IDENTIFICATION OF PHASES IN THE INTERACTION LAYER BETWEEN U-Mo-Zr/Al and U-Mo-Zr/Al-Si.

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ABSTRACT

Out-of-pile diffusion experiments were performed between U-7wt.% Mo-1wt.% Zr and Al or Al A356 (7,1wt.% Si) at 550ºC. In this work morphological characterization and phase identification on both interaction layer are presented. They were carried out by the use of different techniques: optical and scanning electron microscopy, X-Ray diffraction and WDS microanalysis.

In the interaction layer U-7wt.% Mo-1wt.% Zr/Al, the phases UAl_3, UAl_4, $Al_{20}Mo_2U$ and $Al_{43}Mo_4U_6$ were identified.

In the interaction layer U-7wt.% Mo-1wt.% Zr/Al A356, the phases $U(Al, Si)_3$ with 25at.% Si and Si_5U_3 were identified. This last phase, with a higher Si concentration, was identified with XRD Synchrotron radiation performed at the National Synchrotron Light Laboratory (LNLS), Campinas, Brasil.

1. Introduction

Uranium-molybdenum alloys with concentrations of Mo between 6 and 10 wt.% are considered good candidates for fabrication of fuel elements for research and test reactors, in order to reduce the enrichment down to 20 wt.% ^{235}U. These alloys can retain the metastable γU phase at the working temperatures under irradiation.

Post-irradiation examination of U-Mo fuel elements have shown an unacceptable behavior consisting in large swelling and porosity in the surroundings of the interaction layer formed between the uranium alloy and the aluminum matrix [1,2,3]. Although the problem has not been fully understood, results from different investigations would indicate that some of the interaction product formed due to the interdiffusion between U-Mo and Al could be the responsible for these failures.

Modifications to the U-Mo alloy, the Al matrix or both have been proposed looking for the solution to this problem [4].

J.M Park. et al. [5,6] have studied the U-Mo-Zr / Al-Si interaction layer (IL). The main conclusions of these works were that Zr addition to U-7 wt.% Mo and Si to Al, reduces the interaction layer growth rates. A substantial Si accumulation in the interaction layer was measured, whereas Zr only accumulates to a minor extent there. The Zr addition to U-Mo alloy works better when Si is added to Al compared to pure Al. An interaction product with a composition of a Si-rich $U(Si,Al)_2$ was proposed to be present in the IL close to the U-Mo-Zr side.

In this work, the results of the studies of the IL U-7wt.%Mo-1wt.%Zr/Al A356 (7,1 wt.%Si) and U-7wt.%Mo-1wt.%Zr/Al treated at 550ºC, are presented. The characterization of phases was made with different techniques: optical (OM) and scanning electron microscopy (SEM), electron probe microanalysis (WDS) and X-Ray diffraction (XRD). Main contribution of this work is the identification of phases in the IL by XRD, performed with Synchrotron radiation at LNLS.

2. Experimental procedure

Alloys of composition U-7wt.%Mo (U-Mo) and U-7wt.%Mo-1wt.%Zr (U-Mo-Zr) of about 55 g each were prepared in a small arc furnace with a copper crucible under high pure argon atmosphere and non consumable tungsten electrode. The pure components used were: depleted uranium (50 ppm Fe, 60 ppm Mg, 24 ppm Si), molibdenum 99.97 wt.% (< 20 ppm O, <10 ppm N, <10 ppm C, 100 ppm W, 2 ppm Ni) and zirconium 99.85 wt.% (170 ppm Fe, 420 ppm O). Alloys were annealed during 2 h at 1000 ºC for homogenisation in composition and quenched in water to retain γU phase.

Diffusion couples were made by mechanically pressing plates of the uranium alloy with 4N aluminium (Al) and/or commercial aluminium (Al-Si) A356 alloy (7.1 Si, 0.37 Mg, 0.1 Fe, 0.1 Ti, 0.002 Zn, 0.001 Sr all in wt.%).

Couples were sealed in quartz tubes under argon atmosphere, annealed at 550 ºC during 1.5 h and quenched in cold water. The length of thermal treatments results from the compromise between the IL growth and the decomposition of γU phase.

