernulli's equation. The pulse pressure exists for about 10<sup>-9</sup> s and provides cleaning of the work surface at the point of impact and formation of active centers. Duration of the impact pressure is 10<sup>-5</sup>-10<sup>-7</sup> s. It leads to deformation of the spray particle and formation of its physical contact with the surface. During the same period the interatomic bonds providing adhesion of the spray particle with the surface are formed at the interface. The considered phenomenological picture of formation of a thermal spray coating points to the presence of many indicators which coincide with those of such technologies of manufacture of parts and structural materials as hot pressing and rolling of powders. The level of the pressures formed depends also upon the density of the spray material and velocity of particles.

The value of the deformation impact pressure in plasma spraying corresponds to the loads achieved in hot pressing (50-450 MPa), while in detonation spraying it is in excess of the level achieved in pulse hot pressing (500-1500 MPa). This creates technical prerequisites for using thermal spraying as the method for production of free standing components, such as tubes, pipes, crucibles, moulds, dies and other parts [1-6].

The negative point of this technology can be a decrease in strength properties of a material in the as-sprayed state in the case of performing the process in an open atmosphere (in air). The incomplete physical contact between individual particles in the coating, porosity of the layer and oxidation of the surface of the spray particles lead to a decrease in cohesion strength of the layer, which affects the values of tensile strength and impact toughness. Thus, the plasma coating of a copper powder has tensile strength of 70-100 MPa, which is 3-5 times as low as that of a compact material. In the case of a nickel coating these values are 90-130 and 380 MPa, i.e. they are 3-4 times lower [7]. Therefore, one of the basic problems in development of the technology for manufacture of parts involving plasma spraying is that of ensuring the required strength properties of the coating material. The other problem consists in the requirement to decrease the level of residual stresses which grow with an increase in thickness of the sprayed layer.

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Manufacture of parts and different moulds and dies by thermal spraying on a master model is one of the extensively developing applications of this technology. The 0.5-5.0 mm thick metal layer is deposited on the surface of a steel or ceramic model. If necessary, the shell is fitted into a holder and is backed up by a low-melting point metal or epoxy resin.

This work was dedicated to application of plasma spraying for the manufacture of moulds used to make parts of plastic materials.

At present the tooling for plastic injection moulding is mostly manufactured by traditional fitting and machining, which require substantial input of labour of high-skilled machine-tool operators and fitters, sophisticated equipment and expensive tools. Besides, the labour content of the manufacture of the moulding elements proper is 70-90 % of the total labour content of the manufacture of the moulds, and the terms of the manufacture, allowing for the necessity to develop a set of design and technology documents, are up to several months.

The labour productivity can be fundamentally increased and costs of materials and labour, as well as the manufacturing costs of the tooling can be decreased by using a range of thermal spraying methods, and plasma spraying in particular [7]. In their potentialities (precision and complexity of the resulting moulding relief and performance of parts) the spraying methods compete with the methods of galvanoplastics. They are several times superior in productivity and adaptability for industrial production [7].

The necessity of performing tool operations for the manufacture of steel models and single use of the models of heat-resistant self-hardening ceramics are the factors which limit wide practical application of such methods. This determines topicality of development of the process with the ultimate working temperature of the model,  $T_m$ , limited to a level of 70 °C. Solution of this problem allows the use of models made from materials of an organic origin, including wood, wide range of thermoplastic materials with the corresponding low values of heat resistance. Also, this makes it possible to use plastics products proper, subject to duplication, as the models.

The characteristic feature of this process is a decrease in residual stresses in the formed metal shell coatings of arbitrary thickness down to values that exclude their showing up in the absence of adhesion to the surface of the model whose heat resistance is below 70  $^{\circ}$ C.

