

# REACTION LAYER IN U- 7WT%MO /Al DIFFUSION COUPLES

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## ABSTRACT

New results of the reaction layer characterization between  $\gamma$  (U-7wt%Mo) alloy and Al, in chemical diffusion couples, are presented. The analysis was performed using optical and scanning electron microscopy with EDAX and X-ray diffraction techniques. Besides the main components (U, Mo)Al<sub>3</sub> and (U, Mo)Al<sub>4</sub>, already reported, two ternary compounds of high Al content have been identified in the reaction layer when it grew in retained or decomposed  $\gamma$  (U, Mo) phase, respectively. The drastic consequence on the interdiffusion behavior due to the thermal instability of the retained  $\gamma$  (U, Mo) phase is discussed.

## 1. Introduction

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 [1]. The interaction of U-Mo particles with Al matrix in dispersion fuel elements is still a problem of concern. The nature of the reaction products (composition, structure, etc) in the reaction layer is also a requirement from the fuel modeling area [2].

Data have been published for different temperatures and various Mo contents in irradiated [1,3-5] or unirradiated [6-10,12] dispersion fuel samples and out of reactor diffusion experiments [11,12]. In all cases UAl<sub>3</sub> was the major component. In diffusion couples, quantitative determinations of concentrations showed (U,Mo)Al<sub>3</sub> and (U,Mo)Al<sub>4</sub> in U-7wt%Mo/Al at 580°C [11]. In U-10wt%Mo/Al at 550°C [12] three zones in the reaction layer are reported: (U,Mo)Al<sub>3</sub>, (U,Mo)Al<sub>4</sub> and a very thin high aluminum one.

This paper reports new results on the characterization of the reaction layer from further investigation in the U-7wt% Mo / Al diffusion couples at 580°C. This characterization was performed using optical microscopy (OM), scanning electron microscopy (SEM) with EDAX, and X-Ray diffraction (XRD). The identification of the phases is discussed in view of previous data. The effect of the decomposition of the  $\gamma$  (U, Mo) phase is also analyzed related with time and temperature used in fabrication of the fuel elements.

## 2. Experimental

The diffusion couples made from pure Al and an U-7wt%Mo alloy, of previous work [11] were reanalyzed here. The same experimental procedures for metallography and XRD were used.

Diffusion couples had been annealed at 580°C in order to obtain measurable reaction layers in reasonable short times which guarantee no  $\gamma$  phase decomposition

For XRD analysis[11], 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. X-ray diffraction measurements were performed with filtered Cu  $K_{\alpha}$  radiation, in a Phillips PW 3710 X-ray diffractometer, with fixed slit.

### 3. Results

Fig.1 shows the reaction layer at 580°C obtained in [11]. Besides the two zones already reported [12,13], observations with SEM showed the existence of a very narrow third zone (~ 2  $\mu\text{m}$ ) in contact with the aluminum, Fig. 2. No measure of its composition due to the very narrow thickness was made at that time. Micrograph in Fig.2 corresponds to the sample prepared for DRX [10] in which polishing at a small angle from the perpendicular to the diffusion direction results in an enlarged thickness on the analysed surface. Qualitative determination of the composition by EDAX gave ~85%Al. Fig. 3a shows the XRD pattern corresponding to the beginning of the reaction layer at the Al side. The structure of pure Al and  $\text{Al}_4\text{U}$  [14] 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 ternary aluminide  $\text{Al}_{20}\text{Mo}_2\text{U}$  reported in [15]. According to that work it crystallizes with a cubic structure (space group  $\text{Fd}3\text{m}$ ,  $Z=8$ ) and a lattice constant  $a=1.4506\text{nm}$ . Fig 3b shows the pattern for the complete reaction layer showing peaks of  $\text{Al}_3\text{U}$ ,  $\text{Al}_4\text{U}$  and the starting materials.

