SINTERING OF URANIUM DIOXIDE: INFLUENCE OF THE CHARACTERISTICS OF THE POWDERS

H. M. HAYDT, J. D. T. CAPOCCHI, I. NISHIOKA, R. P. A. BUENO, E. F. GENTILE, S. H. L. CINTRA and T. D. S. SANTOS

SINTERING OF URANIUM DIOXIDE: INFLUENCE OF THE CHARACTERISTICS OF THE POWDERS*

H. M. Haydt, J. D. T. Capocchi, I. Nishioka, R. P. A. Bueno,
E. F. Gentile, S. H. L. Cintra and T. D. S. Santos

Departamento de Metalurgia Nuclear
Instituto de Energia Atômica
São Paulo - Brasil

SINTERING OF URANIUM DIOXIDE: INFLUENCE OF THE CHARACTERISTICS OF THE POWDERS

H. M. Haydt, J. D. T. Capocchi, I. Nishioka, R. P. A. Bueno, E. F. Gentile, S. H. L. Cintra, and T. D. S. Santos

ABSTRACT

The purpose of this paper is the characterization of the UO_2 powder produced from ammonium diuranate of different conditions of precipitation, prepared in the Instituto de Energia Atômica, São Paulo, Brazil. The UO_2 characterization includes the determination of the set of physical and chemical properties of the material, affected largely by the preparation methods and, so, have a marked influence on the characteristics of pressing and sintering capability of the pellets and its perfomance as solid fuel. Emphasis is given to the importance of the differential thermal analysis, surface area measurements and O/U ratio. Other properties as, shape and texture of the particles and porosity of the sintered pellets accomplish these informations. Sintering operations realized at 1400°C in argon atmosphere, for 4 hours, corroborated the data foreseen and established by the characterization tests of the uranium dioxide.

INTRODUCTION

The Divisão de Metalurgia Nuclear of the Instituto de Energia Atômica, São Paulo, Brazil, has published the results of some research papers on UO_2 pellets for reactor fuel elements [1-7], besides others on uranium compounds and alloys for the same utilization.

The purpose of this paper is the characterization of the UO_2 powder produced in the division, from ammonium diuranate prepared in another facility of the Instituto, the Divisão de Engenharia Química, by different methods, including also different conditions for the precipitation.

The UO_2 characterization includes the determination of the set of physical and chemical properties of the material, affected largely by the preparation methods and so, have a marked influence on the characteristics of pressing and sintering capability of the pellets and its performance as solid fuel.

ANALYSIS OF THE FACTORS AFFECTING THE SINTERABILITY

The characterization tests are essential in determining the control and the best conditions of the processes for UO_2 production. Stenquist et al [8] presented in 1957 a correlation between surface characteristics and sintering behavior of uranium dioxide powders. The results showed that: 1) UO_2 powders from various sources had a wide variety of surface characteristics; 2) surface area values depend upon both particle size and surface texture; 3) surface area and average diameter can be used as a measure of the sinterability of UO_2 powders.

Clayton [9] noted that the physical properties that are important to the UO_2 powders are: density, microstructure, surface properties (mainly the surface area), particle size distribution and shape. The chemical characteristics are: deviation of the stoichiometric

composition, oxidation resistance and chemical reactivity.

In the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, principally Murray and Williams [10], Belle [11], Chalder et al. [12], Runfors et al [13] and Bel and Carteret [14] characterized in their papers the powders they use, emphasizing respectively the following properties and tests: air stability and factors affecting O/U ratio; particle size, O/U ratio and surface area; chemical analysis, surface area, particle size, O/U ratio and differential thermal analysis; morphology, grain size and surface area, whose measurements were compared with electron micrographs; and O/U ratio; surface area and identification of the phases present by X-rays.

Due to the importance of both physical and chemical properties of the UO_2 powder upon its sinterability and in order to establish the necessary control methods for the production of pellets to be used in power reactors, a meeting on "Characterization of Uranium Dioxide" [15] was held at Oak Ridge, Tennessee, in 1961.

Although the UO_2 characterization may be studied by all the above tests, it is emphasized in this paper the importance of the following ones: differential thermal analysis, surface area measurement and O/U ratio determination. These tests are the most significant to the description of the material behavior not only during the phases of the oxide preparation but also to its performance as nuclear fuel. Other properties as grain size, shape and texture determination revealed by electron micrographs and surface porosity of the sintered pellets, shown by optical microscopy, accomplish these informations.

The differential thermal analysis presents two exothermic peaks, showing the first one the change of UO_2 to U_3O_7, while the second peak shows the change of U_3O_7 to U_3O_8, according to studies carried out by a number of workers [12,16,17,18]. In order to exist the test reproductibility, it is necessary to keep constant the factors affecting the shape of the two peaks of the thermogram. These factors are: heating rate, initial O/U ratio, grain size distribution and surface area.

According to Scott and Harrison [19], there is only one exothermic peak when the surface area is less than $0.05 \ m^2/g$, not showing the change to U_3O_7.

