

REACTION LAYER BETWEEN U-7WT%Mo AND Al ALLOYS IN CHEMICAL DIFFUSION COUPLES.

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ABSTRACT

Several failures in U-Mo dispersion fuel plates like pillowing and large porosities have been reported during irradiation experiments. These failures have been assigned to the formation of a large (U-Mo)/Al interaction product under high operating conditions. The modification of the matrix by alloying Al to change the interaction layer and improve its irradiation behavior, has been proposed. This paper reports diffusion experiments performed between U-7wt%Mo and various Al alloys containing Mg and / or Si. By the use of Optical Microscopy, SEM and X-Ray diffraction, it was found that with a concentration of 5.2wt% or 7.1 wt%Si the interaction layer is constituted mainly by (U,Mo)(Si,Al)₃ and no (U,Mo)Al₄ is detected. As part of the studies of properties of the U-Mo alloys the time for isothermal transformation start at different temperatures of the γ phase is being evaluated for the present U-7wt%Mo alloy. These results are used to plan the future diffusion program that will include diffusion under irradiation at CNEA RA3 reactor.

1. Introduction

The dispersion of U-(7wt% to 10wt%)Mo alloy particles in Al matrix was considered to perform well under irradiation [1]. However qualifying experiments in full size plates had to be interrupted due to excessive swelling [2,3]. This phenomenon was also found, at initial state, in miniplates tested at 80% BU without signs of pillowing [4].

Not only the extent but the behaviour under irradiation of the interaction products are important in U-Mo /Al dispersion fuel. Post irradiation data and past experience suggest to change the characteristics of the interaction layer by alloying the Al of the matrix. First investigations of the irradiation results pointed at Mg as a beneficial presence. Nevertheless, further analysis showed that the influence of Si could be more important [4].

As a first contribution to solve this problem, this paper reports out of pile chemical diffusion experiments, performed at 550°C and 580°C using Al alloys with Mg and/or Si, as main alloying element. Previous experience in interdiffusion between U-7%wtMo/Al was used to set these experiments [5].

It has to be taken into account that the temperature range and/or the time in which diffusion experiments can be planned with a U-7wt%Mo alloy is limited due to the start of the decomposition of the metastable gamma U-Mo phase. The time for isothermal transformation start at different temperatures is being evaluated for the present U-7wt%Mo alloy. Based on these results, the convenience of using an U-9%wt Mo alloy to plan the diffusion studies under irradiation is discussed.

2. Experimental

Materials employed in this study were an arc-melted U-7wt% Mo alloy, pure Aluminium and five commercial Al alloys: three of them containing Mg and the other two Si as main alloying element, Table I.

	Si	Fe	Cu	Mn	Mg	Cr	Ti
6061	0.60		0.28		1.00	0.20	
5052	-	-	-	-	2.5	0.25	-
5083	-	-	-	0.70	4.40	0.15	-
4043	5.20						
AA635 *	7.10	0.10			0.37		0.12

Table I. Compositions of the commercial Al alloys wt% [6].

* Provided by the supplier.

The chemical diffusion couples were triple sandwiches Al/(U-Mo)/Al-alloy. The Al counterpart was used to monitor the reproducibility of the tests. The U-Mo alloy was homogenized in composition by a thermal treatment of 2 hs at 1000°C. The couples were kept tight by a simple mechanical clamp. The details of the experimental set up were described elsewhere [5].

Optical Microscopy (OM), SEM and EDAX were used to characterize the reaction layers' constituents. X-ray diffraction (XRD) was performed for the 4043 and AA635 samples.

Diffusion couples were annealed at 580 °C or 550 °C during 2 hs or (2+2) hs, Table II, in order to obtain measurable reaction layers, in reasonable short times. These times are supposed to be short enough to avoid the γ phase decomposition. Despite of this, certain percentage of decomposition was observed in some of the samples.

For XRD analysis, successive surfaces at a small angle from the perpendicular to the diffusion direction were exposed by a careful polishing, and a spectrum was taken for each one. XRD measurements were performed with filtered Cu K_{α} radiation, in a Phillips PW 3710 X-ray diffractometer, with fixed slit.

