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## POWDER FORMATION OF $\gamma$ URANIUM-MOLYBDENUM ALLOYS VIA HYDRATION-DEHYDRATION

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### ABSTRACT

Gamma uranium-molybdenum alloys has been considered as fuel phase in plate type fuel elements for MTR reactors, mainly due to their acceptable performance under irradiation and metallurgical processing. To its use as a dispersion phase in aluminum matrix, a necessary step is the conversion of the as cast structure into powder, and one of the techniques considered at IPEN / CNEN - Brazil is HDH (hydration-dehydration). The alloys were produced by the induction melting technique, and samples were obtained from the alloys for the thermal treatments, under constant flow of hydrogen, for temperatures varying from 400°C to 600°C and times from 1 to 4 hours, followed by dehydration. A preliminary characterization of the powders was made and the curves of mass variation versus time were obtained and related to the powder characteristics. This paper describes the first results on the development of the technology to the powder formation of the (5 to 10) % weight molybdenum  $\gamma$ -UMo alloys, and discusses some of its aspects, mainly those related to the  $\gamma \rightarrow \alpha$  equilibrium data.

### 1. Introduction

The substitution of the high enriched / low density fuels in the research reactor IPEN-IEA-R1 started in the Nuclear and Energy Research Institute of the Nuclear Energy National Commission, IPEN/CNEN – Brazil with the project BRA/4/047, which covered the development of the  $U_3Si_2$  fuels. Today, IPEN is supplying continuously its reactor with this new fuel, and the technology of the fabrication of the  $U_3Si_2$  based fuel elements is fully developed. But with the

continuous results of the researches on alternative high density nuclear fuels, Brazil continued the development in this area by means of the cooperation project IAEA BRA/4/053, which covered the development of the  $\gamma$ -UMo fuel alloys, planned to be used as a future alternative to the silicide fuel in its reactor. This project is now also closed, but IPEN/CNEN is still continuing to work on the developments suggested by it.

One of the main tasks assigned to the project was the development of the methods to the obtention of the  $\gamma$ -UMo alloys, and IPEN studied both arc and induction melting, since it is known that it has a strong influence on the characteristics of the powders properties. By the considerations described in the work of Oliveira et al. [1], the technique adopted was the second, which enabled the production of a more homogeneous material in only one single step of melting, in amounts of alloy of 1 to 1,5kg.

With the definition of the melting technique, the next important step in the development of the technology of the  $\gamma$ -UMo based fuel elements is the development of a process to the obtention of its powders, and obviously the comprehension of the mechanisms involved in its formation. IPEN-CNEN is now currently working in this direction, and several tests, in laboratory and pilot scales, are being carried out in the development of a hydration-dehydration (HDH) process. Since there is not a specification for a  $\gamma$ -UMo fuel, the HDH studies are covering the broad range of 5 to 10% weight additions of Mo.

The continuous development of the high density fuels technology has not only a technical, but also a strong social impact. Today, the use of low enriched uranium fuels is a world requisite to the non-proliferation of nuclear weapons. Also, this kind of fuel enables the enhancement of the research reactor power, which leads to an increase in the radioisotopes production. Thus, for example, the problem with the increasing demand for the treatment of patients with cancer can be diminished. Since IPEN/CNEN - Brazil is always involved in researches having interfaces with several social areas, in this particular case, the results of the BRA/4/047 and BRA/4/053 projects have and will have a strong importance for our country.

In this paper it is described and qualitatively discussed a small, but important, part of these results, mainly the ones related to the powder obtention and its mechanisms of formation.

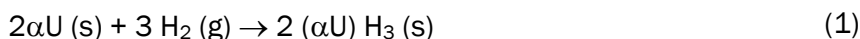
## **2. Powder Obtention Via the HDH Technique**

Traditional techniques for the production of metallic powders of  $\gamma$ -UMo are criogenic milling, machining, atomization and hydration-dehydration (HDH), or its more recent variant, hydration-milling-dehydration (HMDH). Since that a good nuclear fuel must have a good performance under the metallurgical processing and irradiation, and since that the performance is a function of the physical and chemical properties of the dispersed fuel phase, it is of the main importance to understand the techniques of powder fabrication and performance's relationship.

The mechanical and powder metallurgical ones were reported, for example, in the early works by Clark et al [2], where an emphasis was given to the relation between particle properties and metallurgical behavior, and Wiencek and Prokofiev [3], where there is a comparison between atomized and machined powders of  $\gamma$ -U10Mo alloy. Several works on the behavior of atomized powders are being carried out since the works of Hofman et al.[4], Kim et al. [5] and Lee et al [6]. The other ones, called the HDH routes, are studied for example in the works of Balart [7], Solonin [8] and Pasqualini [9,10].

