

GAMMA URANIUM-MOLYBDENUM ALLOYS BEHAVIOR UNDER HYDROGEN ATMOSPHERE

Fábio Branco Vaz de Oliveira¹; Humberto Gracher Riella² ; Michelangelo Durazzo¹

1 Instituto de Pesquisas Energéticas e Nucleares IPEN – CNEN / SP, Rua do Matão, travessa R nº. 400, Cidade Universitária, São Paulo / SP, CEP: 05508-900, email: fabio@ipen.br.

2 Universidade Federal de Santa Catarina, UFSC, Florianópolis / SC.

ABSTRACT

Due to its best irradiation and metallurgical processing performance, gamma uranium-molybdenum alloys are the best candidates for the use as high density / low enriched research reactor fuels. To the fabrication of U-Mo / Al dispersion fuel plates, gamma uranium-molybdenum powder obtention is one of the main processing steps, and to reach this goal, the route considered is hydration-dehydration (H-DH). In this work, some of the experimental results related to the hydration-dehydration of gamma uranium-molybdenum alloys are presented. Additions of 5, 6 and 7% wt% Mo were prepared by arc and induction melting, its as cast structures characterized by optical microscopy, MEV and X-ray diffraction, and related to the results obtained after being thermally treated under hydrogen atmosphere, for several conditions of time and temperature. First examinations showed that the gamma U-Mo alloy hydrogen susceptibility and the yielding in the powder production increases with the decrease in the Mo addition. Since the traditional pre-treatment before the hydration was not considered here, some important conclusions concerning the steps to produce the powder by the HDH process could be taken.

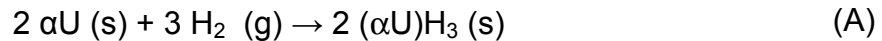
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INTRODUCTION

Due to its high ductility, conventional routes to produce gamma uranium-molybdenum powder, like mechanical crushing, have the disadvantages to present high level of time and power consumption, and the introduction of contaminants in the system. Atomization, another widely utilized technique, presents the disadvantage to produce powders with spherical shape, which leads to problems in

the rolling step of the plates and fuel elements fabrication. Thus, it is necessary to consider a method that avoid those drawbacks, which be capable in the same time to produce powders in the compositions and granulometric specified ranges for its usage as nuclear dispersion fuel ^(1,2,3). The technique considered in IPEN to produce γ -UMo powders is the hydration-dehydration, the best to produce high purity materials.

The idea behind the use of hydrogen to obtain γ -UMo powders is to convert its ductile as cast structure into a brittle one. In the range of compositions considered here, where alpha-uranium is the proeutectoid phase, as cast and even thermally treated structures usually contain some intergranular alpha-uranium as a precipitate, which fortunately has strong hydrogen affinity. The formation of uranium trihydride, given by the following reaction:



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



are the keys to the embrittlement needed, and its ease is achieved by means of a group of operations, which usually comprises a previous gamma-homogenization thermal treatment, followed by another bellow the eutectoid temperature T_e , to convert some of the gamma structure into alpha, hydration (also bellow T_e), dehydration and gamma-quenching of the powder obtained, to recover (most of) its original structure and composition. Some countries are utilizing this route to obtain γ -UMo powders, with relative success ^(4,5). However, some questions arises when we analyze some of the main results in terms of powder yielding, relating to those operations.

In this work, we are presenting and discussing, mainly qualitatively, some of the first results obtained in IPEN on the behavior of those alloys in the presence of hydrogen and its relationship to the powder yielding. Our main objective is to define

a set of values to the HDH process parameters, mainly time and temperature.

We are concerned also to answer some questions on the production of gamma UMo powder, mainly those related to the first operations of pre-thermal treatment, conversion $\gamma \rightarrow \alpha$, and reconversion, considered here unnecessary in some alloys composition.

