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AVALIATION OF γ -U8Mo NUCLEAR FUEL ALLOYS

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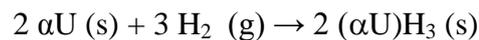
ABSTRACT

Gamma uranium-molybdenum alloys have been considered as the fuel phase in plate type fuel elements for MTR reactors, mainly due to their acceptable performance under irradiation and metallurgical processing. To their use as a dispersion phase in aluminum matrix, a necessary step is the conversion of the as cast structure into powder, and the technique considered at IPEN / CNEN - Brazil is HDH (hydration-dehydration). This paper describes the first results of hydrogen absorption and its relation to powder formation of the 8% weight molybdenum γ -UMo alloy. After their production by induction melting, samples were thermally treated under constant flow of hydrogen for temperatures varying from 500°C to 600°C and times from 2 to 4 hours. Curves relating mass incorporation and time for the above temperatures were obtained, and the results were related to its fragmentation. It was observed that even after the dehydration, samples can be fragmented under specific conditions of isothermal treatments, and that there is a strong correlation between absorption and the rate of gamma decomposition. A value of 568,39°C was obtained for the maximum in the rate of gamma decomposition, which can be also related to the eutectoid transformation temperature of this alloy.

key-words: uranium-molybdenum alloys, hydration-dehydration, powder obtention, high density nuclear fuels.

1.Introduction

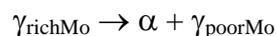
The idea of the use of hydrogen to obtain α -UMo powders is to convert its ductile structure into a brittle one. In the range of compositions where γ -UMo is considered as a dispersed nuclear reactor fuel, mainly 5 to 10% weight in Mo, alpha-uranium is the proeutectoid phase. Thus it is expected that the as cast and even the thermally treated structures contains some intergranular alpha-uranium as cellular precipitates. In terms of powder formation, the alpha phase reacts readily with hydrogen in temperatures from 250°C to 350°C. The formation of uranium trihydride:



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



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



in the gamma plus alpha field, are the keys to the comprehension of how the embrittlement can be achieved via intergranular precipitation.

To produce γ -UMo powders, a group of operations has been used by some countries, the conventional ones reported in the work by CLARK et al,1998 and WIENCEK and PROKOFIEV ,2000. The other ones, called the HDH routes, are studied in BALART ,2000, SOLONIN ,2000 and PASQUALINI,2002 and2004 and are usually carried out in the following sequence, aiming the obtention of γ -U(6 to 7)Mo powders. After the casting operation, an isothermal treatment of homogenization is given to the sample to ensure a good molybdenum distribution in the grains. The next step is carried out by two main routes. The first one comprises a direct thermal treatment in the gamma plus alpha phase field BALLART,2000 and SOLONIN,2000 to partially convert gamma into alpha by means of the reaction (3), followed by dehydration, the inverse (1) reaction. More recently, due to the observation that hydrogen can be easily incorporated by γ -U7Mo mainly in low temperatures, a previous thermal treatment in temperatures from 120°C to 150°C for times varying from 1 to 3 hours, followed by another thermal treatment in gamma plus alpha phase field. Also, the powder is obtained after the DH step.

In both routes, the DH step is the one on which the precipitates cellular structure is broken, leading to the powder formation which, according to the authors above, powder losses originated from the cellular alpha precipitates could be recovered by another isothermal treatment, this time in the gamma field.

However, in some of the experiments carried out in this work, it was observed that, by a correct choice of parameters, the structure of the alloy collapses readily, even without the DH step, and in times and temperatures a bit lower than those mentioned in the previous works. Our suggestion is that the cooling speed has an important role in the fragmentation of the samples. If the same cooling rate was applied to all the samples, we could expect that those ones more susceptible to hydrogen embrittlement are also more susceptible to break by thermal shock. In this paper we are presenting and discussing some of the main results obtained in IPEN on the formation of γ -U8Mo powders instead of γ -U7Mo, where there are the majority of the works in the γ -UMo powder formation, via HDH. Also, according to some time-temperature-transformation diagrams, γ -U8Mo is most gamma stable than γ -U7Mo, thus its use as a fuel phase in nuclear research reactors would be more convenient.

