

FABRICATION RESULTS OF GAMMA URANIUM-MOLYBDENUM ALLOYS FUELS

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ABSTRACT

This paper describes the results on the development of the technology of the fabrication of the gamma uranium-molybdenum alloys in IPEN-CNEN-SP, and presents some of their more recent experimental results. The importance of this class of fuels relies on the fact that they are the fuels considered to be loaded in the first Brazilian Multipurpose Reactor, RMB, stated as one of the tasks in the Nuclear Brazilian Plan, PNB.

The study of γ UMo fuels started with their preparation by the arc and induction melting technique, followed by thermal treatment to the obtention of a better degree of homogenization, under argon atmosphere at 1000°C. Additions of Mo varied from 5 to 10% weight. Samples of both classes of fuels were characterized mainly by X-ray diffraction, density, SEM and optical microscopy with image analysis. The main results of the alloy's production and an emphasis of the use of XRD data in the gamma-UMo powder obtention process are presented and emphasized here.

The results enabled us to study future methodologies to avoid most of the problems encountered in the recent technological approach to the fabrication of the alloys of UMo, which will lead to the production of materials with best efficiency and quality.

1. INTRODUCTION

Gamma uranium-molybdenum alloys has been considered as the best candidates to replace the uranium silicide U_3Si_2 fuel phase in plate type fuel elements for MTR reactors, mainly due to their acceptable performance under irradiation and metallurgical processing. Both fuels are usually dispersed in an aluminum matrix, and the advantages and disadvantages of these classes of fuels were extensively studied in the literature.

The need to the conversion of most of the MTR reactors in the world, due to the RERTR requirements, lead to the gradual replacement of the previous low-density/high-enriched uranium fuels in favour of the high-density/low-enriched ones, and the direction of the researches today passes through the γ UMo fuels, mainly in those with powers above or equal

to 30MW. This is the case of the Brazilian Multipurpose Reactor, RMB, planned to operate with 30MW power. The fuel considered as an initial load is the silicide fuel U_3Si_2 and, with γUMo fuel as its potential first replacement.

In terms of the alloys preparation, the cycle of heating and cooling must be the best to ensure a good homogenization between the alloys addition elements, mainly in the case of γUMo . Being a refractory metal, compositional segregation is sometimes easily obtained, due to the differences of its melting point related to the melting point of the uranium. Thus, the samples are usually submitted to further remelts and thermal treatments after the casting operation, to enable complete diffusion of the elements through the sample, and the obtention of a homogeneous alloy.

This is not the case for the silicide U_3Si_2 , where segregation could lead to the formation of other compounds, like U_3Si or USi , related to the lack or to the excess of silicon in some particular regions of the melting charge. No usual thermal treatments can correct those problems, and new melting operations were usually applied to save this non-conformity.

In this work, the results of the properties of the fuels prepared are shown, mainly in terms of X-ray diffraction and optical microscopy, and also its relation to the obtention of important powder fabrication parameters. The absence or the presence of some important phases in the UMo system is discussed in terms of the usual operations of fabrication.

2. EXPERIMENTAL PROCEDURE

According to the load capacity of the furnace, charges were prepared with uranium masses with nearly 700 – 800g, and the corresponding masses of the addition elements. In the case of uranium silicide a small excess of composition was used, to prevent loss of composition. Additions of 5 to 10% weight of Mo were used in the case of the obtention of γUMo alloys.

Samples were submitted to a cycle of operations of purge and vacuum after their loading into the induction furnace. After the last operation, performed up to the level of a diffusion pump vacuum, chamber was filled with high purity argon gas, to equalize the internal with the external pressure. With the end of these operations, the heating of the samples started, until the observation of the complete melting and mixing of the uranium and the addition elements.

After their solidification, samples were taken off of the crucible, and small pieces of them were analyzed by the previously mentioned techniques of characterization. The same procedure was used in the arc melting technique, but to ensure homogenization, a number of successive operations of remelting was applied to the samples.

3. RESULTS AND DISCUSSIONS

3.1. γUMo Alloys structure and properties – induction melting

First comparison about the main results and those from literature were made by means of the alloys density measurements, via hydrostatic method. The curves below show the variation of the densities as a function of the Mo content, in our case taken as the mean of 5 density

values. In general, a good agreement was obtained between the data and the reported in literature [1,2,3].