### 2. Equipment and materials

The PR-1R plasmatron which uses a mixture of argon and hydrogen as the working gas, and the PM-2M plasmatron using air as the plasma gas were

employed for plasma spraying. The powder of bronze containing 9 % Al and 3-4 % Fe was chosen as the spray material. As shown by investigation of the phase diagram of the Cu-Al system, conditions of slow cooling lead to formation of a structure consisting of a mixture of the  $\alpha$ -phase (Cu<sub>7</sub>Al) and products of the  $\beta \rightarrow \alpha + \gamma_1$  eutectoid transformation occurring at 565 °C [8]. The  $\alpha$ -phase is characterized by high ductility at a low level of strength, whereas the  $\gamma$ -phase (Cu<sub>32</sub>Al<sub>19</sub>) has high hardness at low ductility. However, under conditions of plasma spraving at high rates of cooling of the molten particles the possibility exists of occurrence of martensitic transformation with suppression of the  $\beta$ -phase eutectoid decomposition and formation of a structure consisting of a mixture of the  $\alpha$ -phase providing ductility of the spray material and the  $\beta$ '-phase (Cu<sub>3</sub>Al) increasing its strength (Fig 1). This should favour a decrease in the level of residual stresses in the bulk of the deposited laver.



Fig. 1. Sequence of diffusionless transformations leading to formation of metastable phases in the sprayed structures of the Cu-Al system

The master model was made from wood, which limited the temperature at the "substrate-coating" interface to a value of 70 °C. Therefore, the temperature conditions of formation of a coating in this case were limited by the necessity, on the one hand, to ensure the required cooling rates for the spray material (Cu-Al-Fe alloy) and, on the other hand, to avoid heating of the master model to a temperature above 70 °C. The special system for cooling the coating formation zone was developed to solve this problem.

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# 3. Development of the cooling system and parameters of the plasma spraying technology for the manufacture of parts

The combined binary cooling system was developed to realize the above purpose of the system of cooling the coating formation zone. The system consists of systems for blowing off (cutting off of the plasma jet from the model surface) and spraying of the coolant (Fig. 2) [9]. The object affected by both systems is a dusted plasma jet, and the points of their local effect are the different functional zones (zone of transport of the spray particles within the spraying distance bounds and zone of the spraying spot on the model surface).



Fig. 2. Schematic of the cooling system: 1 - coolant sprayer; 2 - plasmatron; 3 - dusted plasma jet; 4 - slot nozzle of the blowing off system; 5 - cooling spot; 6 -spraying spot; 7 - model; v, ,  $G_1$ ,  $G_2$ ,  $G_3$ ,  $P_1$ ,  $P_2$ ,  $P_3$  and S - process parameters of the cooling system

The blowing off system provides a substantial limitation of heating of the model surface due to cutting off of the plasma jet by the gas screen. In practice, this is achieved by intersecting the plasma jet by a properly formed flow of the process gas, e.g. compressed air. The process parameters of the blowing off system are flow rate  $G_1$ , pressure  $P_1$ , temperature of the process gas, point of its contact with the plasma jet and their relative orientation (attack angle).

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The spraving system is intended for increasing the cooling rate of the sprav particles within the spraving spot zone under the effect of a coolant, e.g. a jet of finely dispersed droplets of distilled water. The intensity of the effect of the system is determined by the following parameters: orientation of the cooling spot relative to the spraying spot, S, flow rate  $G_3$  and pressure  $P_3$  of the sprayed water, pressure  $P_2$  and flow rate  $G_2$  of the compressed air that sprays water and velocity v of the plasmatron moving along the surface treated.

The rational operating parameters of the spraving process in the case of using argon-hydrogen mixture (PR-1P plasmatron) and compressed air (PM-2M plasmatron) as the plasma gases and the powder material of the Cu9Al4Fe alloy were determined on the basis of the criterion of achieving the minimum cost of realization of the process allowing for the following indicators: powder utilization factor (PUF), power consumption N, flow rate of the argon-hydrogen mixture G and its composition ( $H_2$ , Ar), % (Table 1).

Diagmotrop	Doulor	Ampe-	Plasma	agases	Produc-	Deposition	
type	kW	rage, A	Compo- sition	Flow rate, g⋅s⁻¹	tivity, g⋅s⁻¹	efficiency (PUF)	
PR-1R	24,8	420	Ar+20,4 vol. % H <sub>2</sub>	0,6	1,27	0,67	
PM-2M	35,5	185	Comp- ressed air	2,0	1,2	0,63	

Table 1: Technological parameters of plasma
forming process <sup>x)</sup>

<sup>x)</sup> Conditions – powder of Cu9Al4Fe alloy,  $d_p = 40-50 \mu m$ , spraying distance – 0,2 m, model material – wood, with cooling system (CS) application.

