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TECHNOLOGY DEVELOPMENT FOR THE POWER REACTORS FUEL ELEMENT PRODUCTION, AT THE INSTITUTO DE ENERGIA ATÔMICA – SÃO PAULO*

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ABSTRACT

The authors describe the work done at the Divisão de Metalurgia Nuclear of the Instituto de Energia Atômica on the technology of fuel elements fabrication

The obtained results in sintering UO_2 locally produced are discussed in relation to the problems found in the characterization of powders of the oxide The tests used comprise chiefly the BET Fisher and both transmission and scanning electron microscopy methods

Details of the Nuclear Ceramics Pilot Plant of the Instituto de Energia Atômica with relation to the programs to be considered in near future are also included

INTRODUCTION

In the development of UO_2 pellets technology aiming the fuel elements fabrication for PWR type power reactors in the future the Divisão de Metalurgia Nuclear of the Instituto de Energia Atomica has sistematically made experimental studies aiming the characterization of natural UO_2 powders its correlation with the properties of the sintered pellets and the selection of their important characteristics in the texture The characterization of the UO_2 powders produced in the Divisão de Metalurgia Nuclear from purified salts prepared in the Divisão de Engenharia Química seeks the necessary operational control and assures growing experience in this especialized technology The elucidation of the texture aspects in mainly related with the tolerances in the pellets dimensions to be kept up and with the level of permissible rugosity at their surfaces

Finally the data being obtained which constitute a increasing experience in the UO_2 pellet fabrication technology can be better evaluated when the results under irradiation which at present are in planning phase are known

As said before this task accomplished during the last eight years is oriented toward the solution of specific problems of fuel elements fabrication aiming the accumulation of an adequate know how for future expansions with basis in the adaptation and in the changes of technology for the standing conditions

A number of technical papers recently presented by the authors[2 5 13] to other Congresses both of metallurgy and of atomic energy has described details of the work done In this paper the authors resume the main results obtained and go over the data related to the finishing characteristic of the pellets and their textures

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(*) Presented at the III Inter American Conference on Materials Technology August 14-17 1972 – Rio de Janeiro GB

PROPERTIES OF THE UO_2 POWDERS

Natural UO_2 powders utilized until the present in experimental work have been produced at the Divisão de Metalurgia Nuclear from ammonium diuranate of high purity prepared under different conditions, by the Divisão de Engenharia Química. Due to close link between the two Divisions it has been possible to adjust the precipitation conditions of the salt in order to assure firmly the desired characteristics for the UO powders. This articulation is assuring appreciable improvements on the characteristics of that salt and of the UO_2 powders resultant from the different qualities of it in order to meet the specifications which have been set up progressively.

In a initial step the process of treatment was essentially based upon the utilization of the ion exchange process in a uranyl sulphate solution. Although all the characteristics of the powders resultant from this procedure were quite satisfactory this type of ammonium diuranate retained a certain proportion of ion sulphate resulting special characteristics for the powders not only for the sintered pellets but also for the dispersion in the U_3O_8 form used in the fuel element plates.

More recently this process was changed by a solvent extraction method utilizing aqueous uranyl nitrate solution.

The calcining and reducing variables mainly time temperature heating and cooling time rates and time at a lower temperature in the water cooled region of the hydrogen reduction furnaces determine together with the intrinsic properties of the uranium salt their physical and physico-chemical properties and as consequence their sinterability.

The uranium oxides utilized in the development of this work were prepared always from uranium salts produced in the IEA by three different conditions as follows: one called UO_2 type N prepared through the precipitation of aqueous uranyl nitrate solution in a pH near seven the UO_2 type S resulting from ammonium neutralization at 60°C in a pH near 7. In general these salts are previously calcined to U_3O_8 although this technique was not followed in the case of the UO_2 type S which is prepared only by hydrogen reduction at 650°C during one hour. In the other cases calcining operation has been carried out at 500°C for three hours followed by hidrogen reduction at 750°C for one hour both in the cases of UO_2 type N and of UO_2 type D prepared from dissociated ammonia. These marked differences of origin and of treatment determine some properties too much different for the UO_2 powders as it will be shown later.