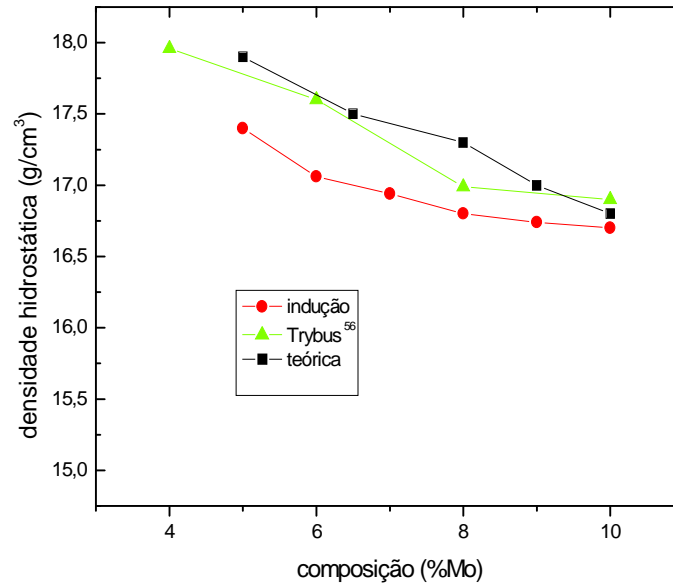


Figure 1. Comparison between the produced γ UMo alloys densities and literature.

In terms of X-ray diffraction, the results for the 5 to 10%wt. Mo alloys are given below. In general, it was observed the evolution of the gamma peaks, from 5 to 10wt% Mo addition, progressively more defined. This reinforces the fact that the higher additions are more suitable to stabilize gamma than the lower ones.

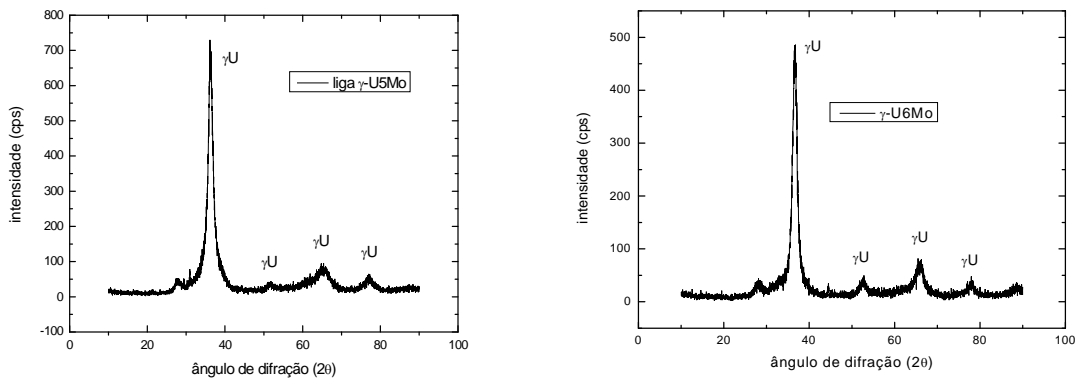


Figure 2. X-ray diffraction spectra, γ U5Mo (left) and γ U6Mo (right).

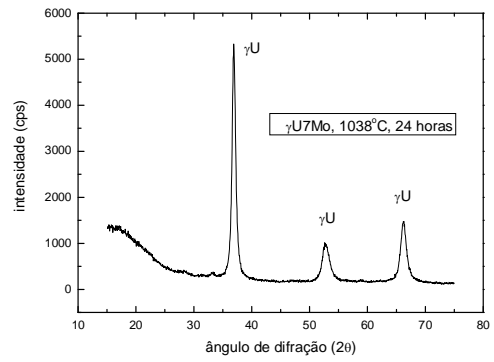
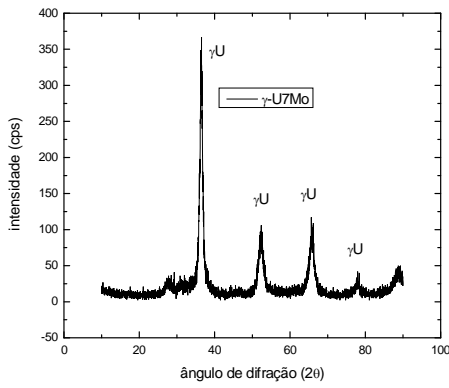


Figure 3. X-ray diffraction spectra, γ U7Mo (left) and γ U7Mo thermally treated (right).

