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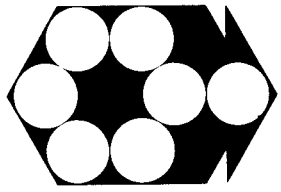

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PREPARATION AND PROPERTIES OF LOWER DENSITY UO_2 PELLETS

BY

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1. INTRODUCTION

For economic reasons, endeavours are being made to raise the burn-up of uranium dioxide - the fuel to which preference is given for light-water reactors - to over 50,000 MWd/t U. The main problems arising in connection with an increase in burnup are cladding problems, fuel swelling and high fission gas pressure. Hence the fuel must guarantee favourable irradiation behavior in this respect. Consequently, increasing use is being made of UO_2 pellets of "medium" density with a defined pore structure and pore size distribution. A report is given below on the fabrication and properties of such pellets.

The term "medium" density denotes a range from 9.8 to 10.3 g/cm^3. On the one side of this is the "low" density range of < 9.8 g/cm^3 (e. g. fast breeder fuel) and on the other side the "normal" density range of > 10.3 g/cm^3 (e. g. fuel for heavy-water reactors).

In principle it is possible to fabricate UO_2 pellets of "medium" density by sintering at low temperatures. Repeated annealing at high temperatures or under irradiation in the reactor may, however, cause after-sintering of pellets fabricated in this manner. As a result, the pore volume decreases with increasing density and is no longer available for matrix swelling and as fission gas space.

It is therefore necessary to fabricate pellets whose structure still contains an adequate pore volume after sintering at high temperatures of > 1600 °C. The cheapest method of manufacturing sintering-inactive UO_2 powder with the required properties is by direct chemical means. It is, however, difficult to produce such UO_2 in large quantities with constant quality. Three other methods can be employed to fabricate UO_2 pellets with the required properties:

A By the use of UO_2 powder (ceramic grade) with reduced sintering activity obtained by heat treatment

B By processing UO_2 powder (ceramic grade) with the addition of returns from pellet fabrication

C By the use of UO_2 powder (ceramic grade) with admixtures which generate a defined porosity by thermal decomposition, e. g. ammonium uranyl carbonate ("AUC").

2. FABRICATION OF SINTERED UO_2 PELLETS OF "MEDIUM" DENSITY

2.1 Processing of UO_2 powder whose sintering activity has been reduced by heat treatment

By suitable heat treatment it is possible to reduce the sintering activity of UO_2 powder by a given amount. Table I shows the main influence of the annealing temperature on important powder properties. Table II contains the specific data of the basic UO_2 powder used and of the additionally treated UO_2 powder. On annealing of the virginal UO_2 powder in an H_2 atmosphere at 1300 °C, the specific surface was reduced by about 25 %, while the flowing behavior, which is important for processing of the powder, improved and the O/U ratio assumed a value of 2.00.

The pellets were fabricated by a pressing and sintering process without the use of a binder [1]. The mean green density of the pellets was 5.3 g/cm^3. Sintering was carried out in a continuous sintering furnace in an H_2 atmosphere at a temperature of 1600 °C with an isothermal holding time of 1.5 h. This produced pellets having a mean

sintered density of 10.3 g/cm^3. With a diam. of about 9 mm and a length of about 10.5 mm, the dimensions of the pellets correspond to those usual for fuel elements used in light-water reactors.

2.2 Processing of UO_2 powder with the addition of fabrication returns

The following alternatives are of considerable importance for the fabrication of pellets, since practically all nuclear pure returns occurring in the production process (pellet scrap, grinding swarf) can be processed in a mixture with 80 to 90 % virginal UO_2 powder. If the returns occurring do not suffice, owing to a high production yield, UO_2 powder heat-treated by the method described under 2.1 - this can be produced relatively simply in the quantities required in a continuous sintering furnace - can be added additionally. The virginal UO_2 powder used for method B was produced from UF_6 via "AUC" conversion and has the following data:

Bulk density:	2.1 g/cm^3
Flowing behavior:	4.8 g/s [1)]
Specific surface B.E.T.	5.95 m^2/g

The returns were prepared by four different methods:

1) Milling of UO_2 return pellets

2) Drying of grinding swarf at about 120 °C in a drying oven

3) Oxidation of UO_2 return pellets to U_3O_8 in air at about 450 °C

4) Annealing of virginal UO_2 powder in H_2

The UO_2 pellets obtained by the four different methods show a large measure of agreement in structure and after-sintering behavior. The same applies for mixtures of the various additions. In the following the discussion will be confined to two selected pellet types denoted by B1 and B2. The powder composition of these is given in Table III.

