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# GAMMA STABILITY AND POWDER FORMATION OF UMo ALLOYS

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## ABSTRACT

A study of the hydrogen embrittlement as well as a research on the relation between gamma decomposition and powder formation of uranium molybdenum alloys were previously presented. In this study a comparison regarding the hypo-eutectoid and hyper-eutectoid molybdenum additions is presented. Gamma uranium-molybdenum alloys have been considered as the fuel phase in plate type fuel elements for material and test reactors (MTR). Regarding their usage as a dispersion phase in aluminum matrix, it is necessary to convert the as cast structure into powder, and one of the techniques considered for this purpose is the hydration-dehydration (HDH). This paper shows that, under specific conditions of heating and cooling, γ-UMo fragmentation may occur with non-reactive or reactive mechanisms. Following the production of the alloys by induction melting, samples of the alloys were thermally treated under a constant flow of hydrogen. It was observed that, even without a massive hydration-dehydration process, the alloys fragmented under specific conditions of thermal treatment, during the thermal shock phase of the experiments. Also, there is a relation between absorption and the rate of gamma decomposition or the gamma phase stability of the alloy and this phenomenon can be related to the eutectoid transformation temperature. This study was carried out to search for a new method for the production of powders and for the evaluation of important physical parameter such as the eutectoid transformation temperature, as an alternative to the existing ones.

## 1. INTRODUCTION

Studies of the hydrogen embrittlement as well as a research on the relation between gamma decomposition and powder formation of uranium molybdenum alloys over a wide range of compositions were previously presented [1]. For the case study of the 8% wt.Mo addition [1,2,3], which are in the hypereutectoid range in the binary UMo phase diagrams but very near of the eutectoid composition, that the curves for the ease of hydrogen reactions, with the gamma alloy matrices, as a function of times and temperatures, presented the same shape of the its time-temperature-transformation (TTT) curves, suggesting that the reaction:

$$2\alpha U(s) + 3H_2(g) \rightarrow 2(\alpha U)H_3(s) \quad (1)$$

can be used to the determination of the maximum decomposition rate of the gamma-uranium matrix, through the reactions:

$$\gamma \rightarrow \alpha \tag{2}$$

in temperatures below the eutectoid equilibrium, a total allotropic transformation, and

$$\gamma \rightarrow \alpha + \gamma' \tag{3}$$

in the gamma plus alpha field, a partial allotropic transformation. Reaction (1) is called hydration (H) and its reverse, dehydration (DH). Both form the basis of the so called HDH technique, usually employed in the range of 5 to 7-8%wt. Mo.

Hydrogen embrittlement of alloys starts with a massive diffusion of the gas to a solid phase. Absorption of hydrogen by the matrix and other phases results in materials with different elastic and thermal properties, leading to the accumulation of stresses in the body of the alloy [4]. Thus, this phenomenon can be explored to fracture and to the powdering of the material, under suitable thermal treatments [1]. For alloys like γ-UMo and others, the ease of embrittlement is also related to its metastable condition, since phases of the UMo binary system behave under hydrogen in different ways. Considering the contribution of this mechanism, the transformations (2) and (3), in the γ or γ + α fields, are keys to understand how the embrittlement can be achieved via intergranular precipitation or intragranular cracking.

To produce γ-UMo powders for use as dispersed-type fuel elements in research reactors, a set of unitary operations, with or without the help of chemical reactions, has been used. Conventional techniques are based on powder metallurgy techniques such as milling, atomization, and machining [5, 6]. The ones supported by chemical reactions are HDH and HMDH (hydration-milling-dehydration) [7, 8, 9, and 10]. It is important to note that the chemical and physical characteristic of the powders, together with the techniques for their fabrication, influences the behavior under fabrication and irradiation of the nuclear fuel plates [11, 12].

An HDH or HMDH technique comprises the following sequence of pre-operations. The first is a thermal treatment in the γ+α phase field, aiming the partial conversion of the γ phase into α by means of reaction (2) and (3), followed by hydration, reaction (1), and dehydration, the inverse of the reaction (1). More recently, owing to the observation that hydrogen can be easily incorporated by γ-U7Mo [1,9,10] mainly in low temperatures, a previous thermal treatment can be given to the samples in temperatures from 120 to 150 ºC, followed by a thermal treatment in the gamma plus alpha phase field.