Experimental studies, in which the optimization criteria were maximum values of the degree of efficiency of the blowing off system  $(q_0/q_1)$   $(q_0, q_1)$  is the heat directed to heating the model by the initial and screened plasma jets, respectively), particles velocities  $v_{p}$  and PUF, allowed determination of the rational operating parameters of the blowing off system. Combinations of the parameters given in Table 2 for the PR-1P plasmatron yield the value of q<sub>0</sub>/q<sub>1</sub> = 2.2 and those for the PM-2M plasmatron - 1.8. In this case with the plasmatrons in a fixed position  $T_m$  is 140-170 and 180-190 °C, respectively, the PUF values are decreased by 3-5 and those of  $v_p$  - by 13-15 %.

Further decrease in  $T_m$  to 70 °C with a simultaneous decrease in residual stresses in the formed structures is achieved by the effect of the spraying system. In the case of using aluminium bronzes the spraying system hardly deteriorates the strength values and provides the possibility of fixation of the  $T_m$  values within a range of 50-100 °C.

It was established that the important parameter of operation of the intensive cooling system was the relative location of the cooling and spraying spots. In the case of coincidence of their centres (S = 0) a sudden decrease in the PUF values ( $\leq$  30 %) and productivity as to spray material, P<sub>s</sub>, is observed, and physical-mechanical properties (strength of the coating is decreased from 45-50 to 5-15 MPa) are fundamentally deteriorated. The maximum effect of utilization of the system is achieved in the case if the cooling zone is superimposed on the spraying spot with its peripheral part (S/ $\Delta \tau$ = 0.5-0.8v, where v is the velocity of movement of the plasmatron and  $\Delta \tau$  is the interval of displacement of the spot centres). The process parameter which is not less important is the flow rate of the coolant, G<sub>3</sub>, which should be kept at a minimum but sufficient level. The ranges of the effective values of the coolant flow rate G<sub>3</sub> and the cooling spot sizes D<sub>cool</sub> can be determined from analysis of thermal processes occurring during formation of the "shell".

Thickness of a layer of the shell coating, h, formed in a single pass is estimated on the basis of mass of the spray powder, m, within the spraying spot zone,  $D_{spray}$ , travel velocity of the plasmatron, v, productivity  $P_s$  and material density  $\rho$ .

$$m = \rho \frac{\pi D_{sprea}^2}{4} h, \tag{1}$$

$$m = P_s \frac{D_{sprav}}{v},\tag{2}$$

$$h = \frac{4P_s}{\rho \pi D_{sprav} \upsilon},\tag{3}$$

At  $P_s = 1.3 \cdot 10^{-3}$  kg/s,  $D_{spray} = 3.5 \cdot 10^{-2}$  m,  $\rho = 7.5 \cdot 10^{3}$  kg/m<sup>3</sup> and  $v = 5 \cdot 10^{-2}$  m/s, the h parameter is equal to  $1.3 \cdot 10^{-4}$  m. Assuming the degree of deformation of the spray particles,  $d_p/h_p$ , to be equal to 10-20 (where  $d_p$  is the diameter of particles of the initial powder material equal to 50 µm and  $h_p$  is the height of the deformed particle), the number of particles which determine thickness of the layer, h, is 20-50. If we assume that heating of the model and the coating formed is realized exclusively due to heat of the spray particles,  $Q_1$ , since