MATERIALS AND METHODS

Alloys of uranium-molybdenum were prepared by arc and induction melting under vacuum. Natural alpha-uranium cylinders and small cylindrical pieces of high purity molybdenum formed the induction charge, while small discs substitutes uranium cylinders to form the arc furnace's charge. Prior to loading the charge into the furnace, the uranium cylinders were chemically treated with nitric acid, in order to remove superficial oxides. The induction charges were assembled inside zirconia crucibles, and then the system was assembled inside the induction coil. In the arc melt samples preparation; the charge was assembled in a copper matrix. In both cases, vacuum to a high level was applied in the chamber prior to the melting operation.

A high level of homogeneity was observed macroscopically in the induction casts, which was later confirmed by optical microscopy. To achieve the same level of homogeneity in the arc samples, 2 to 4 remelts was needed. The molybdenum addition percentage utilized was in the range between 5 and 7% Mo weight. In order to determine its microstructures and composition properties, X-ray diffraction, optical and scanning electron microscopy were utilized.

Samples with nearly the same shapes were taken to the alloys in order to perform the hydration-dehydration experiments, carried out in a thermal-gravimeter (TG) equipment. The samples, each having no more than 400 mg of the as cast alloys, were assembled in alumina crucibles after being surface cleaned, which played the role of our hydration-dehydration reactor. Between each experiment, a cycle of purge and vacuum was performed, in order to keep the internal parts of the equipment free of gases and another contaminants. After a stable vacuum level

of 4×10^{-2} mbar, the furnace was filled with hydrogen, which flowed continuously over the samples during all the experiments.

By means of a controller, the temperature of the sample was monitored. After the system assemblage, the equipment was then programmed to the desired levels of experimental times and temperatures, and a cycle of operation was fixed. The experiments started when the controller was turned-on, and the progress of the reaction between the alloys and hydrogen was constantly measured as a function of time.

The main strategy was to perform experiments over a wide range of temperatures, and to verify the rate of powder production by each one of the conditions. With this in mind, curves relating the powder yielding relatively to the initial mass of the samples were obtained as a function of temperature, and some important conclusions were obtained on the gamma-uranium molybdenum powder obtention by the HDH process.

Since the samples masses in each experiment were not identical, the results were normalized in terms of mass. The amount of powder was measured by the use of the thermal-balance device, taken off the crucible the eventually unreacted UMo alloy core, and let the device take the measurements. A criteria do define the amount of powder was established on the basis that the reaction produced in some experiments a huge unreacted core, with dimensions notably bigger than the fragments. Samples with total fragmentation presented particles with nearly the same dimensions, and no unreacted cores was identified. On the other hand, even in the worst yielding conditions, a thin shell of could be detached from the samples, leading to some powder production.

In all the cases, the use of the pre-thermal treatment step before hydration was avoided. This step is traditionally used with the objective to convert some of the gamma phase into alpha, leading to a fast fragmentation of the samples. We will show that this operation is suitable in conditions where the amount of molybdenum in the alloy exceeds a limiting value. Some of the weak points of this technique will be discussed next.

The experimental conditions are summarized here, where the first numbers

inside the parenthesis represents the sample code, the seconds the temperatures in °C in the hydration operation, and the thirds represents the use (Y) or not (N) of the dehydration step. So, for the U5Mo samples, we had: (701, 900, Y), (702, 450, N), (703, 1000, N), (704, 900, N), (705, 1000, Y), (707, 600, Y), (709, 850, Y), (710, 580, Y), and (711, 560, N). To U6Mo samples, (601, 600, Y), (602, 600, Y), (603, 900, Y), (604, 660, Y), (605, 650, Y), (606, 660, Y), and (607, 660, N). To the U7Mo samples, (201, 700, N), (202, 800, Y), (203, 600, Y), (204, 600, Y), (205, 900, Y) and (207, 600, Y).

RESULTS AND DISCUSSIONS

It is very important to note that, in accordance to previous works, the ease of the hydration process in the production of γ -UMo powders is related primarily with the amount of intergranular α -U phase. The figures bellow shows X-ray diffraction patterns of the alloys, by means of which we can evaluate qualitatively the amount of alpha in each sample.

