Characterization of the reaction layer in U–7wt%Mo/Al diffusion couples

M.I. Mirandou [a], S.N. Balart [b], M. Ortiz [b], M.S. Granovsky [a,b,*]

[a] *Instituto de Tecnología J. Sabato, CNEA – UNSAM, Av. Gral Paz 1499, 1650 San Martín, Pcia. Buenos Aires, Argentina*
[b] *Departamento de Materiales, CAC, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499, 1650 San Martín, Pcia. Buenos Aires, Argentina*

Abstract

The reaction layer in chemical diffusion couples U–7wt%Mo/Al was investigated using optical and scanning electron microscopy, electron probe microanalysis and X-ray diffraction (XRD) techniques. When the U–7wt%Mo alloy was previously homogenized and the $\gamma(U, Mo)$ phase was retained, the formation of $(U, Mo)Al_3$ and $(U, Mo)Al_4$ was observed at 580 °C. Also a very thin band was detected close to the Al side, the structure of the ternary compound $Al_{20}UMo_2$ might be assigned to it. When the decomposition of the $\gamma(U, Mo)$ took place, a drastic change in the diffusion behavior was observed. In this case, XRD indicated the presence of phases with the structures of $(U, Mo)Al_3$, $Al_{43}U_6Mo_4$, $\gamma(U, Mo)$ and $\alpha(U)$ in the reaction layer.
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1. Introduction

For the past several years research in the nuclear fuels for research and test reactors led to the development of aluminum-based dispersion fuels containing U–Mo alloys in γ phase as fuel particles. These fuel elements allow fulfillment of requirements to use low enriched U in research and test reactors [1].

Results of irradiation tests are promising; however, some efforts are focused on the problem of the interdiffusion and reaction between the Al matrix and U–Mo particles. The effect of irradiation temperature on the extent of this reaction has been reported to be important [1–3].

During the fabrication and/or irradiation of the dispersion fuel elements, the fuel particles react with the surrounding Al matrix. This reaction results in the formation of a zone consisting of intermetallic compounds. The low thermal conductivity of these compounds has a major effect on the fuel temperature as well as on the swelling of the fuel.

As it is well known, when two metals are in contact, an interaction zone due to interdiffusion may develop. This is formed by new phases whose composition ranges between those of the terminal components. This produces changes in the specific volume and in the thermomechanical properties of the whole.

Thermal compatibility of U–Mo alloys (2–10 wt% of Mo) with Al in unirradiated or irradiated dispersed fuel samples has been reported [2–10]. A reaction layer to different extents take place, depending on temperature, Mo content of the alloy and decomposition degree of the metastable γ phase. The formation of UAl_3 measured by X-ray diffraction (XRD) for U–2wt%Mo/Al was reported in [4]. Qualitatively microanalysis indicated the presence of UAl_3 for U–9wt%Mo and U–10wt%Mo [6,7]. However, no complete quantitative identification of the reaction layer has been made.

Chemical diffusion couples were used to study the interdiffusion between U–Mo and Al at 580 °C using

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* Corresponding author. Address: Departamento de Materiales, CAC, Comisión Nacional de Energía Atómica, Av. Gral Paz 1499, 1650 San Martín, Pcia. Buenos Aires, Argentina.
E-mail address: granovsk@cnea.gov.ar (M.S. Granovsky).

metallography, microanalysis and X-ray diffraction. In this system the formation of (U, Mo)Al$_3$ and (U, Mo)Al$_4$ has been reported [11].

Antecedents of experiments on diffusion couples were found concerning pure U and Al [12,13]. It has been reported the growth of the reaction layer with non-planar interphase, which leaves islands of pure U inside the reaction zone. Important porosity and cracks characterize this zone. UAl$_3$ is always found as result of interdiffusion. The existence of UAl$_2$ and UAl$_4$ is subjected to some controversy [12].

