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ORNL
FOREIGN TRIP REPORT
ORNL/FTR-3107

DATE: October 31, 1988

SUBJECT: Report of Foreign Travel of Gary M. Crosbie, Principal Research Scientist, Powertrain and Materials Research Laboratory, Ford Motor Company, as a Representative of the Ceramic Technology for Advanced Heat Engines Project

TO: Alexander Zucker

FROM: Gary M. Crosbie

PURPOSE: To participate in a powder processing conference and an IEA Annex II meeting in Berchtesgaden, Federal Republic of Germany, October 10-14, 1988

SITES VISITED:

10/10-11/88	IEA Annex II meeting	Berchtesgaden, FRG
10/12-14/88	Second International Powder Processing Conference	Berchtesgaden, FRG

ABSTRACT:

The traveler attended and presented a technical paper at the Second International Powder Processing Conference and participated in the data analysis of the working group meeting of the International Energy Agreement Annex II.

Of particular interest were discussions and papers about the status of German projects for Si_3N_4 powder synthesis, the fall of certain old ideas regarding desired powder characteristics for sinterability, tests relating Si_3N_4 ceramic properties to powder properties, and advances in understanding hardness of agglomerates and dry-pressing theory. These advances in ceramic technology are likely to be bases for improvements in several energy R&D activities.

In the IEA meeting, the traveler presented a discussion of the X-ray diffraction methods which were used in Ford's contributions to the round robin.

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COMPREHENSIVE TRIP REPORT

STATEMENT OF PURPOSE

Participation in the conference and discussions with researchers at the conference provided important technical information for the ceramic tasks in the DOE Advanced Materials Program and also the DOE Ceramic Technology for Advanced Heat Engines (CTAHE) project. Attending and participating in this conference enhanced the visibility of the DOE/ORNL CTAHE project at a major European/world conference. The subject of the conference was directly applicable to ongoing research activities the traveler is conducting for ORNL.

SUMMARY

The Second International Conference on Ceramic Powder Processing Science meeting was attended by more than 300 participants from 26 countries. Silicon nitride continues to be of strong interest among the various oxides and nonoxides discussed at the meeting. The nitride is still the high temperature toughness leader and continues to attract synthesis, processing, and properties papers. Powder characteristics continue to be an important (but incomplete) basis for predicting the sinterability of powders.

We report here on the status of German projects for Si_3N_4 powder synthesis, the fall of certain old ideas regarding ideal powder characteristics for sinterability, the relationship of Si_3N_4 ceramic properties to powder properties, the progress in describing agglomerates and dry-pressing, and powder characterization discussions from the IEA working group meeting.

Si_3N_4 Synthesis in the Federal Republic of Germany

Information was received about the status of Si_3N_4 powder synthesis projects in the Federal Republic of Germany (FRG).

For the last two years, there have been rumors of pilot-scale production in the FRG. Dr. Wilhelm Flick of Huels Troisdorf AG (previously known as Dynamit Nobel) stated that Huels is now coming on-line with a $SiCl_4$ raw material imide process for making 150-kg batches of high-purity Si_3N_4 powder.

Separately, Dr. Gangolf Kriechbaum of Degussa AG said that he is about 60% certain that Degussa will be presenting its own Si_3N_4 process at the 1989 American Ceramic Society Annual Meeting in Indianapolis. (In particular, he was interested to know that we have a patent on the process we presented at the conference.) The Degussa process is distinguished from ours by absence of liquid ammonia.

Bayer apparently provided Si_3N_4 powders used in a study by Woettig (see bibliography) which have high alpha content and extremely low chlorine contamination by use of low temperature removal of the byproducts. These powders were identified as a "gas phase" process from $SiCl_4$.

As these powders come to market, they may compete with the powders we are working towards in the world market. The recurring question among the potential producers is how big is the market going to be for high purity Si_3N_4.

In a different approach to Si_3N_4 but still with the $SiCl_4$ precursor, the emphasis in a talk given by Schulz and Hausner of the Technische Universitaet Berlin (FRG) was on plasma synthesis of Si_3N_4 powder: problems here are with high beta content, particle size outliers, and chlorine residue from high temperature of synthesis. The plasma approach is more satisfactory with SiC and B_4C, among others.

In a discussion with P. Matje of ESK, he stated that his company buys at least some of its powder from H. C. Starck. He says they are not in competition with us for the Si_3N_4 powder business. "It is difficult!" It is clear, however, that Matje and his colleagues are actively following the nonoxide literature SiC is ESK's core business.

Changing Directions in Desired Powder Characteristics

In a key paper by R. Brook (now with Max Planck Institut, Stuttgart, FRG) a trend was depicted that went from (historical) randomly complex phase mixtures to simple single phase ceramics and is now heading toward complex designed microstructures. Since nondestructive examination methods are not satisfactory, the prevention and removal of flaws through improved powders and processing are critical for the advanced applications. In composites, the strengthening phases are themselves perceived as flaws.

There was also evidence of coming full circle, as some old war horses fell: Monodisperse particle sizes are now out of favor with the university theorists. M. D. Sacks (University of Florida) showed with quantitative analysis that a distribution of particle sizes can lead to the same microstructure as monodisperse in a shorter time and with less shrinkage. Equiaxed shapes are still desirable, but not too perfectly spherical.

Also, it was shown (S. Natansohn, GTE, Waltham, Mass.) that, with extended sintering times, interlocking beta grains could be grown from beta silicon nitride precursors, apparently contravening theories of needed high alpha percentages to get high aspect ratio grains.

The sense of this participant was one of increasing maturity in the understanding: "What we were once convinced of, we now know is not so." The desire is now for some breadth of distribution, but yet there is no qualification as to how much is best at this time. Industry representatives chuckle a bit at this new "discovery" of matters which were at least seen as practical necessities before.

Powder Characteristics for Sintered Silicon Nitride

Powder characteristics for sinterable silicon nitride, in the main, stood unchanged in the discussions. Two studies were reported which allowed separation of variables in relating powder characteristics to sintered nitride properties. The conclusions of these studies reinforce the goals set some years ago in the synthesis project and give it a more solid footing. One can use brute-force on powders to sinter by overpressures and temperatures, but better properties can be obtained at lower temperatures with the right powder characteristics.

In the work of S. Kanzaki (Japan Government Industrial Research Institute), surface area was changed at constant oxygen level and vice versa. At a constant oxygen level, a lower processing temperature was possible with the higher surface area powders leading to a fracture toughness of 6.5 MPa $m^{1/2}$. At constant surface area, a decrease in oxygen level led to finer grain size, higher aspect ratios, and greater fracture toughness.

In the multifactor analysis study by Nietfeld, Wickel, and Woettig (see bibliography), the influence of both purity and powder characteristics provided a quantitative expression to the completeness of the attribution of variance. The powder characteristics mattered the most for the lower temperatures of sintering. It was also recognized that the powder characteristics such as surface area change in the early stages of processing. For 1300°C modulus of rupture, powder impurities have the greatest effect. But there, the differences in measured powder characteristics account for only 40% of the variance across the group. There are powder characteristics not measured which appear to be responsible. (From our work, MAS-NMR for amorphous content was suggested as one to consider.) Carbon content is confirmed to have a detrimental effect on strength.

The detrimental effect of carbon was also reinforced by a poster presentation by Van der Biest (Petten, The Netherlands) in which strength was reduced and grain boundary phases were changed.

Directions in Desired Forming Processes

In forming, an old tension arose *between* the theorists who are at present firmly convinced that pressure filtering (alias slip casting) is the only right way to form *and* the more pragmatic individuals who are trying to advance the understanding of equally established methods such as dry-pressing.

Interesting work about dry-pressing was presented. In work of D. Bortzmayer (School of Mines, ENSMP, Evry, France), simple shear tests were made on powder compacts to estimate the yield locus entirely analogous to the metallurgists' von Mises criterion. (This work could provide the basis for finite element calculations for die designs.)

In work of R. Oberacker (Karlsruhe, FRG), the hardness of the spray-dried agglomerates was measured by compression testing of individual microscopic granules. T. Hayashi (Nagoya University) reported on the use of a cationic lubricant for die-pressing of mullite to achieve a uniform distribution and a K_{Ic} of 5.1 MPa $m^{1/2}$.