However, it was observed that, if a thermal shock treatment is applied to the samples, there is an enhancement in the embrittlement via hydrogen of the alloys, leading to their fracture and thus, powdering, even for the most stable compositions, which are the hypereutectoid ones [1].

In this paper, results for the additions of 6, 8 and 10wt% of molybdenum, are presented and discussed. The first is in the hypoeutectoid field, having the highest rate of decomposition by means of reaction (2). The most stable one, 10wt%, is also the most resistant to the

decomposition, as is shown in the following sections.

## 2. MATERIALS AND METHODS

The method presented in this paper was first devised to enable a massive powdering of the γ-UMo alloys [1], over a broad range of Mo additions, and are briefly described here.

After a series of a small scale experiments, carried out to build the curves of hydrogen absorption-desorption-reabsorption, parameters like the maximum hydrogen absorption temperatures, and temperatures of desorption or dehydration, etc., were obtained.

Samples of similar shapes and average masses of 200 mg were taken from the casts and cleaned, to remove surface oxidation and contaminants, in order to perform the absorption–desorption–embrittlement–thermal shock experiments, carried out in a thermal-gravimeter (TG) analyzer. Prior to each thermal cycle, a cycle of purge and vacuum was performed to ensure that the internal surfaces of the equipment were free of gases and other contaminants. Once a vacuum level of the order of $10^{-2}$ mbar was reached, a constant flow of high purity hydrogen was applied to the samples, up to the end of the experiments. The rate of cooling in the end of the experiments were the same.

Experimental parameters such as temperatures, isothermal times, and heating and cooling rates, were taken as inputs for the thermo-analyzer software, to setting up the experimental cycles. The progress of the hydrogen alloy absorption was measured as a function of time, for the given temperatures, heating and cooling rates. Thermal cycles were mainly defined with temperatures as closest as possible to the binary U–Mo system eutectoid transformation field, where it is predicted the maximum rate of decomposition, given by the reactions 2 and 3.

Powder yielding was obtained by examination of the state of the samples, after the experiments. Its definition and criteria for its evaluation are both given in reference [1].

## 3. RESULTS AND DISCUSSIONS

### 3.1.Microstructure

Micrograph and X-ray spectra of the as cast structures of the γ-U6Mo, γ-U8Mo and γ-U10Mo alloys, are shown in Figs. 1, 2 and 3. For the purposes of this research, homogenization, grain size and the presence of other phases in the parent metal (alloy) are the most important observable parameters. For the purpose of this paper, it is enough to mention that visual analysis showed that the casts were produced with a good degree of homogenization, which is a characteristic of the melting technique of induction when applied to the production of such alloys.

Expected differences between the positions of the peaks of the X-ray diffraction patterns among the three samples can be observed after a more accurate analysis of the X-ray files [1]. The progressive shift is a phenomenon related to the presence of interstitial molybdenum in the γ-UMo body-centered cubic crystalline lattice. However, for the 10% wt addition, it is also shown peaks of the δ-phase, a compound with definite stoichiometry, reported also as δ-$U_2Mo$

phase, indicating some segregation during the production of the alloy, due possibly to local inhomogenization of the induction samples. There is no reported behavior of this phase under hydrogen atmosphere, it is expected that it behaves like the γU10Mo phase, based on the results of the hydration of the alloys of the next section.