Fig. 1 shows that the addition of milled UO_2 returns causes the green density/sintered density characteristic to be displaced to lower sintered density values compared with virginal UO_2 powder. The slope of the curve becomes steeper, i.e. the sintered density changes more with variation of the green density than in the case of virginal UO_2 powder. By suitable selection of the type and quantity of admixture and the green density, it is thus possible to fabricate UO_2 pellets in the

1) referred to a given funnel size

required "medium" density range. A comparison of the various additions showed that heat-treated UO_2 powder effects the greatest reduction in sintering activity, while milled UO_2 returns and UO_2 grinding swarf have approximately the same effect, and U_3O_8 admixture from annealed UO_2 returns has a smaller influence on sintering activity. The complex dependency of the sintered density on the powder parameters [2] will not be dealt with in this connection.

2.3 Processing of UO_2 powder with pore producing admixtures

In principle it is possible to add various admixtures which produce a defined porosity. We will, however, restrict ourselves here to consideration of the method specially developed by us using ammonium uranyl carbonate ("AUC") as mixture [3]. The basic powder for the UO_2 pellets fabricated by this C method was the same as that used for the other pellet types. The powder was mixed with 3 wt.% of ammonium uranyl carbonate in two charges by means of tumbler mixers. The charges differed in the particle size of the "AUC" powder added:

C 1 Powder size: 20 µm

C 2 Powder size: 32 to 37 µm.

The pressing and sintering of the pellets corresponded almost to the above-mentioned conditions. The pellets were likewise sintered in a continuous sintering furnace, but at a lower transport speed and with less compact loading of the sintering vessel. While this is disadvantageous from the standpoint of production quantity, it offers the favourable pellet properties described below.

3. PROPERTIES OF THE UO_2 PELLETS

For the out-pile investigations described below we have in each case selected two alternatives from the three basic types A, B and C. The density and principal fabrication data of these are given in Table III.

3.1 Density measurement and determination of the volume percentage of open and closed sinter pores

Since some of the UO_2 pellet types have a large open pore volume, density measurement by the usual float method presents difficulties and

it was necessary to develop special methods of measurement. For measurement of the geometric density by the float method, the surface is coated with a thin film of varnish. The open pore volume is measured by a penetration method. In this method, a liquid (cyclohexane) is brought together with the UO_2 pellet in a vacuum chamber. When air is let into the chamber, the open pores are filled with the liquid.

As can be seen from Fig. 2, the types A and B do not differ greatly with regard to the distribution of the porosity over open and closed pores. The open pore volume is approx. 60 to 80 % of the total pore volume, the percentage increasing with decreasing geometric density of the pellets. On the other hand, the UO_2 pellets of type C reveal no open porosity within the range of measuring accuracy. This fact was also confirmed by Hg porosimetry. As expected, pellets fabricated by method C did not show any penetration of Hg under pressure, while in the case of the type A and B pellets it was possible to measure the pore size distribution of the open pores accurately. The max. value of the effective pore diam. distribution occurs at 0.9 μm.

3.2 After-sintering behavior

UO_2 pellets of "medium" density would permit attainment of high burnup in an ideal manner provided their dimensions remained stable under the influence of thermal effects and irradi ation, and the volume and arrangement of the pores also remained stable. In reality, however, thermal influences by themselves cause density and structure changes which are discussed below.

The after-sintering behavior was investigated by isothermal annealing in He of 99.99 % purity for periods between 2 h and 80 h in a temperature range between 1600 ^{0}C and 1800^{0}C. As an example, Fig. 3 shows typical results obtained on pellets of types A, B and C. The pellets fabricated by methods A and B, which have a large open pore volume in the basic state, both show a decrease in the open pore percentage. In the case of types A1 and B1, the open pore percentage even disappears completely after long-time annealing. The "AUC" alternatives showed a small degree of densification under all annealing con - ditions.

Fig. 4 shows the after-sintering behavior as a function of time and initial density. With a series of pellets of type B, repeated sintering runs were carried out in the continuous sintering furnace under constant sintering conditions that corresponded to the original (1st sintering) conditions. The green density of these pellets was between 4.9 and 6.2 g/cm^3, so that a relatively large density range was obtained for the sintered material. The sintering temperature was 1,690 ^{o}C. Speaking qualitatively, it can be said that the increase in density under the given conditions becomes smaller with increasing sintered density and thus with the number of sintering runs. The exact conditions are shown in Fig. 4.

3.3 Microstructure and morphology of the pores

Various preparation and imaging methods were used for the ceramographic investigations. Micrographs of polished, unetched sections provide good characterization of the pore structure. In Fig. 5 a comparison is made of the three basic types A, B and C. These micrographs are characteristic of the entire volume of the UO_2 pellets, i.e. the pore structure typical in each case is formed very homogeneously.