Eastern bloc research in powder processing was represented by the freeze drying study of T. Reetz of the Central Institute of Nuclear Research, Rossendorf, GDR. Although this paper provided much consternation to those convinced that faster freezing is better, higher tap density (which often correlates with pressing and sinterability) was achieved in the powder by *slow* freezing. As ice crystals grow, particles are pushed together in between the crystals, and are compressed. Likewise, the injection of slurry into liquid nitrogen seems to give a useful powder, in spite of a gaseous boundary layer that slows heat transfer. Sometimes, an end is reached by reversing conventional, one-dimensional thinking.

In the laser route from SiH_4 presented by S. Danforth, Rutgers, New Jersey, high temperatures and oxide content are apparently needed to get much sintering. A Unamine O™ dispersant for Si_3N_4 in hexane allowed near theoretical packing of the 170-nm particles. This dispersant may apply to the nonaqueous dispersion of other silicon nitride powders.

International Energy Agreement Annex II, Powder Characterization Subtask

In IEA Annex II, A. Dragoo (National Institute of Standards and Technology, formerly National Bureau of Standards) presented combined databases with data plots that were positively received. Areas of discrepancies that would interfere with commerce were identified, such as in the analyses of calcium in the nonoxides. Comparison of our results gives credence to calibrations used in our own powder synthesis project. The consensus was to allow time to review the mass of data before committing to future work. The next meeting was scheduled for the task leaders at the Cocoa Beach meeting in mid-January 1989.

Special talks were given on the second day of the IEA meeting. From TU Berlin (FRG), W. Genthe showed that suspension ICP analysis was useful for Si_3N_4 powders, but not PSZ. P. Matje (ESK, FRG) discussed free carbon analyses of SiC by oxidation in aqueous Cr_2O_7 solutions with an iodate catalyst. The traveler described Ford XRD work with computer analysis (by C. R. Peters) of SiC being of greatest interest. Pompe (Sweden) described an agglomerate factor, $A = d_{sed}/d_{BET}$ such at A^3 is the number of primary particles in an agglomerate. Pugh (Sweden) described leaching studies for powder surface chemical analysis without ultrahigh vacuum instrumentation.

TRAVELER'S ROLE

The principal role was in presenting work done in the CTAHE project. There was much interest in our progress to date. There were many questions of process comparisons -- relative advantages and disadvantages on needed cost and quality issues. The most frequent question was the relation of our process to the UBE Industries patent. (The key difference is absence of organics in ours.)

In participation in the IEA group, the traveler made the one U.S. presentation in the second day of sessions. Participation in IEA provides an opportunity to exchange ideas with the processing people at competing research facilities through a common interest in powder characteristics standardization. One can sense what is important to the others present. This consensus building is important and the survey of methods is now nearing completion.

RECOMMENDATIONS FOR FOLLOW-UP

The conference series is now well established and merits consideration of attendance by technical personnel in future years. The Third International Conference on Ceramic Powder Processing Science will be held in San Diego in February 1990; proceedings will be available for purchase in late 1989. The IEA minutes will be separately distributed to the respective participants.

As the new FRG Si_3N_4 powders are brought to the market, they should undergo ceramic processing and stress-rupture testing as ceramics.

SIGNIFICANT DEVELOPMENTS IN ENERGY PROGRAMS

As this was a technical emphasis meeting, there were only a few displays of engine applications (by FRG conference sponsors) and no displays by major contract projects (as are found at contractors' coordination meetings and American Ceramic Society meetings). The emphasis was on powder synthesis and processing. There were many individuals representing energy programs. Comments on DFVLR (FRG), Belgium, Japan, and U.S. follow.

Based on an interest in G. Woettig's work, I had an opportunity to meet with G. Ziegler of the DFVLR. It appears that there are only limited resources available there for stress-rupture testing. With Woettig's move to Cremer, there has been a decrease in monolithic work, but this does not indicate a lack of interest. The strength at DFVLR is in gas pressure sintering of SSN and SRBSN. Their research interest is to relate quantitative measures of powder characteristics to quantitative measures of microstructure development in the ceramics using analytical electron microscopy. [George Quinn (AMTL), who recently worked there, is another source of DFVLR information.]

Work parallel to that of Woettig's has been under way by R. Leriche (Research Center of Belgian Ceramic Industry, Mons, Belgium). This work reflects an strong interest in the SSN route. There is much speculation as to what will be the consequences of the introduction of free trade in the European Common Market in 1992; no one is sure.

Information on Japan is indirect. There are two new grades of silicon nitride powder -- Sumitomo TC-2 and DENKA 9FW -- both with mean particle sizes below 0.5 µm. A new Kyocera grade of sintered silicon nitride uses 6 wt % Yb_2O_3 as an additive. Government approval has been given for a vehicular advanced gas turbine program (expanding on the previously approved stationary turbine program). Hearsay has this to be an axial, not radial inflow, turbine design to mitigate the possibility of foreign object damage.

In the United States, the purchase of Sohio by British Petroleum (BP America) has caused various discomforts at the U.S. research center, which are not offset by the return to the Carborundum name. This appears to be a case of a foreign purchase of a U.S. company affecting U.S. research strength.

SUMMARY EVALUATION

The topics discussed have meaning for DOE longer-term materials research (but only in a few cases at the commercialization level for automobiles). For the CTAHE project, we were represented in an international forum that included many researchers interested in advanced engine applications of ceramics. For Ford, participation provided a longer view of research than day-to-day requirements for identification of long-term needs in cost and reliability of the materials.

Personally, this meeting was a good opportunity to share and to take in the technical excitement of a relatively "small science" of promising materials. The puzzle to relate powder properties to sintering behavior remains. The success and continued interest in silicon nitride materials will impact the materials use in automobiles in the future.

APPENDIX A

ITINERARY

Dates	Location	Individuals Contacted	Subjects of Discussion
1988			
10/7	Travel from Dearborn, Michigan, to Munich, Federal Republic of Germany		
10/8	Weekend		
10/9	Travel to Berchtesgaden, Federal Republic of Germany		
10/10–11	Berchtesgaden, Federal Republic of Germany	Panel members for IEA Annex II Agreement	Ceramic powders characterization methods
10/12–14	Berchtesgaden, Federal Republic of Germany	Second International Powder Processing Conference attendees	Ceramic powder synthesis and processing studies
10/15	Travel from Berchtesgaden, Federal Republic of Germany, to Dearborn, Michigan		

APPENDIX B

PERSONS CONTACTED

Dr. Peter Matje, Elektroschmelzwerk Kempten GmbH (ESK), 8960 Kempten, FRG

Dr.-Ing. Guenther Ziegler, Head of Ceramic Materials and Microstructural Analysis, German Aerospace Research Establishment (DFVLR), Koeln, FRG, and Professor of Ceramic Technology at Eindhoven University of Technology, Centre for Technical Ceramics (CTK)

Dr. G. Woettig, Cremer Forschungsinstitut, Roedental, FRG

Dr. Wilhelm Flick, Diplomchemiker, Huels Troisdorf AG (previously Dynamit Nobel), Werk Leulsdorf, Niederkassel, FRG

Dr. Gangolf W. Kriechbaum, Diplomchemiker, Degussa AG, Hanau, FRG

A. Leriche, Dr. Sc., Project Leader, Research Center of the Belgian Ceramic Industry, Mons, Belgium

APPENDIX C

LISTING OF LITERATURE ACQUIRED

List of participants*

Abstracts volume*

Product literature from ESK (Appendix D)

Preprint of paper: G. Nietfeld, U. Wickel, and G. Woettig, "Tailoring of Si_3N_4-Powder Properties Concerning Sintering Behavior and Mechanical Properties," presented at Second International Conference on Ceramic Powder Processing Science, October 12–14, 1988, Berchtesgaden, FRG (Appendix E)

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*Available from E. L. Long, ORNL, upon request.

