U-Mo Alloy Powder Obtained Through Selective Hydriding.
Particle Size Control.

S.N. Balart, P. Bruzzoni y M.S. Granovsky.

CNEA, Departamento Materiales

Av. del Libertador 8250, 1429 Buenos Aires, Argentina.

Abstract

Hydride-dehydride methods to obtain U-Mo alloy powder for high-density fuel elements have been successfully tested by different authors. One of these methods is the selective hydriding of the α phase (HSα).

In the HSα method, a key step is the partial decomposition of the γ phase (retained by quenching) to α phase and an enriched γ phase or U_2Mo. This transformation starts mainly at grain boundaries. Subsequent hydrogenation of this material leads to selective hydriding of the α phase, embrittlement and intergranular fracture. According to this picture, the particle size of the final product should be related to the γ grain size of the starting alloy.

The feasibility of controlling the particle size of the product by changing the γ grain size of the starting alloy is currently investigated. In this work an U-7 wt% Mo alloy was subjected to various heat treatments in order to obtain different grain sizes. The results on the powder particle size distribution after applying the HSα method to these samples show that there is a strong correlation between the original γ grain size and the particle size distribution of the powder.

1. Introduction

γ phase U-Mo alloys with a Mo content of 7 to 10 wt% are promising materials for the production of high-density LEU dispersion fuel [1]. In order to manufacture the fuel elements, the alloy must be in the powdered form. The transformation of the massive alloy into the powder is a technological challenge that is currently solved by three different methods: machining, atomization [2] and hydride-dehydride [3-5]. The HSγ method [6] is one of the alternatives in the hydride-dehydride scheme; it is based on the partial decomposition of the γ phase in a cellular structure. This structure is composed by α-U and a second phase that may be either Mo-enriched γ or U_2Mo; it originates at the γ grain boundary and grows towards the center of the grain. Then, the material is treated with hydrogen and the α phase is transformed to UH_3 located at the grain boundary, which causes embrittlement and leads to pulverization *via* intergranular fracture. Finally, the powder is dehydrided and the original gamma phase is recovered through thermal treatments.

Since the fracture mode of the material is intergranular, it was suggested [3] that changing the original γ grain size of the alloy, the final particle size will change accordingly. Thus, the control of the final particle size could be achieved by appropriate thermal treatments of the massive

alloy, prior to the γ phase decomposition and hydriding treatments. The feasibility of this procedure is investigated in this work.

2. Experimental

The experimental work comprised all the steps in the production of the U-Mo powder by the HSα method: alloy casting, thermal treatments, hydride-dehydride process and sieving. In the present work, an additional step (grinding) was included. The starting materials were commercial molybdenum (with the following relevant impurities in μg/g: Al 8, Ni 2 , W 100, O_2 <20) and uranium; the relevant impurities of the uranium were: Al (>200μg/g) and Ni (>200μg/g).

Alloy casting was carried out in an arc melting equipment, under Ar atmosphere. The Mo content of the alloy was 7 wt%.

Thermal treatments were done in a sealed quartz tube under Ar atmosphere. The thermal treatments were carried out in an electric furnace and were finished by quenching in water, without tube breaking. Two different thermal treatments were carried out, as required by the HSα method:

1. Homogenization and grain growth: its conditions were varied according to Table 1.

2. Partial decomposition of the γ phase: 565°C, 24 h.

Table 1. Thermal treatments for homogenization and grain growth.

Treatment	A	B	C	D
Time	2 h	6 h	4 h	1 h
Temperature	980°C	980°C	950°C	1000°C

The hydriding-dehydriding equipment and procedure had been described elsewhere [3].

The progress of the hydriding and dehydriding reactions was followed through the continuous measurement of the system pressure and temperature. With these data, the H:U ratio was calculated.

Grinding and sieving were carried out on the hydrided material. These operations were accomplished manually, in a glove box under low oxygen content atmosphere (N_2 with 3% to 4% O_2 in volume). A glass mortar was used for grinding, and standard meshes (#325 and #125) for sieving. A fixed time of 2 minutes was assigned to each operation. Before exposing to the laboratory air, the powdered samples were stored during 24 h in the glove box in order to allow the passivation of the particles, thus avoiding the spontaneous ignition of the powder.

For the characterization of the samples and the powders, the following techniques were used: Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and X Ray diffraction (XRD).