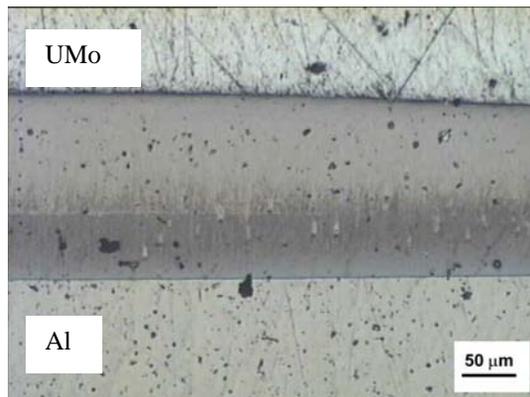


Fig.1

Interdiffusion layer. 2 h 580°C  
Chemical etched. Optical microscopy

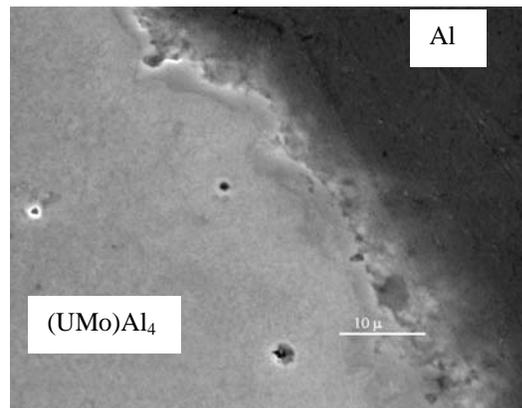


Fig.2

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

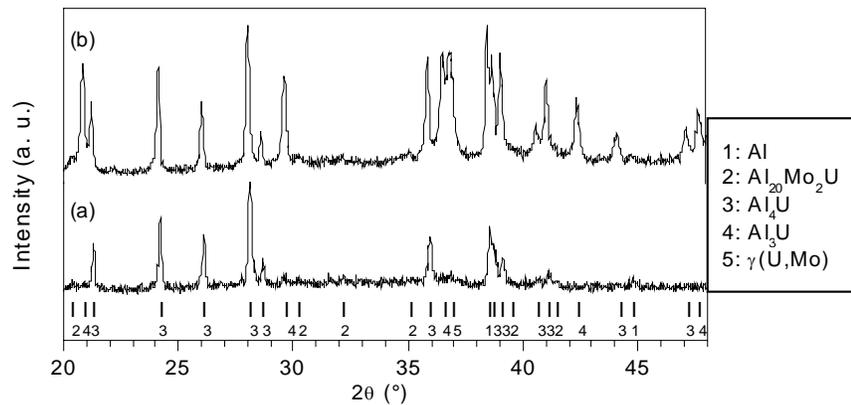


Fig. 3: XRD patterns (a): first appearance of the reaction layer from the Al side. b) Whole reaction layer and starting elements.

In the diffusion couples prepared with the as cast U-7wt.%Mo alloy (not homogeneous in composition), the  $\gamma$  (U, Mo) phase underwent decomposition during the diffusion heat treatment. The microstructure of the reaction layer is observed in Fig. 4. The resultant reaction layer was quite different from the situation in which  $\gamma$  (U, Mo) is retained [13], Fig.1. It presented a very irregular interface in the U-Mo side, islands of unreacted U-Mo and cracks which appeared after 2 h anneal. The width of the reaction layer was approximately 700  $\mu\text{m}$  for 4 h anneal. Chemical etching did not reveal successive layers of different compounds.

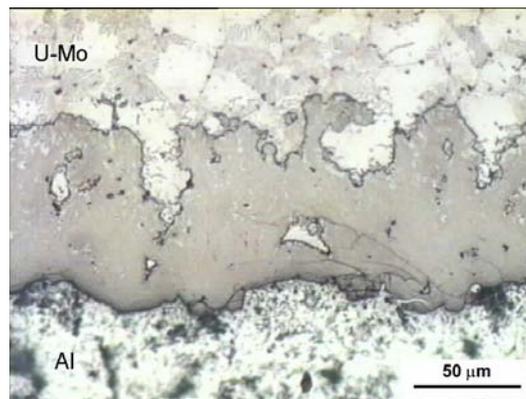


Fig.4 Interdiffusion layer when  $\gamma$  (U, Mo) alloy decomposed during the heat treatment, 2 h. 580°C. Chemical etched. Optical microscopy

The successive XRD spectra taken perpendicular to the diffusion direction were all similar this being a difference from what is described above, when  $\gamma$  (U, Mo) is retained. In the XRD pattern in Fig. 5 the structures of  $\text{UAl}_3$ ,  $\alpha$  (U) and  $\gamma$  (U, Mo) were clearly identified.