Today, atomization is the best considered technique to the production of powders with good performance. Despite this fact, HDH or HMDH has also some good features, which enables it as an alternative technique. Following Balart [7] and Pasqualini [9,10], it is the one which produces powders with purity and particles dimensions closest to the specifications. Another advantage is the cost of the unities, very cheap when compared with the atomization equipments.

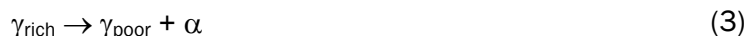
The main responsible for the success of the HDH technique is the high  $\alpha$ -uranium chemical affinity for hydrogen. Hydrogen changes the ductile structure of  $\gamma$ -UMo alloys into a fragile one, by two main mechanisms, as discussed in the work of Powell [11], one related to the intergranular embrittlement and the other by the occupation for hydrogen of the matrix interstitial positions, leading to the creation of tension sources which promotes transgranular fracture. In the range of compositions where  $\gamma$ -UMo is considered as a dispersed nuclear reactor fuel, mainly 5 to 10% weight in Mo, alpha-uranium is the proeutectoid phase, thus it is preferentially formed as a gamma-matrix decomposition product. Thus it is expected that the formation of uranium trihydride, due to the high affinity between  $\alpha$ -U and hydrogen:



in temperatures of 350°C, and the decomposition of the  $\gamma$ -UMo matrix into  $\alpha$ :



in temperatures bellow the U-Mo phase diagram eutectoid equilibrium, or:



in the gamma plus alpha phase field, are the keys to the comprehension of how the embrittlement can be achieved. Both reactions lead to the formation of more  $\alpha$ -U phase in the system.

Since the hydride is formed, its volume is bigger than the volume of the alpha phase and the thermal treatment of dehydration and, as is discussed here, even with a convenient cooling speed, are both capable to break the alloys structure. Thus, the particles formed have, in its majority, the same dimensions of the grains.

The first reported RERTR work on the obtention of  $\gamma$ -UMo powders was the one of Balart [7]. Arc melted alloys of  $\gamma$ -U7Mo and  $\gamma$ -U8Mo were thermally treated at 560°C, previously to the hydration step, for 10 to 24 hours, to partially convert its gamma structure to alpha. The samples were then exposed to a flow of hydrogen for 250°C, and dehydrated at temperatures of 500°C. To minimize losses, the alpha phase remained after the dehydration step was reconverted to gamma, after a thermal treatment of 750°C. Using the same procedure, Solonin [8] obtained the  $\gamma$ -U6,5Mo powders, but for the more homogeneous induction melted alloys.

A more recent development, leading to the HMDH technique, was given in the works of Pasqualini et al [9] e Pasqualini [10]. The arc melted alloys were firstly thermally treated in temperatures between 500°C e 700°C. In the hydration step, differently from Balart et al.[7], a pre-thermal treatment in temperatures from 50 and 190°C, with maximum absorption in 120°C, under 1 atmosphere of hydrogen for 36 hours, was applied to a  $\gamma$ -U7Mo alloy. The strategy for the success was to divide the initial charge of 1 kg into small pieces, each having 50g. The fragments obtained had 5mm of mean diameter, with the smallest having 30 microns, produced by transgranular fracture. Milling was then introduced, to the obtention of the right dimensions, followed by dehydration and reconversion at 700°C for 5 hours.

Thus, for alloys of  $\gamma$ -U $\leq$ 7Mo, the obtention of powders were achieved by the following steps, for both arc and induction melted alloys: thermal treatment at 500°C to 700°C, to partially convert the gamma structure into alpha, hydration in temperatures lower than or equal to 250°C (mainly 120°C), milling, dehydration, and reconversion. However, for additions of Mo >7% weigh, it is demonstrated here that hydrogen embrittles the structure in the same way, leading to the formation of powders with the same characteristics, up to the addition of 8%, with full yielding. For the alloys of 9 and 10% Mo, whose behavior under irradiation and metallurgical processing are the best ones, the obtention of the powders are possible, but with different characteristics

and low yielding, at least in our experimental conditions.

