CHARACTERIZATION OF CALCINED U_3O_8 BY TRANSMISSION ELECTRON MICROSCOPY

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SUMMARY

he dependence of calcination time and temperature on the morph ogy of U_3O_8 powders has been studied by means of Transmission Electr n Microscopy (TEM). TEM is a very good technique for fine powder charac erization and powder processing control. In this work, it can be seen t at during the calcination of ADU, depending on the temperature, some s ntering and modification in shape and size of the particles can occur, pecially in calcination temperature up to 700°C.

INTRODUCTION

This work s part of a detailed development carried out at IPEN leading to the manufacture of nucl r fuels.

Most of nucl ar research reactors are loaded with plate-t pe fuel elements with a dispersion of fis ionable particles in a aluminum matrix. U: e is one of universally selected fuel b cause of its good compatibility whith aluminum powder and cladding, excelle t stability under irradiation and corro ion resistance.

The material commonly known as ADU (ammonium diuranate has been used here to obtain U_3O_8. In the conversion from ADU to uranium oxides, th characteristics of the resulting powder pa ticles are dependent upon ADU preparation [1,2,3] and also thermal decomposition procedures [1,3-9]. To achieve a U_3O_8 powder as a fuel with specific requirements, like high density (>8,0 g/cm^3), low specific surface area (<0,1 m^2/g), particle size in the 44μm-88μm range, and suitable particle morphology, the calcined U_3O_8 powders are initially pressed into pellets, milled, classified, sintered, disaggregated and finally reclassified.

Many steps of the fabrication process is known to strongly modify the properties of the intermediate and final products. However, only ADU calcination has been considered in this work.

The main purpose of this work is to analyse the dependence of the U_3O_8 powders morphology, determined by transmission electron microscopy, on the calcination temperature and time.

Some papers could be gathered about UO_2 particles (from different origins) analysed by transmission electron microscopy technique [2,4,5,7,10,11]. One of them [5] has also been showed U_3O_8 particles which encouraged us to make also this study.

Besides transmission electron microscopy technique, the powders have also been characterized by their pour density and specific surface area to yield informations on their physical behaviour.

EXPERIMENTAL PROCEDURE

The nuclear grade ADU, made by the Chemical Engineering Department at IPEN, has been calcined in six different ways: (A) 600°C for 3 h; (B) 600°C for 6 h; (C) 700°C for 3 h; (D) 700°C for 6 h; (E) 800°C for 3 h; (F) 800°C for 6 h. The lower temperature limit (600°C) has been chosen after thermogravimetric studies; the upper limit (800°C) has been taken in the literature [12,13,14]. Higher calcination temperatures have been previously used [15].

The as received ADU has been dried at 45°C for 24 hours and then ground to 20 mesh size. The calcination has been carried out in Fe-Cr boats in a box-type resistance furnace. The heating rate was less than 200 degrees per hour and, at the end of each heat treatment, U_3O_8 was air cooled outside the furnace.

Specimens from different calcinations have been prepared for electron microscopy by ultrasonic dispersion of a dilute alcoholic suspension. Drops of these suspensions were then placed on the electron microscope copper specimen grids, which had previously been coated with a plastic and carbon film. After drying in desiccator, the specimens were finally examined in a JEM 200 C (JEOL) electron microscope operating at 200 kV.

A special procedure has been used for powder density determinations: a fixed amount of dried powder was introduced in a graduated tube with a standard funnel and carefully measured with a precision of 0.1 ml. This procedure was repeated three times for each powder.

The specific surface area was measured by the volumetric method [16] using nitrogen adsorption. Two determinations on each sample were carried out in a Ströhlein Instruments apparatus (Area-meter II).

RESULTS AND DISCUSSION

Electron micrographs of ADU and calcined U_3O_8 samples have been obtained. The ADU particles observed in the TEM were very fine

with irregular shape, and a strong tendency to agglomerate as shown by the superposition of the particles in Fig. 1. Some modifications in particle shape and size occurred upon calcination. The rounding of the particles as well as neck formation between them have been observed in sample A (600°C for 3 h) indicating the first sintering stage. Powder analysis showed that some necks had broken during preparation of the dispersion but the majority of the necks were retained; moreover several interconnected particles have been found to be in different planes, thereby causing focusing problems (Fig. 2a).

To obtain a better understanding of necking and particle agglomeration, a TEM goniometer stage was used to improve contrast and electron transmissibility. Sample B (600°C for 6 h) was similar to sample A (Fig. 2b).

Fig. 1 - Electron micrographs of as received ADU.