Taylor [16] observes that highly active sinterable powders typically show a U_3O_7 peak between 150 and 180°C. This behavior is typical of powders made at low reduction temperatures from fine-grained precipitates. It is observed also that when the U_3O_7 peak occurs at temperatures progressively higher than 180°C, the powders, when subjected to a standardized sintering test, become less and less sinterable.

Chalder el at [12] noted that the first stage UO_2 - U_3O_7 takes place at a temperature which is markedly dependent on the particle size of the material; the second stage, U_3O_7 - U_3O_8, occurs at a temperature much less dependent on the nature of the starting material. The difference between the temperatures at which the two stages occcur is thus a good measure of the sinterability of the oxide. High percentages of the theoretical density are so correlated to a DTA peak separation between 150 and 200°C.

The effects of the surface area and of the particle size, which are the two most important

physical properties of UO_2 powders, were correlated by Stenquist el al [8], as above, and for a same sintering time, the sinterability increases with the ratio of surface area to average particle diameter of the powder, that is, higher will be the surface area, better will be the sinterability while the powders with small average particle diameters will have greater sinterability than the others with large dimensions.

The sinterability of UO_2 powders is, in that manner, predicted by the determined surface area values.

According, yet, to Chalder et al [12], a powder consisting of small particles, of the order of $1\,\mu$ or less, can be sintered readily to densities in excess of 95% of the theoretical value of 10.96 g/cm^3. Under the same sintering conditions, a material having a particle size of 50-100μ would yield densities of only 70% theoretical. Results included in that paper show that sintered density values higher than 10.44 g/cm^3 are reached when the surface area of UO_2 powders is in the range of 5-8 m^2/g.

The UO_2 powders present different values of surface area according to the used process to reduce the oxide and to the conditions of precipitation of the original salt.

Thus the chemical precipitation process of the ammonium diuranate and its reduction to UO_2 may be controlled by surface area measurements.

An accurate control of the O/U ratio is also necessary during the fuel fabrication. The uranium dioxide has poor air-stability changing to higher oxides, even at room temperature. The change in the oxigen content affects the sintering and the thermal conductivity behaviors. The nonstoichiometric composition plays a definite part in the sintering of the oxide while on the other hand, the thermal conductibility is reduced. By Kingery et al. [20] if the thermal conductibility of $UO_{2.00}$ will be taken as 100, the correspondent values for oxides with O/U ratios of 2.08 and 2.16 will be respectively of 67 and 38. The influence of the nonstoichiometry on both the sinterability and the thermal conductivity is based upon the fact that the departure from stoichiometry presents defects in the crystal lattice. These defects, by one hand, improve the sintering mechanism [21,22,23] but, on the other one, decrease the thermal conductibility [24].

The authors consider, with basis in the above mentioned literature, that the oxides having O/U ratios between 2.06 and 2.16 can take to high density pellets with improved thermal conductibility.

It is possible, finally, to make a correlation of O/U ratio with the particle size and the surface area of the oxide, shortly after reduction. A material of fine particle size will attain, after reduction, a higher oxygen uranium ratio on exposure to air, and will attain it more rapidly than a material of coarser particle size and lower surface area. For example, a material with a one-micron particle size will reach an O/U ratio of approximately 2.20 after two weeks time, whereas a material with a particle size of 50-100 μ, after reduction under identical conditions, will attain a ratio of only 2.03-2.04 in the same time and an extremely fine powder (0.1 μ diameter or less) is pyrophoric on exposure to air at room temperature and oxidizes to U_3O_8 [12].

The departure from stoichiometry of the uranium dioxide may be correlated, in a similar way, with the surface area of the powder, shortly after reduction. Bel and Carteret [14] note that it is posssible to foresee the O/U ratio as a function of the powder surface. According to their experiments, for higher values of the surface area, higher will be the O/U ratio. Their results show, for example, the O/U values of 2.00, 2.21 and 2.29 respectively, for surface areas of 1.2, 10.5 and 19.0 m^2/g.

As mentioned above, the average diameter of the particles can be used as a measure of the sinterability of UO_2 powders [8]. According to Ainscoug [25], the average diameter can be determined by different ways, as by air or liquid sedimentation, by β-back scaterring or by electron micrograph countings. According to him, all three methods are hard ones and not so effective due to the agglomerates. The measurements will be always defective and have no good reproductibility. Powder agglomerates, surface texture, and particle size and shape are easily observed with the electron microscope [8].

The morphology of the particles permits to foresse the pore size distribution and the easiness of a network formation, impairing the powder compactability. According to Muller[26], this pore size distribution in the pellets affects greatly their sintered density.The spherical shape is the best one for pressing and sintering behavior.

The particle texture can be used both to give an idea of the surface area and of the degree of easiness to decrease the average diameter by comminution processes.

Both the morphology and the texture of UO_2 powders are normally observed by electron microscopy.