APPENDIX D

PRODUCT LITERATURE FROM ELEKTROSCHMELZWERK KEMPTEN GmbH (ESK)

ELEKTROSCHMELZWERK KEMPTEN GmbH

Head Office:

ELEKTROSCHMELZWERK KEMPTEN GmbH
Herzog-Wilhelm-Str. 16
D-8000 München 2
Postal address:
Postfach 609
D-8000 München 33
Cable: elektroschmelze münchen
Telex: 522 749 eswm d
Telefax: (0 89) 5 12 01

Company Foundation: 1922

Board of Management:

Dr. Hans Herrmann
Dr. Dieter Normann
Dipl.-Kfm. Hans Zippel

Shareholder:

Wacker-Chemie GmbH, München (99.67%)

Manufacturing Plants:

Plant Kempten, Kempten/Allgäu
Plant Grefrath, Frechen/Cologne

Subsidiary:

Elektroschmelzwerk Delfzijl B.V.
Delfzijl/Netherlands (wholly-owned)

Registered Trademarks:

Kristallit®, Performit®, Silcar®, Tetrabor®, EKabor®, EKrit®, EKasic®, EKasin®, Elastosorb®

Production Program:

Engineered ceramic materials, half-finished and finished products (non-oxide ceramics) of silicon carbide, boron carbide, boron nitride, silicon nitride, borides and nitrides (CaB_6, AlN, TiB_2, EuB_6, LaB_6), ceramic composites, surface hardening by boronizing and nickel-diamond coatings

ESK-Engineered Ceramics – From Powder to the Finished Part

The Elektroschmelzwerk Kempten GmbH (ESK) is Germany's oldest producer of **silicon carbide**, the world's largest manufacturer of **boron carbide** and a major producer of **non-oxide engineered ceramics**. Thus, ESK is not only a raw material supplier but, in addition, uses its own powders to process them into high-grade sintered shapes/components.

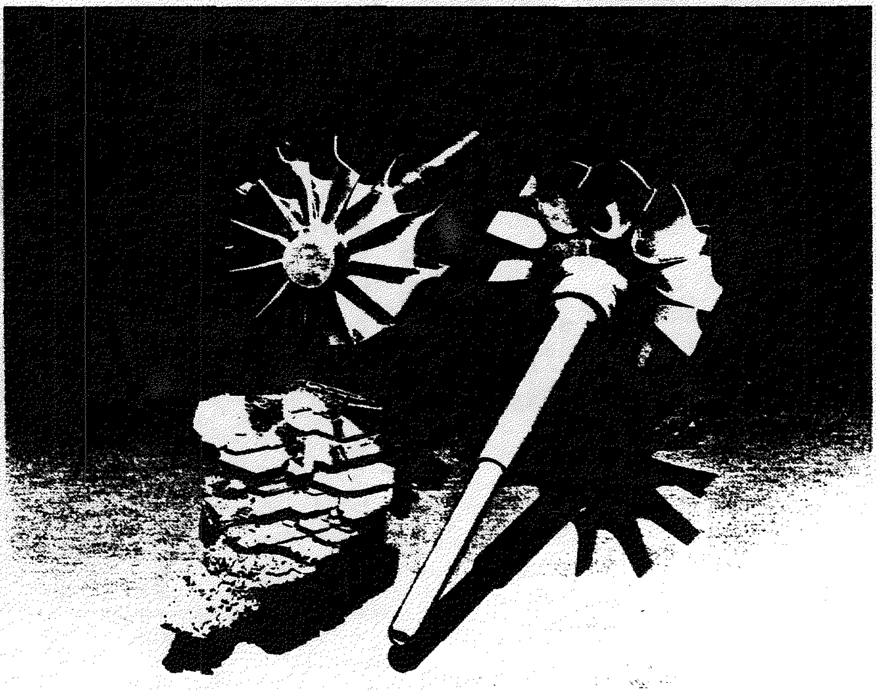

Fig. 1: Silicon carbide turbocharger rotor

Silicon carbide

With its new, worldwide patented process that allows an environmentally clean production, ESK holds a leading position in this sector.

Silicon carbide (SiC) is used in the form of loose grain and for the manufacture of vitrified, resin and rubber bonded abrasive products. In addition, its refractrory applications range from blast furnace bricks to high temperature kilufurniture. In the production of cast iron and steel large quantities of metallurgical silicon carbide are used for alloying, de-oxidation and pre-inoculation. Doped SiC is fabricated into components such as voltage dependent resistors, lightning arresters and similar products.

Boron carbide

Boron carbide, because of its exceptional hardness, is successfully used as a lapping agent in the form of powders and pastes. Also, because of its high boron content, it is used as a source of boron in the manufacture of other boron compounds.

Its high nuclear capture cross-section for thermal neutrons makes it an ideal **neutron absorber**.

In addition to silicon carbide and boron carbide, ESK is also a producer of **nitrides**, such as **boron nitride** (BN), **silicon nitride** (Si_3N_4) and **aluminium nitride** (AlN); **borides**, such as **titanium diboride** (TiB_2), **calcium boride** (CaB_6), **europium boride** (EuB_6) and **lanthanum boride** (LaB_6); wear resistant **nickel-diamond coatings** with adjustable surface friction and **boronizing powders** to produce hard, wear resistant surface layers on metals.

High temperature applications of ceramic materials

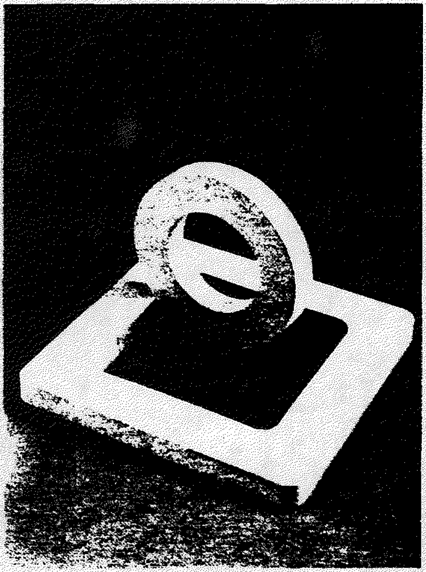

Fig. 2: Boron nitride break rings

High thermal conductivity, excellent thermal shock resistance, exceptional strength – even at elevated temperatures – and chemical stability make nonoxide ceramic materials very useful for high temperature applications.

In high temperature technology, for instance, **thermocouple protection tubes** are made of Si_3N_4, **burner nozzles** of SiC or Si_3N_4, **heat exchanger tubes** of SiC and brazing pads of SiC or Si_3N_4. Metallurgical **crucibles** made of AlN, BN and Si_3N_4 are used for melting high purity semiconductor materials and special metal alloys. **Break rings** for horizontal continuous casting of steels are made of boron nitride, which, in addition to the above properties, stands out because it is not wet by most molten steels.

In **high vacuum technology** a ceramic composite (TiB_2-AlN-BN) is used as **evaporation boats** for continuous evaporation of aluminium to metallize polymeric films and papers at 1450 °C.

One special application of boron carbide is in B_4C/C **thermocouples** for temperature measurements above 1900 °C. They are generally used in sintering furnaces and hot isostatic presses.

Minimizing wear with ceramic materials

Non-oxide ceramics have become the most favoured materials for wear and corrosion resistant applications because of their exceptional hardness, excellent corrosion, oxidation and thermal shock resistance, strength and high thermal conductivity.

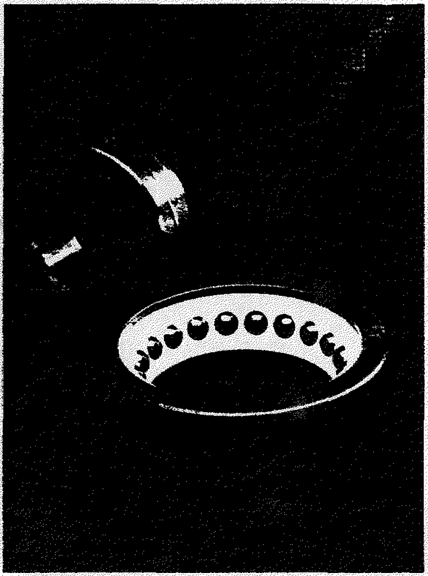

Fig. 3: Silicon nitride ball bearing

In **chemical process machinery**, SiC is most commonly used for **mechanical seal rings, slide bearings** and **shaft protection sleeves**. SiC and Si_3N_4 are used for highly wear resistant **valve fittings** and highly loaded **ball bearings**.

In **mechanical engineering** boron carbide **gritblasting nozzles** and **dressing sticks** are used as well as silicon nitride **cutting tool tips**.

Components for **heat engines** subjected to high thermal and mechanical stress are being developed and procuced of both silicon carbide and silicon nitride.