3. Results

As a general feature no important reduction was observed in the thickness of the interaction layers (IL) between the U-Mo and the Al alloy, respect the one between U-Mo and pure Al. Moreover, for the 5083 alloy it resulted even larger. Table II summarizes the results compared with the Al side. In most of the samples, the interface between the IL and the Al alloy broke apart remaining the greatest part of the layer stucked to the U-Mo alloy. The values reported in Table II correspond to this part of the IL, so the actual thickness may be underestimated.

Sample's name *	Time (hs)	Temp. (°C)	Thickness of the IL with Al (μm)	Thickness of the IL with Al alloy (μm)
6061	2	580	150	129
5052	2	580	139	134
5083	2	550	10	30
4043	2	550	10	15
AA635	2+2	550	20	20

Table II. Diffusion annealings details and resulting IL.
*Samples are named according to the Al alloy used in each one.

Sample's name		% at Al	% at Si	% at Mg	% at Mo	% at U
Pure Al	Near U-Mo	75	-	-	3	22
	Near Al alloy	81	-	-	2	18
6061	Near U-Mo	76	2	-	2	20
	Near Al alloy	75	3	-	2	20
5052	Near U-Mo	76	-	4	2	18
	Near Al alloy	80	-	4	2	14
5083	Near U-Mo	72	-	-	3	25
	Near Al alloy	76	-	-	2	22
4043	Near U-Mo	25	30	-	3	42
	Near Al alloy	51	16	-	3	30
AA635	Near U-Mo	18	38	-	4	40
	Near Al alloy	49	22	-	3	26

Table III. % at of the different elements in the IL between U-Mo and Al alloy measured by EDAX.

3.1. Composition of the interaction layer

Electron microprobe was not available at the time of these experiments, so concentrations were measured by EDAX and are shown in Table III. The compositions of the IL at pure Al side gave the same results for all the samples, Table III, and were in good agreement with previous investigations [5]: two bands, one containing 75 at % Al, 3 at % Mo and 22 at % U corresponding to (U,Mo)Al₃ and the other containing 80 to 82 at % Al, 2 at % Mo and 18 at % U corresponding to (U,Mo) Al₄.

3.1.1. Mg effect

On samples 5052 and 5083, which contain Mg but not Si, both OM and EDAX analysis identified two different zones on the IL, Figs. 1, 2 and Table III. On sample 5052, 4 at% (2.5 wt%) of Mg was found on both zones. This quantity is in good agreement with the original Mg content in the alloy. On sample 5083, on both zones, Mg content, if any, was not found. The content of Al is reduced compared to the Al side.

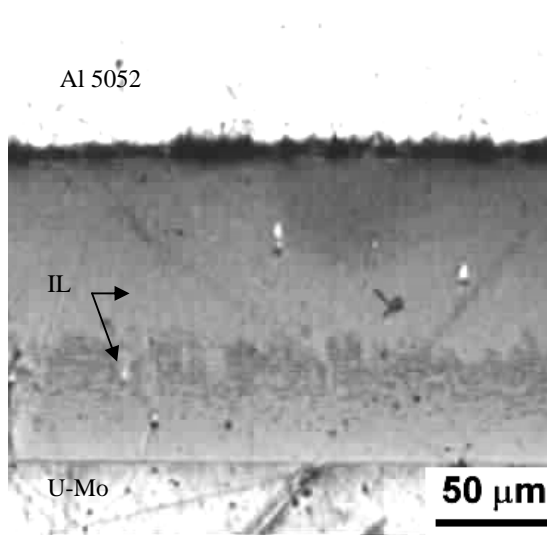


Fig. 1. 5052 sample's interdiffusion layers. 2 hs 580°C. Chemical etching.