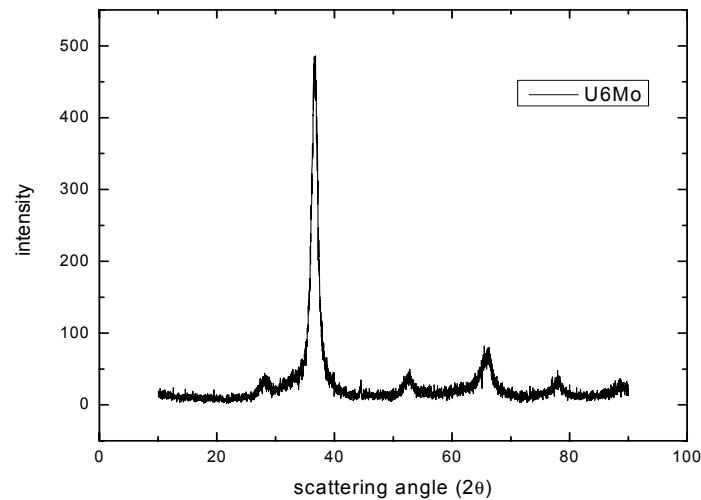


Figure 1 - X-ray diffraction pattern, U6%wt.Mo, induction melting.

Since the peaks of α and γ are very close, for the induction alloys we can see in the figures 1 and 2 that the amount of γ increases with the increase in the

Mo content, or the broadening of the most intense γ peak and the presence of α peaks near 37° decreases with the Mo content. This means that higher Mo contents leads to a reduction in the presence of the α phase, and confirms experimentally that Mo has a favorable effect in stabilizing γ -UMo phase.

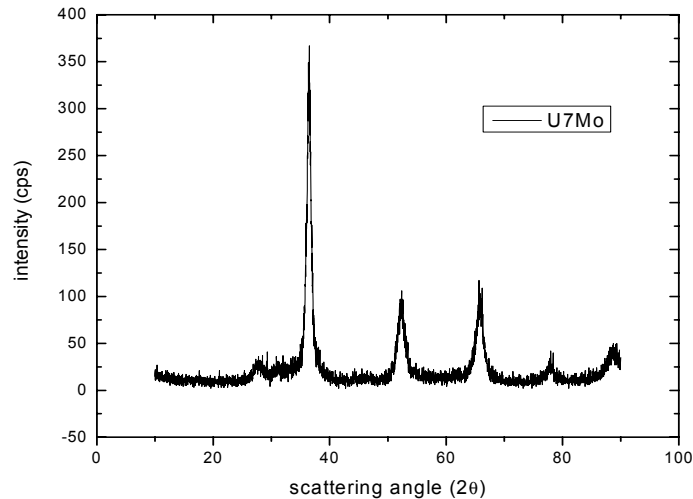


Figure 2 - X-ray diffraction pattern, U7%wt.Mo, induction melting.

Since the reaction of hydrogen and α -U is believed to be the only way to produce γ -UMo powders, we expect that with the increase in the Mo content and temperatures of the isothermal treatments, less powder will be produced. But the definition of an optimal interval of temperatures for those alloys must be stated. In the figures below the results of powder formation as a function of temperature for each of the alloys are presented. Apart of the dehydration treatment applied over most of the samples, the emphasis is given in the first temperature level. Undoubtedly dehydration treatments are very important in order to enhance the formation of powders, but the relation we are trying to fix is on the treatments done over all the hypoeutetoid regions in the U-Mo binary system. The arc-melted alloy was the first to be tested, and it was used to guide us in the choice of the conditions to the remaining tests.