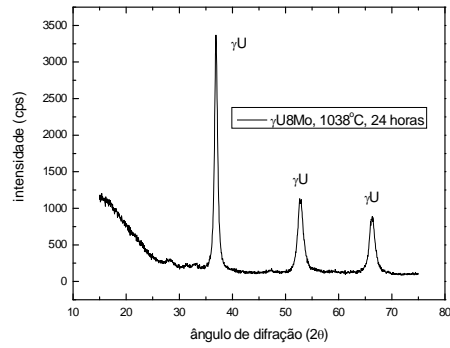
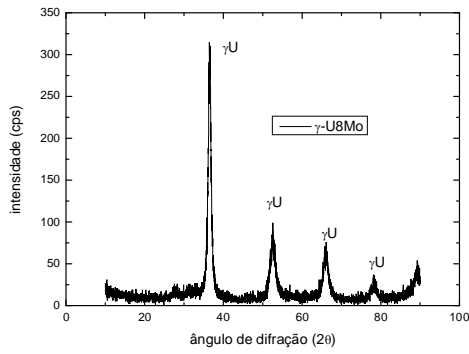


Figure 4. X-ray diffraction spectra, γ U8Mo (left) and γ U8Mo thermally treated (right).

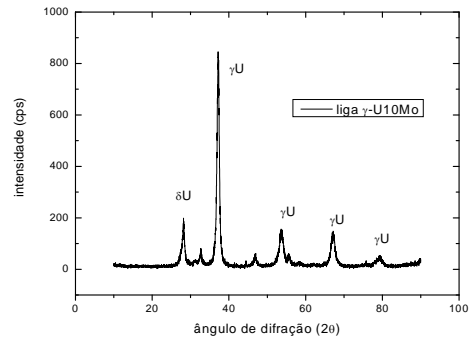
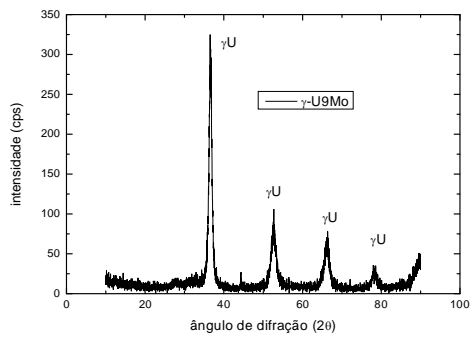


Figure 5. X-ray diffraction spectra, γ U9Mo (left) and γ U10Mo (right).

The sharpening of the gamma peaks is a function of the amount of Mo added but, with 10% addition, peaks of the δ - U_2Mo phase were also present, indicating some inhomogeneity through the eutetoid phase, with excess of molybdenum in some regions of the sample. Thermal treatments, when applied to the alloys, enhanced their gamma concentration by means of the molybdenum homogeneity due to diffusion. It is important to note that, in the UMo binary system, the obtention of gamma is also possible by a metastable process, so there is a strong tendency of the system to the decomposition, in percentages of Mo below the eutetoid, to the alpha phase, and in percentages above, to the delta phase, the unique compound in the UMo system, U_2Mo , which is in turn impossible to revert to gamma, even with thermal treatments.

It was shown also that, by the examination of the figures 3 and 4, what was the result of the thermal treatments in the temperatures above or equal to $1000^\circ C$, for at least 24 hours, below the commonly used and mentioned in the literature. The intensity of the diffraction peaks increased in both cases, indicating and confirming that the molybdenum diffusion in these conditions was enough to the elimination of possible segregation paths. However, as the thermally treated samples presented grain sizes larger than the as cast ones, it was considered convenient to proceed to a closer examination of the as cast structures, before the adoption of some temperature and time to the homogenization step.

It is important to note that no alpha phase was found. The most intense peaks of the alpha phase are at 35° , $35,6^\circ$, $36,9^\circ$, $39,5^\circ$, 51° and $60,3^\circ$. The most intense pure-gamma peaks are at $36,6^\circ$, $52,6^\circ$ and 63° . Despite the fact that we have a substitutional alloy, ADN thus the peaks are slightly deviated from the pure, gamma was the major constituent of the alloys.

Also, it is important to observe that grain sizes of the final gamma UMo alloy will have strong influence in the next fabrication step of a fuel element, which is their fragmentation into powder. Some authors consider that it is possible to obtain, in the homogenization treatments, the correction of the grain size to its usage as the powder fuel phase directly in this step.

As an example, in the next figures are shown some of the microstructures of some of the alloys studied. Here are well emphasized the fact of the huge increase in the grain size with the thermal treatments applied. Also, the enhancement in the number and in the relative area of pores was observed.