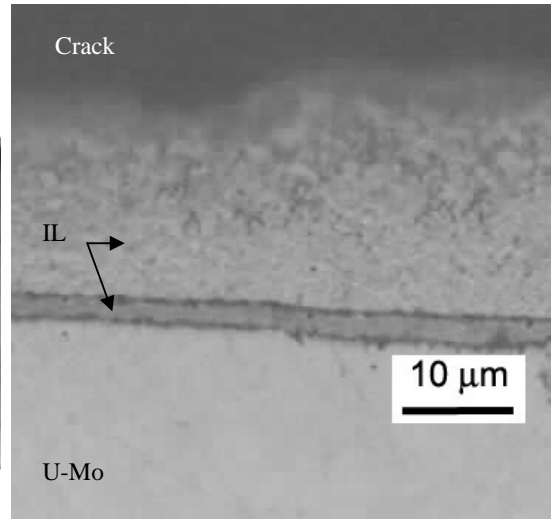


Fig. 2. 5083 sample's interdiffusion layers. 2 hs 550°C. Chemical etching.

On sample 6061, which contains 0.6 wt % of Si besides Mg, EDAX measurements identified ~2 at % of Si across the whole IL which is higher than the 0.5 at % of Si of the initial alloy. The composition of Al, 75 at%, is also rather homogenous. Mg was not detected on this IL. From the OM observations, the presence of two zones is not clearly defined.

3.1.2. Si effect

4043 and AA635 alloys containing 5.2 and 7.1 wt% of Si respectively, presented remarkable differences compared with all the samples which contain Mg as main alloying element. The IL between the U-Mo and these Al alloys resulted slightly wider than the ones between U-Mo and pure Al. The dissolution of Si precipitates was observed in the Al alloys near the interdiffusion layers, Fig. 3.

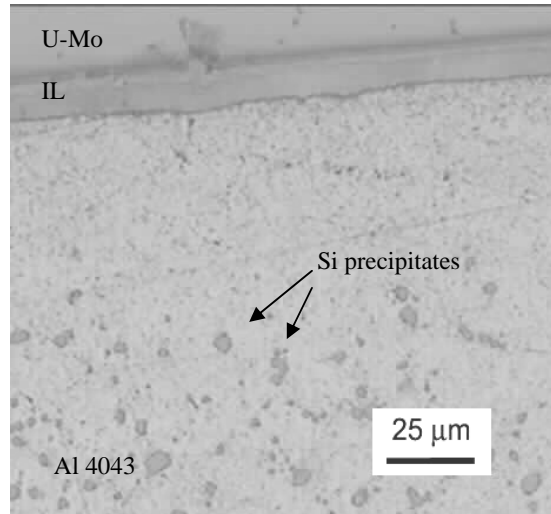


Fig. 3. 4043 sample's interdiffusion layers. 2 hs 550°C. Mechanically polished. Diamond paste 1 μm.

OM and SEM showed that these IL have two zones, the thinner one, close to the U-Mo side, is in fact a two phase region with a very fine microstructure revealed at high magnification, Fig 4. The concentrations for this zone in Table III correspond to the average on window measurements. They indicated a high Si content. The other zone, wider and near the Al alloy, contains 55% less Si than the thinner one.

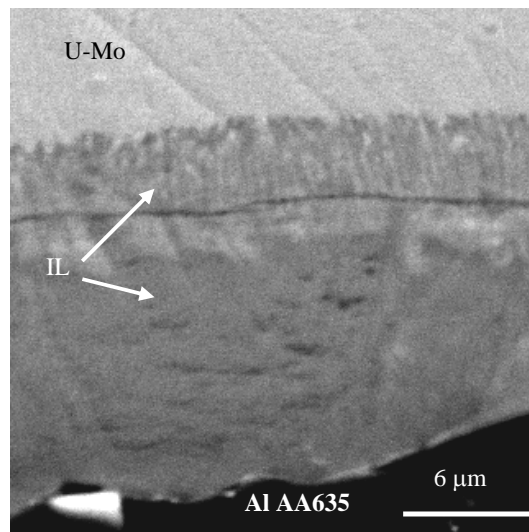


Fig. 4. AA635 sample's interdiffusion layer. (2 + 2) hs 550°C. SEM

3.2. XRD

X-Ray diffraction was performed on the IL of Al Si alloys, Fig.5. Besides the expected peaks associated to the structures of γ U-Mo, Al and Si, the patterns showed the presence of the cubic structures $U(Al,Si)_3$ [7] with lattice parameter $a = 4.205 \text{ \AA}$ and $Al_{20}Mo_2U$ [5]. No $(U,Mo)Al_4$ was found. A small set of weak peaks couldn't be clearly identified.