EXPERIMENTAL PROCEDURE AND RESULTS

The samples of uranium dioxide for the different tests were produced from ammonium diuranate prepared at the Divisão de Engenharia Química of the IEA to be used in nuclear fuels. Two ammonium diuranates of different processes of fabrication were used. One, designated as DUA—N, was precipitaded from aqueous uranyl nitrate solution, purified by solvent extraction method. The second one, DUA—S, was prepared from uranyl sulphate solution, purified by ion exchange process.

From each of the batches of both salts, samples were taken to represent the DUA—N and the DUA—S. These two portions were ground in mortar and classified as -100 mesh.

The resultant powders were, then, calcined at 500°C, for 3 hours, giving by pyrolisis of the original ammonium diuranate, mixtures of higher uranium oxides, called here, calcined, corresponding, mainly to UO_3 and U_3O_8.

The two calcined powders were, later, reduced by hydrogen, at 900°C, for 3 hours, the final product being a uranium dioxide of nonstoichiometric composition and of the type UO_{2+x}.

In order to avoid a gradual oxidation of the reduced powders, they were kept in rubber balls, in argon atmosphere, shortly after removed from the reduction furnace. Besides, some

Fig. 1 - Morphology of the calcined DUA-N agglomerates. The light agglomerates are UO_3 and the dark ones are U_3O_8.
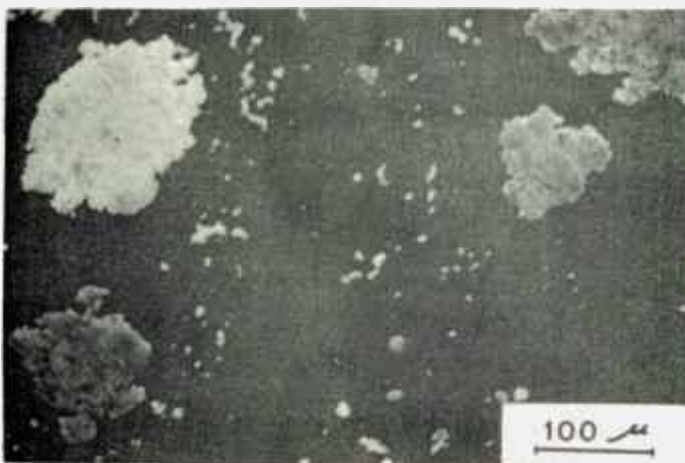

Fig. 2 - Morphology of the calcined DUA-S agglomerates. There are some light agglomerates of UO_3 and some dark ones of U_3O_8.

samples were left, intentionally, on exposure to air to be verified the change of the O/U ratio with the exposure time (Table I).

Table I

O/U ratios for the reduced oxides

sample	O/U[*]
UO_{2+x}N-a	2.08
UO_{2+x}N-b	2.09
UO_{2+x}S-a	2.08
UO_{2+x}S-b	2.09

a – sample shortly after the reduction
b - sample after 5 days to exposition in air
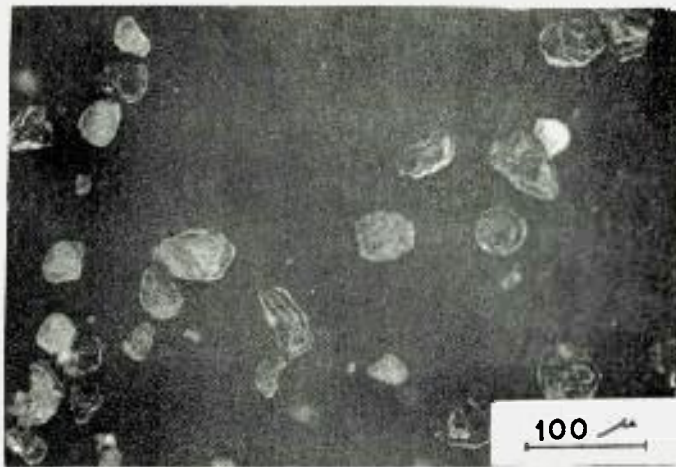* - average of three determinations

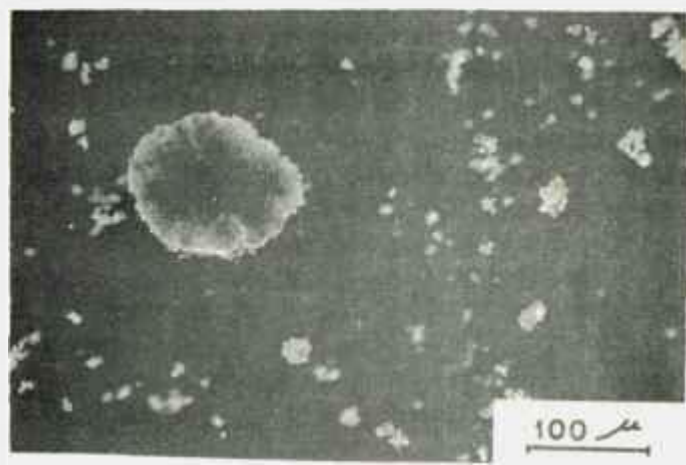Fig. 3 - Morphology of UO_2-N agglomerates.