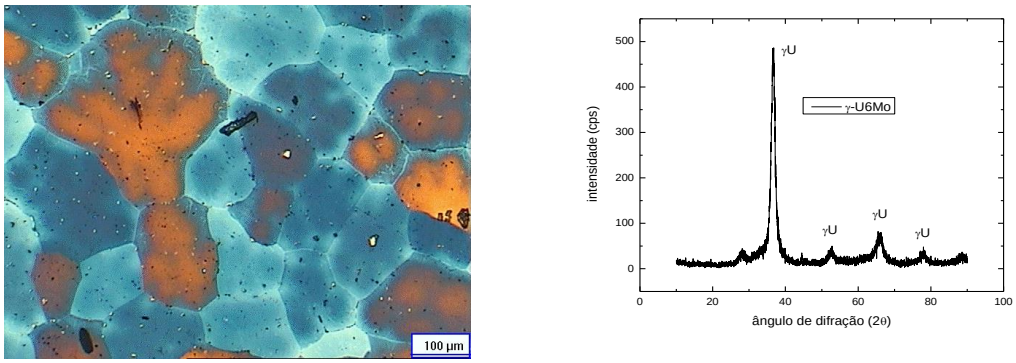


**Figure 1: Micrography and X-ray diffraction pattern, γ-U6Mo.**

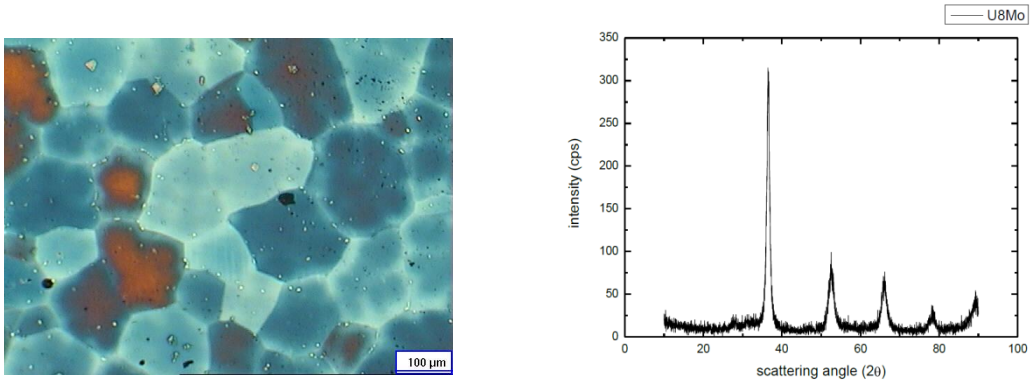


**Figure 2: Micrography and X-ray diffraction pattern, γ-U8Mo.**

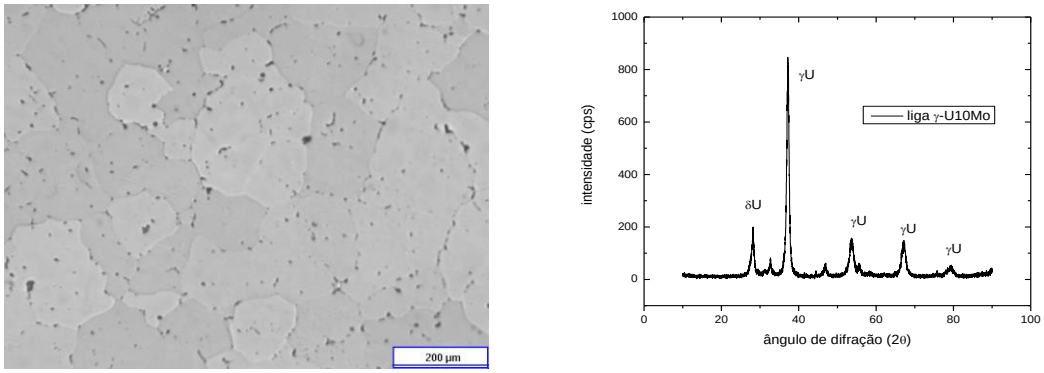


**Figure 3: Micrography and X-ray diffraction pattern, γ-U10Mo.**

### 3.2. HDH treatments and thermal shock

Figures 4 show the behavior of a sensibilization thermal treatment for a sample of γU6Mo alloy, under hydrogen.