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heat of the plasma jet is almost completely cut off by the blowing off system, Q<sub>1</sub> can be estimated as:

$$Q = mc\Delta t, \tag{4}$$

or, allowing for dependence (2), as:

$$Q_1 = P_s \frac{D_{spray}}{v} c\Delta t,$$
(5)

where c is the specific heat of the spray material;  $\Delta t$  is the range of temperatures of the cooling particles,  $T_{melt} - T_m$ . The factor of a low thermal conductivity of the model material of an organic origin ( $\lambda = 0.1-0.5 \text{ W}/(\text{m}^{\circ}\text{C})$ , limitation of heating of the model ( $T_m = 70$  °C) and an insignificant mass (0.1-0.3 kg) make it possible to neglect the heat flow which cools the formed shell in a direction of the coating-model interface as a very small component, as compared with the cooling effect of the coolant. By considering the spraying process to be a successive deposition of the layer components, h thick, on the substrate with a temperature below 70  $^{\circ}$ C, the cooling flow Q<sub>2</sub> can be represented by the following relationship:

$$Q_2 = \frac{\Delta T}{\Delta h} \lambda S_{cool} \tau_{cool}, \qquad (6)$$

or

$$Q_2 = \frac{\Delta T}{\Delta h} \lambda \frac{\pi D_{cool}^2}{4} \frac{D_{cool}}{\nu}, \tag{7}$$

where  $\Delta T$  is the temperature gradient through thickness of the formed layer, h;  $\lambda$  is the thermal conductivity of the coating material and  $\tau_{cool}$  is the duration of the coolant effect. On the basis of expressions (5) and (7) we obtain the following relationship of the process parameters investigated:

$$D_{cool} = \sqrt[3]{\frac{4P_{\lambda}D_{sprav}c\Delta t\Delta h}{\Delta T\lambda\pi}}.$$
(8)

At c = 0.41 10<sup>3</sup> J/(kg °C),  $\Delta t$  = 10<sup>3</sup> °C,  $\lambda$ = 83 W/(m °C), the  $\Delta T$  dependence of D<sub>cool</sub> will have the following form:

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$$D_{end} = 3.4 \cdot 10^{-2} \Delta T^{-\frac{1}{3}}.$$
 (9)

The acceptable minimum values of  $\Delta T$  ( $\leq 0.01$  °C) are determined by the cooling spots  $D_{cool} \geq 0.1 \text{ m} (S_{cool} \geq 7.5 \cdot 10^{-3} \text{ m}^2)$ .

The coolant flow rate  $G_3$ , which provides stabilization of temperature of the model at arbitrary values of  $T_m$  ( $T_m = T_{melt}\Delta t$ ), are determined from the following relationship:

$$G_3 = \frac{P_s c \Delta t}{c_w \Delta t_w + r_w},\tag{10}$$

where  $c_w$ ,  $r_w$  and  $\Delta t_w$  are the specific heat, evaporation heat and temperature of heating of water, respectively, or from the  $\Delta t$  dependencies in the following form:

$$G_3 = 2 \cdot 10^{-7} \Delta t.$$
 (11)

Excess of the calculated value of the coolant flow rate (see Table 2), as well as incorrect orientation of the cooling spot lead to unjustifiable deterioration of the PUF, strength and ductility values.

Plasmotron type	P₁, MPa	V <sub>s</sub> , m⋅s⁻¹	α, grad	P <sub>2</sub> , MPa	G₃, g⋅s⁻¹	V <sub>p</sub> , m Without CS	s <sup>-1</sup> With CS	q₀/q₁	PUF
PR-1R	0,12	5,3	45	0,12	0,22	220	190	2,2	-0,05
PM-2M	0,075	4,2	60	0,15	0,35	130	110	1,8	-0,09

Table 2: Conditions of plasma forming process <sup>x)</sup>

 $^{x)}$  Conditions – powder of Cu9Al4Fe alloy, dp = 50  $\mu m,$  h = 0,2 m, T1 = 150  $^{0}C.$ 

Composition of the plasma gases (argon-hydrogen mixture or air) predetermines a different ratio of microhardness, hardness and wear resistance of respective samples (Table 3). This is attributable, in addition to differences in structure and composition of the phases formed, also to a different degree of heating and deformation of particles, different values of porosity, intensity 15" International Plansee Seminar, Eds. G. Kneringer, P. Rödhammer and H. Wildner, Plansee Holding AG. Reutte (2001), Vol. 3

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of saturation of a structure with intermetallics of the following compositions:  $FeCu_2Al_6$ ,  $FeCu_2Al_7$ ,  $FeCu_{10}Al_{12}$ ,  $FeCu_{10}Al_{18}$  and oxides. Inclusions of this type increase values of microhardness and, at the same time, decrease values of strength and hardness as a result of increase in brittleness. A comparatively large number of such inclusions is characteristic of structures formed by the air plasma jet.