Our main objective is to state a set of optimal parameters to the obtention of good powder yielding, mainly in the hydration step, and to clarify, at least qualitatively, the mechanisms which leads to the γ -UMo powder formation.

2. Materials and methods

Alloys of γ -U8Mo were prepared by induction melting under high vacuum. Natural alpha-uranium cylinders and small cylindrical pieces, each having 3x2 mm, of high purity molybdenum, formed the induction charge, assembled in a high purity zirconia crucible.

Samples with the same shapes were taken from the casts in order to perform the hydration experiments, carried out in a thermalgravimeter (TG) analyzer. The samples, each having approximately 200 mg, were assembled in calcined alumina crucible, after being cleaned and polished to remove surface oxidation, which can interfere in the results. 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 $2,0 \times 10^{-6}$ MPa, a constant flux of high purity hydrogen (5.0 or 99.999% analytic) was applied to the samples until the end of the experiments. The procedure to the verification of the γ -U8Mo alloys embrittlement behavior under hydrogen was very similar to the utilized by TETER et al. ,2008, to investigate embrittlement of U6Nb alloy, concerning gas purity, but in terms of pressure our level of vacuum was high.

All the experimental settings like times and temperatures, ramps, heating and cooling rates, were inserted in the analyzer software, allowing the set up of our experimental cycles. The progress of the hydrogen absorption by the alloys was constantly measured as a function of time. Our main strategy was to perform the experiments over a range of temperatures, mainly those nearly the binary U-Mo system eutectoid transformation, the one in which several TTT diagrams CABANÉ,1959,REPAS,1964,VAN THYNE,1957 predicts maximum rate of decomposition, given by reaction (2). The experiments start when the program parameters are ready and all the system was

filled with hydrogen, which also prevents the presence of oxygen in it. So, curves of hydrogen absorption as a function of time were obtained, and also the ones 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 conditions.

The criteria to define the amount of powder was established on the basis that isothermal treatments under hydrogen atmosphere produces, in almost all the experiments, a remaining solid core, with notably bigger dimensions than its fragments. This parameter considers a fraction of powder with mean diameter less than 1,0mm.

It is important to note that no gamma reconversion treatment was applied to the powders, by the following reasons. The problem with the reconversion is that the alpha phase has very low Mo content; there is not enough Mo dissolved in its structure to retain gamma after quenching. There is a need for Mo diffusion from the gamma powder particles through alpha cellular particles, but after dehydration, they will constitute two spatially non-connected regions and, consequently, solid state diffusion could not be possible.

3. Results and discussions

X ray spectra and micrographies of the γ -U8Mo compositions are shown in Figure 1, where we observe a high degree of homogenization presented by the cast ones, provided by the induction melting technique.

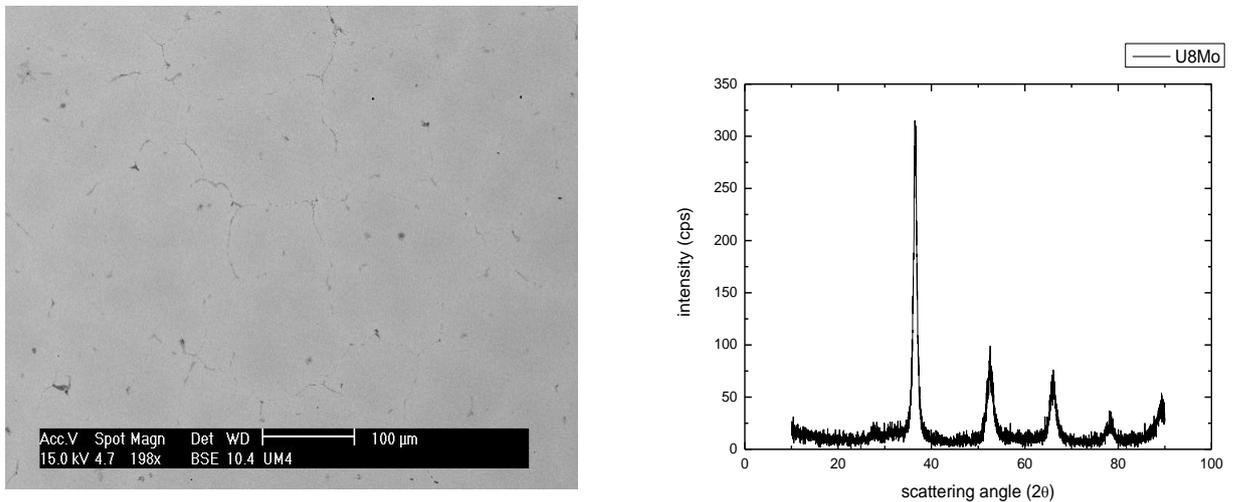


Figure 1 - MEV image and X Ray diffraction pattern of γ -U8Mo alloy.

