

GAMMA DECOMPOSITION AND POWDER FORMATION OF γ -U8Mo NUCLEAR FUEL ALLOYS

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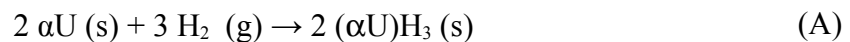
ABSTRACT

Gamma uranium-molybdenum alloys have been considered as the fuel phase in plate type fuel elements for MTR reactors, mainly due to their acceptable performance under irradiation and metallurgical processing. To their use as a 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 is HDH (hydration-dehydration). This paper describes the first results of hydrogen absorption and its relation to powder formation of the γ -U8Mo alloy. After their production by induction melting, samples were thermally treated under constant flow of hydrogen for temperatures varying from 500°C to 600°C and times from 2 to 4 hours. Curves relating mass incorporation and time for the above temperatures were obtained, and the results were related to its fragmentation. It was observed that even after the dehydration, samples can be fragmented under specific conditions of isothermal treatments, and that there is a strong correlation between absorption and the rate of gamma decomposition. A value of 568,39°C was obtained for the maximum in the rate of gamma decomposition, which is related to the eutectoid transformation temperature of this alloy.

key-words: uranium-molybdenum alloys, hydration-dehydration, powder obtention, high density nuclear fuels.

INTRODUCTION

The idea of the use of hydrogen to obtain γ -UMo powders is to convert its ductile structure into a brittle one. In the range of compositions where γ -UMo is considered as a dispersed nuclear reactor fuel, mainly 5 to 10% weight in Mo, alpha-uranium is the proeutectoid phase. It is expected that the as cast and even the thermally treated structures contains some intergranular alpha-uranium as cellular precipitates. In terms of powder formation, the alpha phase reacts readily with hydrogen in temperatures from 250°C to 350°C. The formation of uranium trihydride:



and the decomposition of the γ -UMo matrix into α :



for temperatures below the U-Mo phase diagram eutectoid equilibrium, or:



for the gamma plus alpha field, are the keys to the comprehension of how the embrittlement can be achieved via intergranular precipitation.

To produce γ -UMo powders, a group of operations has been used, the conventional ones reported in the work by CLARK et al [1] and WIENCEK and PROKOFIEV [2]. The other ones, called the HDH routes, are studied in BALART [3], SOLONIN [4] and PASQUALINI [5,6], and are usually carried out in the following sequence, aiming the obtention of γ -U(6 to 7)Mo powders. After the casting operation, an isothermal treatment of homogenization is given to the sample to ensure a good molybdenum distribution in the grains. The next step is carried out by two main routes. The first one comprises a direct thermal treatment in the gamma plus alpha phase field [3,4], to partially convert gamma into alpha by means of the reaction (C), followed by dehydration, the inverse (A) reaction. More recently, due to the observation that hydrogen can be easily incorporated by γ -U7Mo mainly in low temperatures, a previous thermal treatment in temperatures from 120°C to 150°C for times varying from 1 to 3 hours, followed by another thermal treatment in gamma plus alpha phase field, was applied to the samples. Also, the powder is obtained after the MDH step.

However, in some of the experiments carried out in this work, it was observed that, by a correct choice of parameters, the structure of the alloy collapses readily, without the MDH step, with cooling speed having an important role in the fragmentation of the samples. If the same cooling rate was applied to all the samples, alloys more susceptible to hydrogen embrittlement are also more susceptible to break by thermal shock. 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.

Our main objective is to state a set of optimal parameters to the obtention of good powder yielding, mainly in the hydration step, and to clarify, at least qualitatively, the mechanisms which lead to the γ -UMo powder formation.

MATERIALS AND METHODS

Alloys of γ -U8Mo 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 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 200 mg, were assembled in calcined alumina crucible, after

being cleaned and polished to remove surface oxidation, which can interfere in the results. 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 $2,0 \times 10^{-6}$ MPa, a constant flux of high purity hydrogen (5.0 ou 99.999% analytic) was applied to the samples. The verification of the γ -U8Mo alloys embrittlement behavior under hydrogen was very similar to the utilized by TETER et al. [7].

