Hydrogen Absorption-Desorption and Gamma-UMo Nuclear Fuel Powder Production

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Abstract. Gamma uranium-molybdenum alloys has been considered as the fuel phase in plate type fuel elements for MTR reactors due to its performance under irradiation and metallurgical processing. To its usage as dispersion phase in aluminum matrix, a necessary step is the conversion of the as cast structure into powder, and the technique considered at IPEN / CNEN - Brazil was HDH (hydration-dehydration). This work has the aim to study the hydrogen incorporation by gamma-UMo alloys with 8% weight molybdenum. The samples were thermally treated under constant flow of hydrogen, for temperatures varying from 500°C up to 600°C and times of 1 to 4 hours. Some of the curves relating mass incorporation and time for the above temperatures were obtained, and the results related to its microstructures and ease of fragmentation.

Introduction

To produce γ-UMo powders for use as a dispersion phase in MTR type reactors, the technique of atomization is the most widely used, since it produces powders with the best performance in terms of chemical stability under fabrication and irradiation. However, mechanical [1, 2] and chemical routes [3, 4, 5, 6] has also been studied but for compositions of 5 to 7wt% Mo. Since in IPEN / CNEN´s infrastructure there is a well developed unity to hydrogenate metallic materials, the focus of this work is to study the chemical route called hydration-dehydration (HDH).

The idea of the use of hydrogen to obtain γ-UMo powders is to convert its ductile structure into a brittle one. The formation of uranium trihydride, the decomposition of the γ-UMo matrix into α in temperatures bellow the U-Mo phase diagram eutectoid equilibrium, or the decomposition in the gamma plus alpha field, are the keys to the comprehension of how the embrittlement can be achieved via intergranular precipitation.

In this paper we are presenting and discussing some of the main results obtained in IPEN on the formation of γ-U8Mo powders via HDH embrittlement. Since most of the works in literature refers to the γ-U7Mo alloys, it is important to state conditions for the embrittlement of one of the most gamma stable alloys, an advantage in the nuclear reactor applications.

Materials and Methods

Alloys of γ-UMo were prepared by induction melting under high vacuum. Natural alpha-uranium cylinders and small cylindrical pieces, each having 3x2 mm, of high purity molybdenum, formed the induction charge, assembled in a high purity zirconia crucible.

Samples with the same shapes and masses were taken from the casts in order to perform the

hydration experiments, carried out in a thermal-gravimeter (TG) analyzer. The samples, each having approximately 250 mg, were assembled in calcined alumina crucible, after being cleaned and polished to remove surface oxidation.. Prior to each experiment, a cycle of purge and vacuum was performed, in order to keep the internal surfaces of the equipment free of gases and other contaminants. After a vacuum level of $1x10^{-2}$ mbar, a constant flux of hydrogen 5.0, analytic grade, of 1L/h, at a pressure of 1 atmosphere, was applied to the samples until the end of the experiments.

The progress of the hydrogen absorption was constantly measured as a function of time. Our main strategy was to perform the experiments over a range of temperatures, mainly those nearly the binary U-Mo system eutectoid transformation, the one in which several TTT diagrams [7, 8, 9, 10, 11] predicts maximum rate of gamma decomposition to alpha. Since we are dealing with possible absorption and also retention of hydrogen in the structure of the alloys, the absorption isotherms, which predicts maximum at 100°C to 250°C for pure gamma U (not for stabilized gamma-UMo alloys) were taken into account only to set a possible limit for hydrogen incorporation by the lattice. In our analysis of powder formation, where the equilibrium alpha to gamma is important, it is desirable the lattice absorption to be a minimum.

Curves of hydrogen absorption-desorption versus time were obtained, and also the ones related to the powder yielding, a parameter here defined as the relation between the total amount of powder formed and the initial sample masses, for each experimental conditions. The criteria to define the amount of powder was established on the basis that isothermal treatments under hydrogen atmosphere produces, in almost all the experiments, a remaining solid core, with notably bigger dimensions than its fragments.

Results and Discussions

The set of experiments and the results of powder yielding are summarized in table 1, together with the data of the cooling part of the curves, where desorption ends and a new regime of absorption starts. This point is called turning point, or TP, and is here considered as the point where there is a change in the signal of the slope of the cooling part of the curves.