Since there is not any specification regarding  $\gamma$ -UMo powders in IPEN/CNEN, our main goal is to study and understand the behavior under hydrogen of the  $\gamma$  (5 to 10%wt.) UMo alloys. Thus, in this work are presented the first results on the  $\gamma$ -UMo powder obtention, as it was one of the tasks in the technical cooperation project IAEA-Brazil BRA/4/053. Now, the main objective in IPEN is to start the determination of optimal parameters to the obtention of good powder yielding, to setting-up the steps of the HDH process, mainly in the hydration step, since in some of our experiments, fragmentation of the alloy can be achieved readily in this step.

### 3. Experimental Method

Alloys of  $\gamma$ -U(5 to 10)Mo were prepared by induction melting under high vacuum. Natural alpha-uranium cylinders and small cylindrical pieces of high purity molybdenum, each having 3mm x 2mm, formed the induction charge, assembled in a high purity zirconia crucible.

Samples were taken from the casts in order to perform the hydration experiments, carried out in a thermal-gravimeter (TG) analyzer, supplied by the IAEA project BRA4053. The samples, each having approximately 250 mg and same shape, were assembled in calcined alumina crucibles, after being polished and surface cleaned to remove surface contaminants. 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  $2,0 \times 10^{-2}$  mbar, a constant flux of hydrogen was applied to the samples until the end of the experiments.

All the alloys were tested in various conditions of time and temperature, keeping its masses and geometry nearly the same, as it was possible. In terms of process variables, the level of vacuum, the flow of hydrogen through the system, and the heating and cooling were held constant. They enabled us to study the influence of the times and temperatures of hydration, in the production of fragments of the alloys. Dehydration was used as a necessary step to the removal of hydrogen, not necessarily to the production of fragments.

Our main strategy was to perform the experiments over a range of temperatures near the U-Mo eutectoid transformation, the one in which several TTT diagrams [12,13,14,15,16] predicts maximum rate of decomposition, given by reaction (2). The curves of hydrogen absorption as a function of time were obtained, and also the 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 condition.

The criteria to define the amount of powder was established on the basis that isothermal treatments under hydrogen atmosphere produces, sometimes, an unreacted solid core, with notably bigger dimensions than its remaining fragments (powder). It is strongly subjective, but it can help us to analyze the possible yielding for each experimental condition.

## 4. Results

### 4.1. $\gamma$ -U5Mo and $\gamma$ -U6Mo Alloys

Fragmentation of the samples was possible in almost all the conditions of times and temperatures. For times of the order of 1 hour, full fragmentation (100% of powder yielding) was possible in temperatures near that of the theoretical eutectoid transformation, around 565°C, to the maximum tested temperature of 583,37°C (580°C nominal). The minimum temperature tested was 543,77°C (540°C nominal), the fragmentation was about 24%.

For 2 hours of treatment, full fragmentation was possible in temperatures from 533,44°C (530°C nominal) to 591,08°C (590°C nominal), falling drastically at 600,95°C (600°C nominal), where no powder was obtained from the sample.

In the figures below are examples of the TG curves of a  $\gamma$ -U5Mo alloy, during a typical cycle of thermal treatment, together with its typical powder features after the hydration cycle. In the sequence, for comparison, are showed its dehydration curve, together with the resultant powder form.

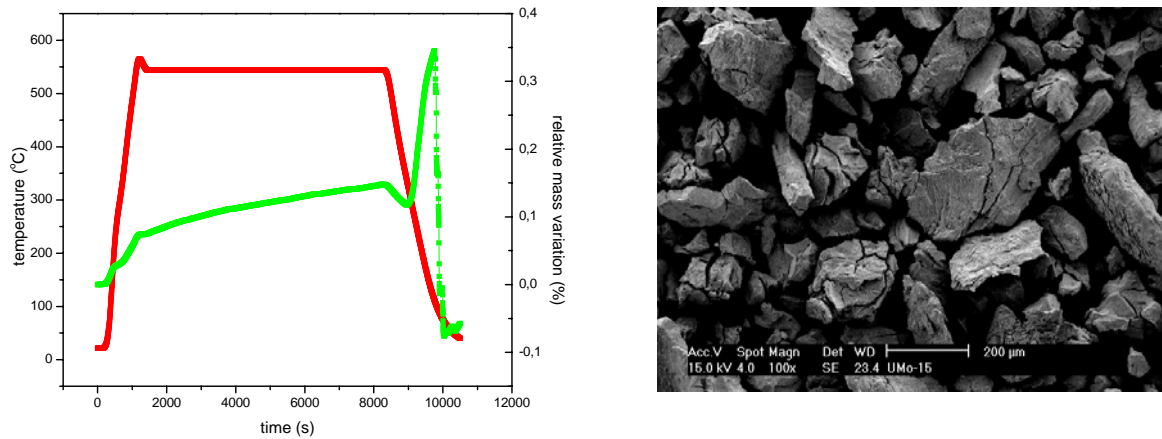


Figure 1 – Typical curves of mass variation (left), and the respective powder structure (right),  $\gamma$ -U5Mo alloy.