Fig. 4 - Morphology of UO_2-S agglomerates.

Different samples of the reduced materials were then sent to the characterization tests. Fig. 3 and 4 show the UO_2-N and the UO_2-S particles, prepared from DUA−N and DUA−S.

The differential thermal analysis curves (Fig.5) correspond to the UO_2-N and UO_2-S powder. Temperature changes, in mV, in an arbitrary scale, are plotted against heating temperatures. Table II resumes the results of this test.
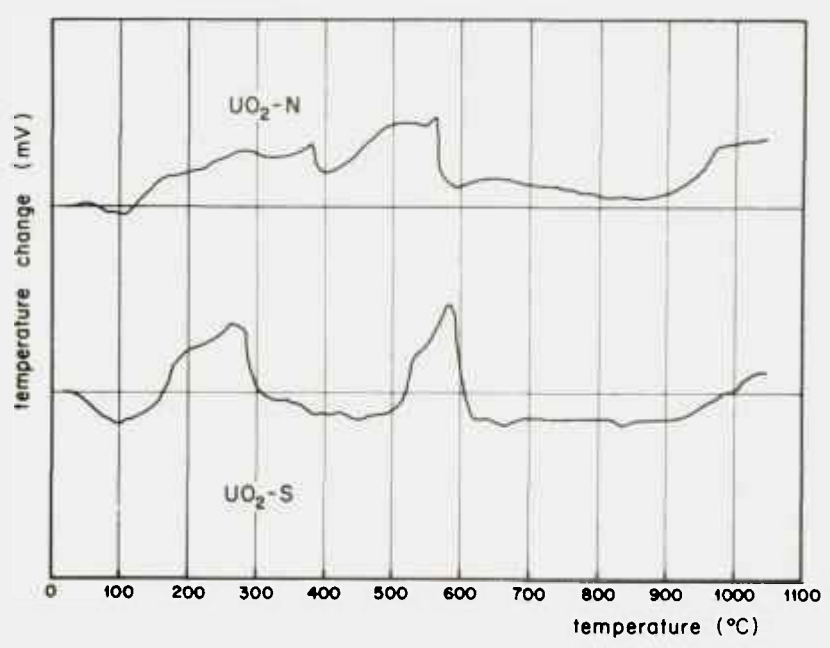

Fig. 5 - Thermograms of UO_2-N and UO_2-S samples. Heating rate: $10°C/min$.

Table II

Peak data from the differential thermal analysis curves

temperatures ($^\circ$C)	UO_2–N	UO_2–S
lower peak		
initial	120	170
maximum	300	270
final	400	400
upper peak		
initial	420	470
maximum	520	580
final	590	610
peak difference	220	310

The values of the surface areas of the original salts, of the calcined intermediate products and of the final products of reduction are summarized in Table III.

Table III

Surface area values determined by the BET technique

sample	surface area (m^2/g) [*]
DUA-N	14.8
DUA-S	18.7
Calcined-N	12.7
Calcined-S	16.4
UO_2-N	7.1
UO_2-S	4.8

[*] average of three determinations

Electron micrographs were taken of the same UO_2 powders (Figs. 6 and 7). Carbon replicas of these powders were obtained by using the technique of dispersing a small amount of powder with amyl acetate on a glass slide and pre-shadowing with platinum. The UO_2 was leached by HF.
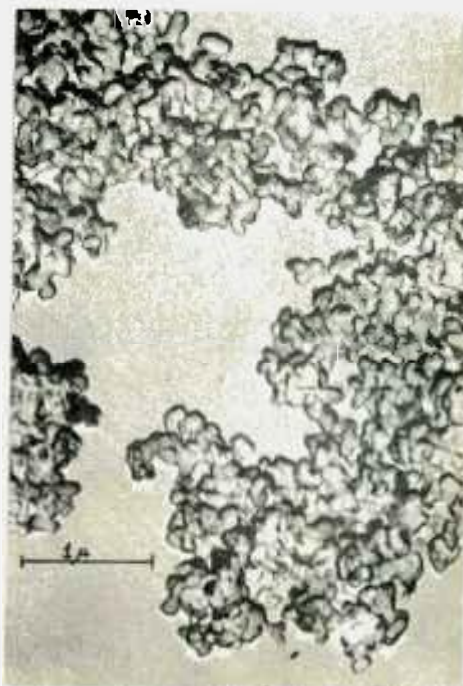

Fig. 6 - Electron micrograph of UO_2-N powder, showing an aggregate of 0.1 to 0.5 μ particles.