Two different configurations of diffusion couples were built. The first one (fig. 1) allows the characterization of the IL by exposing surfaces at different depths, all of them parallel to the diffusion front. This configuration was used for XRD experiments. The second one, (fig.2), allows studying the IL in U-Mo/Al, U-Mo-Zr/Al, U-Mo/Al A356 y U-Mo-Zr/Al A356, under the same experimental conditions.This provides more comparable results. This "multicouple" configuration was used for composition measurements (WDS), OM and SEM observations.

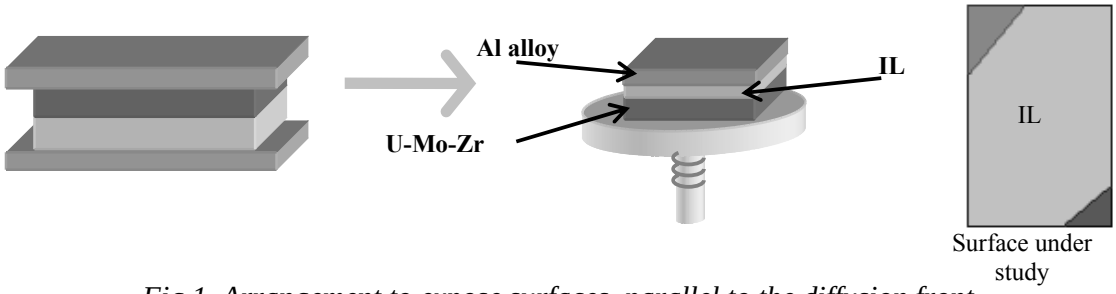

Fig 1. Arrangement to expose surfaces parallel to the diffusion front.

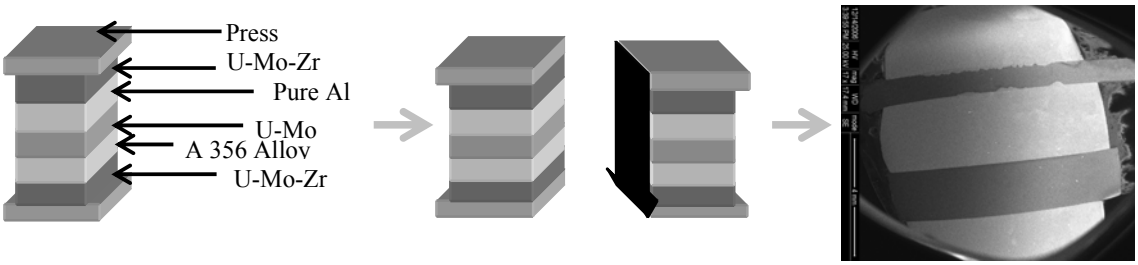

Fig 2. Arrangement to expose surfaces perpendicular to the diffusion front.

The characterization techniques used in this work were OM (Olympus BX60M) and SEM (FEI QUANTA 200) for microstructure observations, electron probe microanalysis EPMA (CAMECA SX-50) to perform composition measurements and X-ray diffraction to identify crystalline structures.

The quantitative compositional microanalysis was made with WDS, under an accelerating potential of 20 KV. The equipment was recalibrated before each analysis session using pure Al, Si, Mo, U and Zr standards.
XRD measurements were performed in two ways: with a PW3710 Philips laboratory equipment using filtered Cu Kα radiation, at room temperature, with fixed slit and with synchrotron radiation at the National Synchrotron Light Laboratory (LNLS), Campinas, Brasil, selecting an energy of 8.048 eV. The diffraction patterns were analyzed using the PowderCell program [7] which allows identifying the different phases and estimating their lattice parameters.

3. Results and discussion

As a consecuence of the thermal treatment, an important amount of γU decomposition was observed in the alloy U-Mo-Zr.

3.1. Interaction layer in U-7wt.% Mo-1wt.% Zr / Al at 550ºC.

The IL interfaces observed in the U-Mo-Zr/Al diffusion couple are irregular with a thickness ranging from 25 to 150 μm, Figure 3. Similar results were reported in [8] for the U-Mo/Al interaction layers at 580 ºC and [10] for U-7Mo/Al6061 at 550ºC.