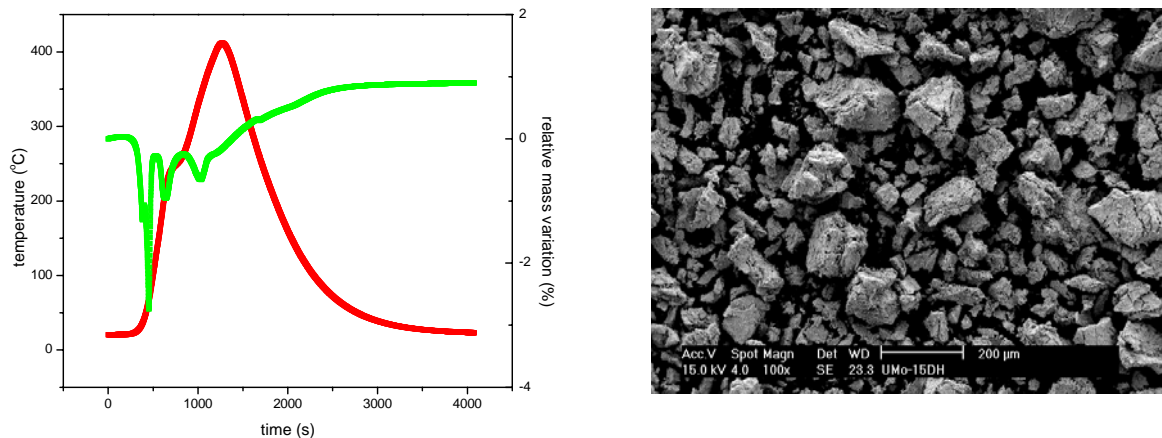


Figure 2 – Typical dehydration curve (left), and the respective powder structure (right),  $\gamma$ -U5Mo alloy.

#### 4.2. $\gamma$ -U7Mo Alloy

For 1 hour of thermal treatment, no full fragmentation was obtained. For 2 hours, only in temperatures near the theoretical eutectoidal transformation. For 4 hours, in the temperature of 482,77°C (480°C nominal), it was obtained 11,4% of fragments. The yielding grew to 100% in the range of 502,53°C (500°C nominal) to 573,22°C (570°C nominal), falling drastically up to 600°C.

The figures below are typical for this alloys, and also the shapes of its particles, very similar to the previous.

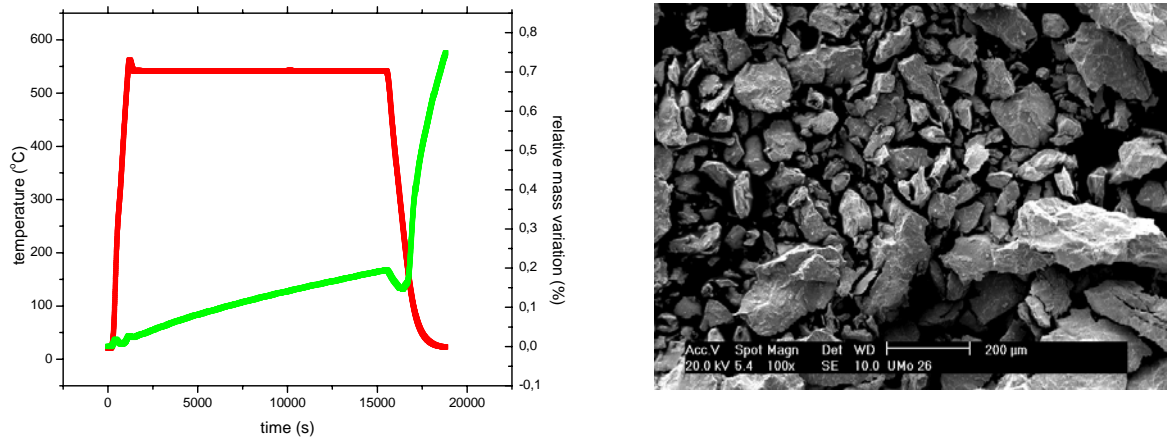


Figure 3 – Typical curves of mass variation (left), and the respective powder structure (right),  $\gamma$ -U7Mo alloy.