Sintering experiments were realized to confirm the sinterability characteristics foreseen by the results of the tests carried out. The UO_2 powders were stored in CO_2 atmosphere, after the reduction. Then they were classified as -65 mesh, pressed in cylindrical dies, without additions of lubrificants and binders. Table IV presents the bulk, tap and limit densities of the classified powders and Table V shows results of the green pellets.
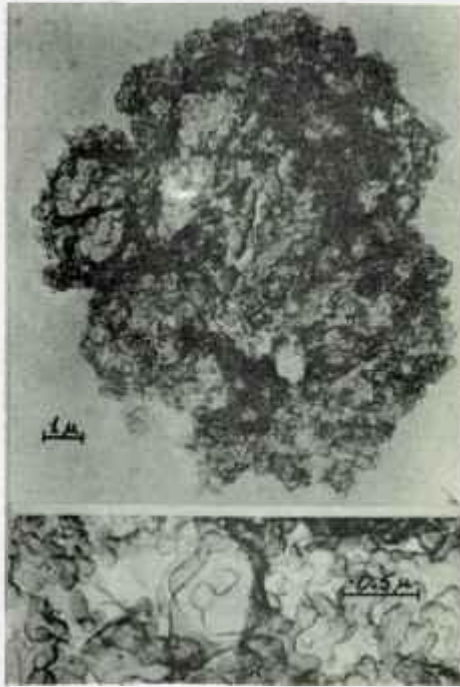
Fig. 7 - Electron micrograph of UO_2-S powder, presenting an agglomerate of about 10 μ. Its texture is showed at the botton of the figure.

Table IV

Bulk, tap and limit densities of the UO_2 powders

type	density (g/cm³)		
	bulk	tap	limit
UO_2-N	1.5	2.3	2.4
UO_2-S	1.3	2.2	2.3

Table V

Characteristics of the green pellets

characteristics	UO_2-N		UO_2-S	
	pressures (ton/cm^2)		pressures (ton/cm^2)	
	1.3	2.7	1.3	2.7
mass (g)	10.39	10.43	10.41	10.49
diameter (mm)	12.04	12.07	12.06	12.06
height (mm)	20.53	16.97	18.46	16.05
density (g/cm^3)	4.45	5.37	4.94	5.72
% theoretical	40.6	49.0	45.1	52.2

Sintering was done in a globar furnace at 1400°C, for 4 hours. Heating and cooling times were controled at a maximum rate of 120°C/hr. It was used an argon atmosphere. The pellets were placed in alumina boats, inside a recrystallized alumina mulfle. The sintered pellets, after visual examination, had their densities calculated by hydrostatic methods. The characteristics of the sintered pellets are in Table VI and the micrographs in Figs. 8 and 9.

Fig. 8 - Microstructure of an UO_2-N pellet, sintered at 1400° for 4 hours. Etched by HNO_3 conc.
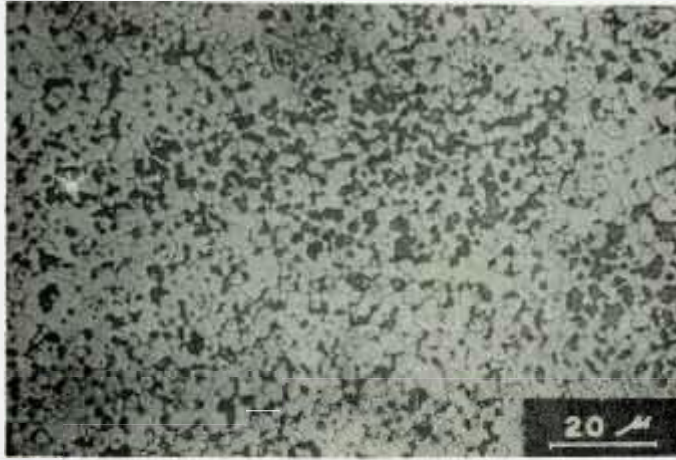
Fig. 9 - Microstructure of an UO_2-S, sintered at $1400^{\circ}C$ for 4 hours. Etched by HNO_3 conc.

Table VI

Characteristics of the sintered pellets

characteristics	UO_2-N		UO_2-S	
	pressures (ton/cm²)		pressures (ton/cm²)	
	1.3	2.7	1.3	2.7
mass (g)	10.30	10.29	10.28	10.36
diameter (mm)	9.05	9.62	9.55	10.12
height (mm)	15.45	13.62	14.62	13.46
density (g/cm³)	10.36	10.56	9.63	10.05
% theoretical	94.5	96.4	87.9	91.7
sintering index	0.91	0.93	0.78	0.83
O/U ratio	2.02	2.01	2.04	2.04

DISCUSSION

The differential thermal analysis curves in **Fig. 5** show that the samples had different behaviors during the tests. UO_2 −N sample presents the difference between the temperatures at which the peaks occur smaller than the one for the UO_2 −S sample. The UO_2 −N peaks are, also, less evident than for the UO_2 −S. An endothermic peak is noted in the UO_2 −S pattern, between 40 e $120°C$ due, probably, to the elimination of adsorved water. According to the results of Table II, the maximum temperature correspondent to the first peak, for both powders, is above the range 150-$180°C$, as observed by Taylor [16], emphasizing low sinterability. On other hand, the UO_2-N sample has a difference between the two peak temperatures much closer to the Chalder's range for high sinterability.

