SYNTHESIS AND CHARACTERIZATION OF GAMMA UMO POWDERS FABRICATED VIA THE HDH TECHNIQUE

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ABSTRACT

In this paper first results of the HDH process parameters and powder characteristics are presented. Addition of 7% wt% Mo was studied, and the preparation of the alloy was carried out by induction melting. After the conventional homogenization and conversion thermal treatments, samples were assembled in a closed vessel, where hydrogen was inserted up to a given pressure. The alloys were then subjected to new thermal treatment under hydrogen atmosphere, to allow the absorption of gas. The progress of the hydration was monitored by the pressure drop of the system during the experiments, and some conclusions about the fragmentation of the alloys were obtained. The powder was then characterized according to the traditional analytic techniques, mainly scanning electron microscopy. Thermo-gravimetric tests were also performed, to closely evaluate the alloy´s behavior under hydrogen in low temperatures. Powders with good quality and with composition nearly maintained under the experiments were obtained, and fragmentation could be possible in temperatures below the previously reported in the literature.

1. Introduction

Gamma UMo powders are widely recommended as the fuel phase in dispersion fuels, due to its good irradiation and fabrication properties, as a possible substitute for the silicide fuels. Several works carrying out during the past years points to atomization as the correct way to prepare the metallic powders of UMo [01,02], due to the minimization of problems like bubble formation, dog-bone and changing of particle size distribution during rolling, due to breakage, interaction layer between fuel phase and matrix, among others.

Despite the above considerations, some good results in terms of performance during fabrication and irradiation were also obtained when plates were fabricated with HDH and HMDH powders [03,04,05]. Thus, to enable IPEN/CNEN to evaluate the behaviour in all the phases of the plates fabrication, our first choice was for the hydration-dehydration as a technique for the gamma UMo powder production.

To produce γ-UMo powders, a group of operations has been used and are usually carried out in the following sequence. γUMo alloy casting operation is followed by an homogenization isothermal treatment, to ensure a good molybdenum distribution in the grains. The next step is carried out by two main routes. The first of them comprises a direct thermal treatment in the gamma plus alpha phase field to partially convert gamma into alpha, followed by hydration-dehydration. In the second, due to the observation that hydrogen can be easily incorporated by γ-U7Mo mainly in low temperatures, a previous thermal treatment is performed in temperatures from 120°C to 150°C for times varying from 1 to 3 hours, followed

by another thermal treatment in the gamma plus alpha phase field. Also, the powder is obtained after the DH step.

Following some of the steps above, in this paper the first experimental results in terms of the process parameters and characterization of the powders obtained by HDH route were presented. Unlike the previously reported tests [06,07], large amounts of U7Mo were also tested, allowing us to work with sufficient amounts of material to the production of the first UMo miniplates and its characterization.

2. Experimental procedure

Production of the γU7Mo alloys was carried out by induction. Thermal treatments of homogenization were performed at the temperature of 1000°C, for 3 days. To the HDH step, a conventional tubular horizontal furnace was used. Due to the experimental constraints, the option was for the work with a fixed amount of hydrogen, with pressure and temperatures ranges in order to avoid absorption by the reaction chamber.

Small pieces of γ-U7Mo alloys, with masses about 150mg, were firstly characterized by means of a thermogravimetric / differential thermal analysis (TG/DTA). Under a constant flow of hydrogen, after some cycles of purge and vacuum, curves of mass gain and temperature with time were constructed, for times of 4 hours and temperatures of 100°C and 75°C. The data generated enabled us to set up experimental parameters to the work with 40 to 50 g of alloys, in another experimental assembly.

After the analysis of the results in the TG equipment, experiments were carried out with alloys placed inside a tubular reactor, after being surface cleaned. With a level of vacuum of 10^{-3} mbar, the system was purged with high purity hydrogen for several times, in order to remove residual air inside the chamber. Hydrogen was then inserted in the system, up to a fixed pressure, and a cycle of heating was programmed to the operation of the furnace. The progress of the reaction between hydrogen and alpha uranium was measured by the reduction of the pressure with time, converted to gain of mass by the UMo sample.