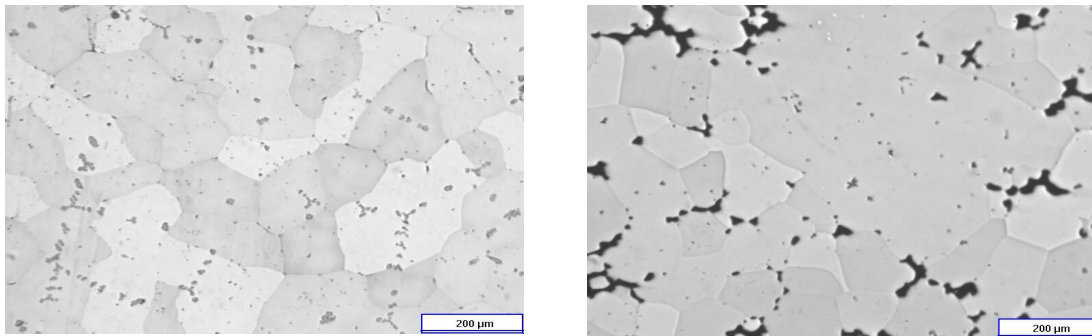


Figure 6. γ UMo alloy as cast (left) and thermally treated (right).

3.2. γ UMo Alloys structure and properties – arc melting

Following the same previously steps, arc melted alloys was also prepared. It was clear for the micrographies and the XRD spectra below that the homogeneity of the alloys was hardly accomplished, even with a number of 5 remelting operations.

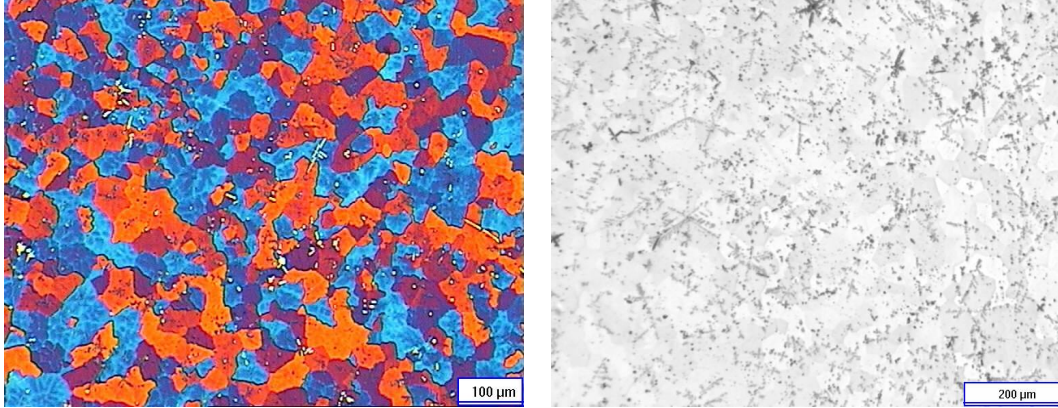


Figure 7. γ U8Mo alloy as cast (left) and thermally treated (right).

In the micrographies above (8% addition of Mo) we observe a huge number of dendritic structures, indicating difficulties in the homogenization process, during melting and even after the application of thermal treatment, in the same conditions of the induction ones. In comparison, the mean size of the grains was approximately the half of the same alloy produced by induction. It was not observed also the huge increase in the grain size after thermal treatment as in the induction alloys. Despite this important fact, relative intense gamma peaks were presented in its XRD spectra.

As shown in the figure below, the position of the peaks are in good agreement with the theoretical and with the peaks of the induction melted samples. The multiplet in the most intense peak could indicate the presence of the alpha phase, low Mo concentration regions in the sample, mainly the dendritic phases.

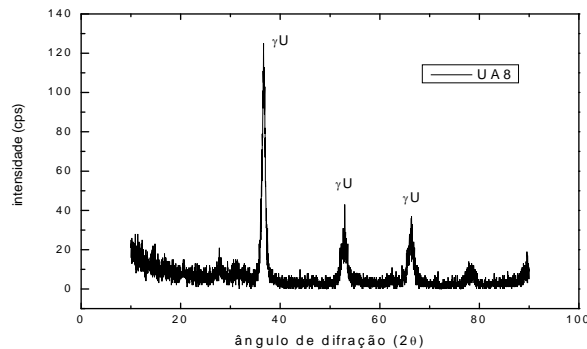


Figure 8. XRD spectra, γ U8Mo alloy, thermally treated.