From each individual experiment we can extract directly from the curves the temperatures of the turning. Isothermal temperatures are given as a real mean observed in the experiments. Those data are shown in the table 1, with the absolute difference DETP between the TP temperature and the classical eutectoid temperature of 565°C, for the γ-UMo system. In figure 1 are shown the mass absorption curves of the γ-U8Mo alloys. It can be noted that there is a correlation between turning points temperatures and the powder yielding, when we take into account the data in table 1.

Table 1 - Isothermal treatments of γ-U8Mo and respective powder yielding.

Temperature [°C]	Time [h]	Yielding [%]	Turning Point Temperature [°C]	DETP [°C]
504,26	4	1,84	99,93	465,07
525,66	3	4,67	139,21	425,79
563,56	2	75,23	139,02	425,98
565,40	4	100	145,41	419,59
568,39	4	100	150,87	414,13
573,53	4	12,58	145,82	419,18
602,33	2	3,30	145,66	419,34

From the graphics, some important results must be considered in the powder formation and its relation to the equilibrium of the metastable gamma uranium-molybdenum phase. We know from the work of Hoffman et al. [11] and from some of the U-Mo time-temperature-transformation (TTT) diagrams, that the rate at which gamma decomposes to alpha in an homogeneous alloy is strongly dependent on the isothermal treatment temperature, being more pronounced when the system is near the eutectoid temperature. Thus, the ease of the HDH process in the production of γ-UMo powders and then the fragmentation are caused primarily by the initial amount of α-U phase, which is continuously formed by a cellular matrix decomposition reaction, leading to its precipitation in the grain boundaries. So, it is logical to suppose that if the molybdenum content is high, more difficult will be the sample's fragmentation.
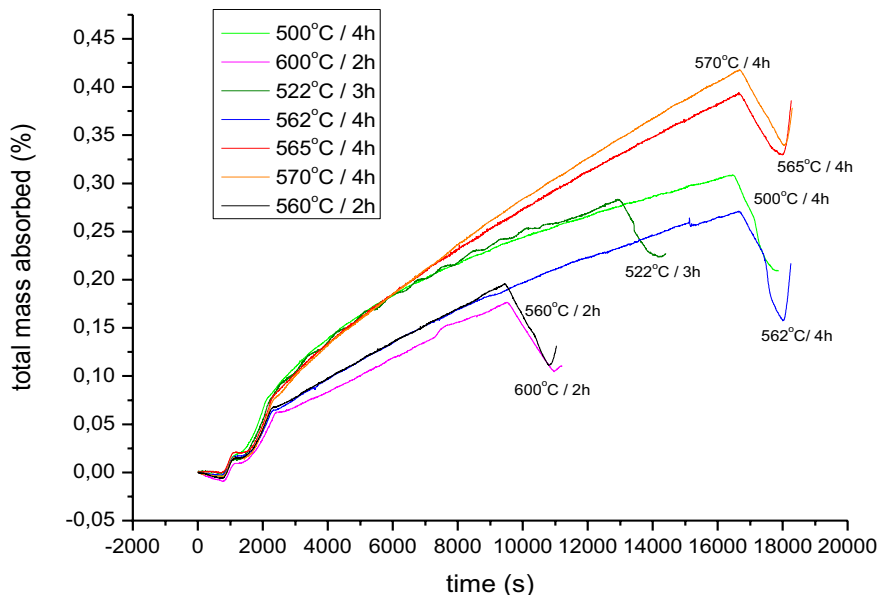