Ceramic materials for power stations

Boron carbide is a particularly suitable material for use as **regulating and control rods** in pressurized and boiling water reactors and in high temperature or fast breeding reactors because of its high nuclear capture cross-section for thermal neutrons, its high melting point and the fact that no longlasting radiating secondary elements are formed under irradiation. For protection against and absorption of neutron radiation B_4C/C and B_4C/silicone rubber composites are used.

Among the many different methods of **flue gas desulferization** used throughout the world, the use of lime and limestone for SO_2 absorption has proved to be the most economical. The liquids conveyed in most of these processes contain solids and, in addition, are very corrosive (pH values are between 1–10). **Valve components** for this application that have to withstand severe abrasive wear and chemical attack are made of **silicon nitride**, a material proven to be particularly suitable after extensive life testing.

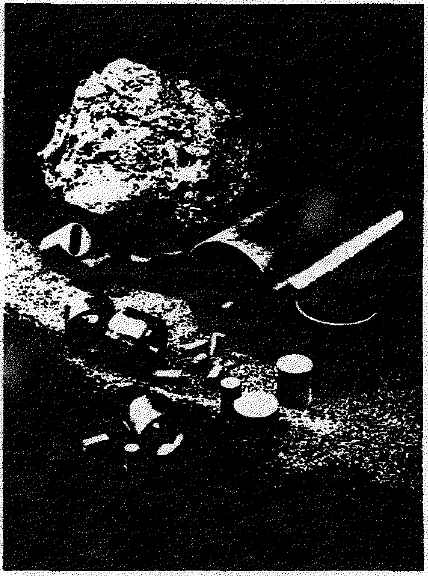

Fig. 4: Boron carbide – From the powder to the finished part.

APPENDIX E

Tailoring Of Si_3N_4-Powder Properties Concerning Sintering Behaviour And Mechanical Properties

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Goslar, FRG

U. Wickel BAYER Bayer AG, PK-F
Uerdingen, FRG

G. Wötting CFI Cremer
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Rödental, FRG

Paper presented at 2nd International Conference on
"Ceramic Powder Processing Science"

Oct. 12 - 14, 1988, Berchtesgaden, FRG

Abstract

Sintering of Si_3N_4 and resulting mechanical properties are essentially determined by the starting powder, by the type and amount of additives and by the sintering conditions. Unequivocal predictions about the effect of individual powder characteristics, however, are still difficult due to superpositions. To evaluate critical characteristics, gas-phase processed Si_3N_4 powders and powders produced by the nitridation of silicon were varied systematically with respect to specific surface area, oxygen- and impurity content. All other powder characteristics, the additive content and the processing conditions are kept constant. Sintering behaviour under atmospheric - as well as increased N_2-pressure and mechanical properties at room- and high-temperatures are discussed as a function of the variations performed. Results are analysed by means of statistical methods.

1. INTRODUCTION

Sintering of Si_3N_4-powder compacts is essentially influenced by the starting powder properties. Besides this, type and amount of additives as well as the processing conditions used play an important role. Together, these variables determine resulting properties. Due to the decisive influence of the starting powder, often great efforts are spent to evaluate the best powder for a given purpose among the various grades offered on market. Such a comparison of the sintering behaviour and of resulting properties in most cases leads to the selection of a certain powder fitting more or less prespecified requirements. The reasons for the observed behaviour, however, are often not quite clear. This seems to be due to overlapping effects of different powder characteristics on sintering and resulting properties, a fact which is often not considered in literature, either. Therefore, controverse statements concerning the controlling factors are found there (1 - 3). Further reasons for these differences may also depend on the comparison of Si_3N_4-powders produced by different methods exhibiting characteristics which usually were not recorded by common powder characterisation methods. Thus, in order to evaluate densification- as well as properties-determining factors, it is necessary to eliminate such parameters. This can be done by restricting powders to be analysed on such ones of a single origin varying only within limited characteristics. A third point which may lead to controverse results is the consideration of starting powder properties in the as-received state, while the preparation of the starting mixture with additives often changes powder characteristics remarkably.

Therefore, the intention of this work is to demonstrate the contribution of individual powder characteristics on sintering and properties, keeping other influencing factors constant as far as possible. In order to take care for the combined effects of the variables considered as well as to be able to analyse such a broad data basis, use is made of statistical evaluation methods. In a previously published part (4), only Si_3N_4-powders produced by a gas-phase process had been treated in this way. This evaluation demonstrated the general feasibility of this method. Now, this first analysis is extended on Si_3N_4-powders produced by nitridation of silicon (5) in order to reveal basic differences between these two powder families. Additionally, a slightly modified set of variables is taken into consideration.

With this respect, 19 Si_3N_4-powders produced by the method of nitridation of silicon (DNP) were investigated and compared with results obtained with the analysis of 11 gas-phase processed powders (GP) mentioned above. In both cases, powders selected reveal deliberately great scatters in characteristics. These differences, however, origin only in slightly modified conditions of constant preparation routes. The variation range itself is arranged around the properties of commercial powder grades (DNP) and a highly developed gas-phase powder (GP), produced in pilot plant scale, respectively. The additive amount used is chosen rather low to reveal intrinsic differences between the powders, avoiding suppression by high amounts of liquid phase created during sintering. It should be mentioned that with this amount of additives and the processing conditions applied, also with other commercially available powders comparable properties were achieved.

It is thought that this type of evaluation provides tools for further improvements of Si_3N_4 starting powders as well as for the selection of appropriate Si_3N_4-powder grades for individual purposes to tailor densification and properties.

2. EXPERIMENTAL PROCEDURE

Due to the reasons discussed above, for the determination of the sintering behaviour of the different Si_3N_4 starting powders, each grade was mixed with only 5 wt.% Y_2O_3 and 1 wt.% Al_2O_3 as additives. Sintering was performed between 1770°C, 1 bar N_2 and 1975°C, 15 bar N_2, partially followed by a second sintering step under 100 bar N_2. Only from sintered samples with high densities, fracture strength values at room- and high-temperatures were determined in 4-point bending (40/20 mm).

The variation range of powder characteristics of the directly nitrided (DNP) as well as of the gas-phase processed (GP) Si_3N_4-powder grades evaluated is given in Fig. 1.

Fig. 1: Variation range of Si_3N_4 starting powder properties

In Tab. 1 the starting powder properties of some selected powders are summarized.

The information in Fig. 1 is twofold: Firstly, it demonstrates the variation in certain powder properties within the DNP- as well as the GP-starting powders. Secondly, it is shown, how different variables are changed during the preparation of the Si_3N_4-powder/additive-mixture. It is obvious that the fineness, characterized by the specific surface area values, as well as the oxygen content (contribution of the additives excluded by calculation) are increased by the processing applied. In contrary, the carbon content is even slightly decreased during burning-out of binders and lubricants. It should be pointed out that for the further evaluation, the characteristics determined from the processed starting compositions are used.

A further variable of the powders exists in the β-Si_3N_4 phase content. This variation, however, is excluded in the further analysis, as high β-values are only represented by two powder grades, giving rise for misinterpretations by the statistical evaluation.

In order to reveal relations between powder characteristics, sintering behaviour and mechanical properties at room- and high-temperatures, different calculations were performed as outlined in Fig. 2.

Fig. 2: Outline of the statistical evaluation method

Primarily, the calculation of the linear correlation coefficients between individual powder characteristics and the "target values" density or mechanical property is performed. Due to the overlapping effects, often only minor fits between such couples result. Therefore, a multiple stepwise non-linear regression analysis is added, starting with the variables of highest influence according to the linear correlation analysis. The stepwise addition of further linear and exponential expressions is continued until a polynomial is developed which best describes the experimental data.

During the stepwise procedure (by means of a computer program) after each addition of a further variable to the fitting polynomial, the improvement of the fit in comparison with the former step is calculated. This improvement is expressed in percent, representing the "extent of influence" of the last variable added on the target value. In the following, mainly these "extents of influence" will be used for discussions.

3. RESULTS AND DISCUSSIONS

3.1 Sintering

Figs. 3 a and b reflect the differences in the densification behaviour between the various Si_3N_4 grades evaluated as a function of the sintering conditions (time at temperature = constant = 1 h). With respect to clarity, only the graphs of the powders with the best as well as with the worst sintering characteristic are shown, which envelope the behaviour of all other grades. Some further typical examples are added.