Surface area measurements show a gradual decrease, (Table III), for the different phases of the process. DUA−S powder presented higher surface areas than the ones for DUA−N, until as calcined. After the same conditions of reduction, it occurred a change in these values, suggesting a more pronounced incipient sinterization of the powder of DUA−S origin. Figs. 1 and 2 show that the grains of the calcined DUA−N present surfaces not so rough as for the calcined DUA−S, what suggests a less surface area, as verified. The UO_2 −N surface area measurements revealed that the powder is in the range of getting densities higher than 95% of the theoretical according to Chalder's results. On the other hand, the UO_2 −S measurements are out of this range, suggesting that the densities of the sintered pellets will be lower.

The morphology of the UO_2 −N and UO_2 −S agglomerates in Figs. 3 and 4 shows how the first ones are more homogenous than the second ones, wich can be also verified by the electron micrographs of Figs.6 and 7. The UO_2 −N electron micrograph shows a particle size between 0.1 and 0.5μ and with roughnesses having a minimum diamenter of about 0.1μ; the agglomerates are easily broken. On the other hand, the UO_2 −S is made of agglomerates with the diameter changing since fraction of micron until about 20μ; in the same way, the roughness changes from about 0.05μ until practically zero; these agglomerates break hardly at sample preparation for electron microscope observation (**Fig. 7**). These differences suggest that the UO_2 −N will have larger surface area than the UO_2 −S, what happens really: $7.1 \, m^2/g$ for the UO_2 −N and $4.8 \, m^2/g$ for the UO_2 −S. With basis in these observations it is possible to admit, according to Vergnon [27], that the UO_2 −S must present better compactability than the UO_2 −N. This hipothesis was configured by the pressing results presented in Table V and, also, by the results of the bulk, tap and limit densities (Table IV), which give better pressing capability for the UO_2 −S. The UO_2 −S agglomerates may present pores, which would not be eliminated during the sintering stages, as studied by Kuczinski [28] and Burke [29]. According to them the morphology and the grain size of the UO_2 −N justify the obtained results in both pressing and sintering operations.

The O/U ratio shows the same values for the UO_2 −N and the UO_2 −N at the same experimental conditions. The obtained results are correspondent to the ones normally closed to to high density sintered pellets, as in general literature (Table I). The light deviation of stoichiometry, besides beneficial to the sintering operation, does not impair the performance of the material as solid fuel and presents a decrease with the sintering operation.

Results of the sintering operations, as in Table VI, reveal that the UO_2 −N has better sinterability than the UO_2 −S. The sintering indexes for the UO_2 −N (0.91 and 0.93) are

significantly higher than the ones for the UO_2-S (0.78 and 0.83), at the same time that they seem to be less sensitive to a press change. Sintered pellets with densities of about 95% of the theoretical (94.5 and 96.4%) were obtained from UO_2-N in the established conditions. Values of the O/U ratio show a more pronounced decrease for the UO_2-N.

The micrographs of Figs. 8 and 9 reveal that the UO_2-N reached a higher sintering grade due to the grain size and to the pore amount and size presented. On the other hand, the UO_2-S has a microstructure with grains much smaller than the ones for the UO_2-N and they are surrounded by a lot of large pores. These microstructures are confirming the presented electron micrographs and they suggest to be necessary higher sintering time and or temperatures to improve the UO_2-S sintering index although the densification may be impaired by the anchoring of the grain growth due to the great amount of pores.

The agreement between the results of the sintering operations and the foresights set up through the characterization tests points out that these tests can be used as methods of estimating the behavior of the UO_2 powders. Future experiences will can fix the powder specifications and the production control to be used in the different stages.

CONCLUSIONS

1. The characterization tests, representing the determination of the physical and chemical properties, presented by the material will be essential to control and to improve the UO_2 production processes.

2. The UO_2 sinterability may be foreseen by the set of results of the differential thermal analysis measurements, surface area and O/U determinations, which are reinforced by other tests as average diameter determination, shape and texture of the grains and porosity of the sintered pellets.

3. Differential thermal analysis results suggest that the UO_2-N will present sintered pellets with higher densities.

4. UO_2-N surface area measurements are in the range that contributes to high density pellets.

5. The micrographs of both UO_2 powders reveal that the UO_2-N presents more favorable sintering structure than the UO_2-S, at the same time justifying the better compactability of the last one.

6. The O/U ratio determinations reveal that the reduced oxides are stable on exposure to air and they are in the range they can take to high density pellets.

7. The results of the sintering operations confirmed the previsions suggested by the characterization tests of the studied powders.