Experimental settings like times and temperatures, ramps, heating and cooling rates, were inserted in the analyzer software. The main strategy was to perform the experiments over a range of temperatures, nearly the binary U-Mo system eutectoid transformation, the nearest one in which several TTT diagrams [8,9,10,11,12] predicts maximum rate of decomposition, given by reaction (B). Experiments start when all the system was filled with hydrogen, which also prevents the presence of oxygen. Curves of hydrogen absorption as a function of time were obtained. Curves of powder yielding for each of the experimental conditions were also obtained. The powder yielding is a parameter here defined as the relation between the total amount of powder formed and the initial sample mass.

RESULTS AND DISCUSSIONS

X-ray spectra and micrographies of the γ -U8Mo compositions are shown in Figure 1.

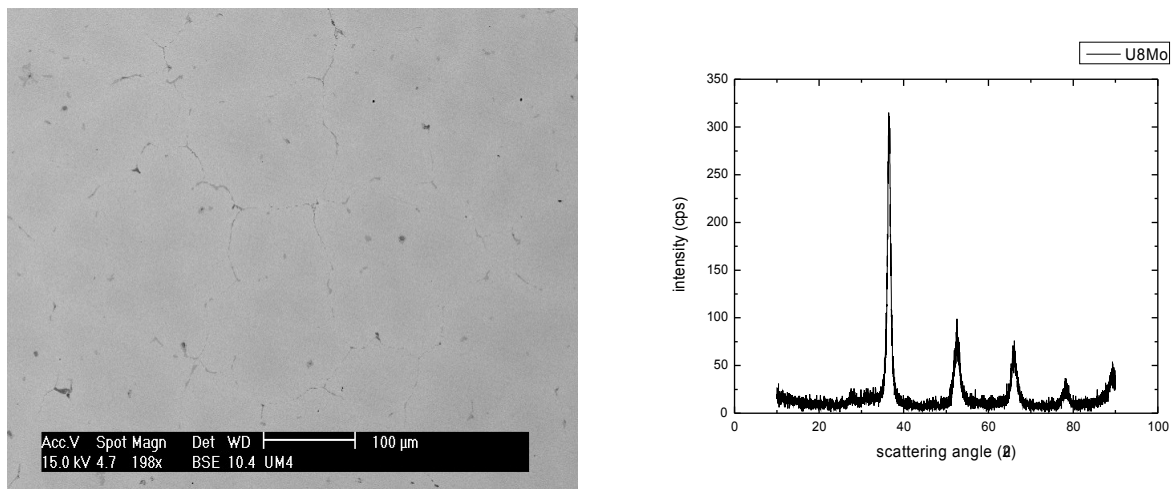


Figure 1 - MEV image and X-Ray diffraction pattern of γ -U8Mo alloy.

The parameters of each of the experiments and the results in terms of powder yielding are summarized in Table 1. We are concerned with the temperatures and times which could lead to powder formation in the isothermal treatments. As discussed above, cooling of the samples had an important role in the sample's fragmentation.

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

Temperature (°C)	Yielding (%)
504,26	1,84
525,66	4,67
563,56	75,23
565,40	100
568,39	100
573,53	12,58
602,33	3,30

In Figure 2 are shown the mass absorption curves, including the points of absorption / desorption changes in the cooling ramps (inflexion points), for the γ -U8Mo alloys.