Fig. 3: Characteristic examples for the densification behaviour of the Si_3N_4-powders evaluated
a) DNP-grades
b) GP-grades

As can be seen, the degree of densification by the one-step sintering cycle applied varies from nearly complete densification already at rather low temperatures to an incomplete sintering even at highest temperatures. It should be pointed out, however, that nearly all samples considered could be densified completely by a two-step sintering cycle with an added gas-pressure step (100 bar), presumed the samples reached density values above about 93 % th. d. during the first step.

It is possible to draw some conclusions about densification-determining factors by opposing the results in Figs. 3 a and b to the powder properties. This reveals, for example, that the well sintering DNP-grade "A" possesses the highest impurity content among this powder group which obviously favours densification. On the other hand, the DNP-powder LC 10 N as well as the GP-grade "f" reveal lowest oxygen contents, resulting in retarded sintering. Finally, samples made of the GP-grade "k" with the highest oxygen amount within this group already reach rather high densities at low sintering temperatures. With increasing temperature, however, density decreases probably due to an "oversintering" effect, meaning vaporization of secondary phase and/or bloating to take place.

Besides these simple relations, further conclusions concerning the effect of different powder characteristics on sintering are difficult. A more extended description of such a broad data basis affords the use of statistical methods. Results for the DNP- as well as the GP-powders are summarized in Figs. 4 a and b, respectively.

Fig. 4: Extent of influence of various powder characteristics on the sintering results
a) samples made of DNP-grades
b) samples made of GP-grades

Fig. 4 a shows the extent of influence of the powder variables specific surface area, oxygen-, carbon- and impurity content on the description of the final (experimentally determined) sintering density as a function of temperature. The summary graph ($\Sigma\Sigma$) reflects the ratio between the theoretical results according to the fitting polynomial developed and the real experimental values. As can be seen, with this analysis a description quality of about 80 % is reached.

Results for the DNP-grades in detail indicate that at low sintering temperatures the impurity content is of greatest importance for the resulting sintering density. This is in accordance with the above mentioned example of experimental DNP-grade "A". Additionally, this finding already points out the necessity to consider not only the sintering behaviour but also other resulting properties. For example, experimental DNP-powder "A" shows a good sinterability but low strength at high temperatures.

Of second importance at lower sintering temperatures, the specific surface area is found, normally discussed as a characteristic for powders' activity. The impact of both, the impurities and the fineness, on density decreases gradually with increasing temperature, while the contribution of the oxygen content simultaneously rises rapidly. Carbon is found here to excert a slightly positive effect over the whole temperature range considered, but it is thought that this result should not be overestimated or discussed (confidential limit ~10 %).

Comparing these dependencies with the ones found for the GP-grades (Fig. 4 b) leads to the surprising result of a contrary sequence of the influencing factors. Here, the oxygen content results with greatest influence at lower temperatures. Its rapid decrease in significance is accompanied by a rising influence of the powder fineness. Impurities remain of secondary importance with this powder group while the carbon content excerts negative effects over the whole temperature range.

The latter is partially anticipated due to reactions between liquid silicate phases and carbon, feasible at high temperatures, which lead to volatile constituents like CO and SiO. Finally, the quality of description again is rather high with an average of above 80 %.

The sequence of influencing factors for the GP-powders can be interpreted with the classical liquid-phase sintering theory (6). Rearrangements can take place after the formation of a sufficient amount of liquid phase of low viscosity. The liquid phase volume created, however, is mainly dependent on the oxygen content. This prime densification step is followed by the solution-reprecipitation mechanism which is mainly controlled by the powder fineness, reflected by the rising importance of the specific surface area.

With the DNP-grades, the impurities seem to take over a part of the role played by oxygen with the GP-powders during the early sintering stage. The reasons therefore are not quite clear at the moment, however, these results may explain frequently reported marked differences in the sintering kinetic of samples based on DNP- or GP-powders (7).

Resuming, it is thought that this type of evaluation revealed fundamental differences between DNP- and GP-powders in the effect of various powder characteristics on densification. Additionally, it is shown that the densification-favouring factors change with the sintering temperature applied. The knowledge of these relationships seems to be a tool to select the best-suited starting powder for specified production conditions as well as to fit desired material properties.

3.2 Room-temperature bending strength

In order to evaluate the influence of Si_3N_4-powder characteristics on room-temperature strength, an identical analysis is performed. Fig. 5 primarily represents the absolute variations in strength values determined from the DNP- and GP-grades, respectively, as a function of sintering conditions. Only those sets were taken into consideration which reached relatively high densities (≥ 3.10 g/cm^3). Additionally, the mean values of some characteristic samples are indicated.

Fig. 5: Variation range in room-temperature bending strength values of all DNP- and GP-grades as a function of sintering conditions (Arrows: mean values of individual grades)

Firstly, it can be seen in Fig. 5 that the strength values react rather sensitive on the sintering conditions. Increasing the temperature in one-step sintering from 1925°C to 1975°C in the case of the DNP-grades, the whole strength level decreases, probably due to beginning "oversintering"-effects, as already discussed above. By means of Fig. 6 (LM/dark-field exposition), the formation of microporosity can be seen caused by these effects.

Fig. 6: LM-dark field exposition of DNP-based sintered Si_3N_4 samples, demonstrating the effect of "oversintering"
a) Sintering temperature = 1925°C
b) Sintering temperature = 1975°C

The same is true with the GP-grades, however, the maximum sintering temperature applicable seems to be even about 50°C lower than with the DNP-grades. This reflects the differences in the sintering activity already discussed in comparing the densification behaviour.

As a second point of interest the fact appears that the strength level of both material groups can be increased by applying the two-step sintering technique under appropriate conditions. This procedure obviously offers a great potential for further strength improvements of sintered Si_3N_4 materials.

Finally, the results of individual grades may be related with certain starting powder characteristics. One peculiar example is the behaviour of the experimental DNP-powder "b", possessing the highest oxygen level. Therefore, it reveals highest sensitivity with respect to "oversintering", resulting in a marked drop in strength with rising sintering temperatures. Concerning this effect, powders low in oxygen, e. g. LC 12 N, react rather insensitive.

For a more complete description of the relations, the use of statistical methods again is necessary. First runs for the powder variables specific surface area, oxygen-, and impurity content, however, resulted in rather low degrees of description of the experimental data by the polynomials developed. Thus, as a further variable, the sintering density is added, improving the quality of description markedly. With this respect, one should keep in mind that sintering densities are essentially determined by powder characteristics, too, as discussed above. Results for the DNP- and the GP-grades as a function of sintering conditions are represented in Figs. 7 a and b:

Fig. 7: Extent of (positive and negative) influence of powder characteristics and sintering densities on the room-temperature bending strength as a function of sintering conditions
a) for samples based on DNP-grades
b) for samples based on GP-grades

As is shown in Fig. 7 a, for the DNP-grades sintered at 1925°C the most intensive and negative influence on strength is excerted by the impurities. The only strength-favouring variable found is the sintering density while the effects of the specific surface area and of the oxygen content can be neglected. With rising temperature, the sequence of effects remains constant, however, the degree of contributions varies. With the two-step sintered samples, the influence of the sintering density must approach zero, as all samples reached nearly theoretical density. According to this calculation, also in two-step sintered DNP-samples impurities still excert the worst effect on strength.

In all cases, the absolute sum of the description values is lower than in the evaluation for the densities. This indicates that the r.t.-strength is essentially determined by other variables than the starting powder characteristics. Among them, processing and sintering conditions are assumed, which influence microstructural characteristics like aspect ratio, grain size, etc.

Again, different effects are found for the GP-grades (Fig. 7 b). The most peculiar result is the positive influence of impurities on the r.t.-strength of the 1875°C sintered samples. One explanation might be that in the case of the GP-grades the impurities present are more easily able to dissolve in the liquid phase while they might remain as particles within the DNP-samples. This suggestion, however, has to be proved by SEM-analysis of fracture surfaces. With this respect it has to be mentioned that the variation of the impurity content was intentionally exaggerated in order to see effects clearly.

