POWDER PRODUCTION OF U-Mo ALLOY, HMD PROCESS. (Hydriding-Milling-Dehydriding)

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ABSTRACT

Uranium-molybdenum (U-Mo) alloys can be hydrided massively in metastable γ (gamma) phase. The brittle hydride can be milled and dehydrided to aquire the desired size distributions needed for dispersion nuclear fuels. The developments of the different steps of this process called hydriding-milling-dehydriding (HMD Process) are described. Powder production scales for industrial fabrication is easily achieved with conventional equipment, small man-power and low investment.

1. Introduction

Powder metallurgy technology offers different alternatives for obtaining uranium-molybdenum (U-Mo) alloy particles in the size range (< 150 μ) needed as raw material for the fabrication of material testing reactors (MTR) nuclear fuel elements. Since as cast U-Mo is a ductile alloy, conventional milling alternatives used with brittle materials are forbidden.

Centrifugal or gas atomization are the two more generalized high yield methods for metallic powder production [1]. The major drawback of these alternatives is that since particles solidify in an inert gas atmosphere flight, big chambers are needed. High initial equipment investment is required for a process where small batches have to be used, limited to a few pounds because of safety conditions required for the management of an alloy with enriched uranium. A cyclonic centrifugal atomization (CCA) process that curves the cooling trajectory of particles, would allow the use of smaller chambers.

Hand and lathe filing, and wheel grinding, have been considered as possible processes. These alternatives are usually associated with additional treatments of classification, purification from introduced debris or rounding of filings by milling and scrap reprocessing. The recently developed process in which γ phase is decomposed in two phases, one of which is α uranium that when hydrided comminutes the alloy [2, 3], needs high control of thermo-mechanical treatments for obtaining desired particle size distribution.

The recent discovery of the massive hydriding [4] of uranium-molybdenum alloys in the γ phase structure allows to obtain a brittle interstitial compound that can be readily milled. This is the starting point for the hydriding-milling-dehydriding -HMD- process of powder production described in this work.

2. Hydriding

Hydriding is a well known process of comminuting materials that form brittle hydrides. Evidence of localized hydride formation in U-Mo was reported in cathodic charge of hydrogen in a uranium 10% weight molybdenum alloy (U-10Mo) [5]. Also it is known that this alloy has low hydrogen [7] solubility that for values over 5 ppm slightly embrittles the material [6]. A massive hydriding of U-Mo

alloy in metastable γ body centered cubic (bcc) phase can be obtained in samples where hydrogen has been solubilized previously.

The equipment used consisted in a vacuum chamber -evacuated with mechanical and diffusion pumps- with a total volume of 6.85 liters *(V')* with a quartz tube inside a resistance furnace. The heating zone is of approximately 2 liters and a needle valve allows the incorporation of hydrogen or argon gases. Batches of more than one kilogram can be processed measuring temperature and pressure. Testing was performed fundamentally using U-7Mo alloy. The alloy was melted in an inert gas induction furnace using high purity molybdenum and natural uranium of different purities. Plates of 5 mm thickness were casted in graphite molds.

Fragments of the alloy are introduced in the quartz tube and heated during one hour in pure hydrogen (H_2) at one atmosphere pressure and 700 °C. Absorption of hydrogen is usually greater than 10 ppm in weight. Sample gas absorption can be detected in a closed chamber by the evolution of pressure and temperature while cooling or heating. Simple calculations can be performed with the suppositions that the chamber has two zones at different temperatures [7] and the ideal gas law:

$$n(t) = \frac{V}{R} P(t)\left(\frac{1}{T(t)} + \frac{V_o}{V T_o}\right) \quad (1); \qquad \frac{dn(t)}{dt} = \frac{V}{R}\left[\left(\frac{1}{T(t)} + \frac{V_o}{V T_o}\right)\frac{\delta P(t)}{\delta t} - \frac{P(t)}{T^2(t)}\frac{\delta T(t)}{\delta t}\right] \quad (2)$$