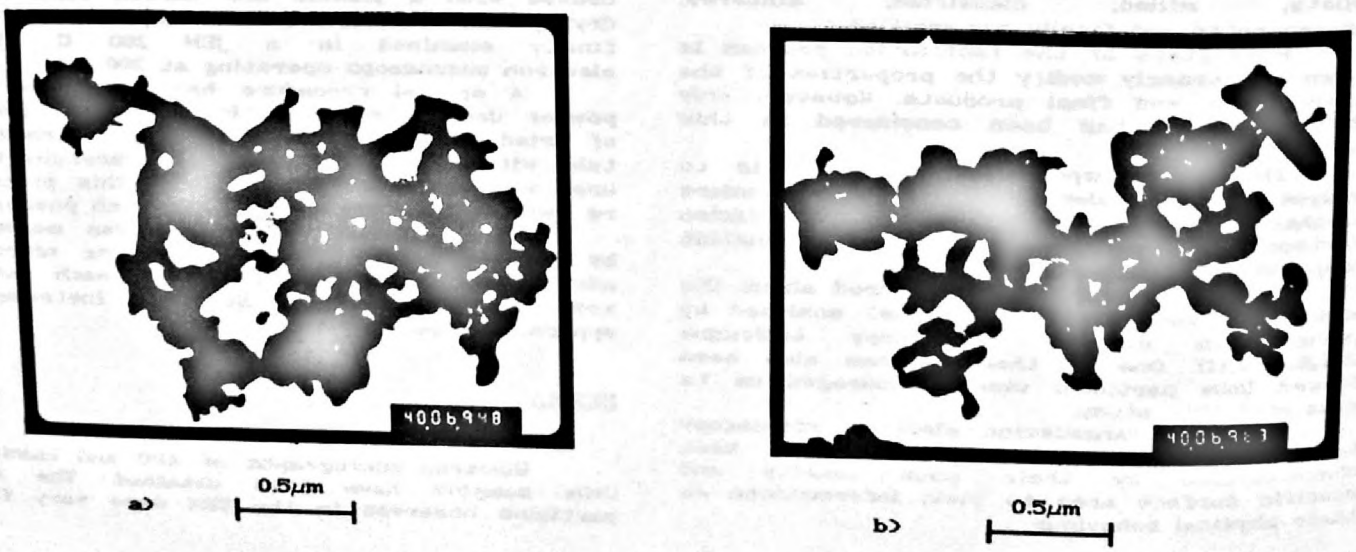

Fig. 2 - Electron micrographs of calcined UsO_8 powders: a) Sample A (600°C - 3 h); b) Sample B (600°C - 6 h).

Particle growth has been observed in sample C (700°C for 3 h) and found not to be so electron transparent (Fig. 3a). Sample D (700°C for 6 h) showed similar results (Fig. 3b). Samples E (800°C for 3 h) and F (800°C for 6 h) had the same contrast (Figs. 4a and 4b) and only after several micrographs they could be distinguished from sample D, indicating that sample D is a transition between samples C and E.

The present observations give evidences of the extreme sintering sensibility of U_3O_8 in good agreement with previous results [1,3,17]. The need to reduce the calcination temperature to avoid U_3O_8 formation (and sintering), which could modify the properties of final UO_2 powders, has been verified [17]. It has been also shown that ADU calcination temperatures higher than 600°C were responsible for the change of the physical state of the particles, due to necking between them and to accelerated growth of the U_3O_8 particles [1]. A rounding of the primary and secondary aggregates has been observed when ADU is calcined above 700°C with further reduction to UO_2 [3]. A strong tendency to U_3O_8 sintering can also be seen in Fig.5 for sample F (800°C for 6 h): narrow necks, tough enough to be broken during ultrasonic preparation, were formed; the apparent fissures near the neck may have originated during the rapid cooling of the powder.