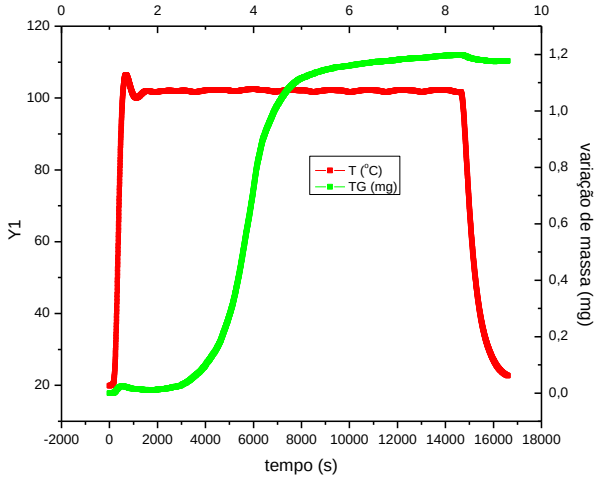


**Figure 4: Mass absorption as a function of time, hidration at 100ºC, 4 hours, γU6Mo.**

For this alloy, it was observed that hydration was a massive process, comparable in terms of the amount of hydrogen absorbed with the presented by alpha uranium, more permeable under hydrogen than the gamma-phase. Previous experiments carried out with the pure alpha-U phase [1] concluded that the start of the reaction (1) occurs at the experimental coordinates (t; T; m; HF) = (1999; 190,2; -0,074; -14,08), with t (time) in seconds, T (temperature) in degrees Celsius, m (mass absorbed) in milligrams, and HF (heat flow) in μV. The maximum rate of hydration occurred at (t; T; m; HF) = (2307; 218,96; 0,446; -14,58) [1].

The approximated coordinates (t, T) for the start of the reaction (1) and the maximum hydration rate for the γU6Mo alloys were obtained at (2115; 102) and (5200; 102), respectively. This indicates that to reach the maximum rate, it is necessary to expose the alloy under hydrogen atmosphere for longer times. There is no need to operate with the alloys at temperatures near the eutectoid transformation point.

For γ-U8Mo alloys, the resulting hydrogen absorption-desorption curves are shown in Figure 5. Since sensibilization thermal treatments [1, 7] produced almost no effect in terms of hydrogen absorption for this composition, temperatures were chosen near the eutectoid, which was, for in this composition, determinant to its embrittlement and subsequent powder formation, together with the important cooling stage, representing the phenomena of thermal shock.

The mass absorption curves, including turning points ($T_{tp}$) of desorption-reabsorption in the cooling ramps of the γ-U8Mo alloys are also taken into consideration. $T_{tp}$ points are defined here as the points where desorption (or loss of hydrogen), as indicated by the decrease in mass after the isothermal treatments, is changed to a massive absorption or reabsorption of hydrogen during cooling.

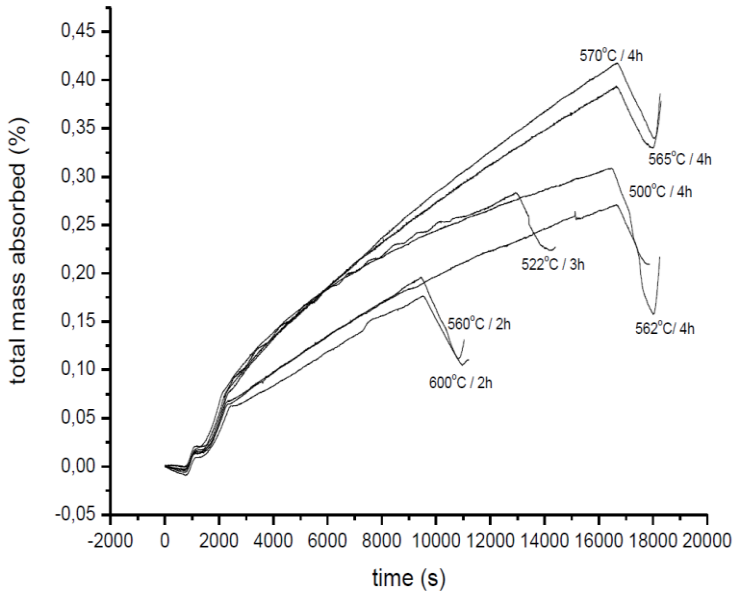


**Figure 5.: Experimental curves of mass absorption for γU8Mo samples [1].**

The temperatures of the turning points (Ttp) were obtained experimentally from the curves. The isothermal temperatures (Tit) were the actual mean temperatures, as indicated by the thermal-analyzer. The experimental conditions, yielding results and thermal cycles and data, are shown in Tables 1 and 2, and Figures 5, 6 and 7.