Conditions of plasma spraying		$\sigma_{s}$ , $\sigma_{s}$	σ <sub>t</sub> ,	σ <sub>1</sub> ,	HV <sub>max</sub> ,	НВ	$\eta \cdot 10^7$ ,	δ,
Plasmatron	CS	wra	IVIFa	IMPa	IVIFa		kg·m⊡s	70
PR-1R	no	8	60-75	25-40	900	80-110	3,6	2-3
PR-1R	yes	<1	80-105	40-55	1800	110-180	6,8	5-10
PM-2M	yes	2,4	70-90	35-40	1700	125-190	7,2	4-8

Table 3: Properties o	f plasma	sprayed	Cu9Al4Fe -	alloy
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An increase of 1.8-2.2 times in the ductility values of the initial material favours a decrease of 4-8 times in residual stresses. This allows formation of the aluminium bronze shell parts of any thickness by avoiding buckling at the absence of adhesion to the model surface.

# 4. Manufacture of press moulds using plasma spray forming process and their practical application

The process developed for the manufacture of press moulds consists of two stages:

- Production of a shell part with a wall thickness of 5-10 mm by plasma spraying of the Cu-Al-Fe alloy powder on the surface of a master model of an organic origin (e.g. wood) or directly on the surface of a prototype part made from plastics;
- 2) Production of permanent and split no-flash moulds by backing up the shell part by a metal-polymer composition followed by its polymerization.

Furyl-epoxy resins with a polymerization temperature of 80 °C were used as the binder. Heat resistance of the composition is 250 °C at a thermal conductivity of 12-28 W m<sup>-1</sup>deg<sup>-1</sup> and shrinkage in solidification equal to no more than 1 %. This ensures high service properties of the moulds made by this technology. It is used under conditions of small-series production of similar-type parts with a developed geometry of the surface, such as toys, shoe soles, furniture and wear accessories, pieces of art, souvenirs, etc.

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The term of manufacture of such moulds using plasma spray forming process is no more than 3-7 days, which is much shorter than in the case of using traditional technologies.

## Conclusions

- 1. The use of plasma spray forming process for making tooling for manufacture plastics parts in small-series production of pieces with a complicated profile allows improvement of technical-economic indices of this process, as compared with traditional methods of metal working, galvanoplastics, cold pressing, electric-spark processing and powder metallurgy.
- 2. The use of the Cu-Al-Fe alloy powders for making shell parts by the method of plasma spraying makes it possible to produce layers with a quenching two-phase ( $\alpha$ + $\beta$ ') structure which combines properties of ductility and strength. This allows a substantial decrease in the level of residual stresses in the deposited layer and formation of the shell parts without considerable limitations as to thickness.
- 3. The developed double system for cooling the coating formation zone makes it possible to control parameters of cooling the spray material and temperature on the master model surface. This permits the use of plasma spraying to deposit layers on the master model surfaces with a heat resistance temperature of up to 70.°C, e.g. made from wood.
- 4. The best results in the level of service properties of the deposited layer of Cu-Al-Fe alloy were obtained in the case of using a mixture of argon and hydrogen as the plasma gas.
- 5. The developed technology for making pressmoulds used to manufacture plastics parts consists of stages of plasma spraying of a shell part and backing it by a metal-polymer composition based on the furyl-epoxy binder. The term of manufacture of complicated-profile moulds by using this technology is no longer than 3-7 days. The technology has found application in the manufacture of toys, shoe soles, souvenirs, etc.

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# Characterization of the Delamination Behavior of Tungsten Based Alloys by Means of Acoustic Emission

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#### Summary

To rank attempts of improving the resistance of thin (<0.5mm) tungsten sheet-material against delaminations, there is a need for a testing procedure which allows to measure the tendency of the material to form delamination cracks. In this contribution, several testing procedures are examined with respect to their ability to initiate delaminations. The reverse bending test turned out to be the most suitable procedure to measure the delamination behavior. The observation of acoustic emission allows an accurate detection of the moment of crack formation and the corresponding bending angle. To get information about the stress distribution during a test, a finite element analysis was carried out. It is shown that specific parameters of the hot rolling process influence the delamination behavior of the sheet material in a significant and reproducible manner. Other fracture patterns like 45° embrittlement were also observed and were correlated to specific hot rolling conditions.