UO_2 pellets of type A have very fine sinter pores which are chiefly located at the grain boundaries. The pores are round and have diam. between 0.05 µm and 5 µm. Fig 6 a) shows an electron micrograph of a UO_2 section. The Triafol replica method was used for this. Structure investigations following after-sintering showed that the number of pores decreases considerably with long annealing times, while the diam. of the individual pores increases. The increase in grain size with high temperature annealing is practically uninfluenced by the fine pores. On the other hand, the pores are displaced due to the migration of the grain boundaries.

The pellets of type B contain the main percentage of their pore volume in irregularly formed cavities arranged about areas with a low number of pores. These cavities form a network that is almost completely connected with the geometric surface of the pellets, as is shown from the porosity measurements. Fig. 6 b) shows in a very impressive form a detail of the pore structure of a B1 pellet. Thermally etched sections of pellets (type B2) are shown in Fig. 7 a) and Fig. 7 b). These micrographs show clearly the large range of the grain size distribution and the irregular shape of the larger pores. The stereoscan micrograph of a section (Fig. 8 a)) shows the bizarre shape of these pores. Isothermal annealing at 1800 °C leads to grain growth in areas without pores and to a rounding off of the larger pores.

Characteristic of the structure of the C1 and C2 types are large, approximately spherical pores which are produced by decomposition of the "AUC" powder and whose size is proportional to the sieved fraction of this powder (Fig. 5 c) and Fig. 5 d)). Method C also permits simple control of the pore size of the UO_2 pellets by the sieving of appropriate powder fractions of the "AUC" powder. Fig. 8 b) shows the characteristic pore morphology of the C type. The slight change in density of the type C pellets found during after-sintering was also confirmed in the structure investigations. The "AUC" pores remain stable on isothermal annealing and even display a tendency to increase in size with long annealing periods and high temperatures.

In summarizing the after-sintering behavior, it can be said that the disappearance of the fine sinter pores of < 1 µm was observed in the case of all types, so that in the temperature range of 1600 °C to 1800 °C under consideration we can expect stability of only the larger pores under isothermal conditions without even including the effects of irradiation.

3.4 Plastic deformation

At high burnup, fuel swelling leads to mechanical interaction with the cladding. Investigation of the plasticity of the fuel is therefore important. For temperatures above 1200 °C, at which thermal activation outweighs the irradiation influence on the mechanical properties of the fuel, these investigations can be made out-pile.

In a high-vacuum compression-creep testing apparatus numerous creep tests were made on UO_2 pellets of "medium" density [4]. The objective of the investigations was to clarify the effect of density reduction on the creep properties of the fuel and to determine to what degree the porosity of the pellets remains available for matrix swelling, despite plastic deformation. The most important results were as follows:

a) Even at high degrees of deformation (over 50 %) the density only increases slightly (e. g. from 90 % to 94 % of the theoretical density).

b) The reduced density influences the steady-state creep rate, compared with high density UO_2, only at a structure factor of the order of 1 to 5, while the stress and temperature dependency of creep is not influenced.

c) A stress-induced redistribution of the porosity takes place which is shown in Fig. 9. Note the compressed zones in the directions of the two diagonals. A porosity accumulation can be seen clearly at the edge of the deformed barrel-shaped creep specimen. The stereoscan micrographs show details of the UO_2 structure after a deformation of 35 % (reduction of the pellet length) at 1700 °C.

3.5 Moisture and "residual" gas measurements

In the case of UO_2 pellets of "medium" density, there is a danger of increased water and "residual" gas contents leading to a chemical reaction with the cladding and thereby preventing the attainment of a high burnup.

Since open porosities could lead to an impermissibly high water content when pellets are stored in air having a natural relative humidity, a series of moisture measurements were carried out. For these the carrier gas method of measurement was selected. The UO_2 pellets are flooded with dry N_2 at a temperature of 400 °C and the water vapour

carried along is split electrolytically in the measuring cell. We have determined the water content of UO_2 pellets with open porosity (types A and B) as a function of the relative humidity of the air, the temperature and the period of storage.

Two important results are shown in Figs. 10 and 11. The quantity of water adsorbed by the pellets at a relative humidity of 100 % decreases as the temperature increases (Fig. 11). The variation of the quantity of water adsorbed as a function of the relative humidity at constant storage temperature produces a curve (Fig. 10) that can be described by the Langmuir adsorption isotherm [5]. This suggests that the equilibrium value of the pellet moisture is brought about by monomolecular adsorption of the water on the surface of the UO_2 pellet which is open to the outside (especially in the open porosity). The deviations at higher relative humidities can be explained by capillary condensation and multi-layer adsorption.

"Residual" gas determination by means of hot extraction at 1650 ^{0}C (extraction time: 30 min) supplied the following typical results:

Types	Total gas [cm^3/g] 1)
A 2	3 - 5×10^{-3}
B 2	19 - 24×10^{-3}
C 1	5 - 12×10^{-3}
C 2	9 - 21×10^{-3}

The composition of the "residual" gas was likewise determined. A typical result is as follows:

H_2:	10	- 12×10^{-3}	[cm^3/g] 1)
N_2:	6	- 9×10^{-3}	"
CO:		1×10^{-3}	"
Total gas:	17	- 21×10^{-3}	"

4. CONCLUSION

The main results of this work can be summarized as follows:

1) s.t.p.