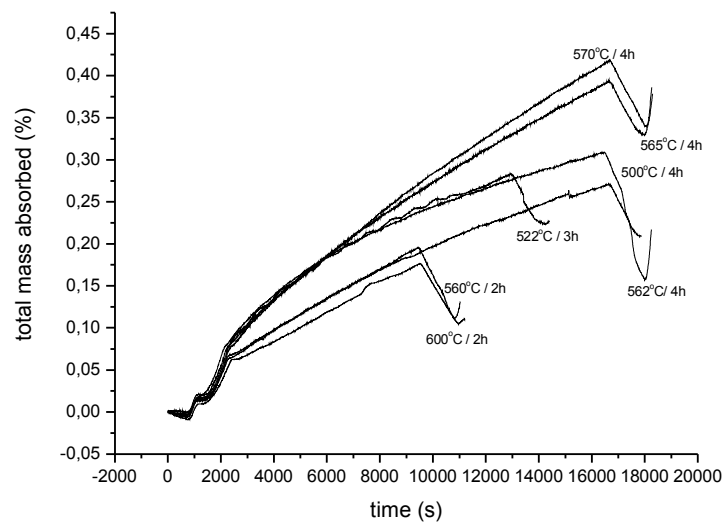


Figure 2 - Hydrogen absorption / desorption curves for the γ -U8Mo samples.

From these curves the temperatures of the inflexion points in the interactions between hydrogen and γ -U8Mo, in the cooling parts of the experiments, were extracted. Those data are shown in the Table 2, with the absolute differences between the isothermal, the inflexion and the classical or stated eutectoid temperature of 565°C, for the γ -UMo system, calculated as:

$$\Delta_{it} = |T_{it} - T_e| \quad (D)$$

$$\Delta_{cm} = |T_{cm} - T_e| \quad (E)$$

where Δ_{it} and Δ_{cm} are the absolute values between the temperature differences of thermal treatment and the inflexion or the absorption to desorption points, from the eutectoid transformation temperature T_e , respectively, where T_{it} is the temperature of isothermal

treatment, and T_{cm} is the temperature of the change of mechanism.

Table 2 - Thermal data from the hydrogen absorption curves.

Isothermal Temperature (°C)	Absorption / Desorption Temperature (°C)	$\Delta_{it} = T_{it} - T_e $ (°C)	$\Delta_{cm} = T_{cm} - T_e $ (°C)
504,26	99,93	60,74	465,07
525,66	139,21	39,34	425,79
563,56	139,02	1,44	425,98
565,40	145,41	0,4	419,59
568,39	150,87	3,39	414,13
573,53	145,82	8,53	419,18
602,33	145,66	37,33	419,34

The first comparison between Tables 1 and 2 shows that there is a correlation between isothermal temperatures, the absorption / desorption temperatures, and the powder yielding, since the yielding can be viewed as influenced by the distance from the isothermal eutectoid temperature of 565°C. Thus, it became interesting to determine the total mass absorption and the respective rates, and to correlate these data also with the powder yielding or to the desorption rates. They were summarized in Table 3, where the amount of hydrogen retained was calculated as the difference between the maximum hydrogen absorbed, given at the end of the thermal treatments, and the amount of hydrogen released at the changing point in the cooling curves.

The rate at the stable hydrogen absorption is a mean value, calculated from the end sections of the isothermal absorption curves, where the absorption is considered to be constant.

Table 3 - Hydrogen absorption data from the isothermal treatments.

Isothermal Temperature (°C)	Hydrogen at the Inflexion Point (%)	Total Hydrogen Absorbed (%)	Rate at the Stable H Abs. (% x10 ⁻⁶ / s)
504,26	0,2091	0,0994	7,94
525,66	0,2237	0,0590	13,12
563,56	0,1115	0,0834	16,54
565,40	0,1573	0,1130	12,62
568,39	0,3298	0,0626	16,46
573,53	0,3401	0,0770	18,48
602,33	0,1044	0,0715	12,72