With the GP-samples sintered at 1925°C, the effect of "oversintering" becomes obvious, caused by high oxygen- and impurity contents according to this analysis. While the sintering density in this case is of remarkably high influence, it again must approach zero with the two-step sintered samples with densities close to the theoretical. On the other hand, oxygen is found to play an essential role. This might be due to the controlling effect of oxygen revealed by the analysis of the densification behaviour of the GP-grades (see Fig. 4 b). Thus, oxygen and, to a minor extent, the specific surface area are thought to substitute the sintering density.

Summing up, the evaluation of the effects of the powder properties and the sintering density on the resulting strength again demonstrates the superposition of different variables. Besides this, essential differences between the two powder groups reveal. In general, the degree of description of the "target value" strength by the variables considered by far is not as good as of the densities, pointing out pronounced effects of further factors. Again, however, the relations found may be used to support the selection of an appropriate powder to suit prespecified properties.

3.3 High-temperature bending strength

In the same way as with the r.t.-strength results, the values obtained at 1100°C and 1300°C are treated, however only samples sintered by the two-step technique are used. Fig. 8 represents the range of data obtained with all DNP- and GP-grades, respectively. Again, the mean values of some characteristic samples are indicated.

Fig. 8: Variation range of bending-strength values at 1100°C and 1300°C of all DNP- and GP-grades (Arrows: mean values of individual grades)

There are only limited possibilities to explain the obtained data, like experimental powder "b" has the highest, LC 10 N, however, has the lowest oxygen content, while LC 12 SX is the purest powder among the DNP-grades evaluated. Concerning the level of the high-temperature strength data it should be mentioned that absolutely no optimization of the additive system and the sintering conditions was performed with respect to this property, e. g. to reach a crystallization of the grain boundary phase, etc.

In order to analyse these data for relations with powder properties, again statistical methods were applied. As variables which still reveal non-negligible correlation coefficients, however, only the oxygen- and the impurity content remain. Results are represented in Fig. 9. The sum of the degree of description of the experimental values by these variables is rather low, indicating that there are several other property-determining factors besides the starting powder characteristics, e. g. the grain-boundary constitution.

Fig. 9: Extent of (positive and negative) influence of powder characteristics on the bending strength at 1100°C and 1300°C
a) for samples based on DNP-grades
b) for samples based on GP-grades

Again, this evaluation reveals marked differences concerning the controlling factors between the DNP- and the GP-grades. At 1100°C strength values of two-step sintered DNP-samples (Fig. 9 a) are found to be negatively influenced by the oxygen- and the impurity content. This is in accordance with results got for the r.t.-strength evaluation (see Fig. 7 a, two-step sintering). As this aggreement is found for the GP-based samples, too, (Fig. 9 b and 7 b) it may be anticipated that the r.t.-strength in this temperature range still excerts a strong influence. On the other hand, this means that the material still reveals mainly a linear elastic behaviour. At 1300°C, however, strength is known to be primarily determined by the viscosity of the liquid phase (8). This is reflected by the essential negative effect of impurities, resulting for both powder groups. All other starting powder characteristics are of diminishing low influence.

4. SUMMARY

The intentions of this work were twice: firstly, it was tried to demonstrate that the sintering behaviour as well as resulting properties usually are not simply related with single starting-powder characteristics. On the contrary, there are several superposing effects which afford the use of statistical methods to clarify their dependencies. With this respect it could be shown by means of such methods how different powder characteristics influence the sintering behaviour as well as resulting properties in a positive or a negative sense. It should be pointed out once more that the effect of individual variables may also change with sintering- or test-conditions. Therefore, each processing route affords a tailored powder or - vice versa - each powder needs adjusted processing conditions. It seems that it is not possible to fulfill all requirements with a single powder grade, as, due to the preparation route, each starting material reveals an own character resulting in an individual property spectrum. The latter is demonstrated by comparing Si_3N_4 powders prepared by direct nitridation of silicon (DNP) with gas-phase processed (GP) materials.

Secondly, the broadness of data obtained within this evaluation should be used as the basis for further work to improve special powder properties to fit specified requirements but also as a guideline for the selection of an appropriate starting powder for certain purposes. In order to be able to draw such conclusions, it is anticipated to include further variables into the analysis to achieve better descriptions, especially for the relations between Si_3N_4-powder characteristics and properties of the sintered parts.

Referring to both points it seems to be obvious that the evaluation method applied is a suited measure to further clarify the relations between starting powder characteristics, sintering behaviour and resulting properties as well as a tool to tailor powder properties to fit special demands.

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Tab. 1

Powder grade	BET m^2/g	O wt%	C wt%	Fe ppm	Al ppm	Ca ppm	Impurities Σ Fe, Al, Ca
LC 12 SX	21,8	2,0	0,10	30	13	10	55
LC 12 S	21,4	2,0	0,15	120	320	40	480
LC 12 N	22,6	1,6	0,12	40	300	50	390
LC 12	21,0	1,9	0,19	60	450	50	560
LC 10 N	14,4	1,5	0,18	100	300	40	440
LC 10	14,6	2,0	0,17	140	450	60	650
GP 14/2	12,4	1,5	0,07	95	30	15	140

HCST

Characteristics of Commercial HCST-Si_3N_4-Powders and one Bayer Trial Product

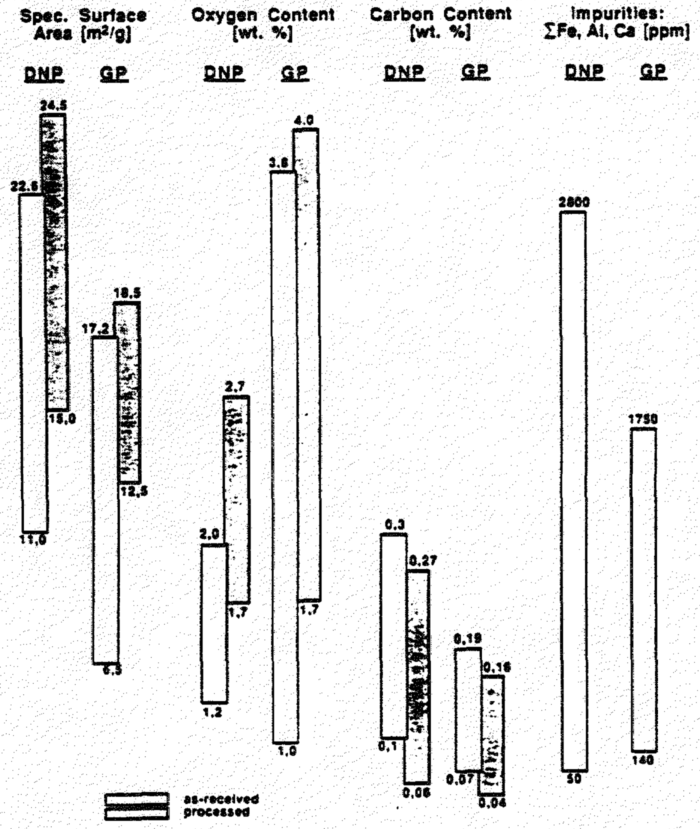

Fig: 1: Variation range of Si_3N_4-powder properties in the as-received and in the processed state

1. Step

Linear Correlation Between Single Powder Variables and "Target Values", e.g. Density, Strength:

⇨ Linear Correlation Coefficients k, e.g.:

- BET of Powders ⟷ Densities (all T_s) : k = 0,75
- C-Content ⟷ R.T. Strength : k = 0,22

2. Step

Multiple Stepwise Non-Linear Regression Analysis
Starting with Variables of Highest Correlation Coefficients k

General Relation*:

$$P = a \cdot V_1 + b \cdot V_1^2 + c \cdot V_2 + d \cdot V_2^2 + \ldots\ldots + i \cdot V_i + j \cdot V_i^2 + C$$

Stepwise Procedure:

1: $P = a \cdot V_1 + C$
2: $P = a \cdot V_1 + c \cdot V_2 + C$
3: $P = a \cdot V_1 + c \cdot V_2 + b \cdot V_1^2 + C$
•
•
•

3. Step

Calculation of the Extent of Description
of the Experimental Results by each Variable in Percent

⇨ Extent of Influence to be Discussed

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* P = Property, e.g. σ, ϱ ; V_i = Variable, e.g. BET; i,j = Regression Coeff.