CHARACTERIZATION TESTS OF THE POWDERS OF URANIUM OXIDES

The most utilized tests are the following:

1) Particle density – The used process is similar to be one developed at Oak Ridge National Laboratory [14] for the determination of the density of UO_2 particles. The equipment is composed mainly of a 20 ml pycnometer thermometer charging tube and vacuum chamber for the introduction of mercury. When U_3O_8 is utilized toluene is used instead of mercury.

2) Average particle size – It is utilized the Fisher Sub Sieve Sizer equipment. The instrument has a device to press the powder to a certain porosity level when air is introduced. The air is supplied by a small compressor through the sample. The resultant head loss is measured by an water manometer. This equipment gives reproducible results in the range of 0.2 to 50 μ.

3) O/U Ratio – The utilized process for the determination of the value of the O/U ratio is analytical and based upon the determination of the contents of total U and hexavalent U respectively.

4) Surface Area – The values of the surface areas of the UO_2 powders were determined through a CG model 10 equipment as shown in figure 1. It makes essentially use of the dynamic method for adsorption initially developed by Nelsen and Eggertsen[4] where a mixture of nitrogen and

helium flows steadily through one layer of the sample the composition of the flowing gas is determined by measurements of thermal conductibility being registred the areas corresponding to adsorption and desorption peaks in a integrator recording potentiometer In order to calculate the saturation pressure of the nitrogen value at around minus 196°C it was used a thermometer of oxygen saturation pressure made at the Divisão de Metalurgia Nuclear with this equipment it is possible to register temperature variations of less than 0 05°C in the liquid nitrogen bath

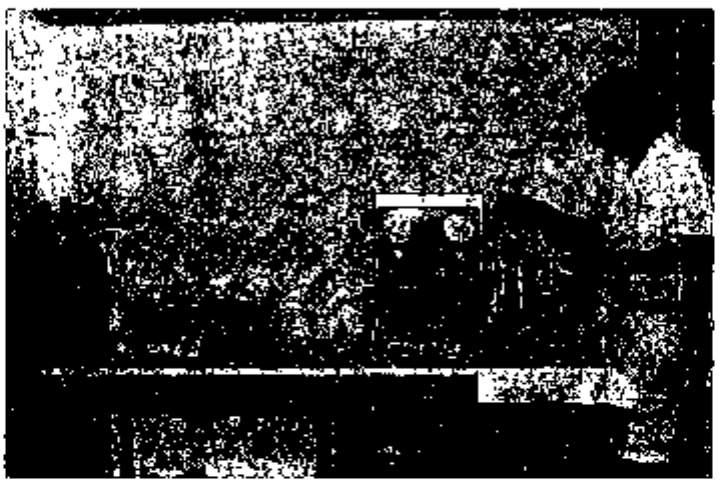

Figure 1 — Surface area determination apparatus used for UO_2 powders

6) X Ray diffraction — In certain cases the control utilizes X ray diffraction data obtained in a Rigatu unit by the powder method

6) Optical microscopy — The examinations are done with powders dispersed in alcool on a glass plate at the metallographic microscopy Leitz MM 5 In order to have uniform dispersions they are obtained by ultrasonics during five minutes

7) Electron microscopy — Different types of powders have been examined under electron microscope and these examinations have been done at the Centro de Microscopia Eletronica of the Instituto de Física Universidade de São Paulo in a electron microscope Siemens-Elmiskop 1 carbon replicas preshadowed with platinum are used To study the textures of the sintered pellets the Divisão de Metalurgia Nuclear has a Cambridge Stereoscan unit model S 4 Such apparatus is being completed with equipment for a two channel X rays spectrometer and a converter connected to a microanalysis recorder

8) Differential thermal analysis — The data of differential thermal analysis have been of great utility to characterize the powders These tests are done at the Divisão de Química do Instituto de Pesquisas Tecnológicas