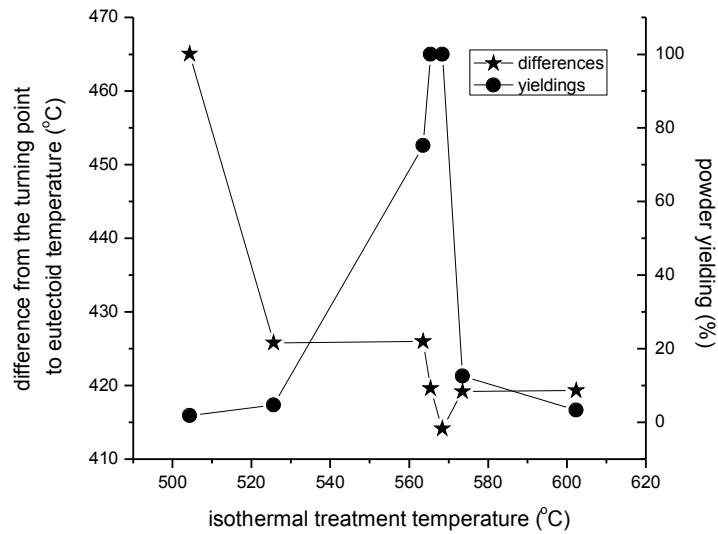


Figure 3 - Δ_{cm} and powder yieldings, from Table 2.

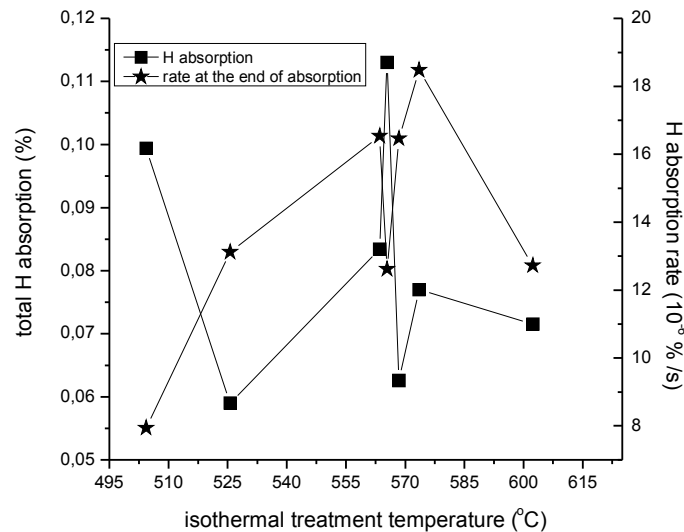


Figure 4 - Hydrogen absorption parameters, from Table 3.

From the graphics and tables above, some phenomena must be considered in the powder formation and its relation to the equilibrium of the metastable gamma uranium-molybdenum phase. First, if a certain amount of alpha is present initially, and by the reaction (A) we know that alpha has the tendency to react with hydrogen, it is expected that the hydrogen absorption in γ -U8Mo must also be influenced by the rate at which alpha is formed. We know from the work of HOFFMAN et al. [13] and from some of the U-Mo time-temperature-transformation (TTT) diagrams, the rate at which gamma decomposes to alpha in any 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.

Also, in the works of VAN THYNE & McPHERSON [10,11] and MGEARY [12], the nose of the TTT diagrams varies strongly, according to the methods used to the determination of the equilibrium gamma - alpha. Following McGEARY [12], the temperature at which there is a maximum decomposition of γ -U8Mo is 525°C, using X-ray diffraction and metallography. According to VAN THYNE & McPHERSON [10,11], resistivity methods indicate a value of 500°C and hardness of 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 3, at a value near 568,39°C or 573,53°C.

For this last condition, we obtained the highest values in the hydrogen absorption and its rates, but it produces only 12% of fragmentation. Since the temperature of the gamma plus alpha to gamma field in the U-Mo phase diagram for γ -U8Mo is approximately 619°C, we are far from the eutectoidal transformation temperature and closer to this line when the treatment is applied at 570°C. Thus, the point of the maximum decomposition is reached when the thermal treatment is performed at 568,39°C, instead of 573,53°C. Another favorable argument is that the temperature of the transition to desorption / absorption is the highest among all, leading to a minimum in the distance from the classical eutectoidal transformation temperature and to a minimum in the energy needed to break the samples by thermal shocks. Since it was considered the same cooling rate in all the experiments, we can conclude from the table 2 that with the smallest thermal gradient the yielding was better. Thus, 568,39°C is the most related one to the eutectoidal transformation. If we use 565,40°C, apart its smallest difference from the classical value and same powder yielding, we cannot have the same results.