3. Results and discussion

Alloy casting

The U-7 wt%Mo as cast material showed a microstructure of grains of average size of 20 μm. There was a depletion of Mo at the grain boundaries. Since the grains were equiaxed with rather uniform size, no attempt was made to break the as-cast structure through cold rolling.
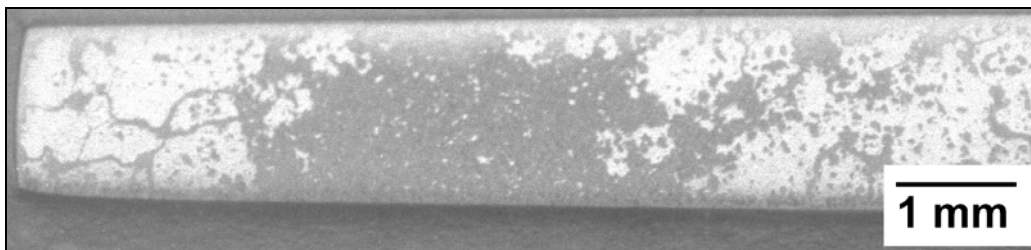
Grain growth treatments.

After the homogenization and grain growth treatments, the samples were observed by OM and SEM.

All micrographs shown below correspond to samples that were subjected to the thermal treatments of grain growth + γ phase decomposition.

Al-containing precipitates are present at the grain boundaries. At 950°C or lower temperatures, the average grain size shows little change as compared with the as cast material. At 980°C or higher temperatures, the grain size increases rapidly up to 1000 μm or higher, but not uniformly. As a result of this, colonies of large (~400 μm) and small (~20 μm) grains coexist. With increasing treatment time, the colonies of large grains grow at the expense of small grains.

Grain growth treatment A (980°C 2 h) represents an intermediate stage in this uneven grain growth process that takes place at 980°C or higher temperature. Fig. I is a macrograph of a transverse section of the sample. Bright areas correspond to large grains and dark areas to small grains; the latter keep the size of the as cast material. Fig. IIa is an enlargement of the region of large grains shown Fig. I.

Grain growth treatment B (980°C 6 h) results in a more advanced stage, increasing the amount of large grains (Fig. IIb).

Fig. I. Sample A: grain growth at 980°C 2 h. Followed by the γ phase decomposition treatment. Transverse section.
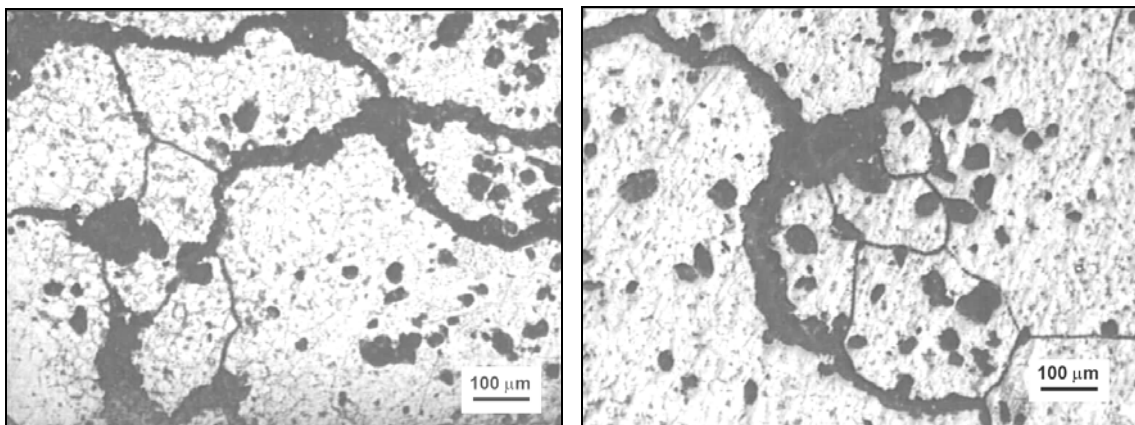
a) 980°C 2 h   b) 980 °C 6 h

Fig. II. a) Grain growth treatment A, zone of large grains; b) Grain growth treatment B. Followed by the γ phase decomposition treatment. Transverse section. The aspect is similar in both cases.

Grain growth treatment C (950°C 4 h) did not significantly increase the grain size of the as cast material (Fig. III); the grains were small and uniform in size. After the decomposition treatment, the appearance of the material at a lower magnification is similar to the dark areas of Fig. I.

