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CURRENT ACTIVITIES IN THE OUT OF PILE INVESTIGATIONS OF THE INTERACTION BETWEEN UMo AND Al OR Al ALLOYS

S. Balart, L. Kniznik, C. Komar Varela, P. Gargano, M. Mirandou, S. Aricó, P. Alonso,
G. Rubiolo, A. Fortis and L. Gribaudo.
Departamento Materiales, GAEN
Comisión Nacional de Energía Atómica
Avda. Libertador 8250 (1429) Cdad de Buenos Aires. Argentina

ABSTRACT

The development of fuel elements based in LEU(Mo) alloys have encouraged worldwide activities such as in pile irradiations, heavy ion irradiation, out of pile experiments and computational simulations. The research program at CNEA launched 7 years ago have included diffusion experiments, the irradiation of a set of microplates in the RA3 reactor and computational methods applied to thermodynamic and kinetic calculations. This work reports the final analysis of the XRD experiments done with Syncrotron radiation on the interaction U(Mo,1%Zr)/Al (7%Si), which *indicated* the precipitation of Zr as Zr_5Al_3 in the interaction zone. Concerning calculations, a successfull database was built to be read by the Thermocalc code to calculate phase equilibria. The diffusion problem was carried out by the DICTRA simulation package which articulates data evaluated by Thermocalc with a mobility database. We present the equilibria obtained in the Al-U system and a first model of UAl_3/Al diffusion couple that simulates satisfactorily the growth of the Al_4U phase.

1. Introduction

The development of fuel elements based in LEU(Mo) alloys to convert high flux research nuclear reactors is in progress, [1]. Dispersed fuel elements in Al matrix could not be qualify due to unsatisfactory behavior revealed in PIE [2]. Modification of the matrix with the addition of Si is nowadays a promissory solution [3, 4]. This situation encouraged worldwide activities such as in pile experiments [4, 5, 6, 7, 8], out of pile experiments [9, 10, 11, 12], heavy ion irradiation [13] and computational simulations [14, 15]

The research program at CNEA has included out of pile diffusion experiments, the irradiation of a set of microplates in the RA3 reactor and computational methods applied to thermodynamic and kinetic calculations. This work reports the activities during the last year in these different areas.

2. Out of pile diffusion experiments

(corresponding author: mirandou@cnea.gov.ar)

During fabrication or in service, the fuel U(Mo) particles, in the cubic γU phase (cI2, W *type*) is in contact with the Al matrix or the Al cladding, interdiffusion occurs and new phases form at the interphase to the detriment of the properties of the fuel element. Out of pile interdiffusion experiments are taken as a first approach to understand this problem.

In our last presentation [16], the results of interaction layers grown at 550 ºC in a multicouple {U-7wt%Mo-1wt%Zr/Al and U-7wt%Mo-1wt%Zr/Al A356 alloy}, Figure 1 and a single diffusion couple U-7wt%Mo-1wt%Zr/Al A356 specially made for XRD analysis were presented. By the combination of different techniques at least two phases $U(Al,Si)_3$ and Si_5U_3 were reported as part of the interaction layer. The use of synchrotron radiation at the Brazilian Synchrotron Light Laboratory (LNLS, CNPq, Campinas, Brazil) was a key technique in the crystallographic characterization. However a few peaks remained without assignment to any phase.

A further analysis of those spectra allowed the identification of the phase Zr_5Al_3 (tI32, W_5Si_3 *type*) from the remaining peaks Figure 2, achieving the complete identification.

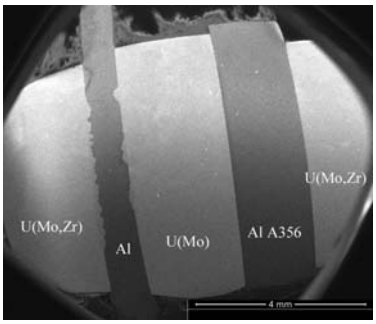

Figure 1: multicouple (U-7Mo-1Zr/Al and U-7Mo-1Zr/Al - 7%Si). Comparison of 4 interaction layers grown simultaneously. [16]

If this new XRD result is taken into account, the composition measurements previously presented in [16] can be explained in a more complete way. There, the measurements performed inside the interaction layer were plotted in a GIBBS triangle, Figure 3. The points aligned from the Al corner towards 50 at%Al and 25 at%Si (circled) correspond to different proportions of Al + $U(Al,Si)_3$, with 25 at% Si.