where n is the quantity of hydrogen moles in the chamber of volume $V' = V + V_o$, V is the volume of the heated zone, R is the ideal gas constant and P and T are the pressure and temperature respectively. Variables depending on time *(t)* are explicitly identified and sub index indicates the volume *(V_o)* of the part of the chamber that is at room temperature *(T_o)*. The values of $V_o/V.T_o$ and V/R are obtained by calculation using a variable temperature and pressure range in which no absorption takes place (n(t) = constant). In figure 1 are represented the absorption velocity during heating and cooling runs of batches of approximately 700 g. Massive hydriding of the material takes place in a temperature range between 50/190 °C and is maximum at around 120 °C. Normally the hydrogen pressure was maintained at 1 bar. Runs performed at 2 bars and 0.5 bars practically doubled and made half respectively the hydrogen absorption rate. Hydrogen flow can reach values of 0.5 lt/min and normally is around 1400 ppm/hr. It is usual to notice during changing conditions of the experiment that absorption velocity is greater during cooling than when heating. Anyway, hydriding of the material is done at constant temperature and pressure. Pressure is maintained constant with a hydrogen gas flow continually incorporated to the chamber and temperature control is needed because the hydriding reaction is exothermic. The process is stopped after less than 15 hours when the rate of gas absorption is lower than 0.02 lt/min and more than 85% of the material has been hydrided. The hydrided alloy is fractured in millimeter size fragments as it is formed.

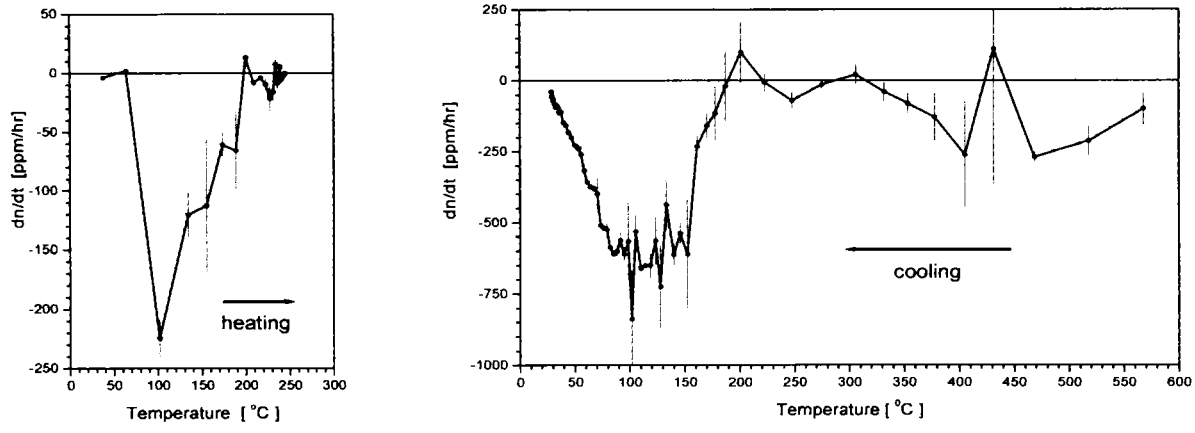

Fig 1. Hydrogen absorption rates during heating and cooling of U-7Mo alloy. Notice the different absorption rates in each case. Error bars are indicated for all data points.

The U-Mo hydride is a dark gray brittle compound of low hardness (Vickers < 300) and when oxidized is dark brown. It is pyrophoric and burns with flame because of hydrogen liberation with temperature. The stoichiometry is MH_X , where M stands for the U-7Mo alloy and X > 2.8. X-ray diffraction (XRD) and Rietveld refinement (Figure 2) show that the structure is of the prototype Cr_3Si (A-15), the same as β-UH_3 [8]. The density (DRX) is 10.39 g/cm^3, much smaller than the U-7Mo which is 17.5 g/cm^3. The hydriding of the U-Mo in γ phase is controlled by hydrogen diffusion but, because of the high density difference between the alloy and the hydride, internal cracks and fractures are formed parallel to the diffusion front and new surface is formed. The consequence is that the rate of hydride formation is greater than the expected 0.5 power law usual in diffusion processes.

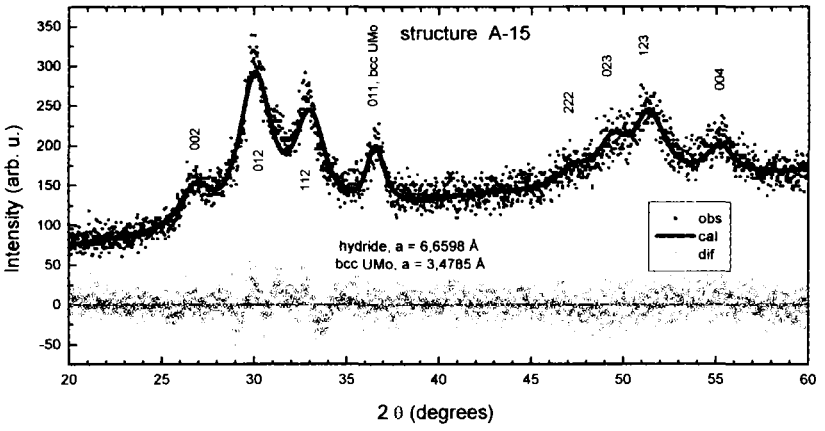

Fig 2. XRD and Rietveld Refinement of U-7Mo hydride A-15 structure. The width of peaks is probably ought to high distortion of the crystal lattice. Some γ phase alloy (bcc) is still present.