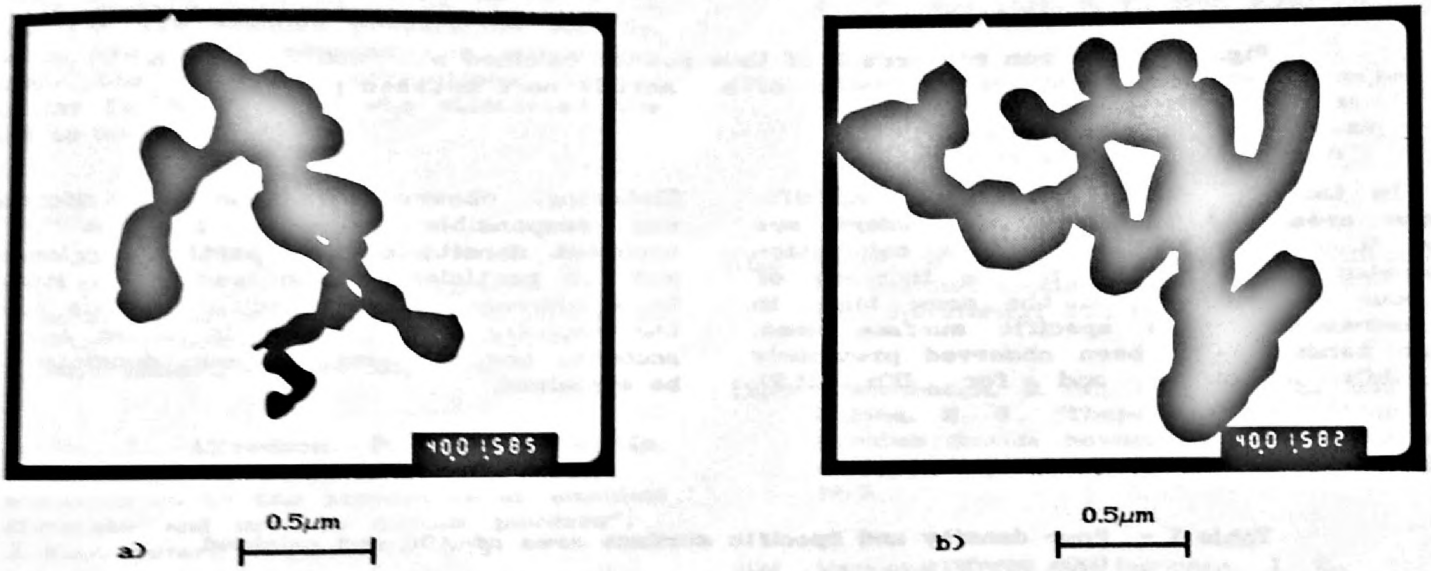

Fig. 3 - Electron micrographs of calcined U_3O_8 powders:
a) Sample C (700°C - 3 h); b) Sample D (700°C - 6 h).

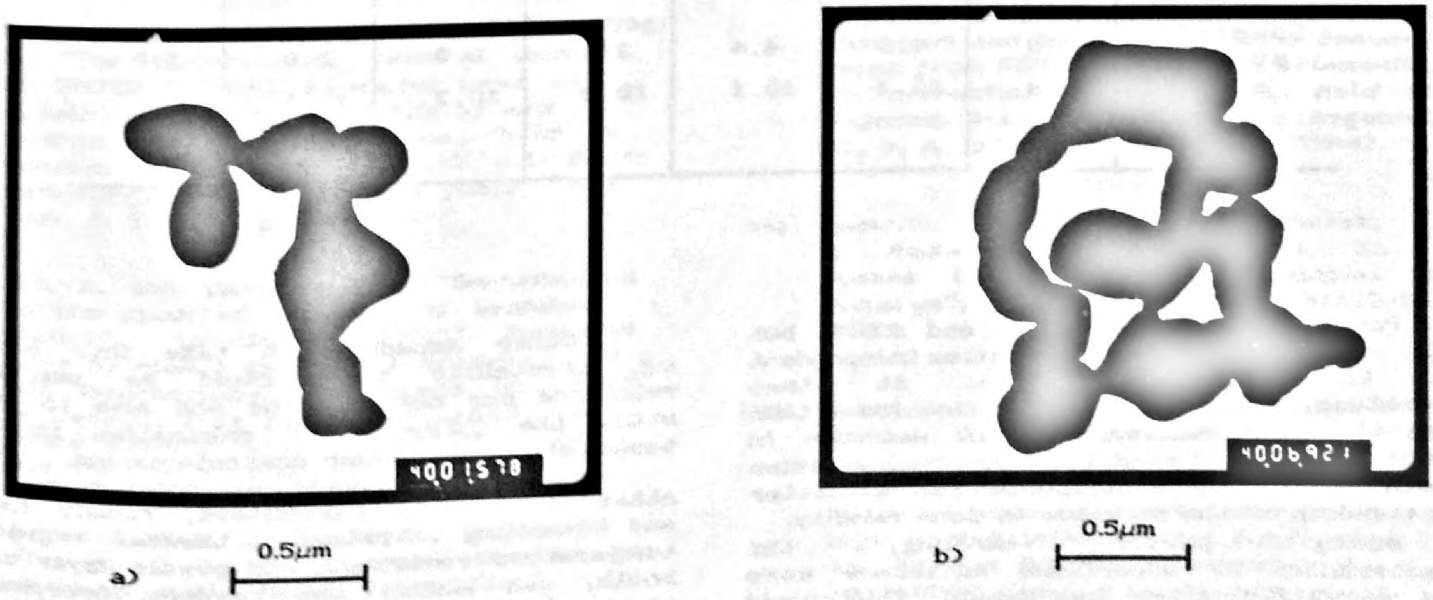

Fig. 4 - Electron micrographs of calcined U_3O_8 powders:
a) Sample E (800°C - 3 h); b) Sample F (800°C - 6 h).