Starting from (U+Mo+Zr) corner, a second set of composition measurements are aligned between (U+Mo+Zr) corner and concentration value 17 at%Al and 30 at%Si (marked with a square). This concentration value, according to XRD results, is considered now as the result of a fixed proportion of U_3Si_5 + Zr_5Al_3. Then, the points in between are the result of different proportions of γU phase (and or αU) + (U_3Si_5 + Zr_5Al_3), suggesting that the interaction layer adjacent to U(Mo,Zr) alloy has a biphasic band formed by U_3Si_5 + Zr_5Al_3.

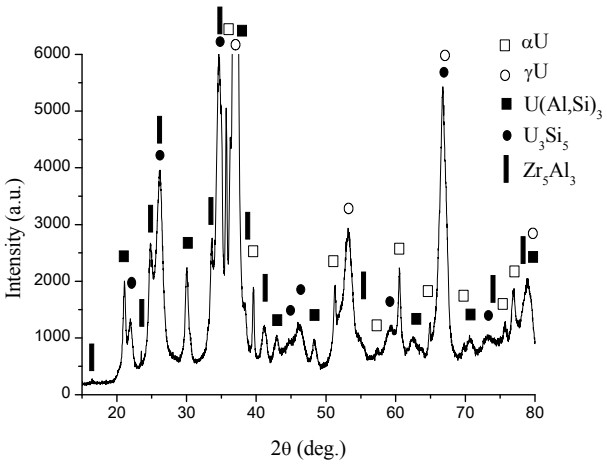

Figure 2. Phase identification in the interaction layer of U(Mo,Zr)/Al 7%Si. 550 ºC . 1.5h XRD Svncrotron Rad.

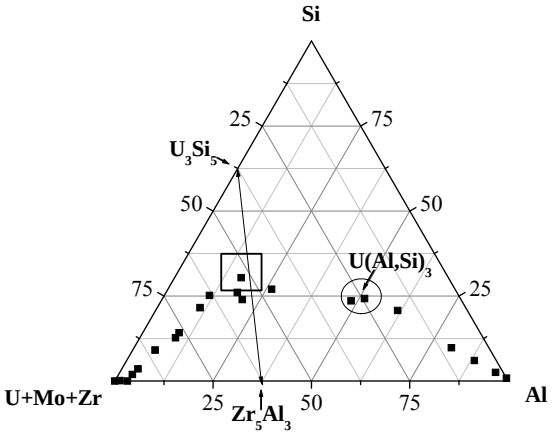

Figure 3 U(Mo,Zr)/Al A356 550 ºC–1.5 h Composition measurements represented in pseudo ternary (U+Mo+Zr)-Al-Si diagram (in at%). WDS

3. In pile irradiation of microplates at RA3 reactor

(corresponding author: mirandou@cnea.gov.ar, cavarela@cnea.gov.ar)

With the objective of studying the effect of neutron radiation on diffusion couples U-7wt%Mo and Al 6061, the irradiation of five microplates was started at RA-3 in 2006. The selected position is the bottom of the core, in a box where the thermal flux is $1x10^{14}$n/cm^{2}s. The microplates were fabricated with U-7wt%Mo and Al 6061 by the use of friction stir welding (FSW) technique. Final dimensions are schematically represented in Figure 4.

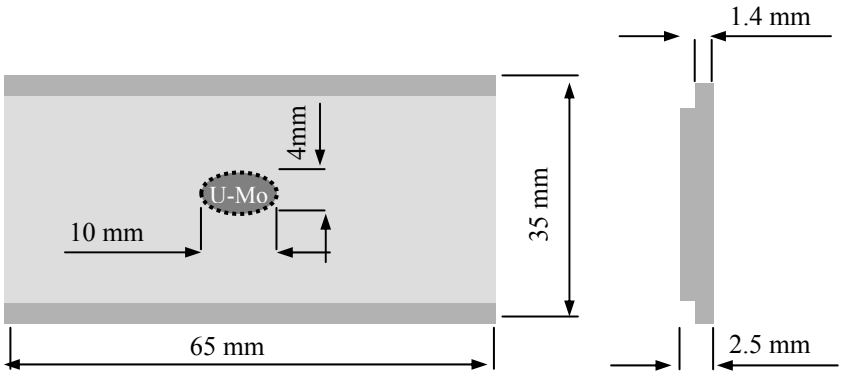

Figure4. Schematic representation of microplates for irradiation experiments.