3. Milling

Before exposing the hydride to air it is needed to do a controlled passivation to avoid burning the material. The general appearance of the interstitial compound is of small platelets 0.5 mm thick with inside small cracks. The milling of the material can be done gently in air by hand using a mortar or in any conventional milling machine in a low oxygen atmosphere. Size distribution control will depend on the choice of the mill to be used. Hydride milled and sieved particles are shown in Figure 3. A decrease in size distribution is expected in the dehydriding of the material because of density differences between the hydride and the final U-7Mo powder. The usual powder specification of less than 50% fines is easily achieved.

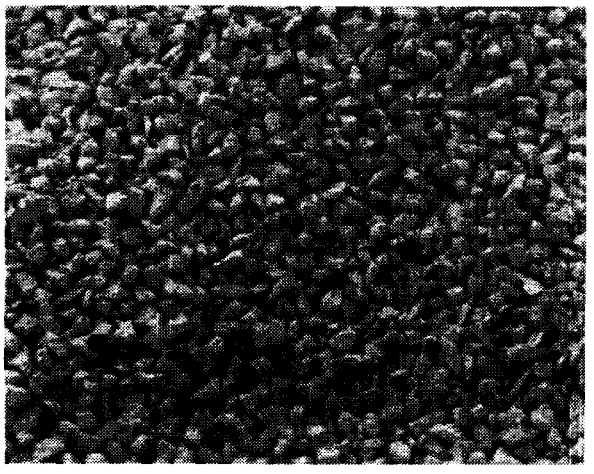

Fig 3. U-7Mo hydride powder. Mean particle size is 80 μ.

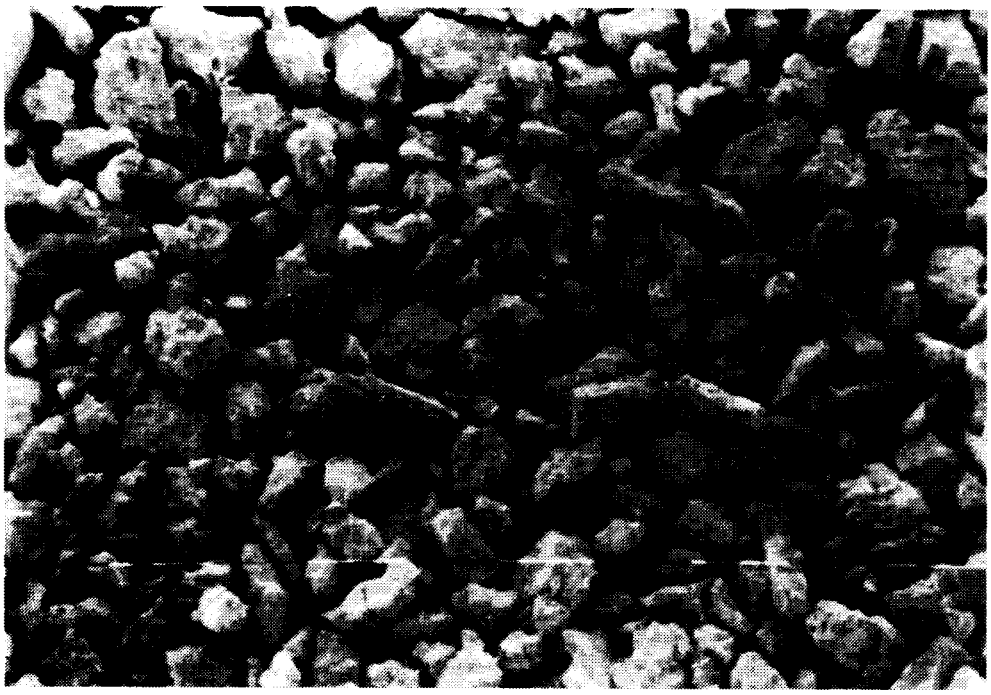

Fig 4. U-7Mo powder obtained by HMD process. Scale bar divisions correspond to 100 μ.