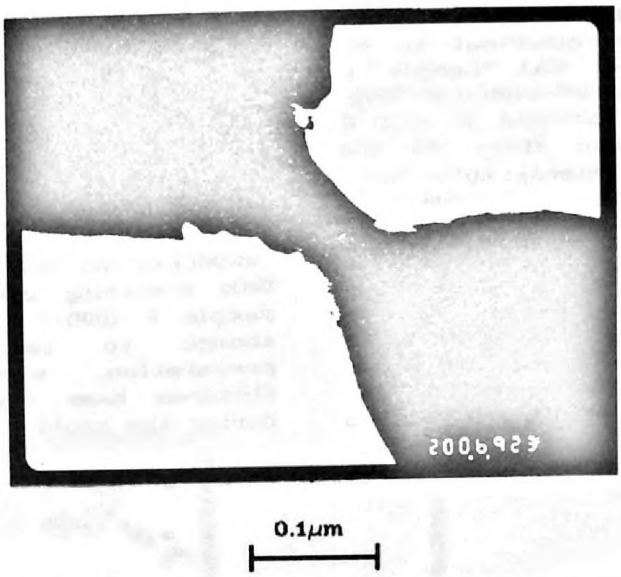

Fig. 5 - Electron micrograph of U_3O_8 powder calcined at 800°C for 6 h (Sample F) showing formation of a narrow neck between particles.

In table I, pour densities and specific surface areas of calcined U_3O_8 powders are shown. It can be noted that the calcination temperature plays a role in the increase of the pour density and, at the same time, in the decrease of the specific surface area. Similar tendency has been observed previously for U_3O_8 [1,9,17,18] and for UO_2 [1,7]. Sintering, observed by electron microscopy, was responsible for the increase in the apparent density of the particle agglomerates and for particles growth leading, by its turn, to a decrease in the specific surface area. If the rounding of particles is taken also into account, the increase in pour densities could be explained.

Table I - Pour density and specific surface area of ADU and calcined U_3O_8 powders.

Sample	ADU	U_3O_8 (A)	U_3O_8 (B)	U_3O_8 (C)	U_3O_8 (D)	U_3O_8 (E)	U_3O_8 (F)
Density (g/cm^3)	1.04 ±0.01	1.19 ±0.01	1.19 ±0.01	1.26 ±0.01	1.37 ±0.01	1.50 ±0.01	1.53 ±0.01
Specific surface area (m^2/g)	6.0 ±0.4	4.5 ±0.2	4.4 ±0.1	2.8 ±0.2	2.8 ±0.2	2.0 ±0.1	1.8 ±0.1

Powders calcined at 600°C and 800°C, but 700°C, have their pour densities independent upon the calcination time. At that temperature, higher the calcination time higher the pour density, with no decrease in specific surface area. Here, transmission electron microscopy contributes for a better understanding of the increase in pour density.

During powder handling, the characteristics of superficial adherence were found to differ after calcination. This could be noticed upon comparing the samples calcined at 600°C (more adherence) and at 800°C (less adherence). This is due to the decrease of specific surface area and to the rounding of the particles.

Other aspects not take into account, e.g. crystallite size, could be useful to reinforce our observations and also to better study the influence of calcination time and temperature on powder characteristics.

Finally, it should be pointed out that other calcination parameters, namely heating and cooling rates, thermal gradient, temperature variations and powder layer in the boats, can modify the powders. Everyone of these parameters have to be properly controlled to obtain powder batches with the same physical properties.

CONCLUSIONS

Transmission electron microscopy is shown to be a good technique for morphological characterization and processing control, in particular, for ADU calcination. The particles morphology showed to be an important feature for a better understanding of powder behaviour. During ADU to U_3O_8 calcination, partial sintering and significant modification in shape and size of the particles can occur. The main morphological change during the calcination process occurs up to 700°C and the influence of time is greater at that temperature.

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