METHODS FOR FABRICATING GAMMA ï URANIUM ï MOLYBDENUM (γ-UMo) ALLOYS AND THEIR INFLUENCE ON POWDER OBTENTION BY THE HDH TECHNIQUE

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ABSTRACT

Gamma uranium-molybdenum (γ-UMo) alloys has been widely considered as the best low enriched ï high density fuels candidates for the substitution of the previously utilized high enriched ones, according to the RERTR requirements. For its usage as dispersions in plate type research reactor fuels, some of the techniques to transform the ingots into powder are highly influenced by the alloys´ properties achieved in the previous steps of melting and solidification. In this work we will briefly introduce the study of two of the main techniques to melt (γ-UMo) alloys, the induction and arc melting, and show some of the differences in properties presented by the casts and its powders, obtained by the technique of hydration-dehydration (HDH) thermal treatments. Samples of the ingots and powders prepared in the range of compositions of 5 to 10 weight % Mo, were characterized by means of scanning electron microscopy, hydrostatic density, and X-ray diffraction. It was verified that highly homogenous alloys can be obtained by the induction technique in only one step, and for those produced by arc, even with smaller loadings, several microstructural problems arises, leading perhaps to its invalidation as a technique for the fabrication of nuclear (γ-UMo) alloys and powders.

1. Introduction

In the nuclear area, the main techniques for fabricating the powders of γ-UMo alloys for its usage as dispersion fuels in nuclear research reactors are cryogenic milling, machining, atomization and hydration-dehydration (HDH). Atomization is the commercially most accepted, but there are works indicating that hydration-dehydration (HDH), as studied by BALLART et al. [1], SOLONIN et al. [2], or its variation, the hydration-milling-dehydration (HMDH) technique, as studied by PASQUALINI et al [3] and PASQUALINI [4], are also suitable to produce powders which obeys more closely the specifications requirements in terms of dimensions and granulometric distributions. This is the main motivation for the adoption of the HDH technique at IPEN / CNEN ï Brazil, to the production of γ-UMo powders.

The responsible for the success of the HDH techniques is the high hydrogen affinity presented by the alpha uranium phase. In the ranges of compositions here studied, an alloy that presents some alpha as intergranular precipitates reacts readily with hydrogen, leading to high yieldings in terms of powder production. The reaction:

$$2\ \alpha U\ (s) + 3\ H_2\ (g) \rightarrow 2\ (\alpha U)H_3\ (s) \qquad (01)$$

are related to the hydride formation, mainly in the grain boundaries. The hydride phase has a volume bigger than that of the alpha phase, and this volumetric difference generate tensions in the alloy that leads to its fragmentation, even without the step of dehydration. Thus, the ease of fragmentation and

subsequent powder obtention implies necessarily in the gamma decomposition during the HDH thermal treatments. The reaction of the decomposition is:

$$\gamma_{matrix} \rightarrow \alpha + \gamma_{poor} \quad (02)$$

which produces precipitates with properties that are function of the HDH temperatures and, also, of the methods of the alloys preparation. The above equilibrium was extensively studied by REPAS et al. [5], VAN THYNE & McPHERSON, D.J. [6], VAN THYNE & McPHERSON, D.J.[7], SALLER, H.A., et al. [8], and more recently by HOFMAN et al. [9]. Their most important conclusions refer to the fact that the higher the molybdenum contents, the higher the gamma stability. Thus, alloys with higher alpha contents are, according to the reactions above, are more convenient to produce higher powder yieldings.

But the methods of powder production are highly influenced by the methods of alloys production, since that, according to the previous works, structure stability is a function of the molybdenum content and thus to the initial composition of the alloys. In all the alloys prepared by the arc melting technique, a subsequent thermal treatment was needed, even after remelts, to enhance their homogenization. In the induction ones, a high degree of homogenization could be obtained in only one step.

In the present work a brief introduction about how the methods of fabricating the alloys influence the choice of HDH condition is given. As there are no references on this issue in literature, our main objective is to show its importance in the nuclear technology, mainly in the fabrication of high density γ-UMo powders.