#### 4.3. $\gamma$ -U8Mo Alloy

Full fragmentation was possible only after 4 hours of treatment, in a narrow range of temperatures between 565,4°C (562°C nominal) and 568,39°C (565°C nominal), falling drastically at 560°C and, in the other extreme, at 570°C, both nominal. In the range of temperatures tested where there was full fragmentation of the  $\gamma$ -U7Mo alloys, no powder was produced at 504,26°C (500°C nominal).

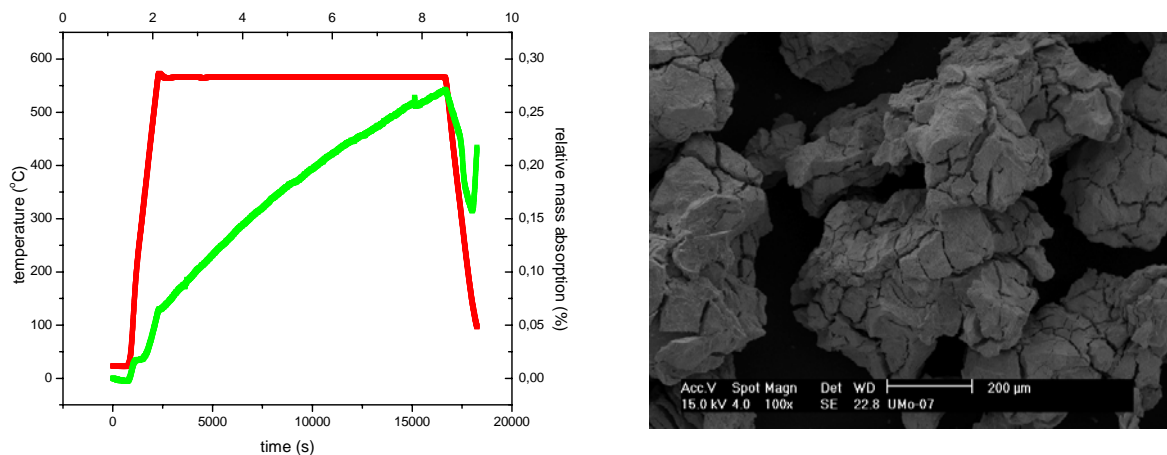


Figure 4 – Typical curves of mass variation (left), and the respective powder structure (right),  $\gamma$ -U8Mo alloy.

This is important in the definition of the conditions of the thermal treatment of hydration, due to the fact that intergranular decomposition is a more efficient mechanism to the promotion of the embrittlement of the samples than the interstitial, which dominates in percentages equal or greater than 8% Mo, since the amount of alpha decrease progressively.

Another important difference is in the cooling part of the curve, in the example and in all the cases studied, always below 151°C. Compared with the previous, it is needed more time of cooling to break the alloy, which enhances its internal surface area and promotes more absorption. In the low molybdenum content alloys, this phenomenon occurs readily at the temperatures of 250°C or above.

#### 4.4. $\gamma$ -U9Mo and $\gamma$ -U10Mo Alloys

For the times of our tests, no full fragmentation was possible for both cases. Formation of powder is given by a progressive superficial mechanism, not by a volumetric one, as suggested for the other compositions. The shapes of the particles are very different from the previous, and what is suggested here is that 9% maybe a well defined frontier, where the contribution of the intergranular embrittlement falls, since the alloys reaches its maximum stability in terms of the decomposition  $\gamma \rightarrow \alpha$  near this percentage of Mo addition.