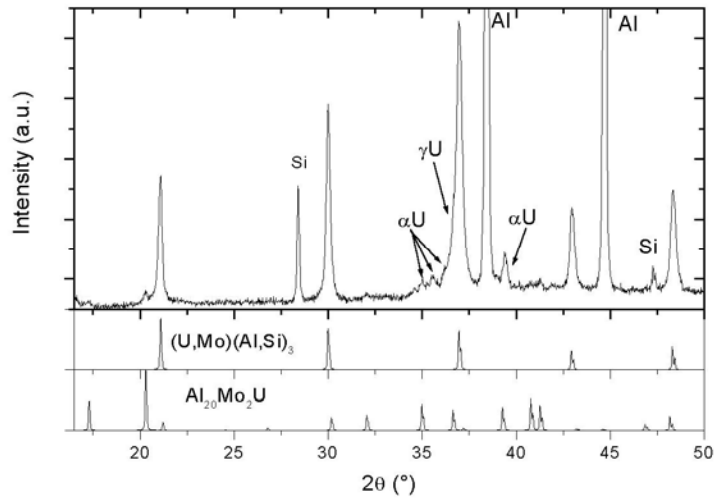


Fig. 5. AA635 sample. XRD pattern

3.3. Changes in the growing kinetics related to γ U-Mo decomposition.

Something remarkable to expose here, is the fact that the IL, for both Si containing samples, didn't show any change in the growing kinetics when the γ U-Mo decomposes. This is really different compare to the pure Al behaviour which finds in the decomposition microstructure a short circuit for diffusion, Fig. 6.

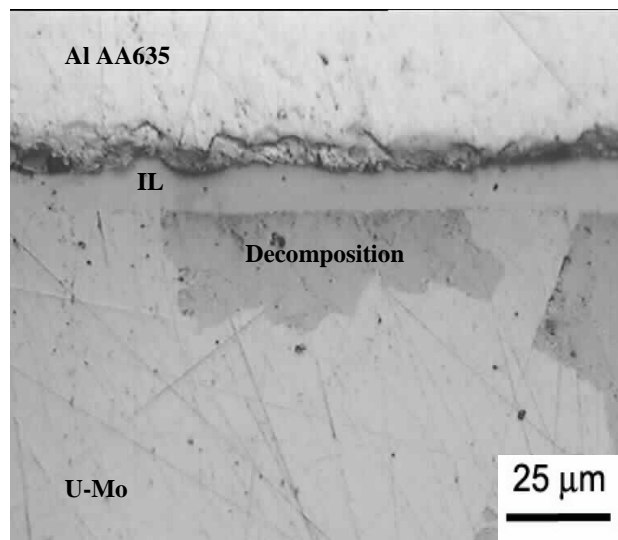


Fig. 6. AA635 sample's interdiffusion layer.(2 + 2) hs 550°C. Diamond paste 1 μm.

4. Discussion

The possible effects on the interaction layer by the addition of a alloying element to the Al have been studied for Mg and Si.

The overall behaviour concerning the layers's thickness for 5052 and 6061 samples showed a slight reduction; for 5083, 4043 resulted bigger respect to the pure Al one.

Concerning the samples with Al alloys containing Mg, the experiences reported in this work, made at 580 °C or 550 °C, do not allow to infer Mg as having any influence on the IL respect to the one with pure Al. Due to this similar behaviour, no longer than two hours experiments were planned and no XRD patterns were performed.