OBTAINED RESULTS

Table I presents the values of obtained results for the surface areas of the three types of powders These values indicate a satisfactory sinterability according to the results obtained by Carpenter[1] by one of the authors[3]

Table I

Surface Area Bulk Density and O/U Ratio for the Uranium Oxides (After Reduction)

Material	Surface Area ($m^2\ g^{-1}$)	Bulk Density $g\ cm^{-3}$	O/U Ratio
UO_2 N	2 7	1 44	2 04
UO_2 S	2 5	1 51	2 06
UO_2 D	1 9	1 24	2 01

Table II shows the results of a typical sizing analysis of the powders as reduced and after milling during 1 and 5 hours in a cylindrical mill 130 mm in diameter placed on rollers that with speed of 85 cm s^{-1} with 12 5 mm diameter steel balls

Table II

Milling Effect on the UO_2 D for Differents Operations Times

Typer s Screen	Weight Retained Percentage		
	0 h	1 h	5 h
20	70 1	0 4	0 2
65	13 6	52 8	84 9
100	5 3	28 1	2 8
150	6 0	12 7	6 3
200	3 7	3 9	2 9
200	1 3	2 1	1 9

Both the type N and the type S UO_2 were easily classified under -20 mesh Type D powder however after the reduction presented lumps of about 40 mm Milling of this material in rubber lined cylindrical mills during 6 hours did not permit to improve substantially its grain size classification destroying only the large agglomerates Therefore in the case of type D UO_2 it was necessary to modify the milling conditions

Different samples of domestic uranium salts besides the ones of UO_2 produced by the authors at the Divisão de Metalurgia Nuclear were taken to sinterability tests in hidrogen at Argonne National Laboratory It was then shown that the pellets produced met the current U S specifications for powder sinterability It was necessary consequently to establish later on the know how for the sintering UO_2 in hydrogen atmosphere in order to get high density pellets It is convenient to emphasize that this is the utilized process in all industrial plants for the production of millions of pellets which are being utilized in the nuclear power reactors

The morphology of the powders of UO_2-D as reduced is being studied through scanning electron microscope The utilized microscope (figure 2) recently installed at the Divisão de Metalurgia

Nuclear of the IEA (september 1971) has permitted also some morphologic studies of preliminar character for the UO_2 N and UO_2 S oxides Initially examinations were done in the ceramic particles without giving any metallic coating at low tensions as 1 to 2 kV later tensions up to 5 kV were used without development of excessive loads at the surface of the samples through the utilization of anti static fluid (Testenal Photowerk Hamburg) At present some sample are being prepared to receive a Au Pd film which enables one to use tensions up to 30 kV

Figure 2 – Scanning electron microscope made by Cambridge Instrument Co model S-4 installed at Divisão de Metalurgia nuclear

The preliminary examinations were done with 2000 X for powders of −325 mesh They presented the UO_2 D as compact agglomerates formed by round grains with small amount of pores The UO_2 S presented also too dense agglomerates but their constituent grains were large and surrounded by a lot of large pores The UO_2 N showed also some agglomerates but presents smaller grains and less pores than in the two previous cases

Under sinterability standpoint it is important to know the morphologic of the particles forming the agglomerates For this objective it is important to coat the powders with metallic films which permits to reach tensions of the order of 20 kV with the possibility of resolutions better than 200Å

PRESSING AND PRE-SINTERING

For the sintering tests of the produced powders compacts of 10 mm diameter were produced in a double effect die The applied load were correspondent to the pressures of 1 and 1 5 ton/cm^2 the authors tried to obtain the largest values of density without the existence of surface flaws

The powders of types S and N needed frequently a previous operation of pre pressing at higher pressures between 1 5 and 2 5 ton/cm^2 Only through this way it was possible to get pellets for such powders without surface defects and with densities larger than 4 5 g cm^3