Grain growth treatment D (1000°C 1 h) produces a mixed structure of large and small grains similar to treatments A and B. So, the grain growth progress at T ≥ 980°C is evidenced in the sequence: treatment A-treatment D-treatment B.

Fig. III shows microstructural details of the decomposed γ phase which correspond to grain growth treatment D, but are common to all grain growth treatments at T ≥ 980°C.
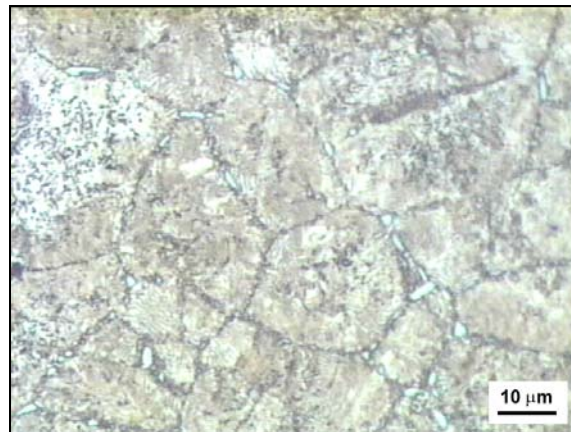
Fig. III. Microstructural details after the grain growth treatment C (950°C 4 h). Followed by the γ phase decomposition treatment. Transverse section.

Decomposition of the γ phase

After the γ phase decomposition treatment, XRD and OM showed, as expected, the presence of a cellular structure of α phase plus enriched γ phase and/or U_2Mo. The degree of decomposition of the γ phase depended strongly on the grain size. Small grain samples showed a nearly total decomposition (dark area of Fig. I and Fig. III). This agrees with the fact that the decomposition starts at the γ grain boundary and advances towards the center of the grain.

In the large regions, the decomposition is partial and located mainly at the grain boundaries (Fig. II). The decomposed region appears as a narrow band adjacent to the grain boundary. Also, spots of decomposed γ phase are observed inside the grains.

Hydriding

Fig. IV shows the progress of the hydriding reaction as a function of the grain size. The hydriding behavior shows a strong correlation with the microstructure. The small grain size sample C, with a high degree of γ phase decomposition, is readily hydrided reaching H:U = 1.9. Sample B, composed mainly of large grains, hydrides slowly and reaches H:U = 0.73. Sample A, which is a mixture of large grain and small grain regions, reacts at a high rate up to H:U ≈ 1; then the hydriding rate decreases. Here, the first, fast stage can be interpreted as the hydriding of regions populated with small grains; the second and slow stage would correspond to the completion of the hydriding reaction at the region populated with large grains. Sample D shows a similar behavior as sample B. Taking into account that UH_3 is the expected reaction product of

α-U and H_2, and that the remaining γ phase does not react with H_2 in the present operating conditions, the degree of decomposition X of the γ phase can be estimated as

$$X = \frac{(H:U)_{max}}{3}.$$

This calculation yields the following values:

Sample	A	B	C	D
Decomposition degree X	40%	24%	63%	33%
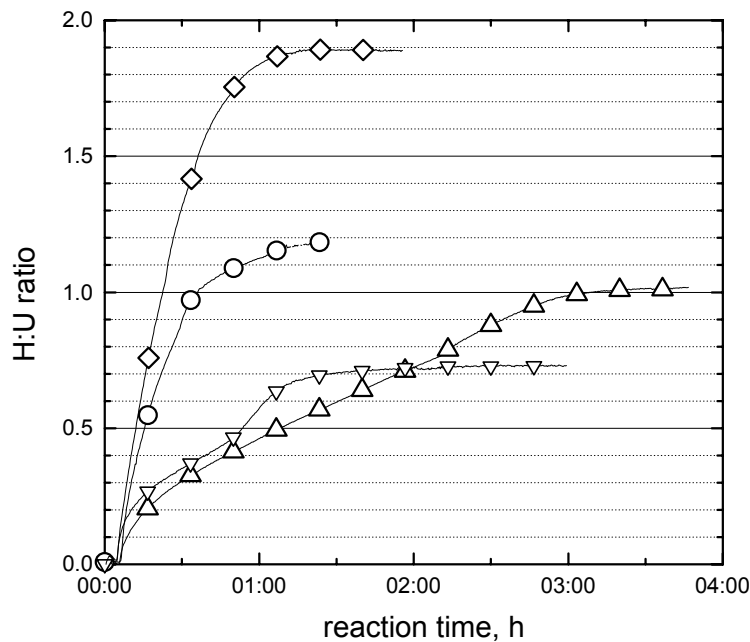
Fig. IV. Progress of the hydriding reaction for the grain growth treatments A (Δ), B (∇), C (◊) and D (O).