On the other hand, although no reduction was observed with Si addition, important changes were found in the components of the IL for these Al alloys. Si presents an affinity with U-Mo alloy resulting in a migration towards it, motivating the presence of a significative quantity of Si in the IL and correspondingly less Al content on it. The Si concentration in the IL is higher than in the initial alloy and is supported by the dissolution of the precipitates next the interaction zone.

As a result of Si presence, the phase $(U,Mo)Al_3$, found next to U-Mo in the case of pure Al, is now $(U,Mo)(Al,Si)_3$, but now is situated close to the Al alloy. It is the widest of the two zones that form the IL. This phase is the same reported in chemical diffusion experiments between U_3Si and Al at 510 to 670 °C [8]; it was also reported for silicide dispersed in Al matrix which has shown a satisfactory behaviour under irradiation [9]. A correlation between the lattice parameter with Si and/or Al in this phase has been published [7,10]. Based on this, and using XRD results of this work, this zone would contain ~25 at%Si, ~50 at%Al and ~25 at%(U-Mo). Nevertheless, according to Table III, the measurements report an excess in U and Mo particularly for 4043 sample. This can be attributed to the small thickness of the IL and the qualitative determination by EDAX. They are plotted on a U-Al-Si ternary representation, Fig.7 a.

For the two-phase zone next U-Mo, some punctual and window EDAX measurements are plotted in Fig.7 b. They appeared located along the line between "1" and "2".

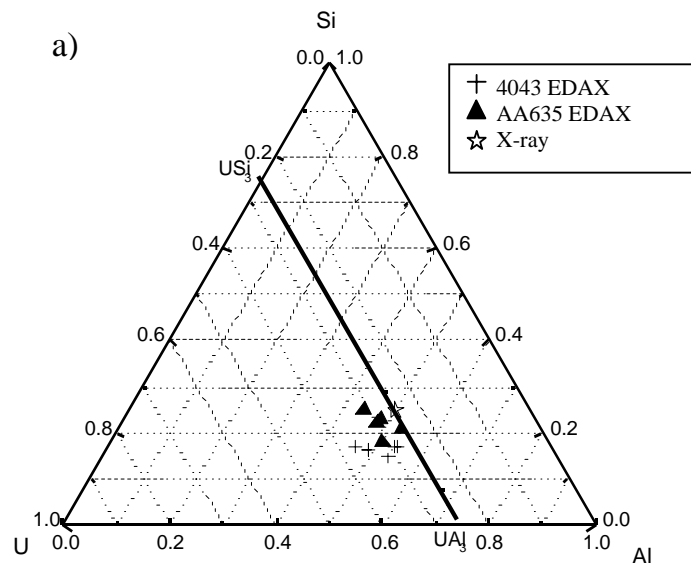


Fig. 7a. U-Al Si ternary representation

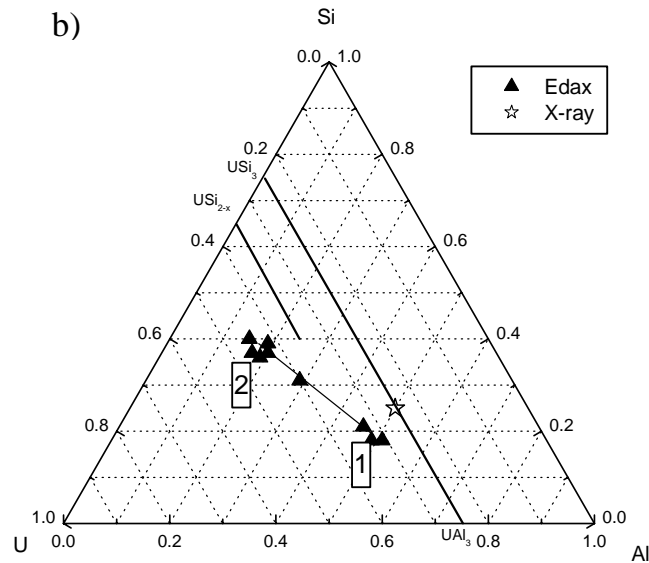


Fig. 7b. U-Al Si ternary representation

Knowing that this is a two-phase zone, it is valid to consider that the points along the line, represent averages of different fractions of both phases. Points near “1” correspond to the phase $(U,Mo)(Al,Si)_3$. The other phase in this zone would be represented by the points near “2” with the same excess in U,Mo concentrations. This let us consider that this phase could be USi_{2-x} , reported in [7] accepting up to 16 at% of Al in solution or 25 at% according to [10]. The structure of this phase could be indexed with the small set of weak peaks mentioned in section 3, but XRD is not conclusive. More experiences should be made to enlarge this zone so that, more definite peaks would be obtained.