This paper reports new results on the characterization of the reaction zone for U–7wt%Mo/Al using chemical diffusion couples. This characterization was performed using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive analysis (EDAX), wavelength dispersive electron microprobe microanalysis with standards (EPMA) and X-ray diffraction (XRD). The effect of the decomposition of the γ(U, Mo) phase is also analyzed.

2. Experimental

Materials employed in this study were high-purity aluminum (99.99%) and an arc-melted U–7wt%Mo alloy fabricated from pure U (impurities are given in Table 1) and Mo (99.9%).

The as-cast U–Mo alloy was metastable γ phase with grain size ∼ 20 μm. Segregation of U at the grain boundaries and precipitates due to the impurities were observed [14].

Part of this as-cast U–Mo alloy was heat treated at 1000 °C during 24 h and quenched at room temperature in order to homogenize the alloy and retain the γ(U, Mo) phase. XRD measurements were used to check it. The grain size obtained by this treatment was 400–1000 μm. Precipitates from the as-cast remained without change.

Diffusion couples were prepared with samples of approximately 2 mm × 5 mm × 5 mm cut from Al and the as-cast and homogenized U–Mo alloy. Larger couples were prepared to be analyzed by XRD in such a way that an irradiated surface of at least 8 mm × 15 mm was obtained. The samples were mechanically polished down to 3 μm diamond paste and ultrasonically degreased in ethyl ether. At this stage, the appearance of the alloy surface was mirror like and no grain boundary microstructure was revealed. In the case of aluminum, an etch

in dilute sodium hydroxide solution was used to remove the oxide layer, immediately before 'setting' the couple. A stainless-steel mechanical clamp was used to keep the couples in tight contact during heat treatments.

Thermal treatments of the couples were performed in sealed silica glass tubes under a high purity Ar atmosphere and ended by quenching into cold water without tube breaking. In order to obtain measurable reaction layers in reasonable short times, interdiffusion anneals were performed at 580 °C. Time at temperature was chosen to prevent the decomposition of the retained γ(U, Mo) phase when the homogenized U–7wt%Mo was used. Experiments performed to check this decomposition gave 2 h as safe time.

Prior to OM, SEM and EPMA analyses, the couples were sectioned parallel to the diffusion direction. Those sections were mechanically polished with carbide paper and diamond paste (6 and 1 μm) on nylon cloth. An electrolytic polishing with Opalu B (phosphoric acid, ethanol and butyl cellosolve), followed by chemical etching with hydrofluoric acid diluted 1:100 in water, was used to reveal the microstructures.

The composition of each zone of the interaction layer was quantitatively determined by wavelength dispersive electron microprobe analysis with a CAMECA S.X.50 electron microprobe. High purity U, Mo and Al were used as standards.

For XRD analysis, successive surfaces at a small angle from the perpendicular to the diffusion direction were exposed by a careful polishing in an abrading machine, especially designed to keep parallelism between each layer, and a spectrum was taken each time. XRD measurements were performed with filtered Cu K$_\alpha$ radiation, at room temperature, in a Phillips PW 3710 X-ray diffractometer, with fixed slit.

3. Results

3.1. Homogenized U–7wt%Mo

At 580 °C, the width of the interdiffusion layer was 25 μm for a 0.5 h anneal. With a two sequential treatments of 2 h a width of 175 μm was reached, which was satisfactory to perform the analysis.

Optical micrographs of typical cross sections of diffusion couples are shown in Figs. 1 and 2. For magnifications up to 700×, the interdiffusion layer presented a planar interface at the U–Mo side. No cracks or po-

Table 1
Impurity content of U (wt ppm) by spectrographic analysis

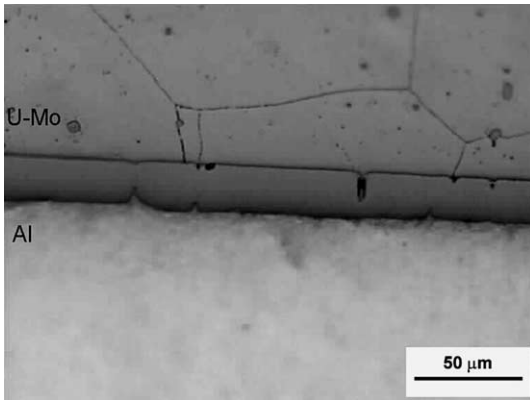| Al	Mn	Cr	Fe	Mo	Mg	Cu	Si	Ti	Co	Ni	Ca
<10	12	<4	27	<3	60	6	24	<4	<3	<6	100