The set of experiments and the results in terms of powder yielding are summarized in Table 1. We are concerned mainly with the temperatures and times which could lead to powder formation in the isothermal treatments, thus no dehydration was applied. But, as we discussed above, cooling of the samples had an important role in the

sample's fragmentation.

Table 1 - Isothermal treatments of γ -U8Mo and respective powder yielding.

Temperature ($^{\circ}$ C)	Time (h)	Yielding (%)
504,26	4	1,84
525,66	3	4,67
563,56	2	75,23
565,40	4	100
568,39	4	100
573,53	4	12,58
602,33	2	3,30

In Figure 2 are shown the mass absorption curves, including the turning points of absorption / desorption in the cooling ramps, of the γ -U8Mo alloys.

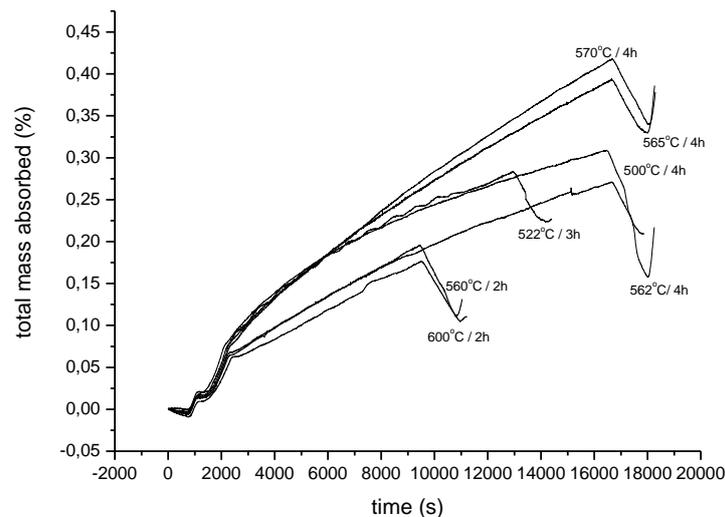


Figure 2 - Hydrogen absorption curves for γ -U8Mo samples.

From each individual experiment we can extract the temperatures of the turning points in the interactions between hydrogen and γ -U8Mo, in the cooling curves. Isothermal temperatures are given as a real mean temperature observed in the experiments. Those data are shown in the Table 2, with the absolute difference between the isothermal, the turning point and the classical eutectoid temperature of 565° C, for the γ -UMo system, and here calculated as:

$$DEIT = |TIT - TE|$$

$$\text{DETP} = |\text{TTP} - \text{TE}|$$

where DEIT and DETP are the absolute values between the temperature differences of thermal treatment and turning point, respectively, from the eutectoid transformation temperature TE, TIT is the temperature of isothermal treatment, and TTP is the turning point temperature.

Table 2 - Thermal data from the hydrogen absorption curves.

Isothermal Temperature (°C)	Turning Point Temperature (°C)	DEIT(°C)	DETP (°C)
504,26	99,93	60,74	465,07
525,66	139,21	39,34	425,79
563,56	139,02	1,44	425,98
565,40	145,41	0,4	419,59
568,39	150,87	3,39	414,13
573,53	145,82	8,53	419,18
602,33	145,66	37,33	419,34

It can be noted that there is a correlation between isothermal temperatures, turning points temperatures, and the powder yielding, when we take into account the data in Tables 1 and 2.

Since the yielding is influenced by the distance from the isothermal eutectoid temperature of 565°C, it was interesting to determine total mass absorption and its rates, and to correlate these data also with the powder yielding. They were summarized in Table 3, where the amount of hydrogen retained was calculated as the difference between the maximum hydrogen absorbed, given at the end of the thermal treatments, and the amount of hydrogen released at the turning point in the cooling curves.