Both Si samples did not show any change in the growth kinetic when the γ U-Mo decomposes. Nevertheless, [5] reports that γ U-Mo decomposition increases significantly the width of the interdiffusion zone between U-Mo and pure Al, changing drastically the morphology of the interface. It seems that the growth of the phase containing Si is not sensible neither to the short circuits of diffusion of the microstructure of the decomposed γ U-Mo phase nor to the α U phase present in it.

These are very hopeful results, but they need to be corroborated at irradiation temperatures. Thermal treatments at 300°C are in progress in order to confirm all of this. The growth kinetics of the phases that constituted a reaction layer may be different so the relative thickness may not be the same at lower temperature.

It is the intention to go further in diffusion studies to determine characteristic parameters like activation energy (experiments at different temperatures) or kinetics (experiments at different times at a single temperature). Previous experience [5] showed that the characteristics of the interdiffusion zones are very different when γ U-Mo phase decomposition occurs, thermal treatments couldn't be longer than two hours, being this a limit for the studies. Due to the importance of knowing the start of the decomposition for each temperature, studies for the

alloy U-7wt% Mo with the same metallurgical characteristics than the alloy of this work are currently being done. Fig. 8 shows the results obtained up to now.

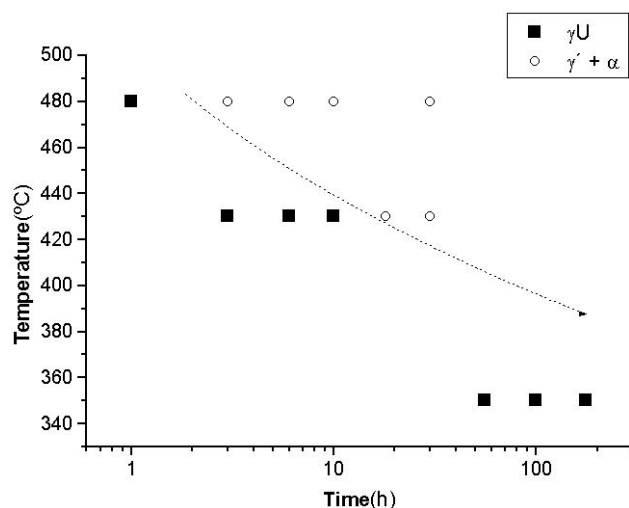


Fig. 8. U-7%wtMo alloy. Time Temperature Transformation diagram [11]

Because of the known effect of Mo on γ U-Mo phase stability, next diffusion studies will be made on U-9wt%Mo alloy.

5. Conclusions

The interdiffusion experiments made between 550 °C and 580 °C allow to conclude:

- 1) Mg additions to Al didn't report any important change on the characteristics or components of the interaction layer respect to the pure Al one.
- 2) Si additions to Al introduced important changes in relation with the phases found inside the interaction layer: $(U,Mo)(Al,Si)_3$ near the Al alloy, a two-phase zone consisting of $(U,Mo)(Al,Si)_3$ and, probably, $(U,Mo)(Al,Si)_{2-x}$ near U-Mo alloy and $Al_{20}Mo_2U$. This last could not be optically located. No $(U,Mo)Al_4$ was found. $(U,Mo)(Al,Si)_3$, which is the main component of the interaction layer, is the phase reported as the interaction product in dispersion Si fuel elements.
- 3) The interaction layer, for both alloys containing Si, is not affected when the γ U-Mo decomposes as remarkably happens in the case of pure Al.

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