Fig. 1. Interdiffusion layer: 0.5 h, 580 °C. Mechanical polished, optical microscopy.
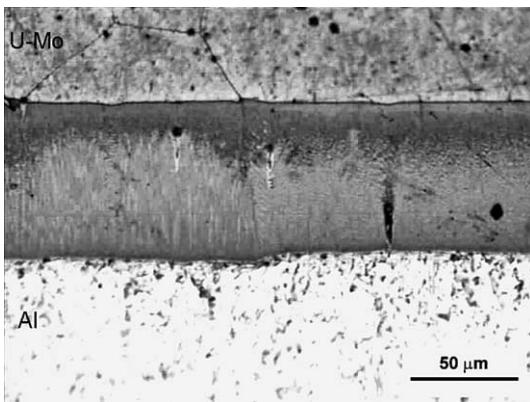
Fig. 2. Interdiffusion layer: 2 h, 580 °C. Chemical etched, optical microscopy.

Fig. 3. Detail of the reaction layer at the Al side. Two treatments of 2 h at 580 °C, SEM.

rosity were visible. Mechanical polishing did not reveal different phases in the reaction layer, showing a uniform surface. An electrolytic polishing followed by chemical etching revealed two different zones, Fig. 2. No clear limit between these two zones was observed, instead a gradual interpenetration of one into the other. The precipitates from the as-cast γ(U, Mo) alloy appeared without change into the interdiffusion zone.

Observations with SEM showed the existence of a very narrow third zone in contact with the aluminum, Fig. 3.

The quantitative distribution of each element across the reaction layer, measured at interval of 1 μm with EPMA, is shown in Fig. 4. Two zones are distinguished in which the atomic percentages of the three elements are fairly constant; their average values are given in Table 2. Between these two zones the concentration grows continuously with no jumps in composition. Measurements inside the U–Mo, close to the reaction layer, did not show the presence of Al. Conversely nei-
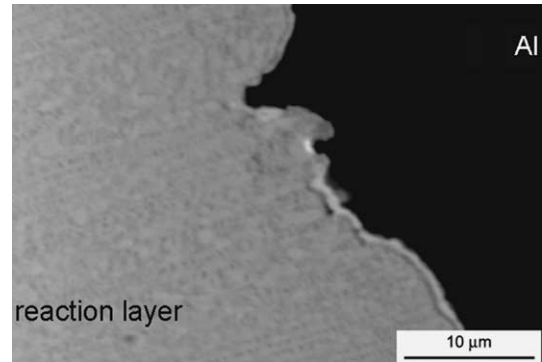
ther U nor Mo were detected in the Al. Due to the very narrow thickness of the third band, it was not possible to measure its composition.

XRD patterns were taken on eight successive surfaces starting at the Al side, across the reaction layer and up to the U–Mo side. Three of them representing the whole behavior are shown in Fig. 5. The intensities of the Al peaks look like those corresponding to a textured sample due to the coarse grains of Al. In Fig. 5(a) the structure of Al_4U [15] was clearly identified. The weak peaks in this pattern indicate the presence of another phase which could be indexed as cubic. The lattice parameter and relative intensities of these peaks suggest that they might correspond to the $Al_{20}Mo_2U$ structure [16]. The next patterns (Fig. 5(b) and (c)) show the successive appearance of the structures corresponding to Al_3U and (γ)U, besides the previous ones.