#### Keywords

Tungsten, sheet, delamination, acoustic emission, reverse bending test

#### 1. Introduction

Tungsten and other high melting materials, e.g. molybdenum, are widely used due to their specific properties (high strength at elevated temperatures, good electrical conductivity, high corrosion resistance, etc.). Both, tungsten

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and molybdenum, have a bcc structure, and they develop a pronounced (001) [110]-texture during the deformation process. Compared to most other metals, recrystallization treatment of these metals causes an embrittlement because during annealing most of the impurities concentrate at the grain boundaries and weaken them. A high degree of deformation causes a large elongation of the grain structure and a strong texture which favors the formation of delamination cracks. A further disadvantage is the high anisotropy, e.g. in highly deformed sheet material, of semi-finished products. The low tensile strength perpendicular to the sheet surface is responsible for the formation of delamination cracks during subsequent treatment by means of punching, bending or cutting. Concerning molybdenum sheet material attempts have been made to investigate the tendency of the material to form delamination cracks [1,2]. Other previous work concerns the investigation of the delamination phenomenon of sheets made of steel [3]. Provided that the thickness of the material is large enough, tensile tests normal to the sheet plane can be performed on notched specimen (notch parallel to the sheet surface in the mid-plane of the sheet). For investigations on thin sheet material with a thickness smaller than 0.5 mm, the main problem is that no procedure is established to measure the delamination strength. The present work points out in which way the characterization of the delamination behavior of thin sheet material can be performed by applying a reverse bending test assisted by acoustic emission. The latter is used to detect the onset of the crack initiation during the test.

## 2. Experimental

## 2.1. Preliminary tests with different types of loading

To evaluate the most appropriate procedure for testing the delamination behavior of sheet material, preliminary tests were performed with different experimental set-ups. In the first tests a tensile load normal to the sheet surface was applied to cause delamination failure in the sheet material. For this purpose blocks made of steel were glued on the sheet material to transmit the force from the tensile test equipment to the sample. Three different adhesives were used. It was found that in no case the bond strength which reached values up to 14 MPa was sufficient to initiate delaminations. Another experimental set-up which was investigated for its suitability for testing the delamination behavior was the thermal shock test. In this test a Nd-YAG laser was used to realize a temperature gradient and therefore thermal

stresses in the material. Although different parameters like pulse energy or duration were varied, metallographic examinations of irradiated spots have shown that these stresses are not high enough to cause delamination. Another attempt to initiate delamination cracks in the sheet material was the three point bending test. The distance between the two outer bearings was varied between 15 and 7.5 mm - all tested specimen show plastic deformation but no delamination cracks occurred.

#### 2.2. The reverse bending test

The most promising experimental set-up for delamination testing of thin sheets is the reverse bending test. This test is performed using a device which transforms the vertical movement of a tensile test apparatus into a bending operation (see Fig. 1). In this set-up the sample to be tested is clamped and pre-strained by a tensile force of 70 N. The test starts with a bending radius of 1 mm. First a bending operation is performed two times up to an angle of 90 degree and back to the starting position. If the sample



Fig. 1: Experimental setup for the performance of reverse bending tests.

shows no damage after these two load cycles, the bending radius is changed to 0.5 mm and another two bending cycles are performed. If still no damage on the sample is visible, the bending radius is reduced to 0.3 mm and the maximum angle is increased to 135 degrees. The continuous counting of the bending angle during the whole



Fig. 2: Illustration of the count of the bending angle during the reverse bending test.

testing procedure means that the bending radius of 1 mm covers the values from 0 to 360 degrees (see Fig. 2). Correspondingly the following cycles using a bending radius of 0.5 mm include 360 to 720 degrees. The last two cycles with a bending radius of 0.3 mm comprise 720 to 1260 degrees bending angles. In the preliminary tests it was found that the surface quality of the edge of the sample influences the results. To eliminate this influence the edges were polished to roughness values (R<sub>a</sub>) lower than 0.1 µm. The length and width of the sample was100 mm and 20 mm, respectively