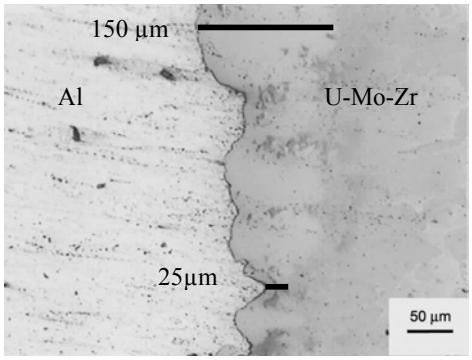

Fig 3. U-7%Mo-1%Zr/Al.Diffusion experiments at 550 ºC (1,5 h). OM micrograph of the interdiffusion zone.

Composition measurements shown that neither the Al incorporates U, Mo or Zr nor the U-Mo-Zr incorporates Al.
XRD patterns performed at different depth are shown in Fig. 4. Besides γU, αU and Al, from the original components of the couple, UAl_3, UAl_4, $Al_{20}Mo_2U$ and $Al_{43}Mo_4U_6$ were also identified. These last phases correspond to the IL. $Al_{43}Mo_4U_6$ according to [8,10] is related to the decomposition γU phase.

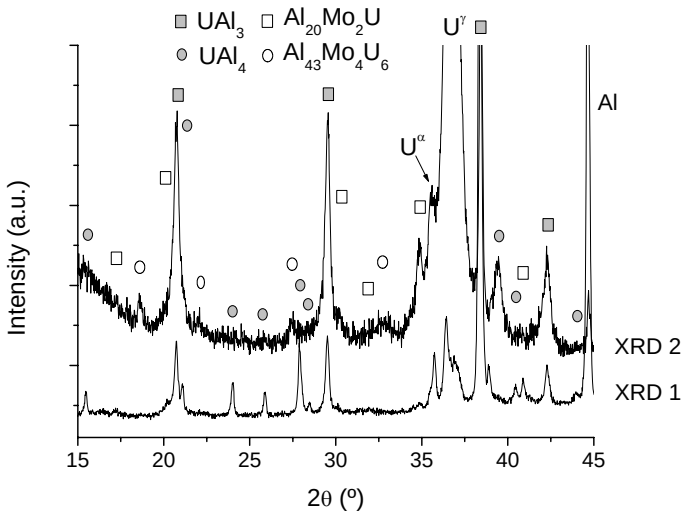

Fig 4. U-7%Mo-1%Zr / Al. XRD obtained in laboratory equipment

3.2. Interaction layer in U-7wt%Mo-1wt%Zr/Al A356 at 550ºC.

The IL observed for the U-Mo-Zr/Al A356 couple is thinner than the one obtained for the U-Mo-Zr/Al couple. This means that the growth of the IL would be reduced by the presence of some of the alloying elements of the Al alloy .The thickness of the IL varies from 3 µm to 12 µm, Fig 5. There, it is also shown that besides the IL, a free precipitate zone (FPZ) appears. This is determined by the absence of the characteristic Si precipitates of the A356 alloy. This effect was also informed in [9,11,12].

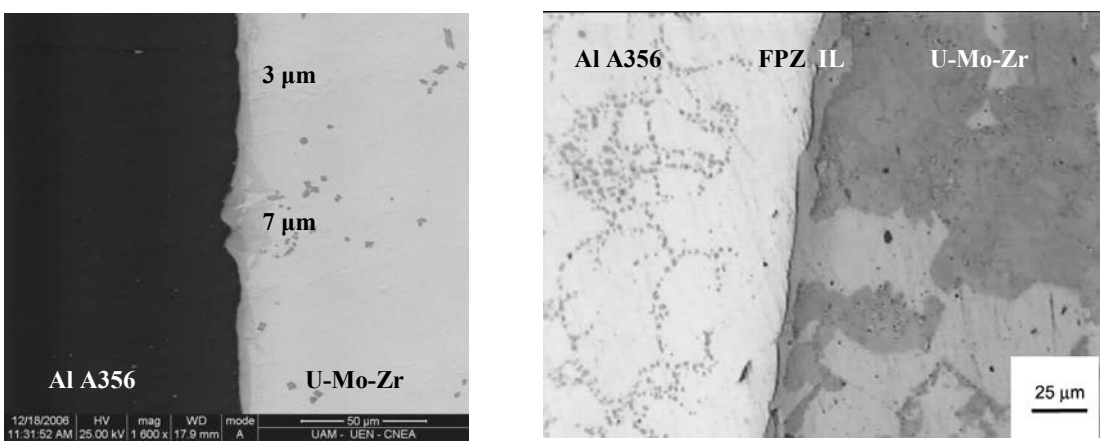

Fig 5. U-7%Mo-1%Zr/Al A356. Diffusion experiment at 550 ºC (1,5 h). a)SEM micrograph b) OM micrograph of the interdiffusion zone.