8. Sintered pellets with densities of about 95% of the theoretical were obtained from UO_2-N with the chosen procedure for experimental production and in the established conditions.

RESUMO

O objetivo deste trabalho é a caracterização dos pós de UO_2 produzidos a partir de diuranato de amônio de diferentes condições de precipitação, preparados no Instituto de Energia Atômica, São Paulo, Brasil. Essa caracterização inclui a determinação do conjunto de propriedades físicas e químicas que o material apresenta, o qual depende muito dos processos de preparação, proporcionando uma influência marcante nas características de compactabilidade e de sinterabilidade das pastilhas e no seu desempenho como combustível sólido. É ressaltada a importância dos ensaios de análise térmico-diferencial, medida de superfície específica e determinação da relação O/U. Outras propriedades como forma e textura das partículas e porosidade dos corpos sinterizados complementam essas informações. Operações de sinterização realizadas a $1400^\circ C$, em atmosfera de argônio, por 4 horas, confirmaram as previsões estabelecidas pelos ensaios de caracterização do dióxido de urânio.

RESUMEN

El objetivo de este trabajo es la caracterización del UO_2 obtenido a partir de diuranato de amónio en diferentes condiciones de precipitación, preparados en el Instituto de Energia Atômica, São Paulo, Brasil. Esa caracterización comprende la determinación del conjunto de propiedades físicas y químicas que el material presenta, muy afectada por los procesos de preparación, y que influen en las características de compactabilidad y de sinterabilidad de las pastilhas y su desempeño como combustible sólido. Se resalta la importancia de los ensaios de análisis térmico diferencial, medida de superfície específica y determinación de la relación O/U. Otras propiedades como forma y contextura de las partículas y porosidad de los cuerpos sinterizados complementam esas informaciones. Operaciones de sinterización realizadas a $1400^\circ C$, em atmósfera de argónio, por 4 horas, confirmaron las previsiones establecidas por los ensayos de caracterización del dióxido de urânio.

RÉSUMÉ

Le but de ce travail est la caractérisation des poudres de UO_2 obtenues à partir du diuranate d'ammonium sous differentes conditions de précipitation, preparé a l'Instituto de Energia Atomica, São Paulo, Brésil.

Cette caractérisation comprend la détermination de l'ensemble des proprietés physiques et chimiques du materiau, celles-ci dependent beaucoup du procédé de préparation, en particulier pour les caracteristiques de compactabilité et de frittage des pastilles et pour son emploi comme combustible nucléaire. L'importance des essais d'analyse thermo-differencielle est mise en évidence, de même que la mesure de surface spécifique et la détermination du rapport O/U.

L'étude d'autres propriétés, comme la forme et la texture (des exture) des particles et la porosité des corps frittés, complete cette étude. Les opérations de frittage realisées à $1400^\circ C$ sous argon pendant quatre heures confirment les prévisons établis pour les essais de caractérisation du dioxyde d'uranium.

16.

REFERENCES

1. Souza Santos, T. D., Barcelos Leite, P. L., and Simões Lopes, I., "Resultados Experimentais de Pastilhas de UO_2 para Uso em Elementos Combustíveis", Paper presented at the III Interamerican Conference on the Peaceful Applications of Atomic Energy, Petrópolis, Brazil, 1960.

2. Pereira da Silva, P. S. C., Souza Santos, T. D., and Freitas, C. T., "Contrôle Dimensional de Pastilhas de Urânia para o Reator Re-Suco", ABM - Boletim da Associação Brasileira de Metais, v.20, nº 85, 1964. pp. 759-770.

3. Souza Santos, T. D., Bidwell, R. M., Freitas, C. T., Haydt, H. M., and Pereira da Silva, P. S. C., "Estudo Experimental das Principais Variáveis para a Produção de Pastilhas de UO_2 para o Reator Sub-Crítico Re-Suco", ABM - Boletim da Associação Brasileira de Metais, v. 20, nº 85, 1964, pp. 711-784.

4. Souza Santos, T. D., Haydt, H. M., and Freitas, C. T., "Fabricação dos Elementos Combustíveis de UO_2 para o Conjunto Sub-Crítico Re-Suco". Metalurgia - Revista da Associação Brasileira de Metais, v. 21. nº 88, 1965, pp. 217-222.

5. Souza Santos, T. D., Haydt, H. M., Freitas, C. T. Capocchi, J. D. T., Cintra, S. H. L., Gentile, E. F., and Puccini, E. C., "Principais Característicos Metalúrgicos dos Elementos Combustíveis Fabricados para o Conjunto Sub-Crítico Re-Suco", Metalurgia - Revista da Associação Brasileira de Metais, v. 23, nº 112, 1967, pp. 175-190.

6. Haydt, H. M., Freitas, C. T., and Capocchi, J. D. T., "Pastilhas de UO_2 de Elevada Densidade", Metalurgia - Revista da Associação Brasileira de Metais, v. 24, nº 123, 1968, pp. 139-144.