**Table 1.: Data from the γU8Mo Hydrogen Experiments.**

| $T_{it}$ (ºC) | time (h) | yield (%) | $T_{tp}$ (ºC) | $\Delta_{eit}$ (ºC) | $\Delta_{etp}$ (ºC) |
|---|---|---|---|---|---|
| 504.3 | 4 | 1.8 | 99.9 | 60.7 | 465.1 |
| 525.7 | 3 | 4.7 | 139.2 | 39.3 | 425.8 |
| 563.6 | 2 | 75.2 | 139.0 | 1.4 | 425.9 |
| 565.4 | 4 | 100.0 | 145.4 | 0.4 | 419.6 |
| 568.4 | 4 | 100.0 | 150.9 | 3.4 | 414.1 |
| 573.5 | 4 | 12.6 | 145.8 | 8.5 | 419.2 |
| 602.3 | 2 | 3.3 | 145.7 | 37.3 | 419.3 |

$\Delta_{eit}$ and $\Delta_{etp}$ are defined as:

$$\Delta_{eit} = \left| T_{it} - T_e \right| \tag{4}$$

and

$$\Delta_{etp} = \left| T_{tp} - T_e \right| \tag{5}$$

from reference [1]. Both parameters are considered, for a first assessment of the powdering mechanism, as absolute values between the temperatures of isothermal treatments and turning points, respectively, and the theoretical eutectoid transformation temperature, $T_e$.

The previously mentioned correlation, between mass absorption curves and TTT diagrams, can be deduced form the data of Table 1 and from the observation of Figures 6 and 7 [1, 2, 3].