In order to remove progressively the agglomerate it was used a pre sintering furnace in a nitrogen atmosphere This furnace has eight zones of independent control of temperature and the operation reached 500°C at the hottest zone where the pellets stayed at this temperature for 60 minutes

Table III shows the densities data obtained

Table III

UO_2 Pellets Density (After Pre-Sintering d_{ps})

UO_2 powders	d_{ps} g cm^{-3}	d_t %
N	5 15	47 0
S	5 01	45 6
D	4 55	41 5

SINTERING OF THE PELLETS

Two furnaces were utilized for the development of the sintering operations in a hydrogen atmosphere The first used (figure 3) had a cylindrical muffle of alumina surrounded by a molybdenum wound electrical resistance Its hottest zone reached 1670°C for 60 cm in length The second furnace of Tammann type (figure 4) had a graphite muffle reaching 1600°C for 80 cm in length in this case the pellets were surrounded by powdered alumina and placed in graphite boats

Figure 3 — Hedin furnace used for the sintering test at 1625°C with hydrogen atmosphere This furnace use a molybdenum resistor for heating

Figure 4 — Tammann type furnace used for sintering tests at 1625°C under hydrogen The muffle is surrounded by the graphite tubular resistor

It was noted that after 1200°C the UO_2 pellets suffered a severe attack in the Tammann type furnace At 1600°C there was some desaggregation of the external layer of the pellets up to 2 mm deep this occurence being studied now by the authors could be explained due to the formation of uranium carbides on the sintered pellets and its later interaction with the hydrogen and the humidity existing at the furnace atmosphere

It is to be noted the graphite resistors of Tammann furnaces is very much affected by the temperature The cumulative experience in utilizing these furnaces shows that the resistors life increase from six hours at 1600°C to some ten hours at 1400°C For these reasons, this type of furnace is used only for operations requiring temperatures less than 1400°C

On the other hand the alumina muffle furnace heated by molybdenum resistors has shown a very efficient operation but its W—WRe thermocouple only lasts about 2 hours when their tips are exposed to the furnace atmosphere The temperature control has been made through a optical pyrometer and the W—WRe thermocouples are used only for calibrations of the optical pyrometer

The hydrogen flow in this furnace is used to be about 12 1/min which is equivalent to about 0 2 1/min cm^2 of transversal section muffle area

It has been observed that flows less than 0 2 1/min cm^2 caused parcial oxidation of the UO_2 N

The densities of the pellets sintered in this furnace correspond to 94 3% of the theoretical density This value satisfy the N 5 North American and Canadian specifications

The pellets present a very good surface in the sintered state Some surface defects are eliminated by a centerless grinding

Although the UO_2-S and UO_2 D powders gave high density pellets they should be used for the sub-critical assembly or for low power critical reactors If these oxides therefore are submited to a comminution operation and pre-compacting under 1 5 t/cm^2 pressure they are likely to provide pellets with densities about 98% of theoretical densities

Table IV presents UO_2 pellets densities sintered at 1625 ± 25°C for 4 hours

Table IV

UO_2 Sintering Pellets Densities (d_s)

UO_2 powders	d_s g cm^{-3}	d_t %
N	10 33	94 3
S	10 17	92 8
D	10 08	92 0

A polished section study of UO_2 pellets was examined under a Leitz Orthoplan ceramographic microscope The microstructure observed in in agreement with the Canadian MET-67specifications

Some other observations were made by the scanning electron microscope Stereoscan S-4 (figure 2)

Figure 5 shows the external surface of a UO_2 D pellet without polishing with 1455 times magnification This pellet presented sintered density of 10 25 g/cm^3 and was obtained with 20 others sintered at 1625°C for 4 hours in the Hedin furnace The heating rate was about 140°C h^{-1} and the cooling rate was 300°C h^{-1} The micrograph obtained by the scanning electron microscope shows a good sintering and no defects in grain boundary