7. Nishioka, I., Bueno, R. P. A., and Capocchi, J. D. T., "Nota Preliminar sôbre a Caracterização de UO_2 para a Fabricação de Elementos Combustíveis", Metalurgia - Revista da Associação Brasileira de Metais, v. 25, nº 143, 1969, pp. 733-740.

8. Stenquist, D. R., Mastel, B., and Anicetti, R. J., "Note on Correlation of Surface Characteristics of Uranium Dioxide Powders with their Sintering Behavior", Journal of American Ceramic Society, v. 41, nº 7, 1958, pp. 273-274.

9. Clayton, J. C., "Characterization of Uranium Dioxide", "Uranium Dioxide Properties and Nuclear Applications", Belle, J. (ed.), Naval Reactors, Division of Reactor Development, United States Atomic Energy Commission, 1961, pp. 91-125.

10. Murray, P., and Williams, J., "Ceramics and Cermet Fuels", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, v. 6, 1958, pp. 538-542.

11. Belle, J., "Properties of Uranium Dioxide", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, v. 6, 1958, pp. 569-589.

12. Chalder, G. H., Bright, N. F. H., Paterson, D. L., and Watson, L. C., "The Fabrication and Properties of Uranium Dioxide Fuel", Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, v. 6. 1958, pp. 590-604.

13. Runfors, U., Schonberg, N., Kiessling, R., "The Sintering of Uranium Dioxide", Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, v.6, 1958, pp. 605-611.

14. Bel, A., and Carteret, Y., "Contribution to the Study of Sintering of Uranium Dioxide", Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, v. 6. 1958, pp. 612-619.

15. Meeting on "Characterization of Uranium Dioxide" held at Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 12-13, 1961, United States Atomic Energy Commssion, TID-7637.

16. Taylor, A. J., "Characterization of Uranium Dioxide Powders for Sintering", Meeting on "Characterization of Uranium Dioxide", Oak Ridge, Tennessee, December 12-13, 1961, United States Atomic Energy Commission, TID-7637, pp. 31-42.

17. Murray, P., and Thackray, R. W., "Differential Thermal Analysis of Uranium Oxide", Atomic Energy Research Establishment Report, AERE-M/R-632, January, 1951.

18. Clayton, J. C., and Aronson, S., "Some Preparation Methods and Physical Characteristics of Uranium Dioxide Powders", Westinghouse Electric Corporation, Bettis Atomic Power Division Report, WAPD-178, December, 1958.

19. Scott, K. T., and Harrison, K. T., "Some Studies of the Oxidation of Uranium Dioxide", Journal of Nuclear Materials, v. 8, n⁰ 3, 1963, pp. 307-319.

20. Kingery, W. D., Ross, A. M., and Belle, J., "Thermal Conductivity", "UO_2: Properties and Nuclear Applications", Belle, J. (ed.), United State Atomic Energy Commission, 1961, pp. 177-189.

21. Williams, J., Barnes, E., Scott, R., and Hall,A., "Sintering of Uranium Oxides of Composition UO_2 to U_3O_8 in Various Atmospheres", Journal of Nuclear Materials, v. 1, n⁰ 1, 1959, pp. 28-38.

22. Burke, J. E., "The Science and Technology of Sintering", Proceedings of a Symposium held at the Pennsylvania State University, May 28-30, 1962, Klingsberg, C. (ed.), Office of Naval Research, Gordon and Breach, Sciences Publishers, New York, 1962, pp. 165-178.

23. Scott, R., Hall, A., and Williams, J., "The Plastic Deformation of Uranium Oxides Above 800°C", Journal of Nuclear Materials, v. 1, n⁰ 1, 1959, pp. 39-48.

24. Readey, D. W., and Handwerk, J. H., "Nuclear Fuel Materials", Proceedings of the American Ceramic Society Symposium, Washington, April, 1966, pp. 47-60.

18

25. Ainscough, J. B., "Some Properties of UO_2 Powders and Sintered Pellets with Particular Reference to ADU Oxide", Meeting on "Characterization of Uranium Dioxide", held at Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 12-13, 1961, United States Atomic Energy Commission, TID-7637, pp. 1-30.

26. Muller, N. G., "Pore Structure and Sintering of UO_2", Meeting on Characterization of Uranium Dioxide", held at Oak Ridge National Laboratory, Oak Ridge, Tennessee, December 12-13, 1961, United States Atomic Energy Commission, TID-7637, pp. 139-145.

27. Vergnon, P., "Compression des Poudres", Comissariat à l'Energie Atomique, Serie Bibliographies, n.º 70, 1966.

28. Kuczinski, G. C., "Theory of Solid State Sintering","Powder Metallurgy", Lesziynski, W. (ed.), Interscience Publishers, New York, 1961, pp. 11-29.

29. Burke, J. E., "Recrystallization and Sintering in Ceramics", "Ceramic Fabrication Processes", Kingery, W. D. (ed.), M.I.T. Press, 1963, pp. 120-131.