3.2. Effect of the decomposition of the γ(U–Mo) phase

In the diffusion couples prepared with the as cast U–7wt%Mo (not homogeneous in composition) the γ(U, Mo) phase underwent decomposition during the diffusion heat treatment. The corresponding microstructure is observed in Fig. 6. The interdiffusion layer that resulted was quite different from the previous case. It presented a very irregular interface in the U–Mo side. Islands of unreacted U–Mo were present, being greater near the U–Mo side. Cracks appeared after 2 h anneal. The width of the reaction layer was approximately 700 μm for 4 h anneal. Chemical etching did not reveal successive layers of different compounds, as Fig. 6 shows.

XRD successive spectra were obtained as described in Section 2. Two of them are shown in Fig. 7. The peaks in the pattern of Fig. 7(a) close to the Al correspond to two structures: (U, Mo)Al_3 and the hexagonal compound $Al_{43}Mo_4U_6$ [17]. The XRD pattern taken deeper in the reaction layer to the U–Mo side, Fig. 7(b),
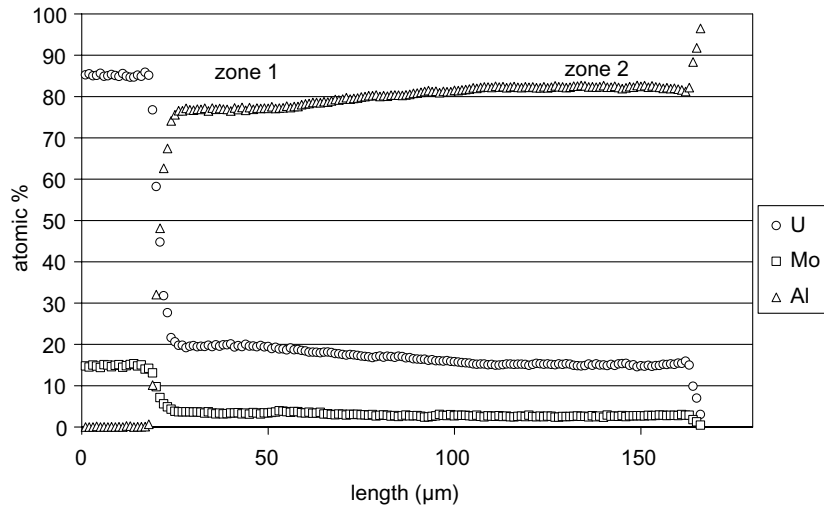
Fig. 4. Quantitative distribution of Al, U, and Mo (at.%) across the reaction layer in sample of Fig. 3.

Table 2
Average composition of aluminum, uranium and molybdenum, in zones fairly constant of the interdiffusion layer

	Average composition (at.%)			
	Al	U	Mo	Width (μm)
Zone 1	76.9 ± 0.3	19.6 ± 0.2	3.4 ± 0.2	25
Zone 2	82.3 ± 0.2	15.1 ± 0.2	2.6 ± 0.1	56

Two treatment of 2 h at 580 °C.

contains peaks that correspond to $\alpha(U)$ and $\gamma(U, Mo)$, besides those shown in Fig. 7(a).

4. Discussion

The results of the present study confirm the fact that provided $\gamma(U, Mo)$ phase is not decomposed, the interaction layer was uniform and had smooth or planar interface, similar to what has been observed in experiments performed with fuel elements with or without irradiation [2,7–9].

The composition values obtained by EPMA, Table 2 and Fig. 4, and the structures determined by XRD are in accordance with UAl_3 and UAl_4 being the major components in the reaction layer at 580 °C. In fact, they should be referred as $(U, Mo)Al_3$ and $(U, Mo)Al_4$ be-
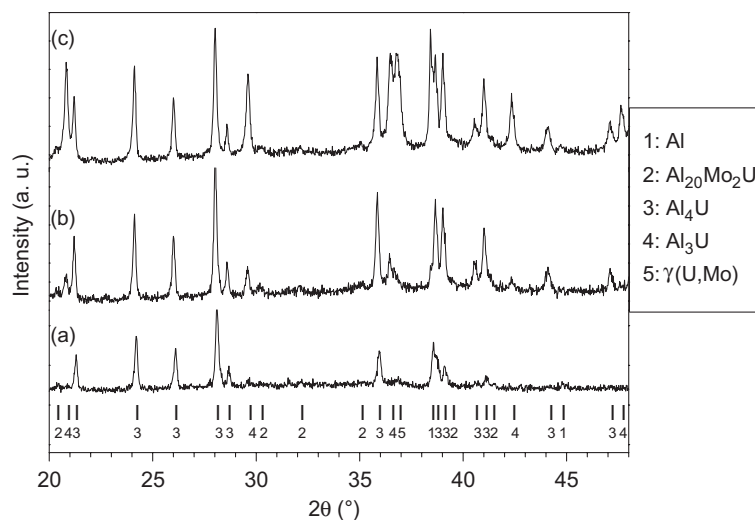