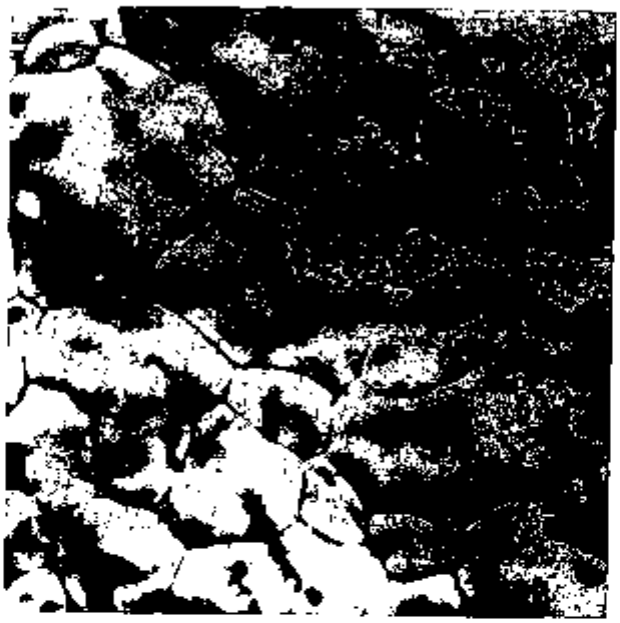

Figure 5 — Pellet surface without polishing sintered at 1625°C for 4 hours under hydrogen atmosphere in the Hedin furnace made by UO_2 D powder (1455 X) The micrograph obtained by a scanning electron microscope shows the perfect sintering and the grain boundaries without flaws

Figure 6 presents the surface of a fractured pellet obtained in the same conditions above specified It was made with UO_2 N powder Observe the UO_2 grain fineness

Figure 6 — Surface examination of a fractured pellet obtained in the same condition of that pellet of figure 5 made with UO_2 N powder (1299 X) Note the fine grain texture of this UO_2 pellet

PELLETS SURFACE GRINDING

The clearance between the cylindrical surface of pellets and the internal surface of the canning tubes is so small that surface grinding by a centerless machine is necessary

For the two projects being develloped at the Divisão de Metalurgia Nuclear the following limits have been set

a) maximum surface rugosity 2

b) maximum diameter deviation 0 01 mm

There are also some other requirements on the surface finishing of the pellet basis

The sintered pellets are ground in three centerless grinders locally built

The values obtained are referred to a single centerless grinder although when in experimental production the three ones will be used

The grinding operation was made by vertical introduction because of the small number of test pellets With a single pass the mean pellet diameter of 8 30 ± 0 06 mm was reduced to 8 202 ± 0 006 mm These pellets were made by UO_2 N powder and have presented 510 kg/cm^2 of Knoop hardness (Test with 100 g load) The mean grain size was 15 7 microns

The grinding operation in present Pilot Plant operation will be carried out with three machines in series thus avoiding severe passes which would cause surface craks Experiences made in order to verify the influence of the severity of a pass on the surface cracks showed that reductions about 0 4 mm may cause these cracks which could be observed with a 5 x magnifying glass

The surface roughness of the ground pellets has been studied with scanning electron microscope making comparison between the electrical signals emitted from the ground surface and the ones emitted from a Knoop indentation These first results showed that roughness is less then two microns The figure 7 shows the pellet surface fractured by Knoop indenter penetration (1083 x of magnification) This picture obtained by scanning electron microscope makes evident the intrinsic great brittleness of UO_2 S in comparison with the other two kinds of powders UO_2 D and UO_2 N