Fig. 2: Outline of the statistical evaluation method

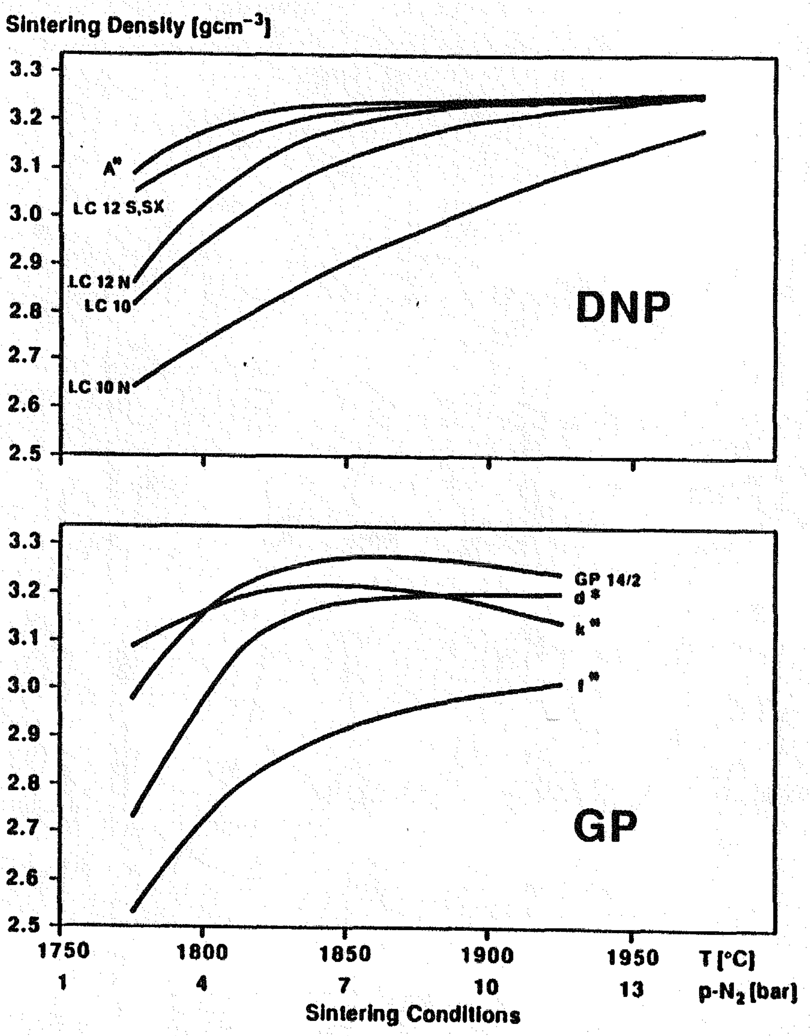


Fig. 3: Comparison of the sintering behaviour of DNP- and GP-Si_3N_4-powders (*experimental grades)

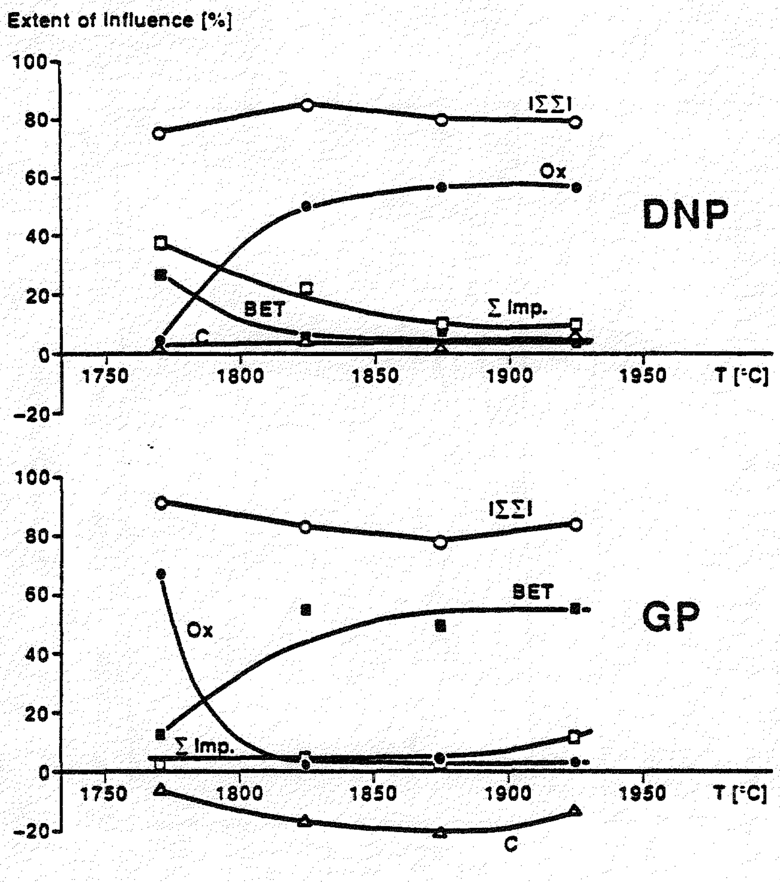


Fig. 4: Extent of influence of various powder characteristics on the sintering results of the DNP- and GP-grades

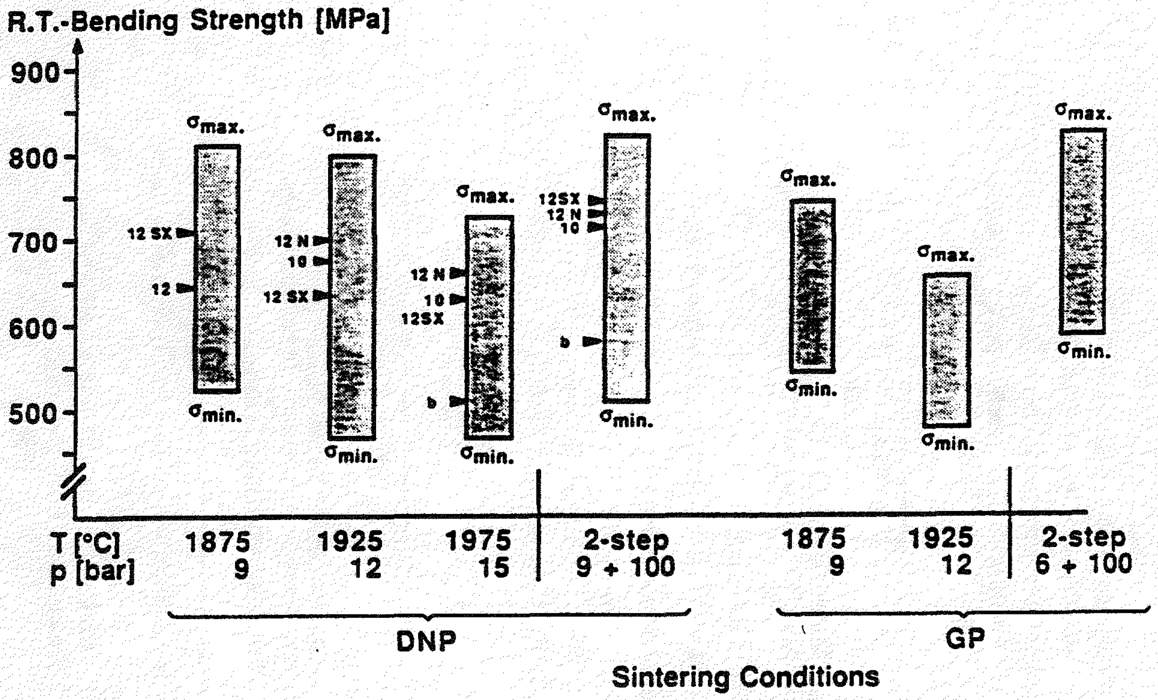
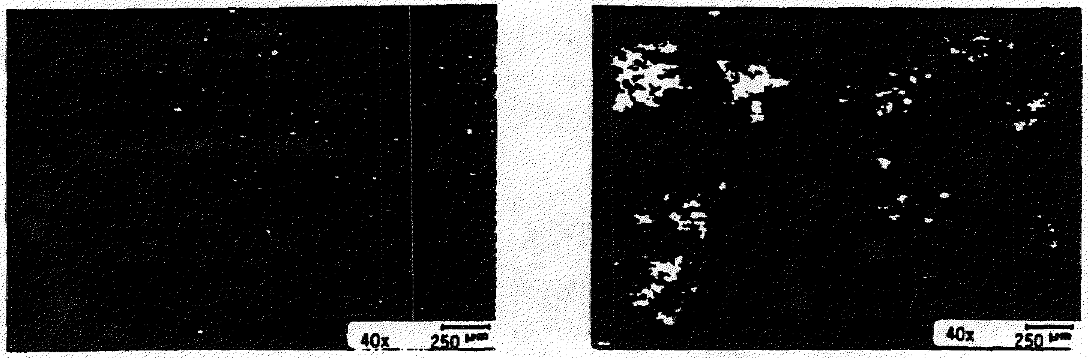