3.3. Example of application - γ UMo powder obtention and XRD data.

To illustrate the use of the XRD data, let us consider the following analysis [1]. To the obtention of powders of γ UMo by the hydration-milling-dehydration technique (HMDH) [4,5], it is necessary to know the diffusion profile of hydrogen through the alloy fuels sample. The main equations to be used considering a plane alloy profile are:

$$\frac{c(x,t) - c_0}{c_s - c_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \exp\left[-(2n+1)^2 \frac{\pi^2}{4} \frac{Dt}{h^2}\right] \cos\left[\frac{(2n+1)}{2} \left(\pi \frac{x}{h}\right)\right] \quad (1)$$

where $c(x,t)$ is the concentration of hydrogen in the position x at time t , c_0 is the initial concentration of hydrogen in the sample, c_s is its concentration in the surface, D is the hydrogen-alloy diffusion coefficient, and h its total length. The other equation considered could be related to the mean hydrogen concentration cm , where we have:

$$\frac{cm(t) - c_0}{c_s - c_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(1)}{(2n+1)^2} \exp\left[-(2n+1)^2 \frac{\pi^2}{4} \frac{Dt}{h^2}\right] \quad (2)$$

Considering that there was no hydrogen initially present in the samples, $c_0 = 0$, and we are now leading to the estimation of the c_s parameter. It could be obtained taking the following initial hypothesis. If the flow of gas is Constant, the external alloy surface, with coordinates $(-x,0)$ and $(x,0)$, x representing its half width, is constantly supplied with a Constant amount of hydrogen. Thus, we can suppose that the speed with the hydrogen is adsorbed in the surface will not interfere in the analysis.

If c_s is proportional to the external surface of the alloy, and if we suppose also that over this area a defined amount of hydrogen is available to be adsorbed, by means of the equation:

$$\chi_{H_s} = N_{H_s} / (N_{H_s} + N_{M_s}) \quad (3)$$

the number of sites available can be estimated. For a specific amount of atoms in the surface, if they represent the external atoms of a monocrystalline layer of them, and if their main structure are the gamma, thus body-centered cubic, the number of interstitial tetrahedral positions comprised by this layer of atoms is 6, considering only the center of the faces, and in the tetrahedral sites, it is 3. Considering hydrogen diffusion in this 9 positions, the Best estimative for c_s is it is equal to 9 times the amount of atoms in the surface (layer) of the metal. Supposing the alloy's density is homogeneous, then c_s could be given by:

$$c_s = 9 \cdot \rho_x \cdot a \quad (4)$$

where ρ_x is the γ U_xMo density, and a is the thickness of the monocrystalline layer considered here, equals to the unitary cell parameter. Here c_s is given in unities of $[M]/[L]^2$. Here it is considered that all the interstitial positions are occupied.

Thus, the parameter a can be found as a function of the Mo content, as indicated in the Table 1, to the studied alloys, considering only the most intense peaks and using equation (5). The values of c_s were obtained by the equation (4). It was observed that the values obtained are

slightly different for the pure gamma U structure, according to the literature [3] the value is 3,524Å. Using:

$$n \lambda = 2 d_{hkl} \sin(\theta) \quad (5)$$

where we have $n = 1$ and $\lambda = 1,54\text{Å}$, we can build the Table 1 below. Here it is considered the calculations by the (1,1,0) plane, the minimum set of Miller indexes in a body-centered cubic lattice.

Table 1. Calculated values of cs by means of a , $\gamma\text{U}_x\text{Mo}$ alloys.

$\gamma\text{U}_x\text{Mo}_x$	θ (°)	a (Å)	ρ (g/cm ³)	cs (µg/cm ²)
5	18,07	3,5107	17,46	5,5167
6	18,39	3,4517	17,10	5,3121
7	18,25	3,4772	17,00	5,3202
8	18,22	3,4828	16,80	5,2659
9	18,26	3,4754	16,74	5,2360
10	18,59	3,4158	16,71	5,1370

Now, it is enough to know the total alloys surface exposed to the hydrogen, to use the equations (1) and (2), and thus to understand the diffusion of hydrogen as a function of some of the alloys properties.

4. CONCLUSIONS

In terms of fabrication, good agreement with previous fabrication results was obtained with induction rather than the arc melting technique. In this case, even with thermal treatments, the remnant phase alpha could not be removed, leading to the conclusion that there are some important changes to be done in the arc system or in its operation.

In general there were observed, for all the alloys produced by both techniques, a good agreement with the expected gamma peaks. A slight deviation of the pure gamma position was also expected, due to the fact that they are substitutional alloys. With the XRD data, some important estimation could be done related to the behavior of hydrogen in the process of gamma UMo powder obtention, by means of the HMDH technique.

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