The remaining small peaks in this case fit satisfactorily with another ternary compound:  $\text{Al}_{43}\text{Mo}_4\text{U}_6$  [16], hexagonal (space group  $P6_3/mcm$ ,  $Z=2$ ) with lattice parameters  $a = 1.097\text{nm}$ ,  $c = 1.769\text{nm}$ .

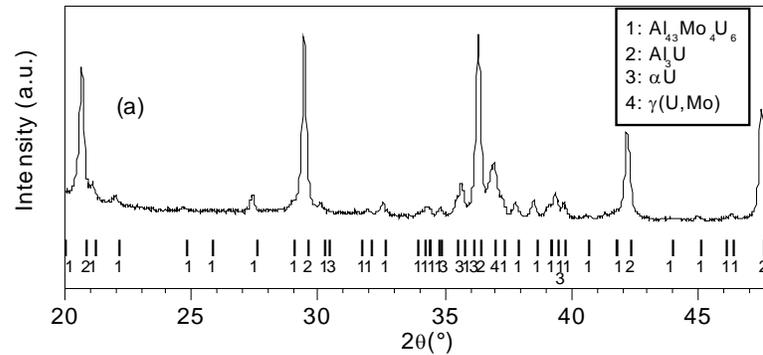


Fig. 5 XRD patterns for the reaction layer in a diffusion couple with decomposed  $\gamma$  (U, Mo) alloy.

Experiments at  $480^\circ\text{C}$  (which is of interest in the dispersion fuel elements fabrication) were performed. The width of the reaction layer was  $\sim 2\ \mu\text{m}$  for a 3 h anneal. This time was chosen from a series of experiments as the maximum possible to avoid the decomposition of the retained  $\gamma$  phase. Then, dealing with U-7wt% Mo the type of characterization of the reaction layers done in this work, is limited to temperature above  $500^\circ\text{C}$ .

#### 4. Discussion

The presence of the binary structures  $\text{UAl}_3$  and  $\text{UAl}_4$  in the reaction layer between U-Mo alloys and Al up to  $580^\circ\text{C}$  has been a common result of several works [11,12] and is also the case here. In fact, the compounds should be referred as  $(\text{U}, \text{Mo})\text{Al}_3$  and  $(\text{U}, \text{Mo})\text{Al}_4$  because Mo is detected in both phases replacing U in approximately the same proportion as in the original U-7wt% Mo alloy.

In this work, further investigation on the XRD pattern of the diffusion layer at  $580^\circ\text{C}$  indicated the existence of the  $\text{Al}_{20}\text{Mo}_2\text{U}$  cubic structure reported in [15]. Ryu et al [12] reported that the Al composition of the third band named L3 was 87% and higher Mo content than in the original alloy. The difference between the stoichiometric composition for  $\text{Al}_{20}\text{Mo}_2\text{U}$  and the reported measurements in [12], can be explained if a range in composition is assumed for the ternary phase. Indeed [15] studying the isotypic compound  $\text{Al}_{20}\text{Mo}_2\text{Ce}$  measured considerably divergence from the ideal composition, being Mo atoms replaced by Al. The X-ray density of  $\text{Al}_{20}\text{Mo}_2\text{U}$  range from  $4.225\ \text{gr}/\text{cm}^3$  to  $4.067\ \text{gr}/\text{cm}^3$ , and the content of Al range from 87 to 89 at. %.

Hofman [17] suggested that early measurements in diffusion couples, PIE results from RERTR 1 and 3, CEA IRIS 1 and the third component of the reaction layer in [12], can be

related with the metastable compound  $Al_7Mo$  taking into account the concentration of Al and the probably cubic structure.

The ternary aluminide  $Al_{20}Mo_2U$  found in this work, in the reaction layer of diffusion couples, includes the above results. Moreover we suggest that the metastable binary phase  $Al_7Mo$ , obtained in rapid cooling experiments [18], would be stabilized by the progressively addition of U in the ternary system.