The powder obtained was analysed by the help of a scanning electron microscope, its form and approximate composition could be obtained.

3. Results and Discussions

3.1. Synthesis

The results of the TG /DTA experiments are shown bellow, in the Figure 01, where we can observe the increase in the absorption of hydrogen at some fixed value of temperature. This behavior confirmed the previously reported in literature [03,05], where it was mentioned that hydrogen treatments comprising expositions in temperatures between 120°C and 250°C allows the alloy to be more sensitive to the hydrogen action.

Figure 01 show that, for 100°C and 4 hours treatment, mass absorption reached some limiting value, which keeps itself constant even after cooling, indicating complete reaction of the alloy with hydrogen. In absolute terms, the mass gain was of 1,177mg, corresponding to 1,34% of the initial mass sample, very near of the theoretical value of 1,24%, needed to the complete hydration, by means of the reaction:

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

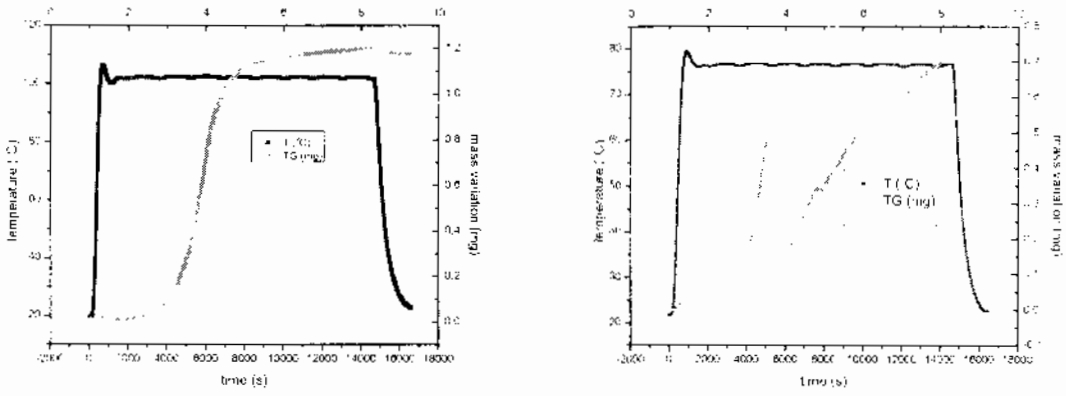


Figure 01 – Mass variation with time, left: U7Mo, 100°C / 4 h, right: U7Mo, 75°C / 4h.

At the end of the experiment, the sample presented itself totally fragmented; no dehydration was needed to first turn the metal into powder. It is reasonable to state that, for the experimental conditions adopted, a time of 2 hours was enough to complete the process.

To the same alloy at 75°C, it is shown that there was the rupture of the structure in a temperature value very far from the previously reported in literature, 120°C. This fact is not necessarily related to complete hydration, or, in other words, complete hydration and dehydration is not a necessary condition for the start of the breakage phenomena of the alloys. We can observe that practically all the mass absorbed by the alloy was lost easily in the interval of (5363; 76,26; 0,601) ≤ (t;T;Δm) ≤ (5399; 76,27; 0,008), where t stands for time, T for temperature and Δm for gain of mass. The final mass of 0.008mg corresponds to the amount of hydrogen retained in the alloy after the new absorption step. The hydrogen release velocity was performed with a mean rate of 16,472µg/s.

After the initial phase of mass fall, where all the hydrogen incorporated by the alloy and which di not react with alpha uranium was released, the fragments formed were responsible for the new growth in the gain of mass up to the end of the experiment. After the constant temperature phase, and similarly to the previous case, the maximum value stands in the coordinates (14744; 67,53; 0,723). Even working with a lower value than the previously reported, an amount of 0,54% of the initial mass was able to be retained.