Particle size distribution

Due to the pyrophoricity of the hydrided material, the grinding and sieving operations were carried out in an atmosphere with low oxygen content. High pyrophoricity was observed in a highly decomposed material, condition C.

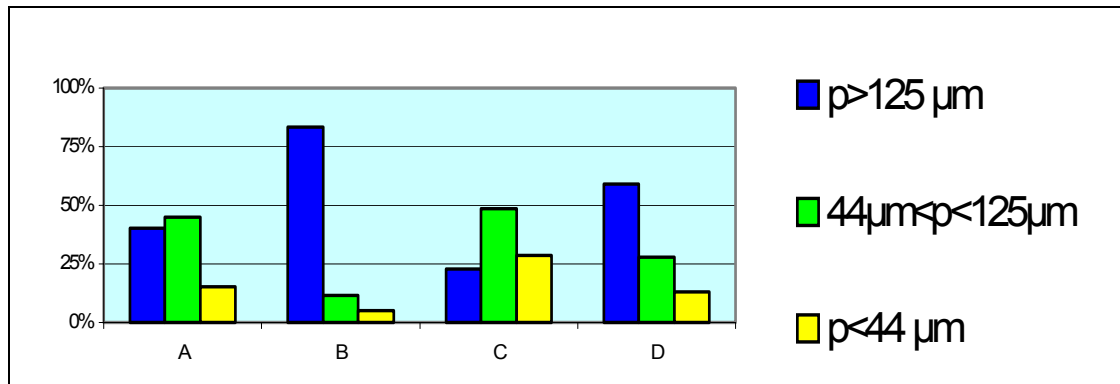The particle size distribution after grinding is shown in Fig. V.

Fig. V Particle size distribution after grinding; *p* = particle size according to the sieving behaviour.

A strong correlation was observed between the γ grain size and the particle size after grinding. The B and D conditions with coarse grains, show also a majority of coarse particles. The A condition, which contains coarse and fine grains, shows an increasing amount of intermediate size particles. The C condition with only fine grains has the maximum amount of intermediate size particles, which are suitable for fuel manufacturing.

Particle morphology

The particle morphology was investigated by SEM and OM. The present results concern the B and C conditions, which were the most relevant regarding the final particle size distribution.