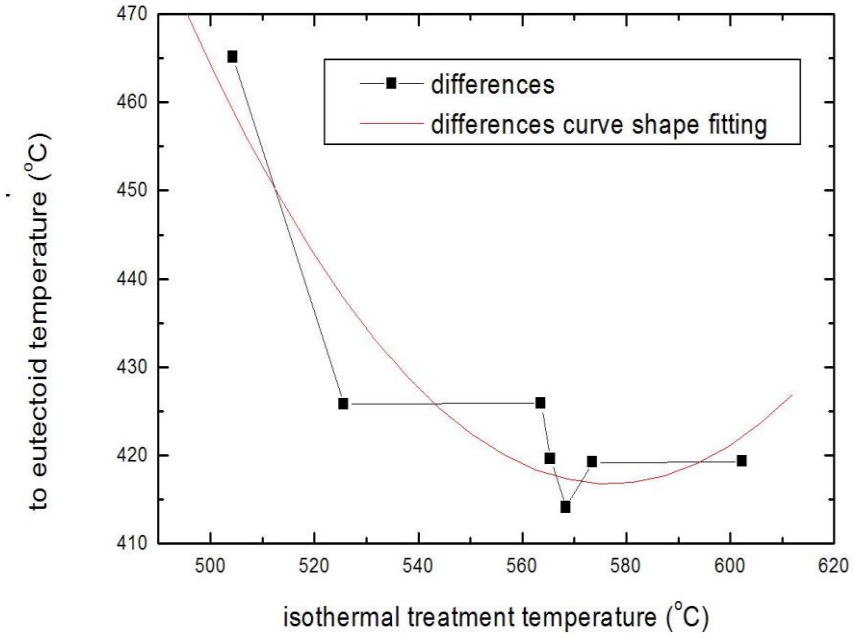


**Figure 6.: $\Delta_{etp}$ and powder yielding, γU8Mo [1]**

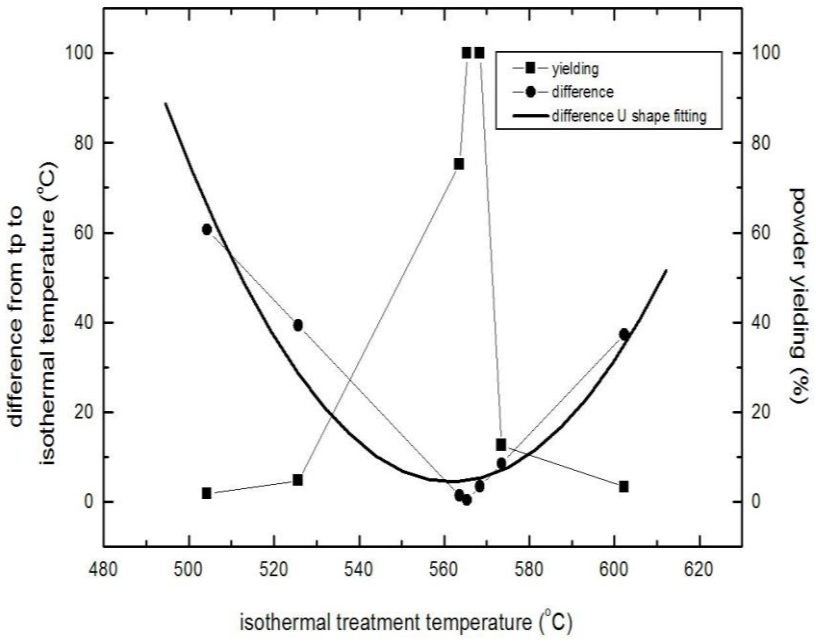


**Figure 7.: $\Delta_{eit}$ and powder yielding, γU8Mo [1]**

Results are summarized in Table 2, for the amounts of hydrogen retained by the samples, calculated as differences between the maximum hydrogen absorbed, at the end of the thermal treatments, and the amount of hydrogen released at the turning point in the cooling curves.

**Table 2.: Hydrogen Absorption Data and Powder Yielding, γU8Mo. [1]**

| Isothermal Temperature (°C) | Hydrogen at the $T_{tp}$ (%) | Total Hydrogen Absorbed (%) | Rate at the Stable H Absorption (% × $10^{-6}$/s) |
|---|---|---|---|
| 504.3 $(500)_T$ | 0.2091 | 0.0994 | 7.94 |
| 525.7 $(522)_T$ | 0.2237 | 0.0590 | 13.12 |
| 563.6 $(560)_T$ | 0.1115 | 0.0834 | 16.54 |
| 565.4 $(562)_T$ | 0.1573 | 0.1130 | 12.62 |
| 568.4 $(565)_T$ | 0.3298 | 0.0626 | 16.46 |
| 573.5 $(570)_T$ | 0.3401 | 0.0770 | 18.48 |
| 602.3 $(600)_T$ | 0.1044 | 0.0715 | 12.72 |

A typical curve of mass absorption for γU9-10Mo is given below. The amount of mass absorbed is nearly 10 % less than the absorbed by the γU8Mo sample, when considering the same thermal cycle, as can be seen by direct comparison of Figs. 5 and 8.

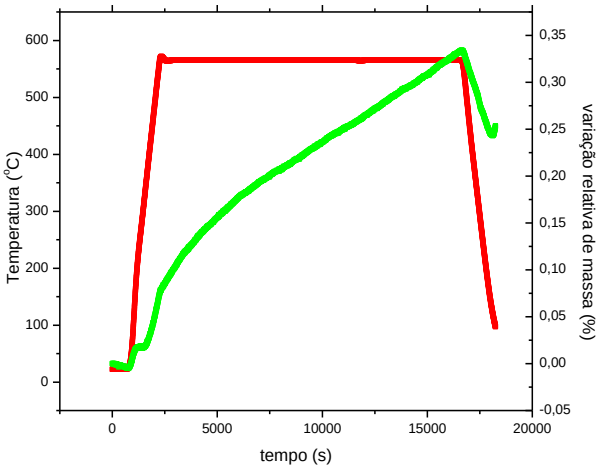


**Figure 8.: Experimental curves of mass absorption for γU10Mo samples [1].**

Again, a thermal shock phase was necessary for the enhancement of hydrogen absorption by the samples, but since at this composition the alloy is in its most stable state, cellular decomposition, as given by reactions 2 and 3, are not enough to produce some amount of absorption necessary for the embrittlement of the alloy.

It is also suggested by the observation of Figure 8 that longer thermal cycles than the chosen here are necessary to produce the same yielding, for example, of the samples of γU8Mo. Experiments with different temperatures and cycles, and sensibilization treatments for this composition, did not obtain different results than the presented in Figure 8, suggesting that hydrogen is mainly adsorbed than absorbed by the alloy´s bulk.