Composition measurements were taken across the IL starting from the Al A356 and ending in the U-Mo-Zr alloy, at 1 µm steps. The values obtained were plotted in a isothermal pseudo-ternary Al, Si, (U+Mo+Zr) diagram, Fig. 6a. The same points are overlapped with the 400 ºC isothermal ternary diagram (Fig 6b) proposed by Dwigth in [13]. In Fig.6a points distribution

suggests the presence of two phases inside the IL. The first one, starting from the Al corner, is assigned to the phase $U(Al,Si)_3$ informed in the diagram in Fig.6b [13]. This phase has a Si concentration near 25 at.%. Next points, closer to the U-Mo-Zr, indicate that the second phase in the IL would have a Si concentration around or above 30 at.%. This result was also observed in another U-Mo-X / Al-Si diffusion couples, where the presence of a second phase richer in Si than $U(Al,Si)_3$ was reported [5, 6,11].

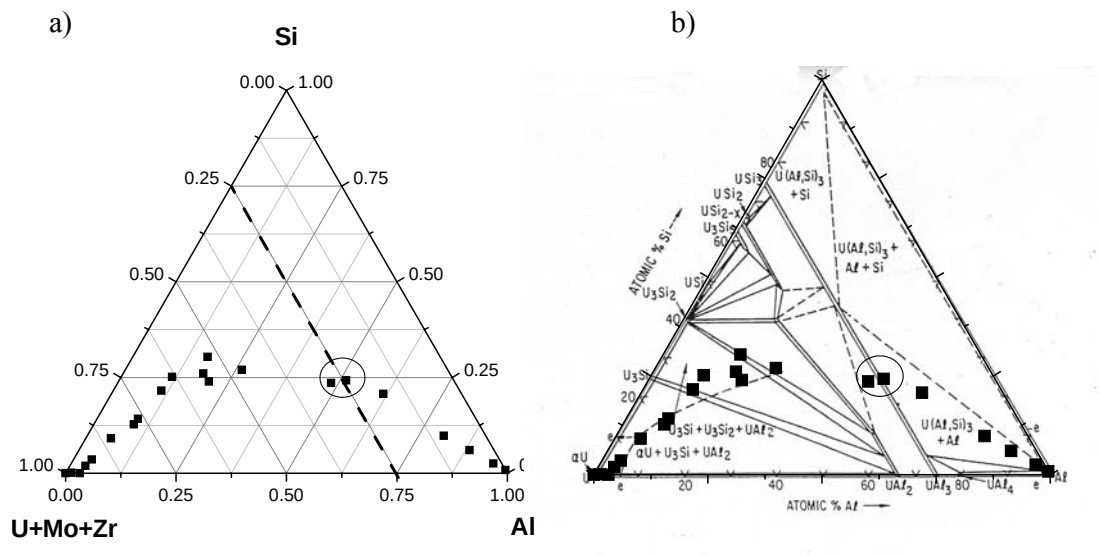

Fig 6. U-7%Mo-1%Zr/Al A356. Diffusion experiments at 550 ºC (1,5 h). a) WDS results in the interdiffusion zone . b) WDS results overlapped with isothermal sections Al, Si, U at T=400ºC (Fig 17 in [11]).

Phases identified with XRD with synchrotron radiation (fig 7) are γU and αU, corresponding to the component U-Mo-Zr, and two phases: $U(Al,Si)_3$ and Si_5U_3 corresponding to the IL.
Both phases have also been identified in a U-7Mo/Al A356 tested at 550ºC and presented in this meeting [14]. The remaining peaks could not been assigned to any phase yet. The analysis is still in progress.
The estimated lattice parameter of $U(Al,Si)_3$ was 4,21Å. According to the correlation presented by Dwight [13] between the Si at% in this phase and its lattice parameter, the value obtained in this work corresponds to 25at% Si, Fig.8. This value is equal to that obtained by EPMA in this work, Fig.6a.