1) Three methods of fabrication produce UO_2 pellets having the required density range between 9.8 and 10.3 g/cm^3:

   A UO_2 powder with reduced sintering activity

   B UO_2 powder with UO_2 returns

   C UO_2 powder with the addition of ammonium uranyl carbonate.

2) Pellets of types A and B have a large percentage of open pores, while those of type C all have closed porosity.

3) On isothermal annealing, the percentage of open pores of types A and B decreases or disappears. Pellets of type C show the smallest degree of densification.

4) The structures of the three types A, B and C differ in a characteristic manner in respect of pore size distribution and pore morphology.

5) On plastic deformation, the major part of the porosity remains available for matrix swelling.

6) On the basis of the law of water adsorption and desorption, a drying process can be defined for moist UO_2 pellets with open pores.

An important factor to be considered in the evaluation of these results is that the investigations have largely been carried out on samples taken from large production charges. Thus the results are in no way coincidental, but are based on near fabrication conditions and in some cases already form part of specifications for fuel elements. For instance, UO_2 pellets with reduced density have already been used for fuel elements of the reactor for Stade Nuclear Power Station.

The working out of fabrication methods, the exact characterization of the pellets and the after-sintering and deformation tests form the basis for current irradiation tests. These in-pile experiments represent a continuation of the experimental program described and should lead to further optimization of the pellet properties in respect of the desired increase in burnup.

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TABLE I: INFLUENCE OF HEAT TREATMENT ON UO_2 POWDER CHARACTERISTICS (ANNEALING IN H_2)

HEAT TREATMENT	BULK DENSITY g/cm^3	FLOWING BEHAVIOR g/s 1)	SPECIFIC SURFACE m^2/g 2)	O:U RATIO
as received UO_2	2.1	poor	5.33	2.16
1000 °C-UO_2	2.2	4.6	4.48	2.04
1100 °C-UO_2	2.8	6.2	1.78	2.00
1200 °C-UO_2	3.0	7.4	1.89	2.01
1400 °C-UO_2	4.1	8.2	1.47	2.00

1) using a special funnel
2) B. E. T.

TABLE II: CHANGE OF PROPERTIES OF THE UO_2 POWDER USED FOR PELLET PREPARATION (ANNEALING IN H_2)

POWDER CHARACTERISTICS	AS RECEIVED UO_2	1300 °C-UO_2
BULK DENSITY g/cm^3	1.7	2.0
FLOWING BEHAVIOR g/s 1)	3.7	5.0
SPECIFIC SURFACE m^2/g 2)	4.38	3.24
STOICHEIOMETRY O:U	2.06	2.00

1) using a special funnel
2) B. E. T.

TABLE III: PELLET DENSITY, SINTERING TEMPERATURE AND COMPOSITION OF POWDERS OF THE SPECIMENS

SPECIMEN DESIGNATION		MEAN SINTERED DENSITY g/cm^3	SINTERING TEMPERATURE ^oC	COMPOSITION OF ADMIXED POWDER wt.%
A	A1	9.96	1700	UO_2 annealed at 1100 ^oC
	A2	10.33	1600	UO_2 annealed at 1200 ^oC
B	B1	9.81	1700	5 % grinding swarf 5 % U_3O_8
	B2	10.07	1700	10 % UO_2 returns
C	C1	10.15	1700	3 % "AUC" powder, particle diam. < 20 µm
	C2	10.10	1700	3 % "AUC" powder, particle diam. 32 - 37 µm

LIST OF FIGURES

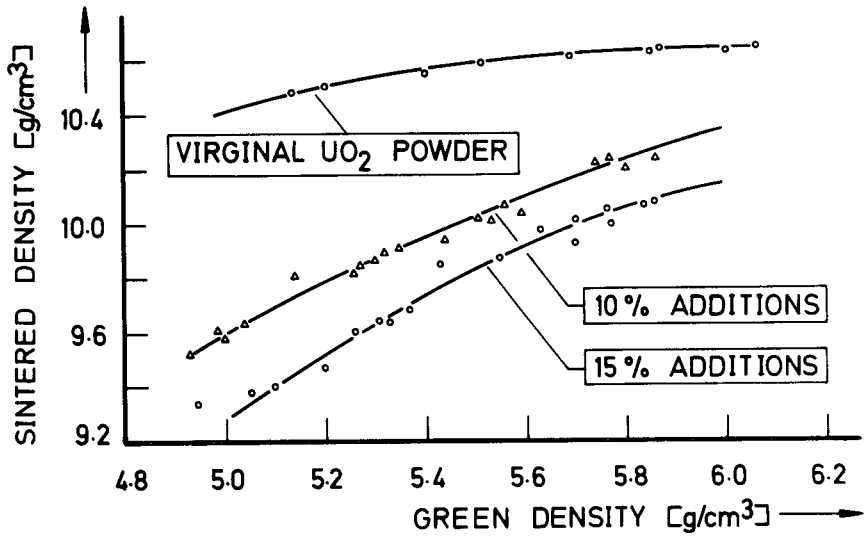


FIG. 1: Relation between green density and sintered density of UO_2 pellets with different percentage additions of UO_2 returns