Fig. 5. XRD patterns at different depth into the interdiffusion layer: (a) close to the Al side, (b) deeper inside the layer and (c) close to the U–Mo side. Two treatments of 2 h at 580 °C.
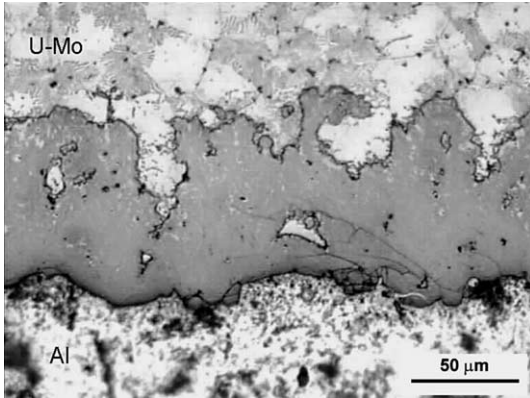
Fig. 6. Interdiffusion layer when γ(U, Mo) alloy decomposed during the heat treatment, 2 h, 580 °C. Chemical etched; optical microscopy.

cause, as Fig. 4 and Table 2 indicate, Mo is detected in both phases replacing U in approximately the same proportion as in the original U–7wt%Mo alloy.

The $Al_{20}Mo_2U$ cubic structure found by XRD, Fig. 5, is tentatively assigned to the thin band in Fig. 3, because it appeared from the beginning in the sequence of XRD spectra. Composition measurements by EPMA are necessary to assure this identification. Further diffusion anneals at longer periods of time to enlarge band thickness are in progress.

The quantitative results of EPMA in this work, Fig. 4, showing no penetration of Al into the U–Mo alloy confirm the qualitative results discussed in [8].

The γ(U, Mo) metastable phase is known to suffer decomposition during isothermal treatments above 400 °C [18]. This decomposition starts at grain boundaries and yields α(U) and γ(U, Mo) enriched in Mo in a complex microstructure. It seems that the presence of

the decomposition products enhances Al diffusion at the grain boundaries, causing a thicker interaction layer and promoting the formation of the U–Mo islands, as shown in Fig. 6. This behavior has also been observed in dispersed fuel samples [1,4,5].

The results of XRD show important differences with respect to the case of no decomposed γ(U, Mo), Figs. 5 and 7. UAl_3 is clearly identified in both types of samples. In Fig. 7(a) the small peaks besides the corresponding to UAl_3 are not readily identified. In dispersion fuel samples, when decomposition of γ phase occurred, using neutron diffraction technique [4,10], the presence of UAl_3, UAl_2 and α(U) was reported. In this work an attempt to identify the peaks in Fig. 7(a) with the rest of the compounds from the binary phase diagrams was not satisfactory. A search concerning data on ternary compounds was made. It was found that $Al_{43}U_6Mo_4$ [17], hexagonal with lattice parameters $a = 1.097$ nm, $c = 1.769$ nm, fit quite satisfactorily concerning peak positions, as can be seen in a detail of the pattern of Fig. 7, shown in Fig. 8. It remains a discrepancy in the intensity of the peaks, that could be explained taking into consideration the sample characteristics: it was not a powder sample, therefore crystallographic texture effects may be present; the different phases are not distributed in the irradiated surface at random, therefore it is not likely that using fixed slit (variable irradiated area), intensities have a good coincidence with theoretical ones.