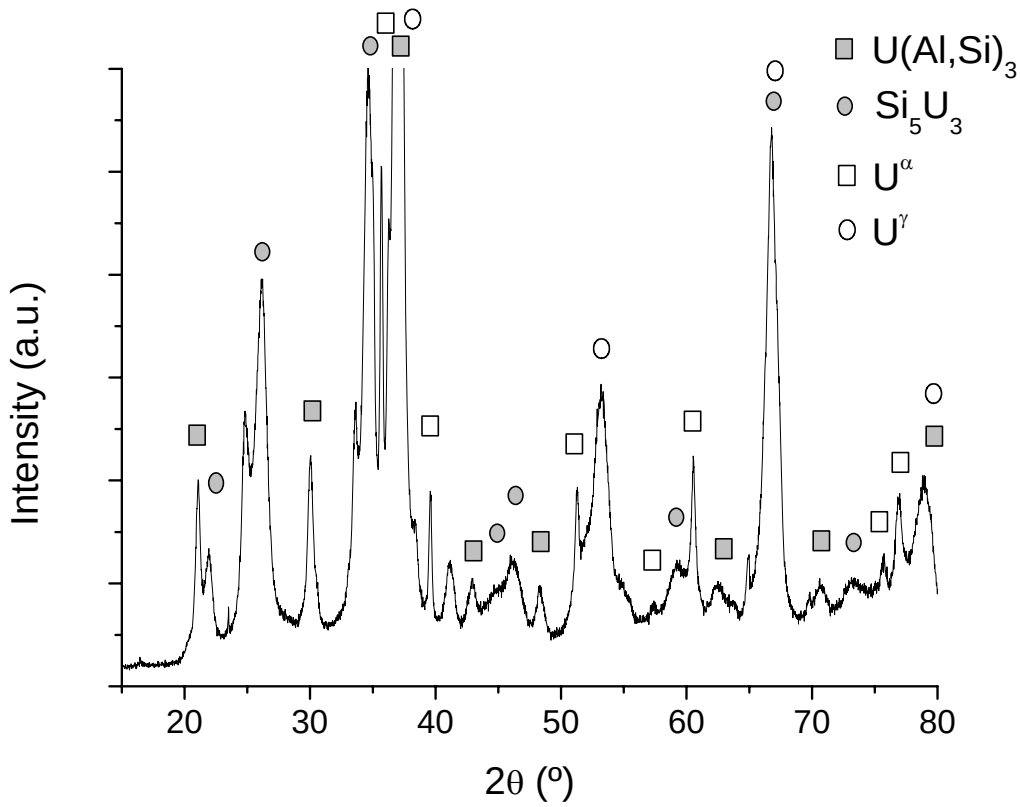

Fig 7. U-7%Mo-1%Zr/Al A356. Diffusion experiments at 550 ºC (1,5 h). XRD pattern obtained with synchrotron radiation.

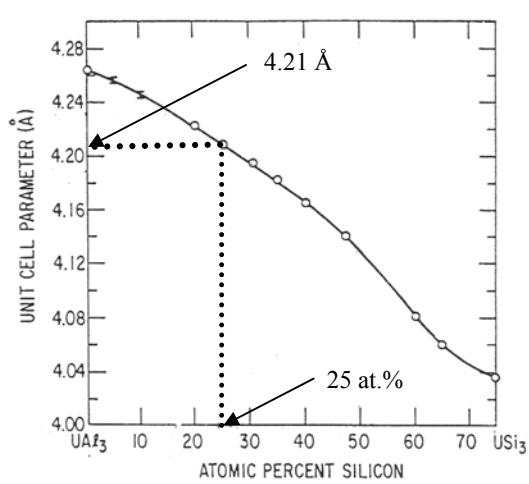

Fig 8.Llattice parameter for $U(Al,Si)_3$ vs its at% Si content (fig 19 in [11]). Arrows indicate experimental results in this work verifying the correlation.

5. Conclusions

In the U-7 wt.% Mo-1 wt.% Zr/Al interaction layer (*550 ºC, 1,5 h*) the phases UAl_3, UAl_4, $Al_{20}Mo_2U$ and $Al_{43}Mo_4U_6$ were identified.
When pure Al is replaced by Al A356, the phases $U(Al, Si)_3$ with 25 at.% Si and Si_5U_3 were identified in a U-7wt.% Mo-1wt.% Zr/Al A356 interaction layer (*550 ºC, 1,5 h*).

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