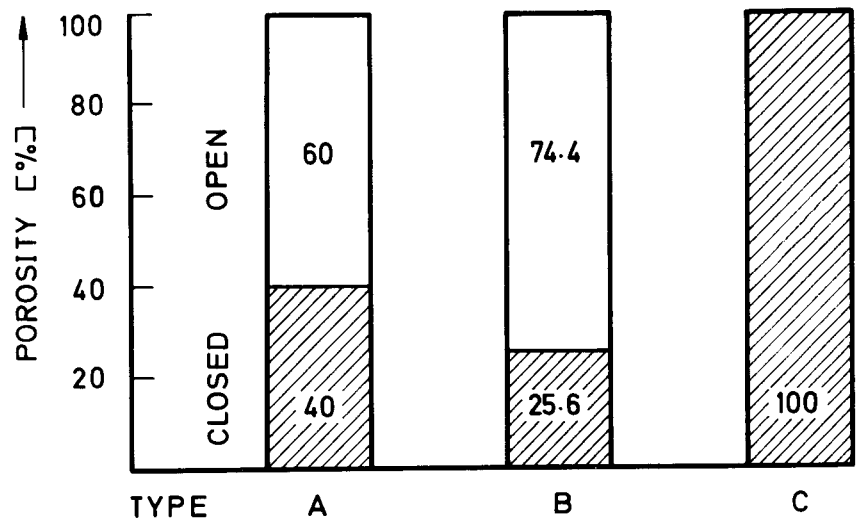


FIG. 2: Characteristic distribution of open and closed porosity of UO_2 pellets type A, B and C with mean sintered density of 10.1 g/cm^3

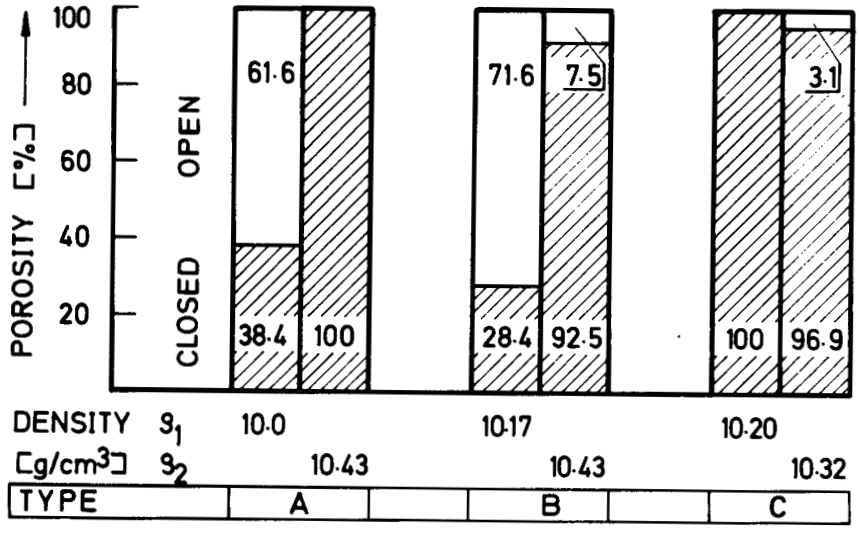


FIG. 3: Change in density and porosity of UO_2 pellets by isothermal annealing (80 h, 1800 °C)