Fig.6 is a redrawing of the schematic ternary graph of the Al rich corner of the Al-Mo-U system, suggested by [17], which include the present results.

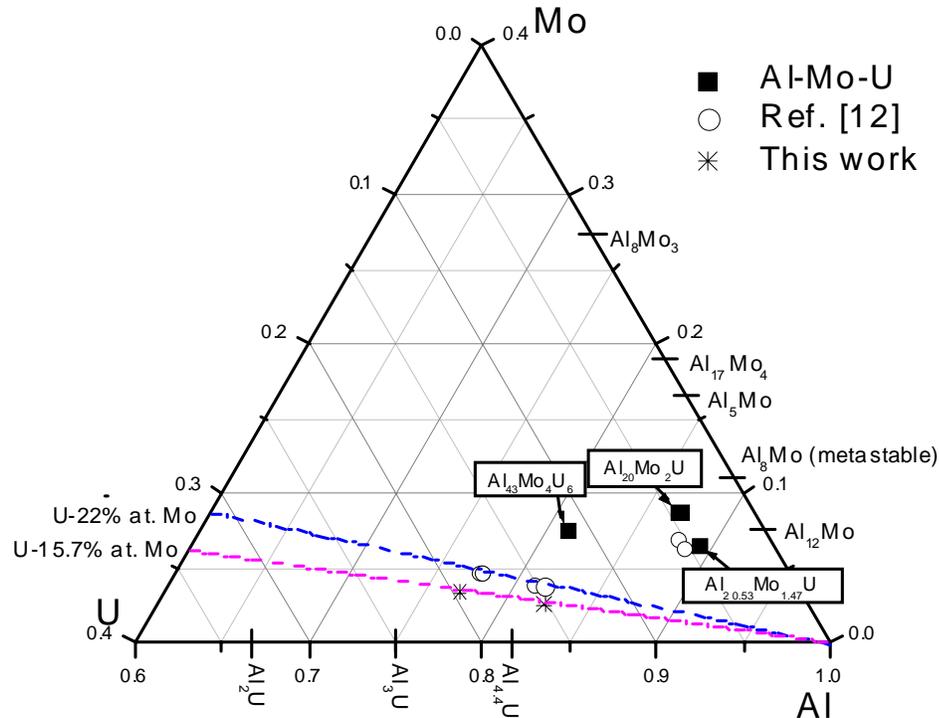


Fig 6 Ternary representation of the Al rich corner of the system AL-MO-U. Measured concentrations and binary and ternary compounds

The  $\gamma$  (U, Mo) metastable phase is known to suffer decomposition during isothermal treatments above  $400^\circ C$  [19]. This decomposition starts at grain boundaries and yields  $\alpha(U)$  and  $\gamma$  (U, Mo) enriched in Mo in a lamellar microstructure. The presence of the decomposition products enhances even more the rapid diffusion of Al at the grain boundaries, resulting in a thicker interaction layer and promoting the formation of the U-Mo islands, as shown in Fig. 4. This behavior has also been observed in dispersed fuel samples [5]

The results of XRD (Figs. 5) show important differences respect to the case of not decomposed  $\gamma(U, Mo)$ .  $UAl_3$  is clearly identified in both types of samples. In Fig. 5 the small peaks besides the corresponding to  $UAl_3$  were not readily identified. In this work an

attempt to identify the peaks in Fig. 5 with the rest of the compounds from the binary phase diagrams as reported in[10] was not satisfactory. The fitting with the simulated pattern for  $\text{Al}_{43}\text{U}_6\text{Mo}_4$  is considered more suitable.[13].

## 5. Conclusions

The detailed study of the reaction layer between (U-Mo) alloy and Al at 580°C, when  $\gamma$ (U-Mo) is not decomposed, showed that the compounds constituting the layer were identified as (U,Mo)Al<sub>4</sub>, (U, Mo)Al<sub>3</sub> and Al<sub>20</sub>Mo<sub>2</sub>U. No Al in solution into the  $\gamma$  (U-Mo) alloy was detected.