The rate at the stable hydrogen absorption is a mean value, calculated from the end sections of the isothermal absorption curves, where the absorption is considered to be almost constant.

Table 3 - Hydrogen absorption data from the isothermal treatments.

Isothermal Temperature (°C)	Hydrogen at the Turning Point (%)	Total Hydrogen Absorbed (%)	Rate at the Stable H Abs. (% x10 ⁻⁶ / s)
504,26	0,2091	0,0994	7,94
525,66	0,2237	0,0590	13,12
563,56	0,1115	0,0834	16,54
565,40	0,1573	0,1130	12,62

568,39	0,3298	0,0626	16,46
573,53	0,3401	0,0770	18,48
602,33	0,1044	0,0715	12,72

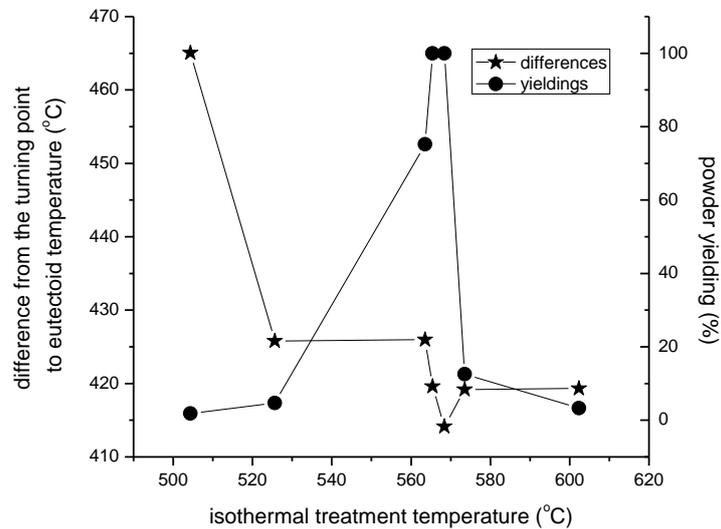


Figure 3 - DETP and powder yieldings, from table 2.

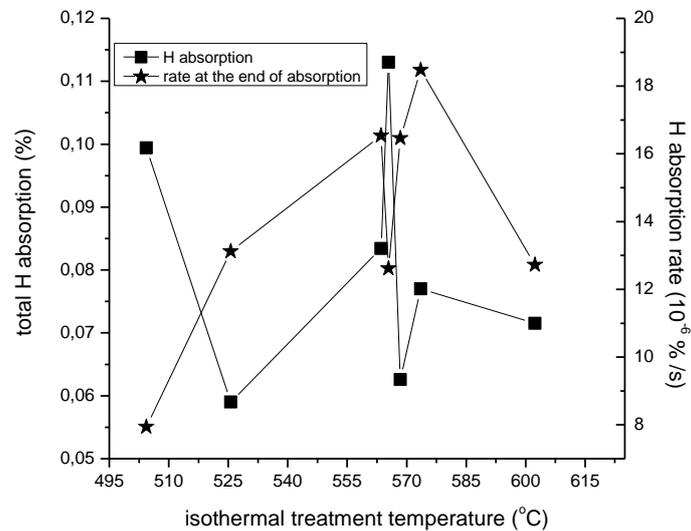


Figure 4 - Hydrogen absorption parameters, from table 3.

From the graphics and tables above, some important facts must be considered in the powder formation and its relation to the equilibrium of the metastable gamma uranium-molybdenum phase. First, if a certain amount of alpha is present initially, and by the reaction (A) we know that alpha has the tendency to react with hydrogen, it is expected that the hydrogen absorption in γ -U8Mo must also be influenced by the rate at which alpha is formed. We know from the work of HOFFMAN et al. ,1998 and from

some of the U-Mo time-temperature-transformation (TTT) diagrams, that the rate at which gamma decomposes to alpha in an homogeneous alloy is strongly dependent on 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 γ -UMo powders and then the fragmentation are caused primarily by the initial amount of γ -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 will be the sample's fragmentation.