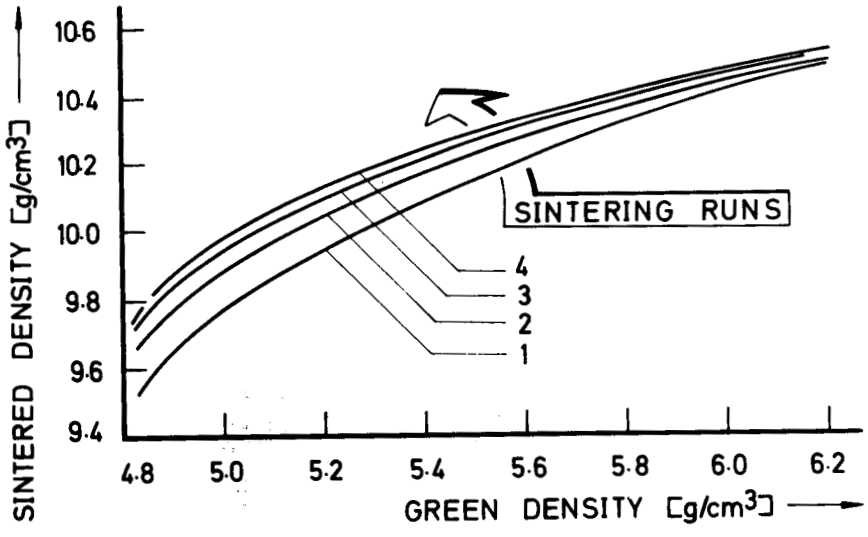
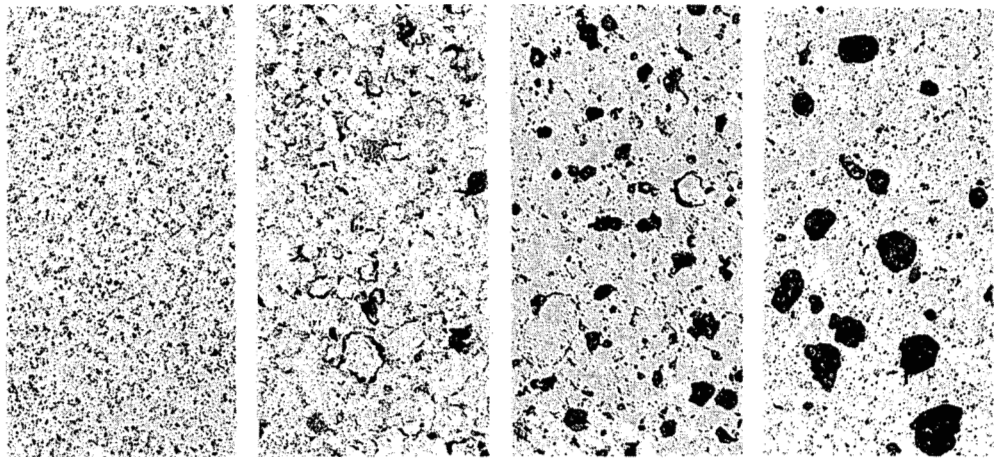


FIG. 4: Repeated sintering runs in a continuous sintering furnace



F G. 5: Comparison of the pore s ructure of UO_2 pellets a) type A1, b) type B1, c type C1 and d) type C2

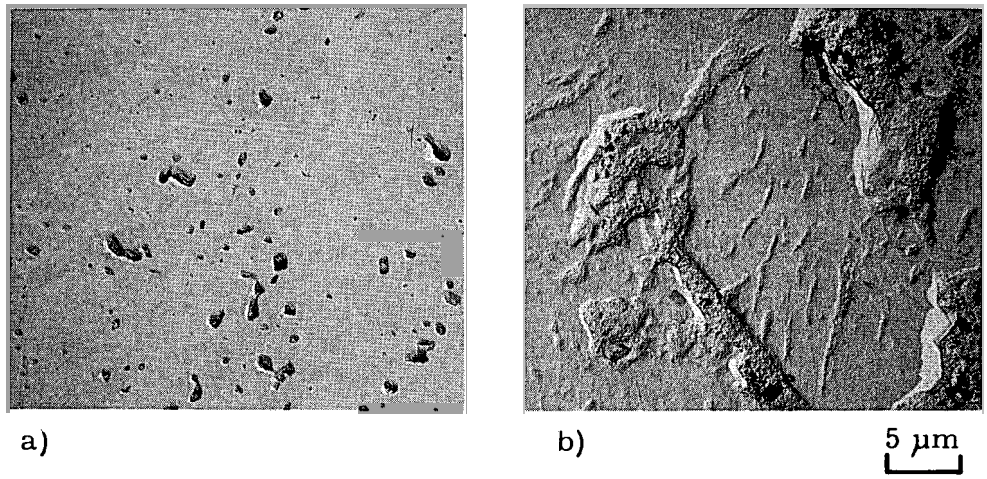


FIG. 6: Representative electron micrographs (replica method) from UO_2 specimens a) type A2 and b) type B1