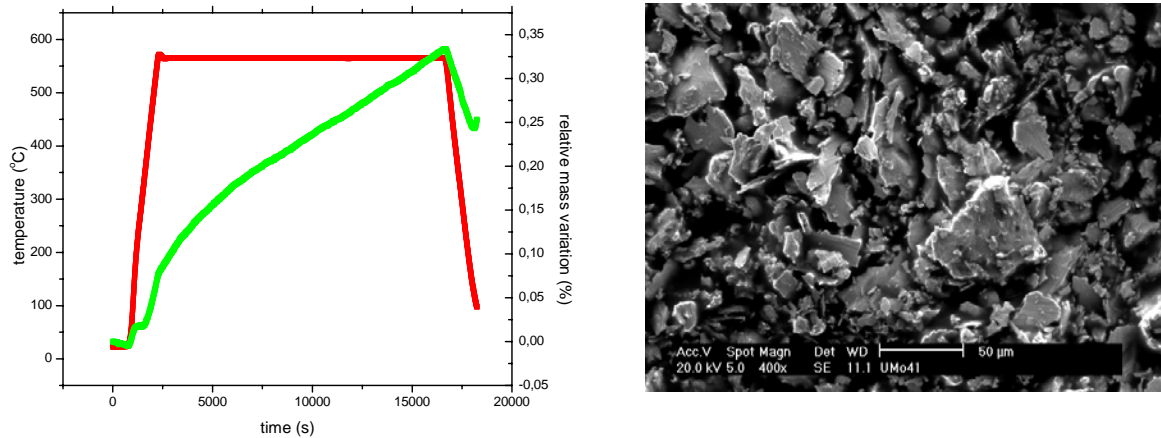


Figure 5 – Typical curves of mass variation (left), and the respective powder structure (right),  $\gamma$ -U9Mo alloy.

#### 5. Powder Formation, Suggested Mechanisms

We are now able to make a brief discussion on how the equilibrium  $\gamma \rightarrow \alpha$  is related to the powder formation, and to suggest a mechanism for the  $\gamma$ -UMo alloys fragmentation phenomenon, from the graphics and figures above. First, if a certain amount of alpha is present initially, and by the reaction (1) it is known that alpha has the tendency to react with hydrogen, it is expected that the hydrogen absorption must also be influenced by the rate at which alpha is formed. We know from the work of HOFFMAN et al. [17] and from some of the U-Mo time-temperature-transformation (TTT) diagrams that the rate at which gamma decomposes to alpha in a homogeneous alloy is strongly dependent of 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  $\gamma$ -UMo powders and thus the fragmentation are caused primarily by the initial amount of  $\alpha$ -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 the sample's fragmentation and, thus, the first point to be examined is the total amount of hydrogen absorbed by the samples.

Also, if it is considered that curves of hydrogen absorption can be used to study equilibrium data, it is advisable to take into account the works of Van Thyne & McPherson [14,15] and McGearry [16]. For example, according to these authors, the nose of the TTT diagrams varies strongly, as a function of the methods employed to the determination of the gamma - alpha equilibrium. It was determined several different temperatures of maximum decomposition according to the methods employed. For example, for a  $\gamma$ -U8Mo alloy, McGearry [16] found the value of 525°C, using X-ray diffraction and metallography, and according to Van Thyne & McPherson [14,15], resistivity methods indicate a value of 500°C and hardness of 570°C. For this composition and the others, since this work deals with powder fragmentation, and thus, with mechanical properties of the alloys, it is reasonable to suppose that it confirms the value of the hardness method. In fact, if we take into account that more alpha leads to a higher increase

in the total hydrogen absorption and, thus, to an ease of the sample fragmentation. This occurred for this composition, at a value near 568,39°C, which is closer to the reported 570°C.

According to Powell [11], incorporation of hydrogen by alloys like UMo occurs by two main mechanisms, one due to the creation of tension sources in the matrix which its interstitial positions occupied by hydrogen, and the other, the more prominent here, by the intergranular precipitation of alpha, in the low Mo content alloys, from 5 to 8%. The former is always present and is related to the increase in the absorption with temperature, even in the high molybdenum content alloys.

From the graph and figures above, it is now suggested a possible mechanism of powder formation, based mainly on the change of the rate of absorption which follows a brief period of mass loss, as showed in the curves. 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, so it is expected, as it was observed, that absorption increases with time in the cooling region.

This increase in incorporation, due to the gamma and alpha phases, allows the estimation of the surface area created, and thus of the dimensional parameters of the particles produced in each experiments.

## 6. Conclusion

The obtention of powders was studied in a wide range of composition, and the emphasis was given in IPEN to the obtention of the ideal conditions of isothermal treatment under hydrogen. Undoubtedly, the dehydration reaction is very important in order to retry the matrix 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 observed in the experiments carried out at IPEN is that, using a convenient set of parameters, fragmentation of the structure into powder can be obtained even in the alloy considered as having a high Mo content, of 8 and 9%Mo, but in more restrictive conditions of temperature, mainly those 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 is obvious that times of treatment could be extended, in order to provide more hydrogen to hydrate the intergranular  $\alpha$ -U or to provide more hydrogen atoms to the occupation of the interstitial matrix sites, as suggested by the work of Powell [11]. Our goal here is to have clues about the predominant mechanism involved in the formation of powders of the alloys, and its range in terms of molybdenum content.

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