When decomposition of  $\gamma$  (U, Mo) phase occurred, the width of the reaction layer increased considerably. The growth with a non-planar interphase left islands of unreacted  $\gamma$  (U, Mo). The compounds due to the reaction, identified by XRD, were (U, Mo)Al<sub>3</sub> and possibly  $\text{Al}_{43}\text{U}_6\text{Mo}_4$ . No UAl<sub>4</sub> was found when gamma decomposed.

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## References

- [1] M. Meyer, G. L. Hofman, S. Hayes, C. Clark, T. Wiencek, J. Snelgrove, R. Strain, K. H. Kim. J. Nucl. Mater, 304 (2002) 221-236.
- [2] S.Hayes, G.Hofman, M.K.Meyer, J.Rest and J.L.Snelgrove. Proc. 24rd. International Meeting on Reduced Enrichment for Research and Test Reactors .November 3-8 2002, San Carlos de Bariloche, Argentina.
- [3] M. Meyer, G. Hofman, R. Strain, C. Clark, J. Stuart, in: Proc. 23rd. International Meeting on Reduced Enrichment for Research and Test Reactors RERTR. Las Vegas USA. Oct. 1-6, 2000, 202.
- [4 ] G. Hofman, J. Snelgrove, S. Hayes, M. Meyer. International Meeting on Research Reactor Fuel Management, March 17 –20, 2002, Ghent, Belgium, 50.
- [5] G. Hofman, M. Meyer. International Meeting on Reduced Enrichment for Research and Test Reactors. November 3-8, 2002. San Carlos de Bariloche, Argentina
- [6] V. G. Aden, V. V. Popov, A. Rusanov, V. Troyanov. International Meeting on Research Reactor Fuel Management, RRFM'99, 201.
- [7] K. H. Kim, H. J. Kwon, J. S. Lee, H. J. Ryu, J. M. Park, Ch. Kyu Kim, in: 23rd International Meeting on Reduced Enrichment for Research and Test Reactors. October 1-6, 2000. Las Vegas, Nevada, USA.
- [8] K. H. Kim, D. B. Lee, Ch. K. Kim, G. Hofman, K. W. Paik. Nucl. Eng. and Design. 178 (1997) 111-117.

- [9] R. H. Gibadullin, A. D. Karpin, R. H. Gibadullin, A. D. Karpin, Yu M. Pevchikh, V. V. Popov V. N. Sugonayev, V. M. Troyanov. International Meeting on Research Reactor Fuel Management, March 17 –20, 2002, Ghent, Belgium
- [10] J. S. Lee, C. H. Lee, K. H. Kim, V. Em. Journal of Nuclear Materials. 306 (2002) 147-152
- [11] M. Mirandou, S. Balart, M. Ortiz, M. Granovsky, G. Hofman. 24<sup>th</sup> International Meeting on Reduced Enrichment for Research and Test Reactor, November 3-9, 2002. Bariloche Argentina.
- [12] Ho Jin Ryu, Young Soo Han, Jong Man Park, Soon Dal Park, Chang Kyu Kim. Journal of Nucl Mater. 321 (2003) 210-220.
- [13] M. Mirandou, S. Balart, M. Ortiz, M. Granovsky, J.of Nucl. Mater to be published
- [14] V. Y. Zenou, G. Kimmel, C. Cotler, M. Aizenshtein. Journal of Alloys and Compounds 329 (2001) 189.
- [15] S. Niemann, W. Jeitschko. Journal of Solid State Chemistry. 114 (1995) 337
- [16] S. Niemann, W. Jeitschko. Z. Metallkd. 85 (1994) 5, 34
- [17] E.A. Logan, J.N. Pratt, M.H. Loretto. Materials Science and Technology 5 (1989) 123
- [18] D. Blake, R. F. Hehemann, in: Proc. of the Third Army Materials Technology Conference, Vail, Colorado, USA, February 12-14, 1974; J. J. Burke, D. A. Colling, A. E. Gorum, J. Greenspan (eds.); Brook Hill Publishing Company, Chestnut Hill, Massachusetts, USA (1976) 189 .
- [19] G. Hofman private communication.