Also, in the works of VAN THYNE & McPHERSON ,1957 and McGEARY 1955, the nose of the TTT diagrams varies strongly, according to the methods used to the determination of the equilibrium gamma - alpha. Following McGEARY 1955, the temperature at which there is a maximum decomposition of γ -U8Mo is 525°C, using x ray diffraction and metallography. According to VAN THYNE & McPHERSON,1957, resistivity methods indicate a value of 500°C and hardness of 570°C. Since we are dealing with powder fragmentation, it is reasonable to suppose that our work confirms that the value at which the γ -U8Mo suffers a more pronounced change in hardness is that on which there was a more pronounced production of alpha phase, which leads to a higher increase in the total hydrogen absorption and, consequently, to an ease of the samples fragmentation. This occurs, according to Table 3, at a value near 568,39°C or 573,53°C.

For this last condition, we obtained the highest values in the hydrogen absorption and its rates, but it produces only 12% of fragmentation. Since the temperature of the gamma plus alpha to gamma field in the U-Mo phase diagram for γ -U8Mo is approximately 619°C, we are far from the eutectoidal transformation temperature and closer to this line when the treatment is applied at 570°C. Thus, the nose point, e.g., the point of the maximum decomposition, is reached when we work at 568,39°C, instead of 573,53°C. Another argument favorable to this observation is its turning point temperature, the highest among all, which leads to a minimum in the distance from the classical eutectoidal transformation temperature and to a minimum in the energy needed to break the samples by thermal shocks. As we considered the same cooling rate in all the experiments, we can conclude from the Table 2 that with the smallest thermal gradient the yielding was better. So, 568,39°C is the most related one to the eutectoidal transformation. If we use 565,40°C, apart its smallest difference from the classical value and same powder yielding, we cannot have the same results.

In spite of the absorption at 568,39°C being less pronounced when compared with those of 504,26°C, 573,53°C and 602,33°C, we are leading to the following conclusions. Absorption of hydrogen occurs by 2 main mechanisms, given for example in the work of POWELL, 1976 one related to the interstitial positions and the other related to the intergranular precipitation of alpha. If the distance from the eutectoid increases, we are far from the condition which leads to a more alpha precipitation and, thus, the mechanism related to the first, also called fragilization by hydrogen saturation and tension sources creation, are not enough to produce fragilization and, consequently, good powder yielding. This fact can explain good absorption, but low yielding, when the samples were treated in above mentioned temperatures. At 602,33°C, for

example, if we double the time and consider the same rate of absorption, we will obtain near the double of the mass absorbed in two hours. The same is considered valid for the other experiments, when the time was less than 4 hours

So, it is demonstrated here, at least for this composition, that a good yielding is possible only in temperatures very close to 565 to 568°C, and that 568,39°C, instead of 565°C, can be considered the closest value of the eutectoidal temperature transformation.

Another aspect is the characteristic of the powder formed, which can be inferred by the huge increase in the absorption rates, mainly in the cooling part of the curves. In all the experiments where there was good yielding, it was observed that at some point in the cooling ramp there was a change in the mechanism of mass absorption. If we consider that absorption is a phenomenon that depends on the amount of the free area existent in the system, it is expected that the higher the surface of the material exposed to the gas, the higher the absorption, and then we can estimate dimensional parameters of powders, like mean diameters, for example.

So, the huge change of the rate of absorption which follows a brief period of mass loss can be explained by the following considerations. 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, like it was observed, that absorption increases with time in the cooling ramp region.

Thus, there is a creation of a number of sites by the particles detached from the initial samples, which can be capable to absorb more hydrogen until saturation is reached. This creation of new absorption sites can be related to the difference between the total amount of hydrogen absorbed at the maximum in the isothermal treatment and the minimum in the cooling ramp, after which the system undergoes a new increase in the absorption rates. This increase allows us to do some estimates on the surface area created, and to the dimensional parameters of the particles produced in each experiment.

Finally, at this level of the samples hydrogen exposition, it is important to observe that, due to the low solubility of hydrogen in uranium and uranium alloys and to the strong tendency to form hydrides, it is expected that the main mechanism of embrittlement of uranium alloys must be due to the stress induced by alpha uranium hydride formation TETER, 2008, mainly in the low stabilized alloys of γ -UxMo alloys ($x < 8$). At this level of stability, both mechanisms must play a concurrent role to the phenomenon. It is logical to infer, thus, that stress induced alpha formation

contribution must decrease with the increase in the Mo content in γ -UxMo alloys (for nuclear fuel applications $8 \leq x < 10$).