For the arc U5Mo alloys, good results were obtained in almost all the

temperatures, mainly for those treated in the binary fields (experiments 702, 711, 707). This can be explained by its high alpha content and poor homogenization relatively to the induction melted ones. Thus, as we mentioned earlier, this behavior corresponded to the expected. The best results were achieved between 560°C to 600°C (711, 707). Since the entire samples became fragmented, and no solid core remained, this indicates that there is a range of suitable temperatures above and below the eutectoid isotherm, which can be used to obtain directly the powder (707), without the DH operation. The main advantage in treat samples in the gamma plus alpha region is the low amount of second phase formed with respect to that of the alpha plus delta field (702).

To verify the behavior in the gamma field, samples were treated in temperatures far from the γ to $\gamma + \alpha$ limiting line (experiments 701, 703, 704, 705 and 709). When followed by a second thermal treatment (701, 705), some powder was obtained, even in low amounts, but this fact shows that there are possibilities to obtain high hypoeutectoid γ U-Mo powders without the conversion of γ to α , as is usually done, in temperatures below the eutectoid isotherm.

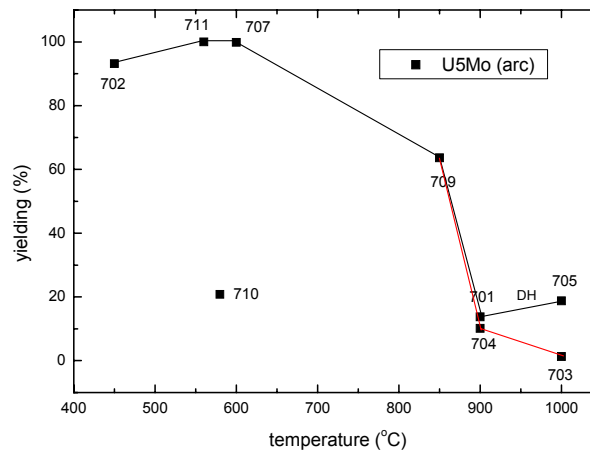


Figure 3 – Powder formation as a function of temperature, arc melted sample, U5%wt.Mo.

To observe the effect of the reconversion α to γ , an U5Mo sample was treated firstly in a temperature near the eutectoid isotherm, and then in the gamma field

(experiment 710). It is shown that, instead to the obtention of a result near the maximum, the rising of the temperature to the gamma field leads to the stabilization of the gamma structure, which results in low yielding, the powder formation was mainly due to the first isothermal treatment.

The general behavior of the low molybdenum induction melted samples were the same respecting to the maximum powder yielding, 600°C was the maximum for both the U6Mo and U7Mo (experiments 601, 602, 203 and 204), as we can see in the figures 4 and 5 bellow. Again, a good result was obtained in the gamma plus alpha field, and for both compositions, 2 hours followed by dehydration was good enough. Another results were that with the increase in the amount of the gamma content, the need to a dehydration treatment increases also. Poor yieldings were obtained in samples only treated with the T1 isotherm and far from the eutectoid isotherm (experiments 603, 201, 202 and 205).

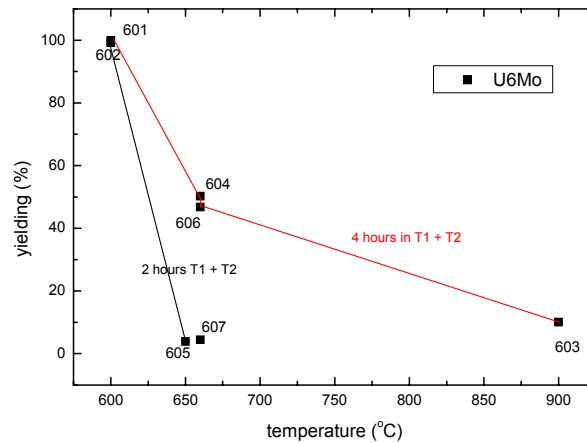


Figure 4 – Powder formation as a function of temperature, induction melted sample, U6%wt.Mo.