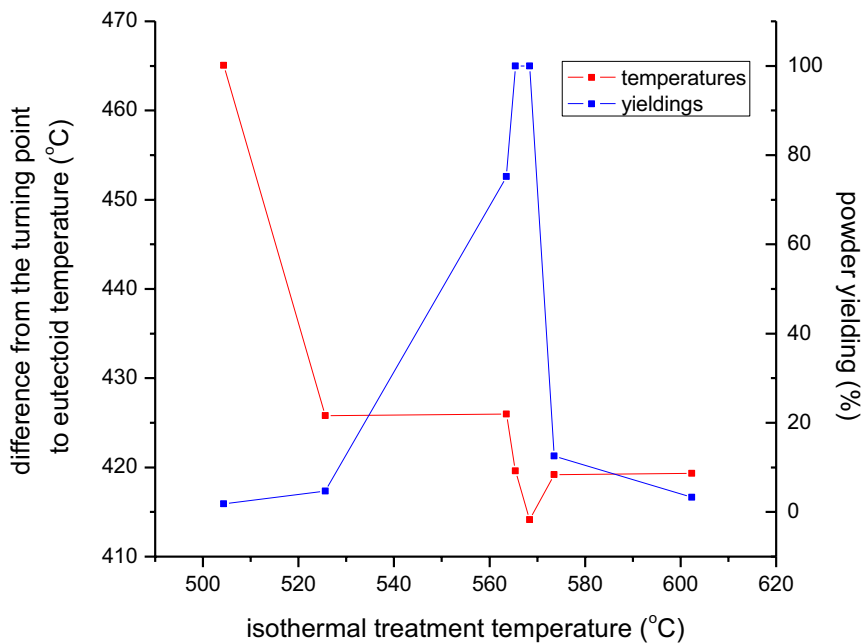Fig. 1 - Hydrogen absorption-desorption curves for γ-U8Mo samples.

Fig. 2 - DETP and powder yielding.

According to Van Thyne & McPherson [9,10], resistivity methods indicate that the value for the maximum decomposition gamma to alpha is at 500°C, and hardness indicates 570°C. Since we are dealing with powder fragmentation, it is reasonable to suppose that our work confirms that the value at which the γ-U8Mo suffers a more pronounced change in hardness is that on which there was a more pronounced production of alpha phase, which leads to a higher increase in the total hydrogen absorption and, consequently, to an ease of the samples fragmentation. This occurs, according to table 1, at a value near 568,39^{o}C.

So, the huge change of the rate of absorption which follows a brief period of mass loss can be explained by the following suggestions, and also in accordance with the work of Powell [12]. Hydrogen diffuses through the samples at a determined rate, and reacts with alpha uranium as it is precipitated in grain boundaries during the isothermal treatment. With the progress of the reaction, absorption increases, increasing also the hydrogen absorbed by the gamma uranium-molybdenum lattice.

At a specific point, where the isothermal treatment ends and the cooling ramp starts, the differences in the crystalline structure of the parent phase and uranium trihydride, which leads to differences in thermal expansion or contraction, leads to the sample collapse. This collapse leads to the increase in the absorption rate and, also, to the observed powder formation. Powders are parts of the initial alloy with high surface exposed to the action of hydrogen, so it is expected, like it was observed, that absorption increases with time in the cooling ramp region.

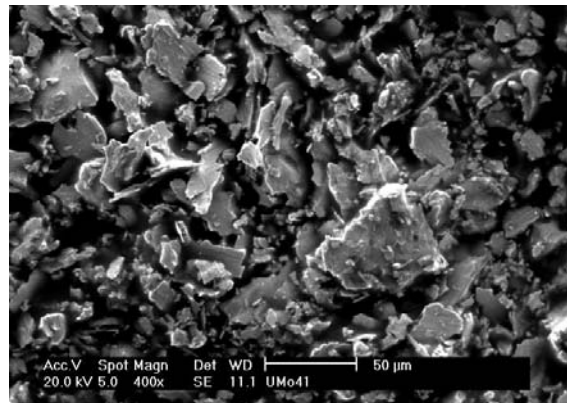In the figure below, a micrography of the γ-U8Mo powder obtained after the processes here described, is displayed.

Fig. 3 – Powder of γ-U8Mo alloy.

Conclusions

The conversion of the gamma as cast structure into alpha is thoroughly mentioned in the literature as a pre-requisite to the obtention of good powder yielding. What was experimentally demonstrated here is that, using a convenient set of parameters, the fragmentation of the structure into powder can be obtained even in a high Mo content alloy, like 8%Mo, but in more restrictive conditions of temperature, mainly those near and above the eutectoid isotherm.

The most important conclusion is related to the set of the isothermal conditions which leads to good yielding and its relation with the equilibrium between gamma and alpha phases. In terms of process, thermal shock leads to maximum yielding at 568,39^{o}C. Thus, we determined here that we are close to the eutectoid temperature transformation of the U-Mo system and to the nose point in the time-temperature transformation diagrams at this temperature. So, hydration of the alloys could also be used as a method to find some important values of equilibrium properties in the uranium-molybdenum system.

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