In the B condition, the most abundant fraction is that of particles larger than 125 μm. This fraction is composed by particles with sizes up to ~1 mm (Fig. VI). Most of them correspond to the original γ grains. The grain boundaries are easily identified on the particle surface, showing an intergranular fracture mode. These particles are similar to those described in our previous works [3].
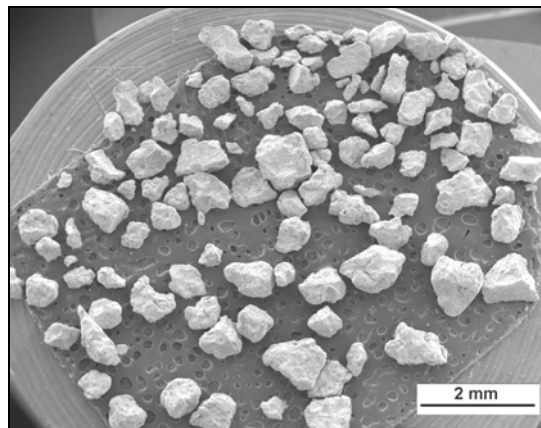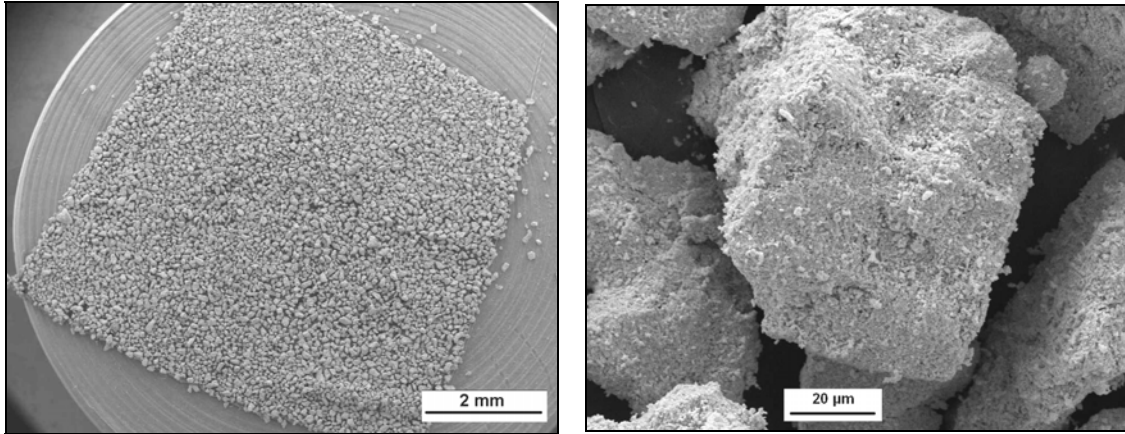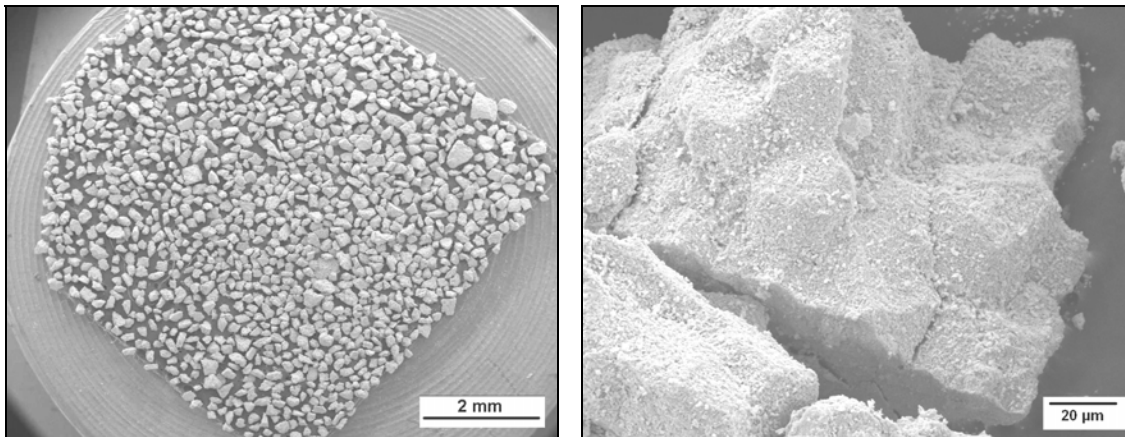

Fig. VI. A condition (Grain growth at 980°C 6 h): fraction of particles larger than 125 μm. SEM micrograph.

In the C condition, the most abundant fraction correspond to particle size *p* in the range 44 μm < *p* < 125μm. These particles are shown in Fig. VII. Most of these particles appear as agglomerates of several γ grains.

Fig. VII. C condition (Grain growth at 950°C 4 h): fraction of particles with 44 μm < *p* < 125μm. SEM micrographs.

The coarse grain fraction of the C condition is mainly composed of particles with $p \approx 200$ μm (Fig. VIII). As in the case of the intermediate size particles, these coarse particles are aggregates of original γ grains. A great number of particles in this fraction present intergranular cracks, which suggests that a more energetic grinding should further reduce the size, thus increasing the amount useful particles.

Fig. VIII. C condition (Grain growth at 980°C 4 h): fraction of particles with *p* > 125 μm. SEM micrograph.

As a consequence of the great extent of the γ phase decomposition, the particle surface in the C condition shows an important roughness at a scale of ~1 μm. This surface roughness may be responsible of the high reactivity of these particles in the presence of air during the grinding operation. The surface roughness of the C particles of intermediate size is similar to that of the coarse C particles.

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4. Concluding remarks

This work has demonstrated that in the HSα method of U-Mo alloy pulverization, there is a strong correlation between the particle size and the original γ grain size. In the case of coarse grain samples, the resulting particles are individual grains. In the case of fine grain samples, the resulting particles are agglomerates or several original γ grains.

The C condition with fine grains shows the best yield of particles with adequate size for fuel manufacturing (50%); the fine particles remain within the limits of the current specification proposed for the powder produced by atomization (<30%). The percentage of coarse particles (currently ~20%) might be reduced by further grinding of this fraction.

Further work should be carried out with a material of higher purity. It should focus in obtaining intermediate grain sizes in the range between B and C conditions. The extent of the decomposition reaction is other variable to be considered.

5. References

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