Four of the microplates have been extracted from the reactor and have been put in individual stainless steel (SS) containers to be situated in the decay pool. The last one is still under irradiation. The dose rate is measured regularly in order to translate them safely to the Hot Cell Lab. Up to date, microplates 05-001 and 05-005 are ready to be translated safely in a lead container. Some details are given in Table 1. Post irradiation experiments are planned to be started during the first part of 2010 and they will include metallographic preparation and optical observations.

Table 1.Details of irradiated microplates

Microplate	Total time of irradiation **(h)**	Dose rate outside the SS container at 5/09	Dose rate outside a lead container at 6/08
05-001	1187.3 (approx. 49 days)	124 mrad/h	4 mrad/h
05-002		325 rad/h	
05-003	4673.8 (approx. 6.5 months)	1.05 rad/h	
05-004	9946.51 (approx. 14 months)	2.4 rad/h	
05-005	2856.9 (aprox. 4 months)	350 mrad/h	

4. Computational calculation

(corresponding author: kniznik@cnea.gov.ar)

4.1. Calculation approach to describe the growth of intermediate phases by diffusion.

4.1.1. Calculation method.

In an U/Al diffusion couple interdiffusion occurs at the interphase leading to the growth of intermediate phases. The composition of these phases arises from the phase equilibrium diagram, as it was experimentally verified [17, 18,]. As a first approach, we present here the modeling of thermodynamic properties and diffusion controlled transformations in a Al_3U ($L1_2$, cP4, spatial group 223 [19]) / Al (A1, cF4, spatial group 225 [19]) couple where Al_4U (D1b, oI20, spatial group 74[19]) phase is expected to grow. For thermodynamic equilibria calculations we used the CALPHAD method [20] implemented in the THERMOCALC software [21] together with data from Kassner and co. [22] and the database in [23]. Resulting phase diagram is shown in Figure 5. For kinetics simulations the DICTRA software [24] was used together with data from Ryu and co. in an out of pile experiment with a U-Mo/Al couple [25]..

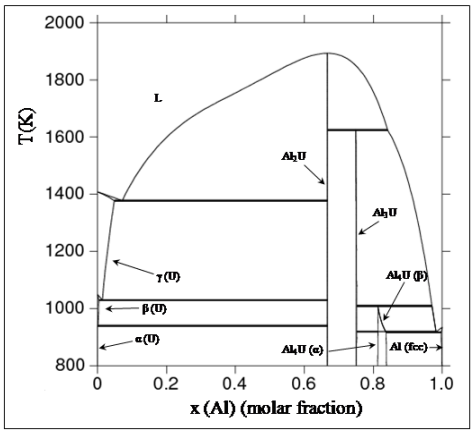

Figure 5. Equilibrium phase diagram calculated for the U-Al system.

DICTRA software solves Fick`s laws [26].

$$J_k = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial z} \qquad (1)$$

for the diffusion flux J at the interphase in a certain concentration gradient assuming local thermodynamic equilibrium established by THERMOCALC functions. The model needs the knowledge of the diffusion coefficients D_{ki}. In a binary system, there is a unique chemical interdiffusion coefficient for each phase that can be written in terms of the tracer diffusion coefficients D^* in the absence of volume change:

$$\widetilde{D} = \left(D_i^* x_j + D_j^* x_i\right) \cdot \phi \qquad (2)$$

where ϕ is the *thermodynamic factor* in that phase:

$$\phi = 1 + \frac{\partial \ln \gamma_{Al}}{\partial \ln x_{Al}} = 1 + \frac{\partial \ln \gamma_U}{\partial \ln x_U} \quad \text{or} \quad \phi = \frac{x_i}{RT} \frac{\partial \mu_i}{\partial x_i} \qquad (3)$$

where the equality holds due to Gibbs-Duhem relation and γ is the activity coefficient. Stoichiometric compounds as Al_3U and terminal Al solution had to be artificially given a certain solubility range in order to obtain a finite value for the thermodynamic factor [27].