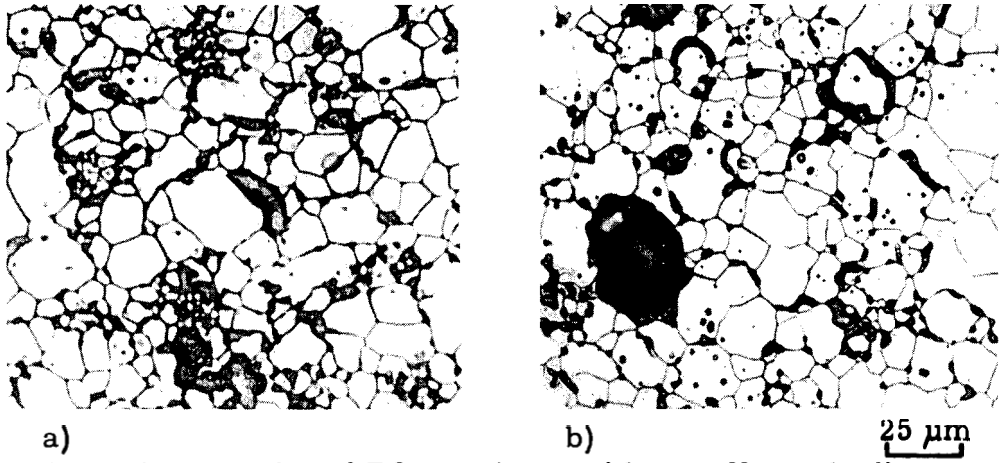


FIG. 7: Micrographs of B2 specimens (thermally etched) a) as received, b) treated for 2 h at 1800 °C in H_2