4. Conclusions

Apart of the dehydration treatment applied by the various works on HDH γ -UMo powder obtention mainly in the compositions of 5 to 7 wt% Mo, the emphasis was given here in the isothermal absorption treatments. 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 experimentally demonstrated here is that, using a convenient set of parameters, the fragmentation of the structure into powder can be obtained even in a high Mo content alloy, like 8%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.

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 in the gamma plus alpha phase field. Since time acts on the enhancement of diffusion processes, which tend 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 pretreatments of 150°C to 250°C are questionable, at least for a range of compositions now defined as %Mo \leq 8, if we take a look at our good yielding.

The most important conclusion is related to the set of the isothermal conditions which leads to good yielding and equilibrium between gamma and alpha phases. In terms of process, thermal shock could be achieved with the alloy treated at 568,39°C, so it is easy to break it in this temperature. Also, we know that the greater the production of alpha, the greater the yielding.

Thus, we determined here that we are close to the eutectoid temperature transformation of the U-Mo system and to the nose point in the time-temperature transformation diagrams at the temperature of 568,39°C, instead of the classical 565°C. So, hydration of the alloys could also be used as a method to find some important values of equilibrium properties in the uranium-molybdenum system.

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REFERENCES

CLARK, C.R., MEYER, M.K., STRAUSS, J.T., Fuel Powder Production from Ductile Uranium Alloys, *Proceedings of the RERTR Meeting*, São Paulo, Brazil, October 1998.

WIENCEK, T., PROKOFIEV, L.G., Low-Enriched Uranium-Molybdenum Fuel Plate Development, *Proceedings of the RERTR Meeting*, Las Vegas, Nevada, march 2000.

BALART, S. et al., U-Mo Alloy powder Obtained by a Hydride-Dehydride Process, *Proceedings of the RERTR Meeting*, Las Vegas, Nevada, march 2000.

SOLOVIN, M.I., et al, Development of the Method of High Density Fuel Comminution by Hydride-Dehydride Processing, *Proceedings of the RERTR Meeting*, Las Vegas, Nevada, March 2000.

PASQUALINI, E.E., et al, Scaling up the Production Capacity of U-Mo Powder by HMD Process, *Proceedings of the RERTR Meeting*, Bariloche, Argentina, November 2002.

PASQUALINI, E.E., Set up of U-Mo Powder Production by HMD Process, **2004 International Meeting on Reduced Enrichment for Research and Test Reactors**, Chicago, USA, October 2004.

TETER, D.F., et al., Hydrogen Decreased Ductility of a U6%Nb Alloy, *Los Alamos National Laboratory document LA-UR-04-3343*, Los Alamos, United States.

CABANÉ, G., DONZÉ, G., Stabilisation de la Phase γ dans les Alliages Ternaires a Base d'Uranium Molybdene, *Journal of Nuclear Materials*, v.4, 1959, pp.364-373.

REPAS, P.E., et al., Transformation Characteristics of U-Mo and U-Mo-Ti Alloys, *Transactions of the ASM*, v.57, 1964, pp.150-163.

VAN THYNE, R.J., McPHERSON, D.J., Transformation Kinetics of Uranium-Niobium and Ternary Uranium-Molybdenum Base Alloys, *Transactions of the ASM*, v.49, 1957, pp.576-597.

VAN THYNE, R.J., McPHERSON, D.J., Transformation Kinetics of Uranium-Molybdenum Alloys, *Transactions of the ASM*, v.49, 1957, pp.598-621.

MCGEARY, R.K., Development and Properties of Uranium-base Alloys Resistant in High Temperature Water, *USAEC report WAPD-127-I*, April 1955.

HOFFMAN, G.L., MEYER, M.K., RAY, A., Design of High Density Gamma-Phase Uranium Alloys for LEU Dispersion Fuel Applications, *Proceedings of the RERTR Meeting*, São Paulo, October 1998.

POWELL, G.L., et al., Internal Hydrogen Embrittlement of Gamma-Stabilized Uranium Alloys, *Corrosion*, v.32(11), November 1976, pp. 442-450.