We found in the literature values for Al self-diffusion coefficient and for tracer impurity diffusion coefficient of U in Al matrix [28] and no information of values in the intermediate compounds. In Ref. [25] concentration profiles are shown for a U-10%Mo/Al diffusion couple and estimations for integral values of the interdiffusion coefficients in the intermediate phases: $\widetilde{D}_{\text{int}}$. In order to make use of these values independently of the experimental concentrations values, we calculated the average value of the interdiffusion coefficient $\widetilde{D}_{av}$ for each phase [29, 30,]:

$$\widetilde{D}_{av} = \frac{\widetilde{D}_{\text{int}}}{C(X_2) - C(X_1)} \qquad (4)$$

$C(X_i)$ are the equilibrium values from the calculated equilibrium diagram.

Finally D^* values for each species, required to construct DICTRA data base, were obtained by using $\widetilde{D}_{av}$ values together with the thermodynamic factors calculated from our thermodynamic data base.

$$\widetilde{D}_{av} = \left(D_{Al}^* x_U + D_U^* x_{Al}\right) \cdot \phi = D^* \left(x_U + x_{Al}\right) \cdot \phi = D^* \phi \qquad (5)$$

where we used the same value D^* for Al and U tracer diffusion coefficients. Values for $\widetilde{D}_{av}$ and D^* are shown in Table 2.

Table 2**.** Average values $\widetilde{D}_{av}$ for the interdiffusion coefficients estimated from Ref [25] and D^* used in our DICTRA data base.

Phase	$\widetilde{D}_{av}\left(m^2/s\right)$	$D^*\left(m^2/s\right)$
Al_3U	1.57×10^{-10}	1.34×10^{-14}
Al_4U	9.15×10^{-13}	1.54×10^{-13}

4.1.2. Calculation results.

We applied the moving boundary model [26] to the problem of interdiffusion in an Al_3U/Al couple. Total length was taken as 1200 μm with two initial regions of 600 μm each filled with Al_3U and Al. In between, a small Al_4U region of 0.01 μm length was introduced (Figure 6a). Initial Al molar fractions were 0.751 (Al_3U), 0.814 (Al_4U) and 0.999 (Al). Global composition resulted in x(Al)=0.875 (molar fraction), meaning that final equilibrium would only exhibit the presence of Al_4U and Al. Temperature and pressure were set as T=823.15K and P=10^5Pa. Figure 6b schematically shows the interphases displacement due to Al_4U growth. Al_4U phase evolution

can be seen in the Al concentration profiles of Figure 7a for initial time, for 5h and after 40h of simulation.

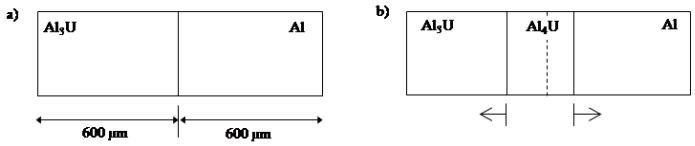

Figure 6**.** a) Initial conditions. A small Al_4U region was placed in the interphase, b) Interphases displacement.

Interphase displacement as a function of time, Figure 7b, exhibits the correct proportionality with the square root of t. The Matano plane was taken as coincident with the original interphase [29]. It can be noticed that the interphase Al_3U/Al_4U moves farther than Al_4U/Al interphase, indicating that Al diffuses in Al_3U fastest than U in Al.
After 40 h the width of Al_4U region is 361.7 µm. A direct comparison with experiment is not possible. The value in Ref [25] involves the effects of Mo dissolved in U [11] and of the growing of both Al_3U y Al_4U. Penetration depths reported in Ref [17] involves the whole interphase without distinction among different composition regions. Finally, in Ref [18] width measurements of the interphase as a function of time are presented for an Al_3U/Al couple but experiments are performed at high pressure ($2x10^7$ Pa or higher).