Despite of the absorption at 568,39°C being less pronounced when compared with those of 504,26°C, 573,53°C and 602,33°C, we are leading to the following conclusions. Absorption of hydrogen may occur by 2 main mechanisms, mentioned in the work of POWELL [14], one related to the interstitial positions and the other related to the intergranular precipitation of alpha. If the distance from the eutectoid increases, we are far from the condition which leads to a more alpha precipitation and, thus, the mechanism related to the first, also called embrittlement by hydrogen saturation and tension sources creation, are not enough to produce embrittlement and, consequently, good powder yielding. This fact can explain good absorption, but low yielding, when the samples were treated in above mentioned temperatures. At 602,33°C, if we double the time and consider the same rate of absorption, we will obtain near the double of the mass absorbed in two hours. The same is considered for the other experiments, when the time was less than 4 hours

Thus, it is demonstrated here, at least for this composition, a good yielding is possible only in temperatures very close to 565 to 568°C, and that 568,39°C, instead of 565°C, can be considered the closest value of the eutectoidal temperature transformation.

Another aspect is the characteristic of the powder formed, which can be inferred by the huge increase in the absorption rates, mainly in the cooling part of the curves. In all the experiments where there was good yielding, it was observed that at some point in the cooling ramp there was a change in the mechanism of mass absorption. If we consider

that absorption is a phenomenon that depends on the amount of the free area existent in the system, it is expected that the higher the surface of the material exposed to the gas, the higher the absorption, and then we can estimate dimensional parameters of powders, like mean diameters, for example.

Thus, the huge change of the rate of absorption which follows a brief period of mass loss can be explained by the following considerations. 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, the sample collapses, and 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. It is expected that absorption increases with time in the cooling ramp region.

If there is a creation of a number of sites by the particles detached from the initial samples, they can be capable to absorb more hydrogen until saturation is reached. This creation of new absorption sites can be related to the difference between the total amount of hydrogen absorbed at the maximum in the isothermal treatment and the minimum in the cooling ramp, after which the system undergoes a new increase in the absorption rates. This increase allows to some estimates on the new surface area after fragmentation, and to the dimensional parameters of the particles produced on each of the experiments.

Finally, at this level of the samples hydrogen exposition, it is important to observe that, due to the low solubility of hydrogen in uranium and uranium alloys and to the strong tendency to form hydrides, it is expected that the main mechanism of embrittlement of uranium alloys must be due to the stress induced by alpha uranium hydride formation [7], mainly in the low stabilized alloys of γ -U_xMo alloys ($x < 8$). At this level of stability, both mechanisms must play a concurrent role to the phenomenon. It is logical to infer, thus, that stress induced alpha formation contribution must decrease with the increase in the Mo content in γ -U_xMo alloys (for nuclear fuel applications, $8 \leq x \leq 10$).

CONCLUSIONS

Apart of the dehydration treatment applied by the various works on HDH γ -UMo powder obtention mainly in the compositions of 5 to 7 wt% Mo, the emphasis was given here in the isothermal absorption treatments. Dehydration phenomena is very important to recover the original composition, which must be free of hydrogen, but it is not essential to the fragmentation of the alloys, as we have demonstrated here.

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 near and above the eutectoid isotherm. Isothermal treatments in temperatures far from the

eutectoid were also applied to some samples, leading to low yielding, but revealing the possibility to the obtention of high gamma powder contents.

It was determined in this work that thermal treatments near to the eutectoid temperature transformation of the U-Mo system and to the nose point in the time-temperature transformation diagrams, thermal shock with good yielding occurred at 568,39°C, near of the classical 565°C. 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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