To understand the mechanism which causes the delamination failure during the test, a finite element simulation was carried out. The evaluation concentrated on the elements in the middle of the sheet thickness where delamination cracks occur during the test. From the different stress components the stress in the direction perpendicular to the sheet plane was assumed to cause the phenomenon of delamination cracking. Its course during the reverse bending test is illustrated in Figs. 3-8. The pictures on the left side illustrate the calculated deformation of the tested sample, and on the right side the level of the corresponding stresses normal to the mid-plane of the sheet is plotted. The local X-axis has its origin at the end of the clamping jaw and is "running" along the neutral axis of the sheet.





Fig. 3: Deformation of the sample at a bending angle of 90 degrees.

*Fig. 4: Stress normal to the sheet plane versus spot on the sample at a bending angle of 90 degrees.* 



Fig. 5: Deformation of the sample at a bending angle of 135 degrees.

*Fig. 6: Stress normal to the sheet plane versus spot on the sample at a bending angle of 135 degrees.* 



Fig. 7: Deformation of the sample at a bending angle of 180 degrees.

Fig. 8: Stress normal to the sheet plane versus spot on the sample at a bending angle of 180 degrees.

The stress perpendicular to the sheet plane shows a significant change from increasing compressive stress during the bending from 0 to 90 degrees to increasing tensile stress during the reverse bending from 90 to the starting position. This corresponds to the fact that delamination occurs during back bending. A typical delamination crack initiated by the reverse bending test is displayed in Fig. 9. In Fig. 10-12 micrographs of other crack types occurring during the test are shown. A well-known crack pattern is the 45° cracking caused by a heat treatment at too high temperatures during the manufacturing process. In previous work the occurrence of this type was correlated to the formation of areas with (111)-texture planes having an orientation parallel to the sheet surface during hot rolling [4]. These areas exhibit recrystallization at lower temperatures than others and are therefore responsible for embrittlement.



Fig. 9: Delamination crack in a tungsten sheet after reverse bending test.



Fig. 10: Surface crack diverted to a delamination crack in a tungsten sheet after reverse bending test.



Fig. 11: 45 degree crack type in tungsten sheet after reverse bending test.



Fig. 12: Scale-type crack in tungsten sheet after reverse bending test.

# 2.3. Crack detection by acoustic emission measurement and definition of the critical angle

The development of a testing procedure requires a method for the detection of crack initiation during the reverse bending test. Due to the small cross section of the tested samples very small forces are necessary for bending the sheet material. Most of the force applied by the tensile test apparatus is necessary to move the bending test device. An arising damage in the tested

sample causes therefore no significant change in the measured force. A technique that enables the accurate detection of crack initiation and propagation is the acoustic emission measurement. Acoustic emission (AE) is the elastic energy that is spontaneously released by materials when they undergo deformation. Sources of AE include many different mechanisms of deformation and fracture [5]. This effect can be used to detect crack initiation and crack growth during load cycles applied to structures. An advantage of the method is that inaccessible areas of the structure under test are monitored since the acoustic waves emitted by a crack spread out in the whole structure. The application of AE include different fields like process control (e.g. welding, pressing of powder), proof testing of pressure vessels, quality assurance and material science and inspection. The frequency range of interest to study AE reaches from the audible region up to some MHz. In the present work the acoustic waves were detected using piezoelectric sensors which cover the frequency range between 200 and 900 kHz (Dunegan SE-650P). To minimize the noise in the measurement chain the sensor signal is pre-amplified by a factor of 34 dB and then digitized and stored in a personal computer. For data acquisition, storage and analysis a system of the type Vallen AMS3 was used.