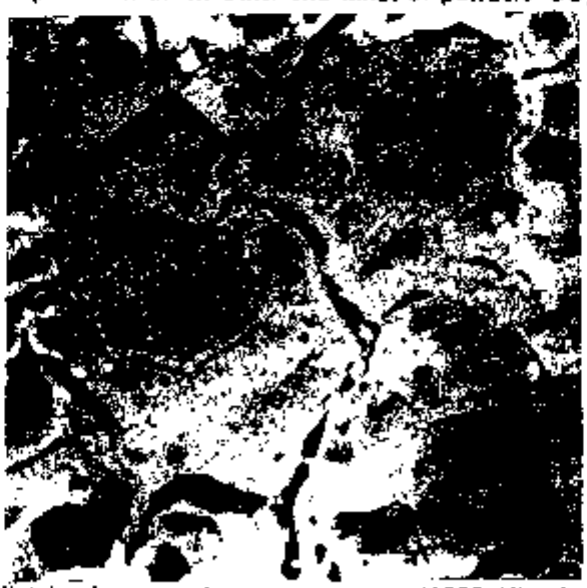

Figure 7 — Fractured pellet by knoop indenter penetration (1083 X) obtained by scanning electron microscopy This micrograph shows the UO_2 -S inherent brittleness

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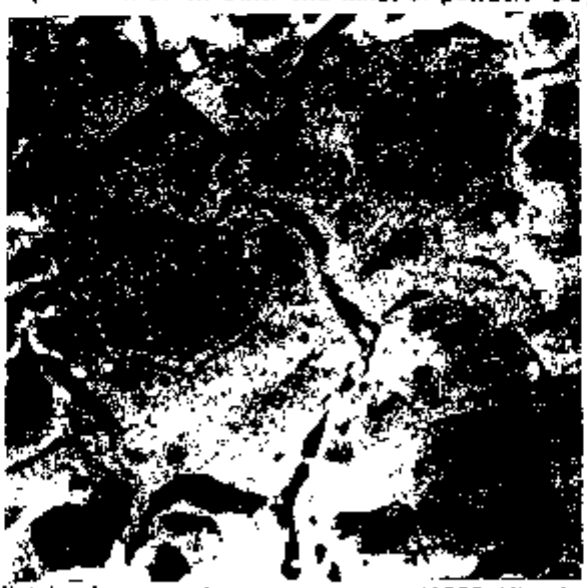

Figure 7 — Fractured pellet by knoop indenter penetration (1083 X) obtained by scanning electron microscopy This micrograph shows the UO_2 -S inherent brittleness

CONCLUSIONS

1) The Divisão de Metalurgia Nuclear has been performed extensive studies on the influence of some UO_2 powders properties on the manufacture of sintered UO_2 natural pellets at 1625°C under hydrogen atmosphere UO_2 pellet fabrication within specified density surface quality and dimensional reproductivity are the objetives of these studies

2) The manufactured powders show wide differences in their characteristics as reflected by the values of particle density particles average size O/U rate surface area and texture observed by optical microscopy and scanning electron microscope and in some cases by examination by X Ray difraction and thermo differencial analysis

3) The sintering tests made with type N UO_2 powders at 1625°C for 4 hours have given average densities of 10 33 g/cm^3 This value is equivalent to 94 3% of UO_2 theoretical density The pellets density manufactured under the same conditions with types S and D powders were 10 17 and 10 08 g/cm^3 respectively which correspond to 92 8 and 92 0% of UO_2 theoretical density

4) The main results obtained by scanning electron microscope powder examinations were presented These results showed large structural differences among those powders

5) The pre sintered pellets behaviour during sintering operations at 1625°C for 4 hours in hydrogen atmosphere proved that the type N UO_2 powder was the best, due to the density values and surface quality obtained

6) The ceramographic study of UO_2 pellets was done with a Lertz Orthoplan microscope The UO_2 pellets satisfied the specifications used

RESUMO

Os autores descrevem o trabalho realizado na Divisão de Metalurgia Nuclear do Instituto de Energia Atômica na tecnologia de fabricação de elementos combustíveis

Os resultados obtidos na sinterização de UO_2 produzidos no próprio Instituto são discutidos com relação aos problemas encontrados na caracterização dos pós desse óxido Os ensaios usados compreendem principalmente o de BET o de Fisher e os de microscopia eletrônica de varredura e de transmissão

Também são incluídos detalhes da Usina Piloto de Cerâmica Nuclear do Instituto de Energia Atômica relacionados com os programas a serem desenvolvidos em futuro próximo

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