The U6Mo alloys presented good results in temperatures not very far from the eutectoid isotherm (experiments 601 and 602), and in those representing the limiting line between the gamma and alpha plus gamma fields (experiments 604 and 605). All the experiments were carried out in the same DH conditions, the differences in the final yieldings thus showing the high sensitivity the hydration

operation has with temperature. To verify the behavior in the gamma but near from this line, 3 treatments at 660°C were carried out (604, 606 and 607), one without T2 step (607). This was the worst case, indicating again the need to T2 to obtain some result for this composition. The sample treated with T2 below the usual value presented poorer result than that treated at the usual, which confirmed previous data in the literature relating to the dehydration or T2 step ^(3,4,5).

Another interesting result was obtained on those alloys, mainly the relative unexpected yielding in the 900°C isotherm (603), followed by a conventional dehydration step, indicating again that another mechanism of powder formation, together with that given by the reaction (01) is acting on the samples, and must be considered in the production of high-stabilized γ U-Mo powders. The behavior of the U7Mo alloys was the same when compared to that of the U6Mo alloys. It is interesting to observe the growth in the powder yielding in the experiments 201, 202 and 205, confirming the considerations above on the U6Mo experiment 603.

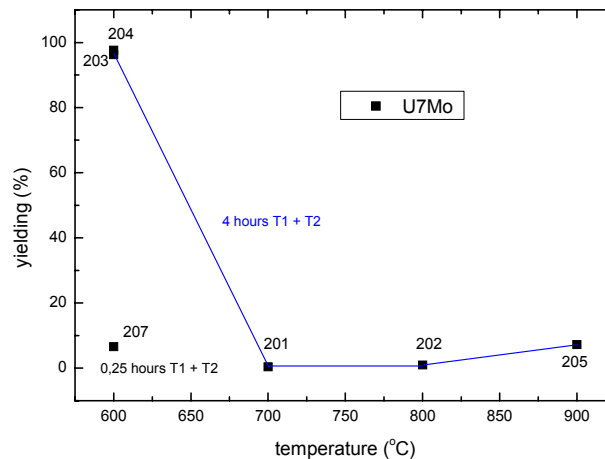


Figure 5 – Powder formation as a function of temperature, induction melted sample, U7%wt.Mo.

The results above can be explained by the following arguments. Production of alpha is favored by thermal treatments carried out in the biphasic fields and also by its initial amount in the as cast alloy. In this case, our Mo alloys has more intergranular alpha in its structure, and this alpha phase, having very higher

reactivity with hydrogen than gamma, will readily consume the hydrogen of the furnace's atmosphere. Since there is low molybdenum in the grain of the gamma matrix, its stability is low, thus the rate of the decomposition reaction $\gamma \rightarrow \alpha$ increases with the decrease in the Mo matrix content, as is shown in some equilibrium studies and time-temperature-transformation U-Mo diagrams.

In the case of low-stabilized γ -UMo alloys, treatments in the biphasic fields tend to decompose gamma, producing more alpha, increasing the formation of the hydride, and leading to the samples fragmentation even without the dehydration treatments. If these alloys were isothermally treated in the monophasic field, by means of diffusion the composition will tend to be homogeneous with time and temperature, which leads to a decrease in the sample's alpha content, reducing the possibility of reaction with hydrogen, which leads to low yieldings. If we think in terms of temperature, the production of powders in the monophasic field is an advantage, since that maximizes the amount of gamma and removes the need to quench the powder after the dehydration process. But we still have to lead to the problem of the low yielding.

We still have to consider the fact that the arc-melted alloy was less homogeneous when compared with the induction melted ones. Regions of high alpha content inside the grains were found, in contrast with the highly homogenized induction structures, as we can see in the next figures. In the first case, the amount of transformation by means of the reaction (A) is higher, also contributing to enhance the yieldings. But those inhomogenities must be eliminated, so the arc melted samples must be gamma-homogenized, justifying its usage as one of the operations prior to the traditional hydration-dehydration processes utilized by some countries. Thus, in the arc-melted alloys, the need of the gamma-homogenization thermal treatment must be considered, and if applied, probably will lead to a similar behavior presented by the induction-melted samples.