In the laboratory scale experiments, the behavior of the pressure drop with time, for hydration, and pressure increase with time, for dehydration, is shown in the next figures. For the previously sensitized γ-U7Mo alloys, in this experiments were introduced a mean value of 1604 mbar of hydrogen in a pre-evacuated system of nearly 10^{-3}mbar pressure (-902 mbar indicated above represents the measurement head indicator limiting value). It is observed in Figure 02 (left) that the absorption was instantaneous and, after 6 hours of experiment, all the gas inserted was absorbed.

Dehydration is shown in Figure 02 (right), where we can observe also the great capacity of hydrogen retention by the alloy. In the marks A, B and C, the pressure of the system was forcedly reduced, for the safety of the system.

Very similar results were early published by Balart et al. [03], for the hydration of γ-U7Mo. The progress of the reaction was followed also by pressure measurements. According to the authors, it was observed that at a specific point, pressure started to drop, indicating the start of hydrogen consumption by the samples. Pressure continues to fall but, after some time, it

tends asymptotically to reach the value before hydrogen had been inserted into the reactor, indicating the end of the reaction or the process of hydrogen incorporation by the sample.

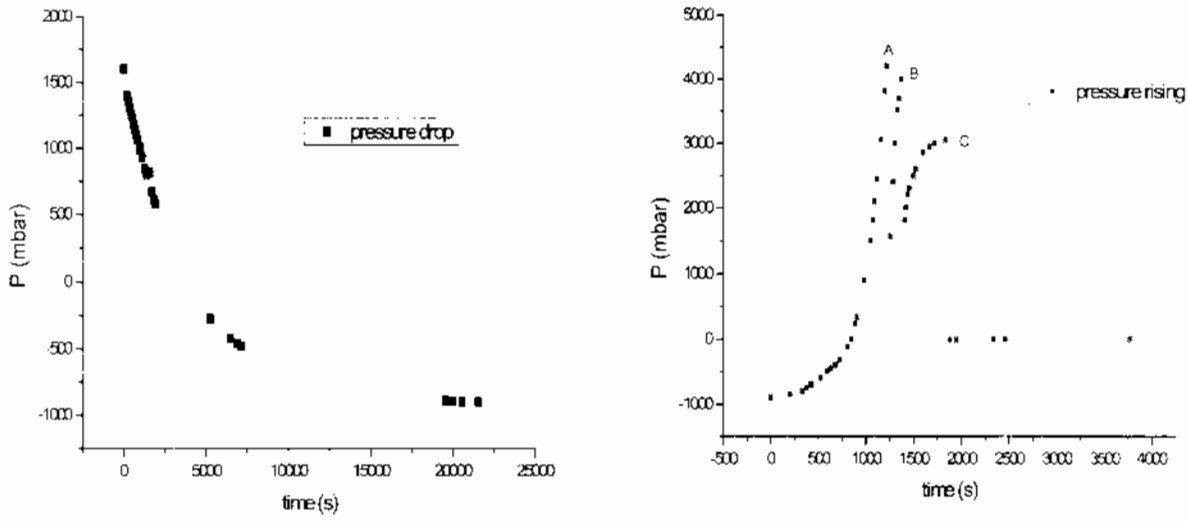


Figure 02 – Hydrogen absorption, γU7Mo (left); hydrogen desorption, γU7Mo (right).

3.2 Characterization

Typical images of the powders formed after the laboratory scale experiments are shown bellow. It is clear that an adjustment of the particle size was needed to attain the specifications of the dispersion fuels in the fabrication of the plates. The good quality of the powders was verified also visually, with a metallic grey color.