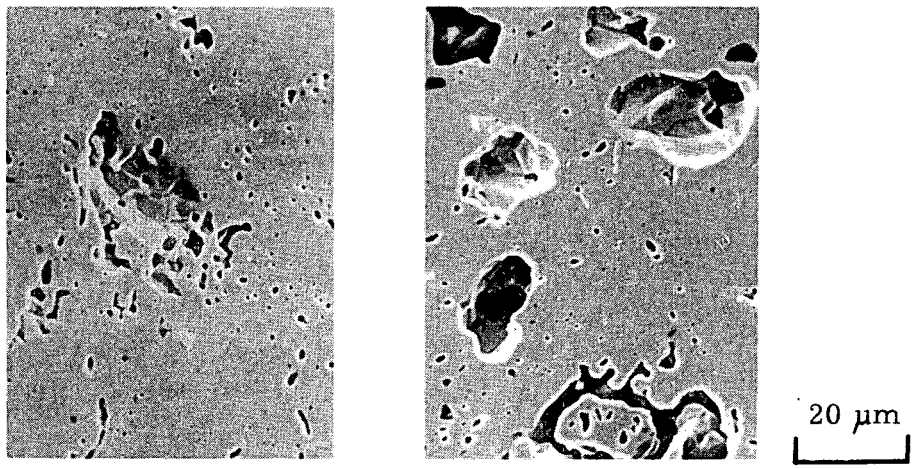


FIG. 8: Stereoscan micrographs a) of a B1 specimen, b) of a C2 specimen

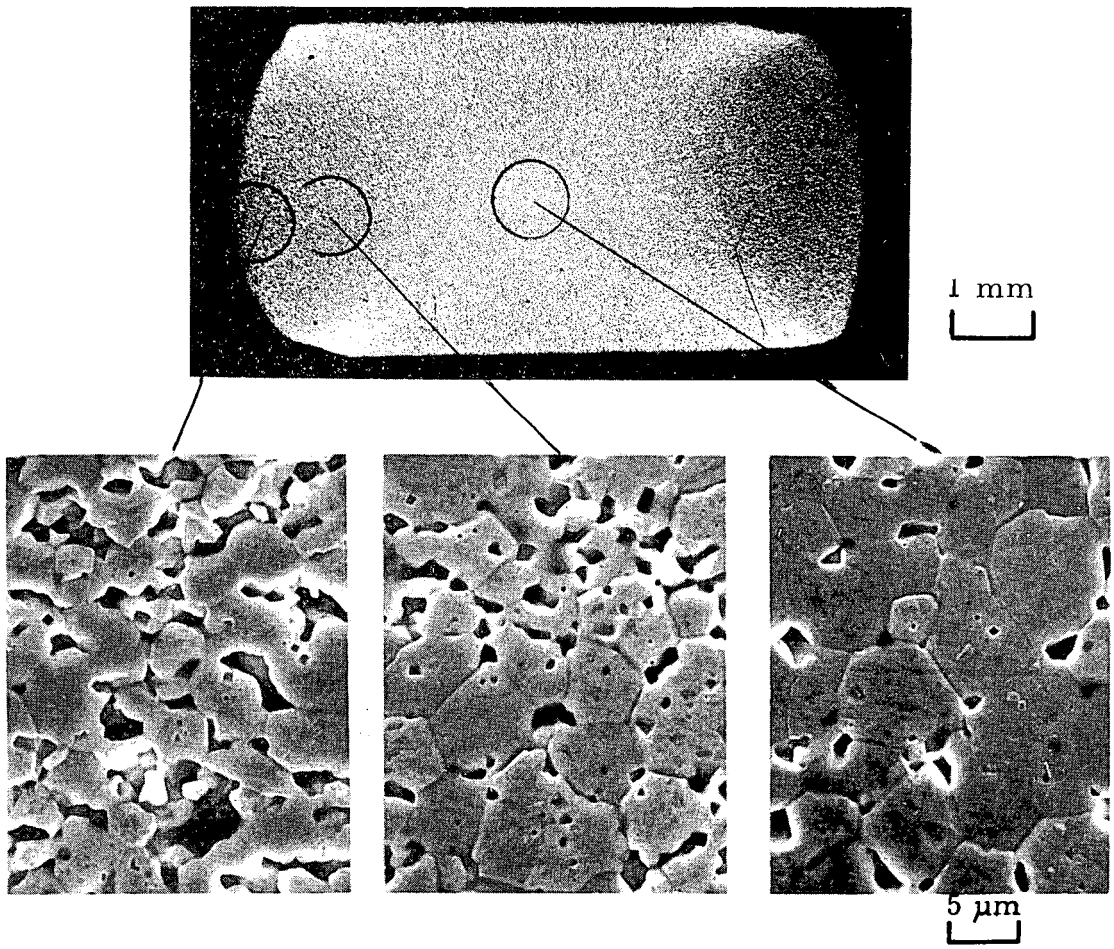


FIG. 9: Micrographs from a UO_2 pellet after compression testing (35 % deformation) showing grain growth and redistribution of pore structure

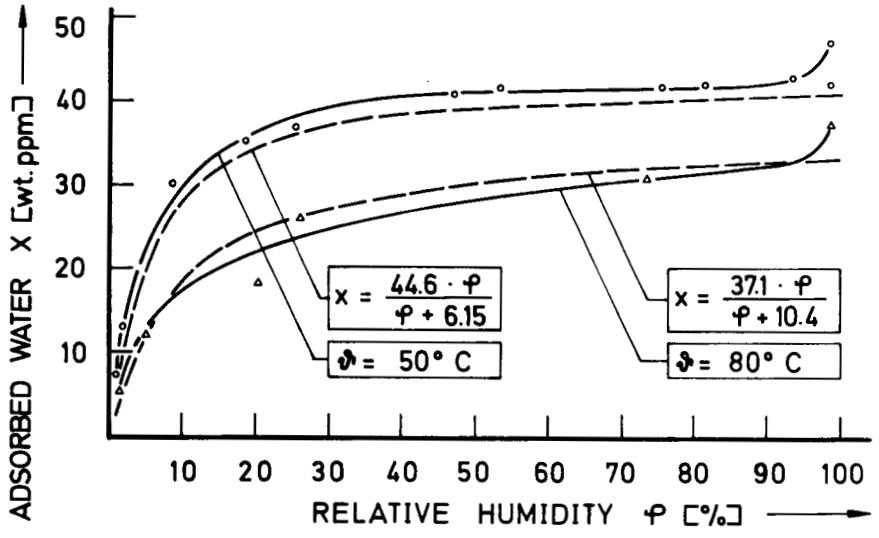


FIG. 10: Relation between adsorbed water x and relative humidity φ and comparison with Langmuir adsorption isotherms (pellet type B)

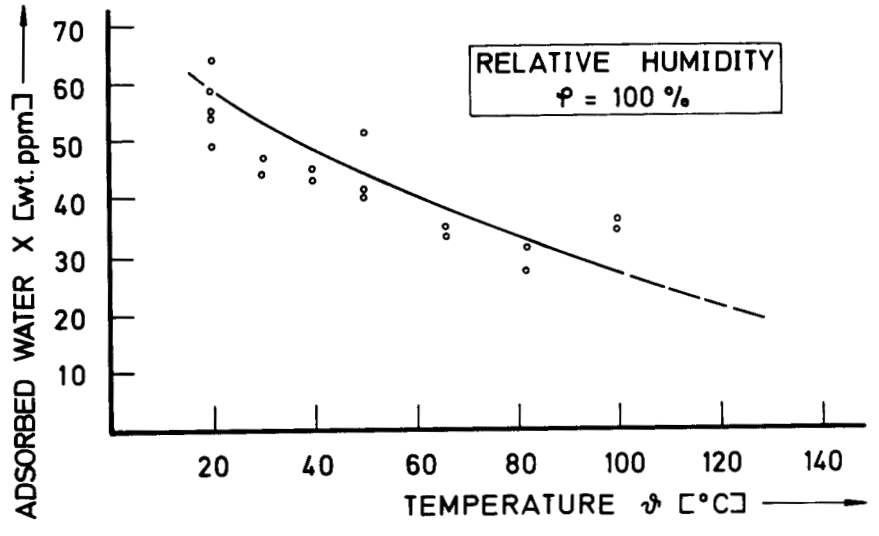


FIG. 11: Adsorbed water of UO_2 pellets as a function of the temperature of the atmosphere