5. Conclusions

The characterization of the reaction layer between (U–Mo) alloy and Al by the quantitative determination of the composition and crystal structure of the component phases, showed the strong dependence between the
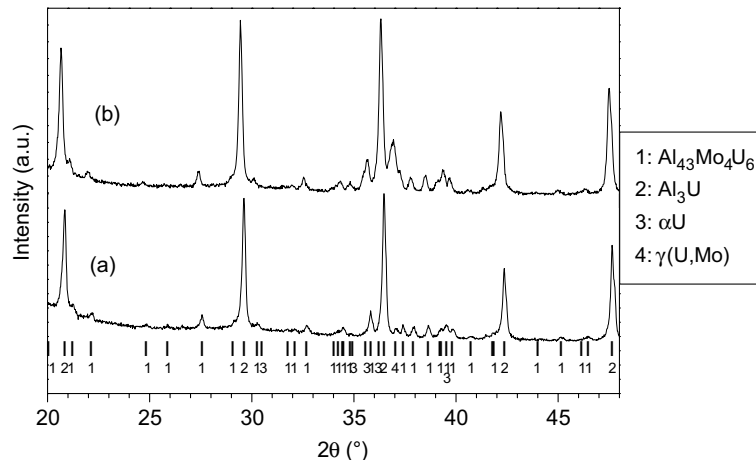

Fig. 7. XRD patterns for the reaction layer in a diffusion couple with decomposed γ(U, Mo) alloy: (a) near Al side, (b) deeper into the layer.
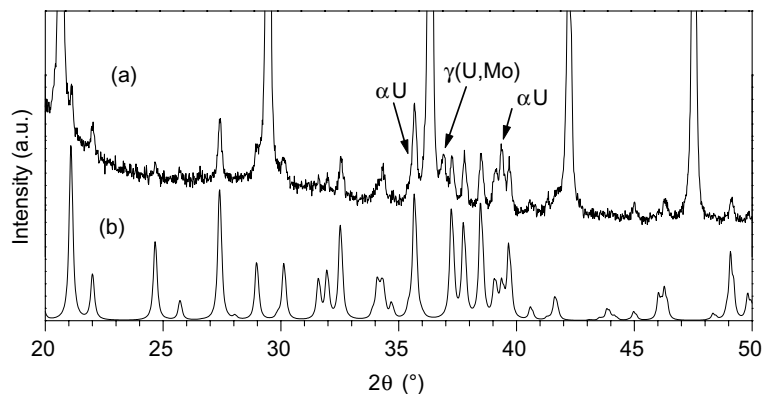
Fig. 8. (a) Closer examination of XRD pattern in Fig. 7. Peaks out of scale correspond to (U, Mo)Al$_3$ structure. (b) Simulated pattern of Al$_{43}$Mo$_4$U$_6$ structure.

(U–Mo) alloy being retained as γ phase and the kind of the resultant reaction layer. The results showed that when γ(U, Mo) phase did not decompose:

- The reaction layer for the interdiffusion (U–7wt%Mo)/Al at 580 °C is uniform and has smooth interface with no cracks or porosity.
- The compounds constituting this layer were identified as (U, Mo)Al$_4$, (U, Mo)Al$_3$ and Al$_{20}$Mo$_2$U.
- No Al in solution was detected into the γ(U–Mo) alloy.

When decomposition of γ(U, Mo) phase occurred, the width of the reaction layer increased considerably. The growth with a non-planar interphase leaves island of unreacted γ(U, Mo). The compounds due to the reaction, identified by XRD, were (U, Mo)Al$_3$ and possibly Al$_{43}$U$_6$Mo$_4$.

The results of the present work are a step forward to the knowledge of the interaction of (U–Mo)/Al from the qualitative previous studies [4,6,7]. They also point out certain risks in the formation of the reaction layer which is a critical parameter in the dispersed fuel elements fabrication, as mentioned in Section 1 [1,2].

Acknowledgements

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