The highly homogenized structure is one of the main advantages in the use of the induction to produce alloys. For the induction-melted samples, composition homogeneity is not a problem; gamma-homogenization treatment is not a necessary step, since the as-cast alloys has homogenous compositions.

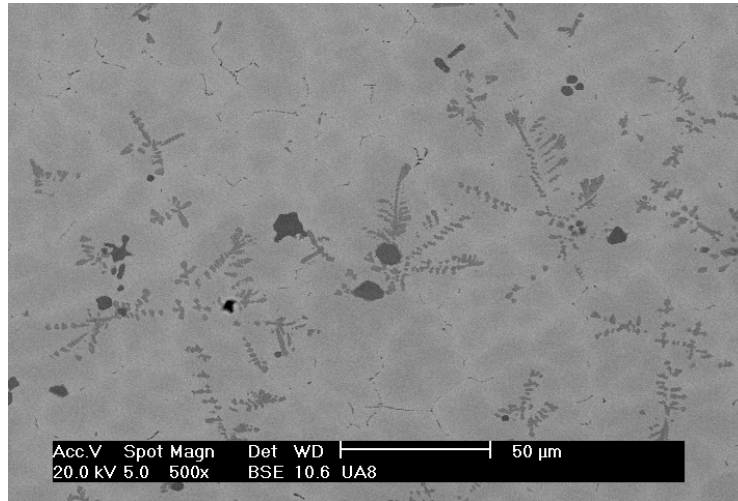


Figure 6 – Micrography of the arc melted sample.

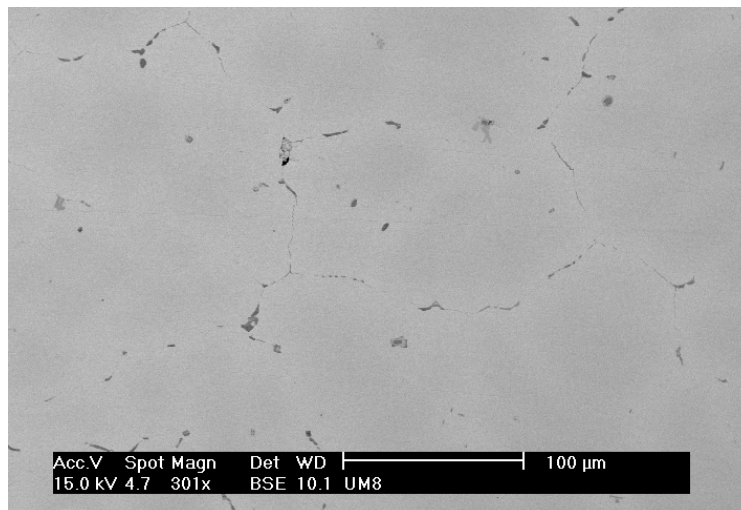


Figure 7 – Typical micrography, induction-melted samples.

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 without this step in all of the compositions tested, but if we increase the Mo content, the more difficult is the production of powders in a suggested single step.

Since alpha is formed in the as cast structure mainly as intergranular precipitates, what is expected with those treatments is that more amounts of alpha precipitates, will be formed. Since time acts on the enhancement of diffusional processes, which tends to homogenize the composition, reducing microsegregation and internal surfaces, and since that precipitation is a phenomenon that is favored by such inhomogenities, we are leading to the conclusion that such treatments are questionable for alloys whose compositions lies in the range of at least 5 to 7%, if we hydrate the alloys near and above the eutectoid isotherm. But in this case the use of a reversion treatment must be considered because we are still in the field where gamma decomposes to gamma plus alpha. The problem with the reversion is that the alpha phase has very low Mo content; there is not enough Mo dissolved in its structure to retain it after quenching.

HDHs in temperatures far from the eutectoid were applied to some samples, leading to low yieldings but revealing the possibility to obtain high gamma powder contents. The question here is how to obtain high yieldings in a region where gamma dominates.

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