2. Experimental procedure

To the arc melted alloys, natural metallic uranium discs were used as charge. Molybdenum was used as a charge in small cylinders with 3 mm height and 3 mm diameter. Both materials were assembled in the copper plate of the furnace, its chamber closed and mechanical vacuum was applied to the system. After a suitable level of pressure, the vacuum valve was closed and a flow of argon was inserted inside the chamber. The arc was opened by means of an arc-starter, and applied over the sample until a high level of mixing between uranium and the molybdenum charges was obtained. The typical time to reach this configuration over the charges was about 40 seconds to 1 minute, maximum values to avoid damages in the chamber.

This procedure was repeated several times until, after visual inspection, the observation that the molybdenum charge was well homogenized in the sample. The main disadvantage in applying several remelts over the samples is the formation of an external oxide layer on the samples, deleterious to the quality of the alloy. Maximum masses of the alloys were about 30g.

For the induction melts, natural metallic uranium cylinders with 7 cm height and 2 cm diameter, and the same small cylinders of molybdenum were used as charge. Uranium cylinders were surface cleaned with 65%vol. nitric acid, and inserted together with molybdenum, in a zircônia crucible, inside the furnace chamber. A cycle of purge and mechanical vacuum was applied and, after 3 operations, argon was inserted and the power of the furnace was raised until the melting of the samples. Masses of 700 g were utilized in each melting operations. The internal surfaces of the as cast alloys were analyzed by scanning electron microscopy, X-ray diffraction and its hydrostatic densities were also measured. Some of the results are discussed bellow.

3. Comparison between Arc and Induction Melting Techniques

Theoretical densities were obtained from some existent data in literature, for the 5 to 10 % weight molybdenum, and were shown in figure 1, together with the experimental determinations. The literature data are from the paper of TRYBUS [10].

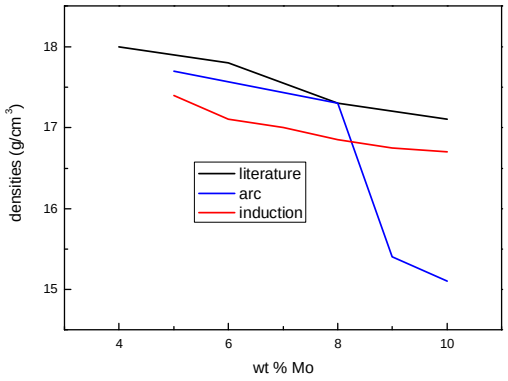

Figure 1 ï Densities of uranium with additions of Mo, for the methods here studied.

In terms of densities, alloys prepared by both methods behaved the same way up to 8% Mo, the fall in the densities were almost at the same ñrateò. After 8% Mo, the fall in the densities of the samples prepared by arc was substantial, and must be due to some closed porosity, which doesnôt constitute a problem in terms of powder obtention. It was observed also that this parallelism between the arc and induction density curves was possible only after the application of at least 2 remelts in the arc samples. In the case of the induction ones, no remelts were necessary, even working with charges 30 times heavier.

However, the most important difference in terms of quality is microstructural. It was observed that the structure of the induction alloys was mainly constituted by an homogeneous γ-UMo matrix plus some intergranular porosities, as we can see in the figure 2. In the case of the low-Mo alloys (5 to 7%wt. Mo), some α-U is also present in the grain boundaries. In the arc samples, a big number of dendritic structures and some intragranular regions containing α-U, even after the operations of remelts, were observed, which indicates some incompatibility between the speeds of cooling and diffusion of molybdenum in uranium in the samples, the first one faster than the second.

Structures containing high amounts of alpha uranium are the main responsible for the ease on the hydration-dehydration operations, but they are also related to a low degree of homogenization of both constituents of the samples. Thus, it is expected that, in the hydration of the arc melted samples, the rates of hydrogen absorption must be higher than that the induction rates. But if we are looking for homogeneous powders, it is necessary to work with the induction ones, and to try to find methods to enhance the hydrogen incorporation by these alloys.

Factors affecting the solidification of the alloys are mainly those related to the furnaceôs project, like its geometry of melting (crucibles) and charges (how to assemble the charge into the crucible), possible impurities introduced in the charges by the crucible and the arc base materials, and mainly the cooling system.