Fig. 5: Variation range in room-temperature bending strength of all DNP- and GP-grades as a function of sintering conditions (Arrows: mean values of individual grades)



a) T_s = 1925°C b) T_s = 1975°C

CFI

Optical Microscope Images
(Dark Field)
of DNP-Si_3N_4-Based Sintered Samples

Fig. 6

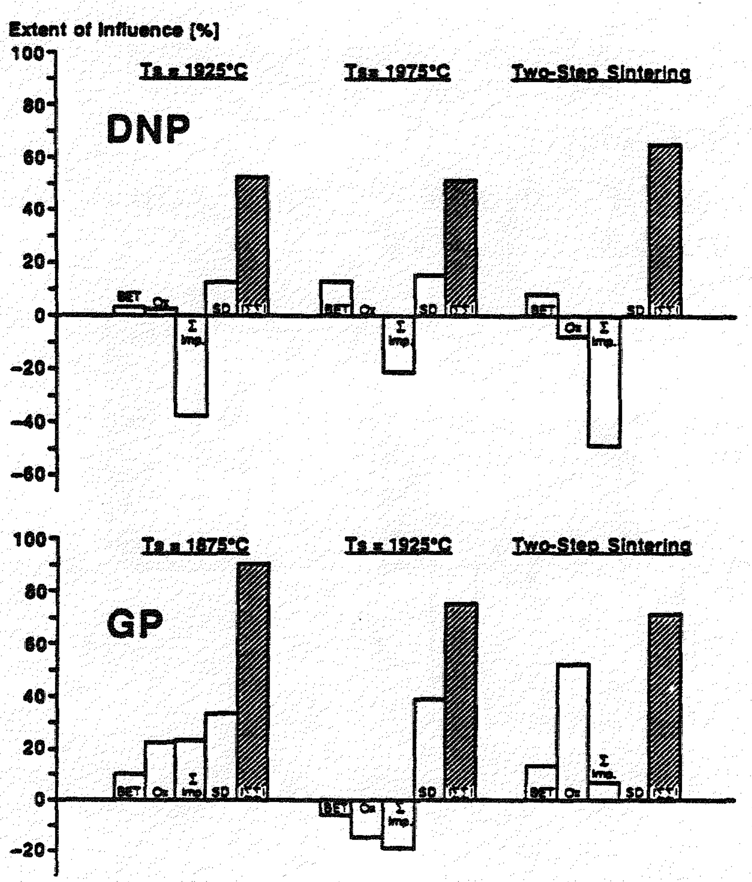


Fig. 7: Extent of (positive and negative) influence of powder characteristics and the sintering density on the room-temperature bending strength of the DNP- and GP-based samples

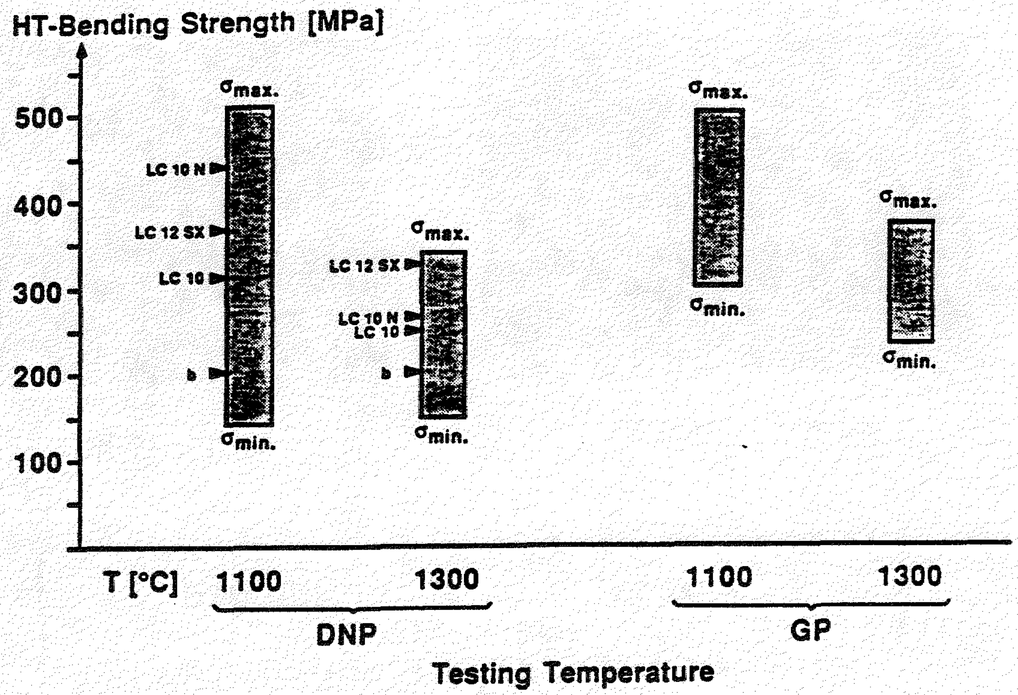


Fig. 8: Variation range in bending strength values at 1100°C and 1300°C of all DNP- and GP-grades (Arrows: mean values of individual grades)

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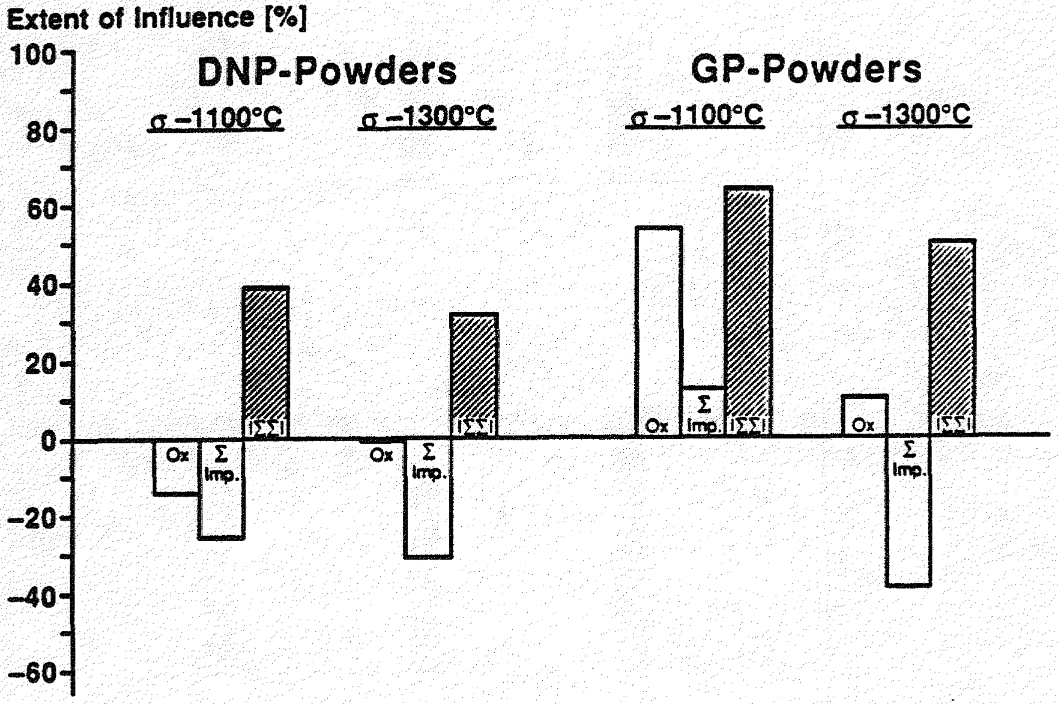

Fig. 9: Extent of influence of DNP- and GP-powder characteristics on bending strength at 1100°C and 1300°C

APPENDIX F

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