4. Dehydriding

In vacuum conditions hydrogen liberation from the hydride powder begins at 125 °C. As hydrogen evacuation takes place, the particles surface densify and diffusion rate decrease. For a complete removal of hydrogen the powder is submitted during one hour at 700 °C in a diffusion pump vacuum. After cooling, controlled passivation must be done before air exposure of the material. Measured hydrogen content is less than 50 ppm, probably attributed to water adsorption at the particles surface after air exposure than to remnant hydrogen. Figure 4 is a general view of the final U-Mo powder particles retained in a 44 μ sieve. XRD of the powder is shown in Figure 5 indicating the major presence of the U-Mo metastable γ phase. Some traces of uranium oxide are detected and are attributed to excessive oxidation in air during the hand milling of this laboratory sample.

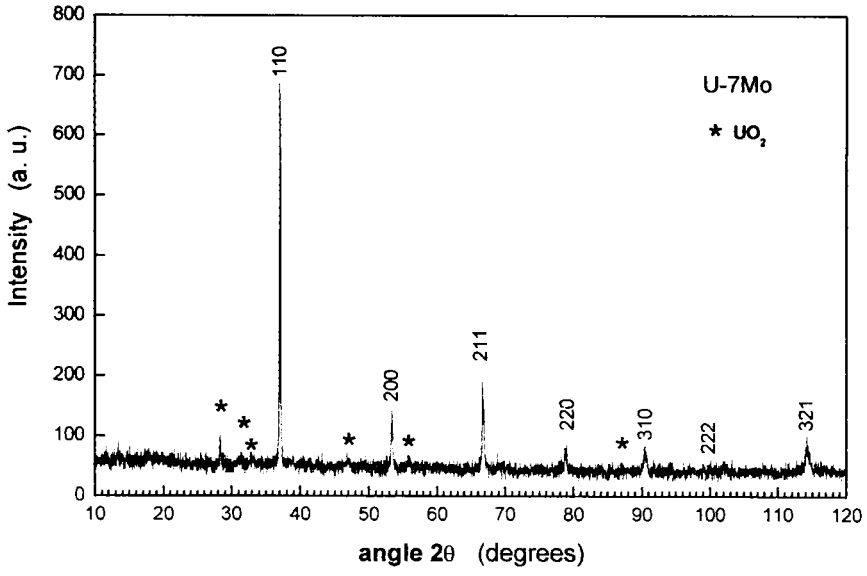

Fig 5. X-Ray Diffraction of U-Mo alloy obtained by hydriding, milling and dehydiding.

5. Conclusions

The development of the HMD process has been done simultaneously with the initiation of basic research to study the up to now unknown properties of the massive U-Mo hydride. Additional thermodynamic data, equilibrium stoichiometry and interstitial hydrogen positions still have to be elaborated. Hydrogen in solution, crystallographic orientation and macro and micro stress field alloy conditions are fundamental in the kinetics and massive hydriding of γ phase U-Mo, as in the formation of other hydrides.

One important aspect of the hydriding of U-7Mo alloy is that fractures are not as fine as in α-U hydride which produces nanometric size powder. In the case of the U-Mo hydride fractures are macroscopic with micron size internal cracks. Brittle transgranular fractures are produced during comminution giving as result polyhedrical shaped particles.

The developed process (Figure 6) is susceptible of improvements. Higher pressures can be used to increase hydrogen rate absorption; temperature and pressure controls can be automated; etc. The process is fully scalable to maximum U-Mo powder production using enriched uranium compatible with security standards. Low man-power and equipment investment are required.

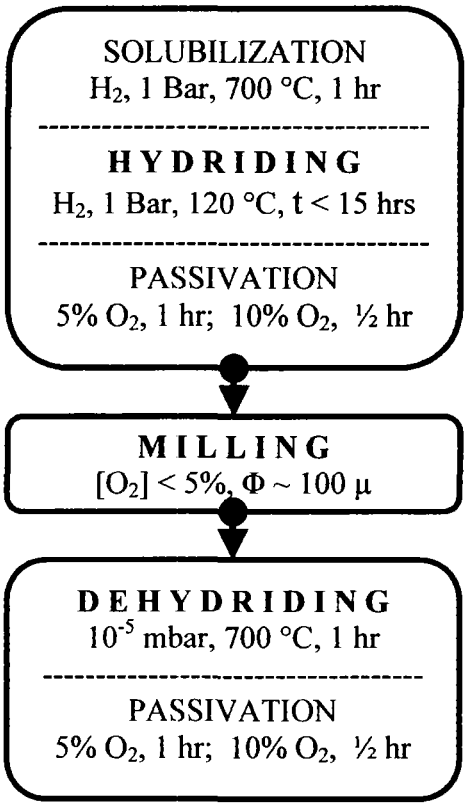

Fig 6. Flow diagram of the HMD process for U-Mo industrial powder production.

6. Acknowledgements

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7. References

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