As an example, X-ray spectra and micrographies of the γ-U8Mo compositions are shown in the figures 2 and 3, where we observe a high degree of homogenization presented in the induction sample. Dendrites are regions of low molybdenum concentration, and thus, the most suitable to promote high rates of hydrogen absorption, due to the high affinity presented by hydrogen and α-U. They form, by chemical reaction, uranium trihydride, which leads, after dehydration, to the formation of powders. However, the remaining alpha uranium constitutes a loss of material, because there is no possibility to reconvert it to gamma, as it is usually segregated out of the gamma matrix.

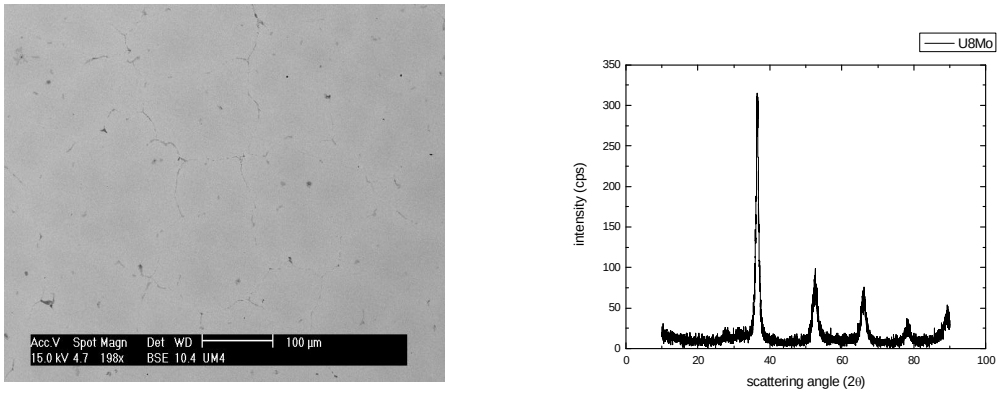

Figure 2 - MEV image and X-Ray diffraction pattern of γ-UMo alloy, induction melted.

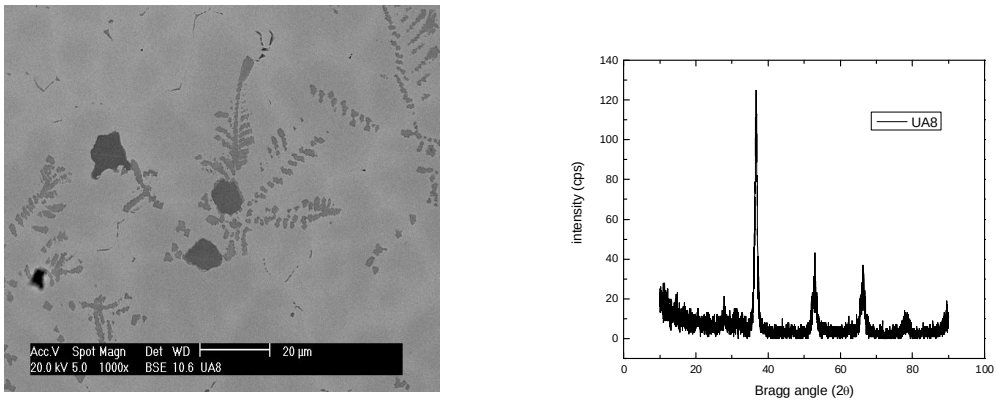

Figure 3 - MEV image and X-Ray diffraction pattern of γ-UMo alloy, arc melted, thermally treated, same composition as the induction sample.

4. Hydrogen Absorption

The experiments with hydrogen absorption for both alloys were carried out exactly at the same conditions of gas flow and sample´s masses and form. As an example, we can see below that the rates of absorption for those produced by arc melting was higher than for those produced by induction.