Preliminary investigations have been carried out to determine the threshold value of the AE signal amplitude which enables a distinction between signals caused by crack initiation, and propagation from other signals caused by friction within components of the experimental set-up. For this purpose samples where loaded in the described reverse bending procedure until signals with different amplitudes where measured during the test. The tests were stopped and the samples were investigated using light and scanning electron microscopy for the inspection of the surface and by metallograpic sectioning. These preliminary tests showed that the different damage patterns which are shown in Figs. 9-12 cause signal amplitude values above 80 dB<sub>uV</sub>. Signals with lower amplitudes could not be correlated to damage and where therefore assumed to be caused by friction. This assumption is confirmed by the fact that these signals occur mainly when the direction of bending is changed to the reverse direction (see Fig. 13). The bending angle at which the first signal with an amplitude above 80 dB<sub>uV</sub> is detected is called the "critical angle" since the damage of the sample occurs at this angle in the reverse bending test.



Fig. 13: Test record of an acoustic emission measurement during a reverse bending test. The points indicate the amplitudes of the measured signals and the line gives the bending angle. The signal marked by the arrow determines the "critical angle".

From Fig. 13 it can be seen that the analysis of the signal amplitudes enables an easy and accurate determination of the crack initiation during the test. The transient record of the signal in Fig. 13 which indicates the "critical angle" is shown in Fig. 14. Two signal types can be distinguished. The first mode occurs from 15 to 30  $\mu$ s, the second signal mode starts approximately at 30  $\mu$ s and has a longer signal duration and a higher amplitude. The first mode is a typical feature of the acoustic emission of delamination cracks. For comparison a signal generated by a scale-type crack (see Fig. 12 for the crack pattern) is shown in Fig. 15. The first signal mode is hardly noticable but the second mode is clearly visible.



*Fig. 14: Transient record of the signal in Fig. 13 which indicates the "critical angle". The signal was caused by a delamination crack.* 



Fig. 15: Transient record of a signal which initiated by a scale-type crack.

#### 3. Results

To show the effect of manufacturing parameters on the properties of the sheet material the results of two differently manufactured qualities were compared. The differences in the conditions concern mainly the hot rolling process. The results are shown for sheet material produced under standard condition (type 1) and optimized condition (type 2). From each type 12 samples were tested, 6 of them where cut out of the sheet material along the rolling direction and another 6 where cut in transverse direction. The critical angle which is determined as described in chapter 2.3 gives the load limit of a sample tested in the reverse bending test. To characterize the loadability of the two types of sheet material the mean value and the standard deviation of the critical angle were compared. The values are given separately for the stripes which were cut along the rolling direction and in perpendicular direction. The results are summarized in Fig. 16



Fig. 16: Critical angle for two differently manufactured types of tungsten sheet material tested along the rolling direction and in the transverse direction.

From Fig. 16 it can be seen that the tungsten sheet of type 2 reaches higher average values than type 1 in both directions. Another advantage of the type 2 material is the extremely small standard deviation of the critical angles.

The common methods of material characterization are not sensitive to this difference in the loadability of the sheet material. For example the material hardness was determined by microhardness measurements on the metal-lographic section according to Vickers applying a test load of 1 N. The difference in the obtained average values is not significant since it is smaller than the scatter of the data. The materials structure was investigated using light and scanning electron microscopy. The light microscopic investigations do not show significant differences in the structure of the two material types. The grains are elongated in a distinctive manner and their size is of the order of some micrometers. In the electron channeling contrast, the sub-grain structure becomes visible. The method is described for example by Stickler [6]. Examples of the sub-grain structure are shown in Fig. 17 (type 1) and Fig. 18 (type 2). The type 2 material appears more homogeneous and shows a slightly bigger subgrain size than the type 2 material.



*Fig. 17: SEM image of the sub-grain structure of the type 1 tungsten sheet in the electron channeling contrast.* 



*Fig. 18: SEM image of the sub-grain structure of the type 2 tungsten sheet in the electron channeling contrast.* 

#### 4. Discussion

Acoustic emission enables the accurate detection of crack formation and propagation in metals. From a simple amplitude analysis of the acoustic signals, the load limit of a sheet material tested in the reverse bending test can be determined precisely. Additionally, information about the crack type is obtained by the waveform analysis. Common characterization methods, like hardness measurement and metallographic investigation do not have the potential to recognize the differences in the loadability of sheet material. The combination of reverse bending test and acoustic emission measurement is therefore a simple method to evaluate the delamination behavior especially of thin sheet-materials.

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