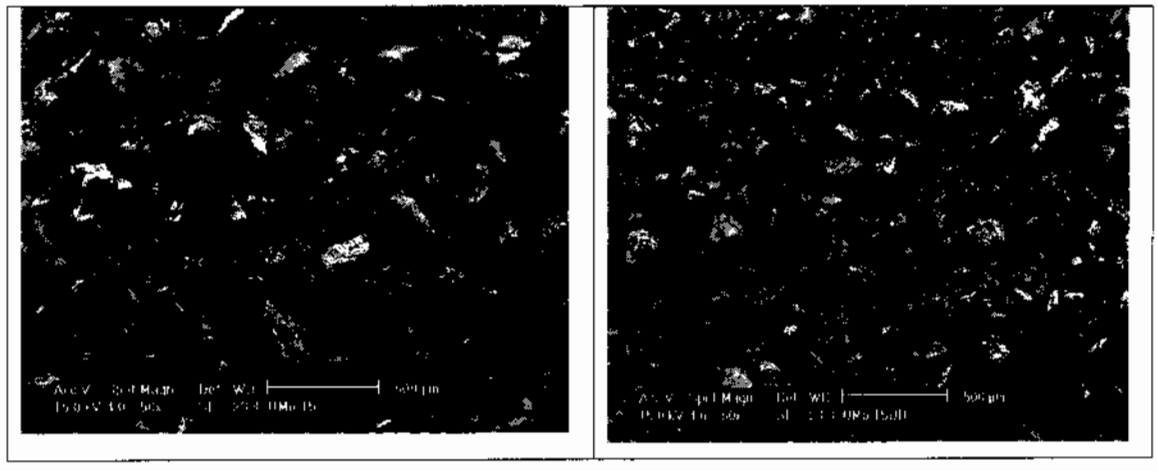
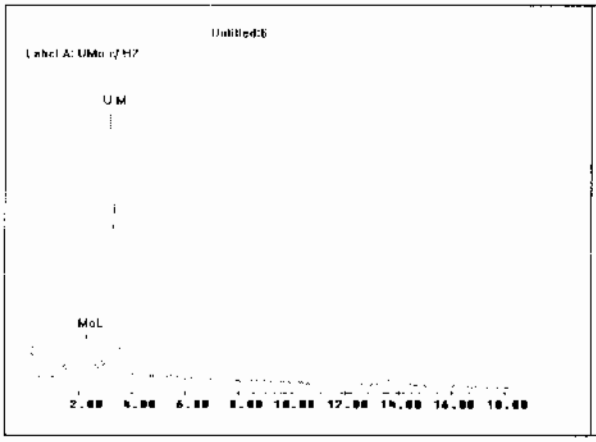


Figure 03 – SEM image of γU7Mo powders . Left: after hydration, right, after dehydration.

The semiquantitative results above were performed taking as principle that only U and Mo was presented in the sample, oxygen or other impurities were not considered in the calculation of the percentages. Despite of the precision of the method in this range of composition, we can conclude that it was maintained nearly constant during the fabrication of the powders.



Element, Wt %, At %, K-Ratio, Z, A, F

MoL, 6.27, 14.23, 0.0503, 1.1782, 0.6810, 1.0000
U M, 93.73, 85.77, 0.9011, 0.9884, 0.9726, 1.0000
Total, 100.000, 100.000

Figure 04 – Semiquantitative analysis, UMo powder, after hydration step, γU7Mo.

4. Conclusions

For the γU7Mo alloy and lower, pre-treatment under hydrogen can be introduced at least at 75°C, sufficient condition for the start of the fragmentation of the pre-sensitized alloy and above the previously temperature reported in literature, equals to 120°C. Obviously that, working with large amounts of alloy, times of fragmentation could be very different. However with the reduction of the hydration temperature powders with good quality were also obtained. Full compositional and structural characterization was still in conclusion.

5. References

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Acknowledgements

To Dra. Elita U.F. Carvalho and Dr. Luciano Pagano, coordinators of the Project IAEA / Brazil BRA3012, and to Dr. Ivan Salatti, from the Nuclear Energy National Comission, for the support provided.