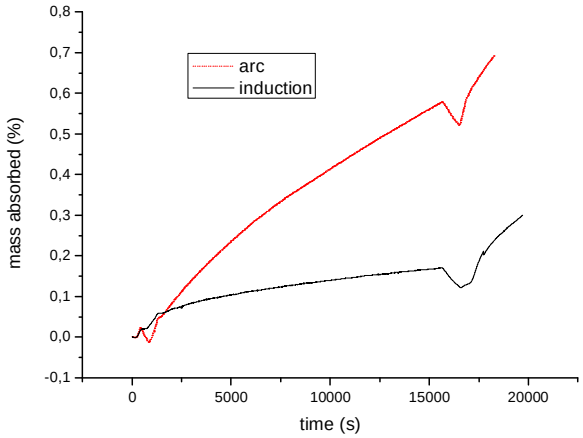

Figure 4 ï Comparision of hydrogen absorption between arc and induction melted samples, same composition.

For the figure above we conclude that arc melted samples are more capable to absorb hydrogen than induction samples, since the rate of hydrogen absorption by the arc sample is approximately 4,5 times higher than that for the induction one. But, as denoted in the micrographies, inhomogenities in composition are the main responsible for this high absorption rate. If gamma uranium is considered the more favorable phase for a high density fuel, such anomalies are undesirable, and must be treated as a process or method of fabrication loss.

Finally, in the case of the induction-melted alloys, the structures are much more homogeneous, presenting grains of a continuous gamma matrix and, sometimes, alpha precipitates in the boundaries, mainly in those of 5 to 7% weight Mo compositions. Thus, no homogenization thermal treatment is needed. If we take as comparison the same compositions, as the initial Mo content presented by the arc alloys, easiest is the powder obtention, but of an alloy with no homogeneous composition.

As an example, in the figure 5 are presented a micrography of a powder produced after thermal treatment under hydrogen applied on a γ-UMo induction alloy.

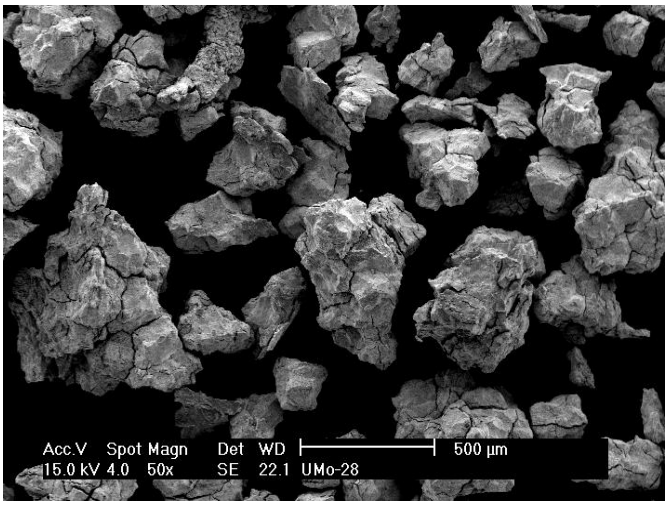

Figure 5 ï Powder particles of γ-UMo alloy.

5. Conclusion

The difficulty of the obtention, in one single step, a microstructural homogeneous alloy by the method of arc melting, its abrupt reduction in the values of densities in compositions greater than 8% wt. Mo, lead us to the conclusion that, to the obtention of the same quality presented by the induction melted alloys, some features of the arc melting process must be changed, like the furnaceôs geometry, number of remelts, geometry of loading, and mainly the cooling systems and thermal treatments conditions. Our main solution to avoid the problems of homogeneity in the arc samples was the change in the number of remelts. However, the remelts promotes also the formation of oxides, introducing impurities in the alloys.

Thus, the use of induction as a method of fabricating γ-UMo alloys are the choice here in IPEN-CNEN / Brazil. However, for low molybdenum alloys, where the problem of homogeneity is not too serious, arc could be used, conditioned to the application on the samples a sufficient number of remelts.

The important fact relating to the techniques of fabricating γ-UMo alloys is that the arc-melted alloys present, in all compositions, several dendritic structures, which are regions of low molybdenum concentration, mainly constituted by alpha-U phase, which leads to the application of an homogenization thermal treatment. But, as our experiences shows, they are not enough to eliminate all the dendritic structures, which are responsible to the differences in composition inside the grains.

This can be an advantage in the production of the powders, but at a cost of the loss of homogeneity. To the best preservation of the structural integrity of the alloys and their compositional homogenization, the induction melting techniques is considered here the best choice to produce the powders of high gamma content alloys.

6. References

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