To explain the differences of behavior under hydrogen among the additions, first physical parameter we consider is density, together with the amount of phases presented in the samples. Differences in the densities of the γ-UMo alloys, which has a mean value of 18 g/cm$^3$, α-U (19.1 g/cm$^3$) and α-$UH_3$ (10.9 g/cm$^3$) phases, can explain the mechanism of creation of thermal stresses in the bulk of the alloys, mainly if an initial amount of α is present in the samples. Hydrogen absorption occurs at a different rate in alpha phase than in gamma, thus the facility to powdering of the γ-U6Mo even at low temperatures, and γU8Mo, together with thermal shock. Embrittlement can be enhanced by reaction (1), and thus influenced by the rate at which alpha is formed.

For the determination of U-Mo TTT diagrams, some experiments were conducted [13, 14, 15, 16] to determine the rate at which gamma decomposes to alpha, in a homogeneous alloy. Similar curves, but based on empirical data, are given in the works of Van Thyne and McPherson [14,15] and McGeary [16], where the inflexion or nose points of the TTT diagrams changes, according to the methods employed for the determination of the gamma-alpha equilibrium. From McGeary [15], maximum decomposition of γ-U8Mo occurs at 525 ºC, as determined by X-ray diffraction and metallographic techniques. According to Van Thyne and McPherson [13,14], resistivity methods indicated a value of 500 ºC, and hardness methods, 570 ºC.

Since the present study deals with powder fragmentation, it is reasonable to suppose that the value where there is a change in hardness for the γ-U8Mo, according to Van Thyne and McPherson [13,14], is the one where there was a higher concentration of alpha phase, leading to a higher increase in the total hydrogen absorption via hydration and to more powder formation. With the results obtained in our hydrogenation experiments, and according to Figures 6 and 7, maximum absorption temperature occurs at a value near 568.4 ºC. Thus, decomposition is more pronounced when the system is closer to the eutectoid temperature, as is shown in this paper, Figs. 5 to 7.

The γ+α→γ transition temperature in the U-Mo phase diagram for γ-U8Mo is approximately 619 ºC, which is far from the eutectoidal transformation temperature and closer to this transition line, when the treatment is applied at 570 ºC. Thus, the inflexion point, i.e., the point of the maximum decomposition, is reached at 568.4 ºC, instead of 573.5 ºC. The corresponding turning point temperature is then at a minimum distance from the classical eutectoidal transformation temperature, and can be related to a minimum in the energy, equation (7), to break up the samples by the thermal shock technique.

For the most stable compositions, absorption in the lattice, related to the presence of the interstitial positions in the alloy, is the main mechanism of hydrogen incorporation. If intergranular precipitation, a mechanism which is related to reactions 2 and 3 and most likely to occur with less hypereutectoid additions, is also present, both are responsible for the mechanical instability of the alloys, mainly under thermal shock.

However, the rates of absorption for hypereutectoid alloys, as shown here, is very far from the hypoeutectoid compositions, by means of a direct comparison of Figs. 4, 5 and 8.

## 4. CONCLUSIONS

In the experiments carried out in this study, uranium-molybdenum samples had collapsed in different conditions of times temperatures, due to differences in the rate of hydrogen absorption presented by those two different classes of alloys. It was observed a massive incorporation of hydrogen by the 6wt% hypoeutectoid composition, even in very low temperatures. However, this incorporation was only possible at the end of the experiments, mainly in the cooling ramp of the mass absorbed x time curves, for the 8-10wt% hypereutectoid alloys.

Thus, it is shown here that, if H(M)DH of alloys is the chosen process for the obtention of gamma powders, a thermal shock step is necessary, mainly for higher Mo additions. The observation of the final fragmented state of the samples, together with the observations above, leads to the conclusion that a thermal shock step must be considered for the embrittlement and powdering of the hypereutectoid compositions.

It was also suggested by the experiments a temperature of 568.4oC for the eutectoidal transformation temperature. The method utilized here can be viewed as an alternative for the previously stated in literature, to the determination of TTT diagrams.

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