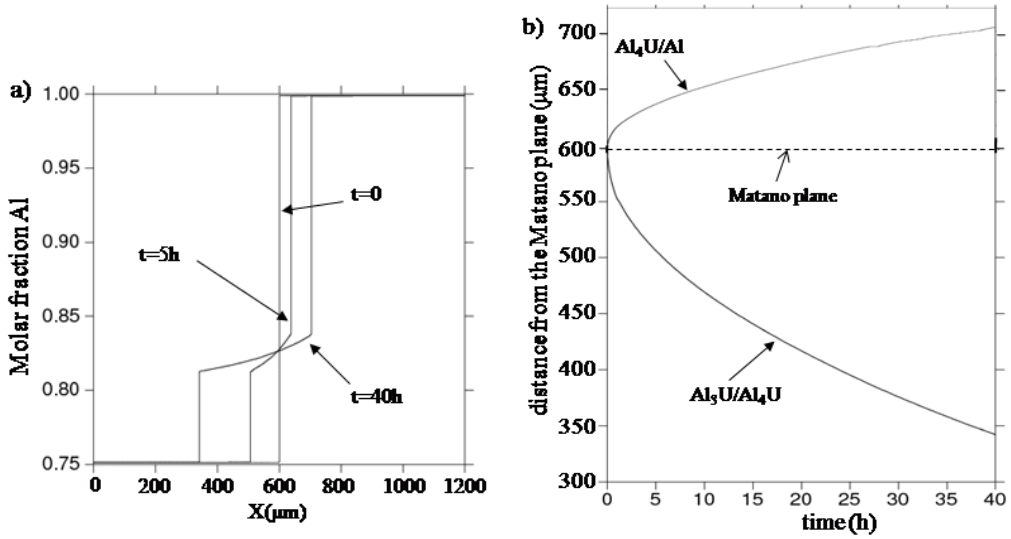

Figura 7**.** a) Al concentration profiles at t=0, t=5hs, t=40hs, b) Interphases positions Al_3U/Al_4U and Al_4U/Al.

We can conclude that our simulation satisfactory models the diffusion growth of Al_4U in an Al_3U/Al couple. An adjustment of the diffusion parameters will be possible by comparison of a simulated U/Al couple with experiment reported by De Luca and co. [17]. This calculation is now being undertaken.

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5. References

1 M.K. Meyer et al, J. Nucl. Mat. 304 (2002) 221-236.
2 A. Leenaers et al, J. Nucl. Mater. 335 (2004) 39-47.
3 G.L. Hofman et al, Proceedings of the 2004 RERTR Int. Meeting, Nov. 7-12, Vienna, Austria.
4 M. Ripert et al. Transaction 10th Int. Topical Meeting ENS RRFM, April 30-May 3, 2006, Sofia, Bulgaria.
5 G. Hofman, 2007 RERTR Int. Meeting. Sep23-27,2007, Prague, Czech Republic.
6 D.F. Sears et al, Transaction 10th Int. Topical Meeting ENS RRFM, April 30-May 3, 2006, Sofia, Bulgaria.
7 V. Popov et al, Transaction 9th Int. Topical Meeting ENS RRFM, April 10-13, 2005, Budapest, Hungary.
8 J.M.Park et al.2007 RERTR Int. Meeting. Sep23-27,2007, Prague, Czech Republic.
9 J.M. Park et al, J. Nucl. Mater. 374 3 (2008) 422-430.
10 M. Mirandou et al, J. Nucl. Mater. 384 (2009) 268-273.
11 F. Mazaudier et al, J. Nucl. Mater. 377 (2008) 476-485.
12 L. Olivares et al.2007 RERTR Int. Meeting. Sep23-27,2007, Prague, Czech Republic.
13 N. Wieschalla et al. J. Nucl.Mater 357(2006) 191-197.
14 D. Wachs et al. 2006 RERTR Int. Meeting. Cape Town, South África. Oct 29-Nov 2 2006.
15 J.Garces et al 2005 RERTR Int. Meeting Nov 6-11. 2005 Boston Mass. USA.
16 M. Mirandou et al 2007 RERTR Int. Meeting. Sep23-27,2007, Prague, Czech Republic.
17 L.S. DeLuca et al, Unclassified Document KAPL-1747, UC-25, Metallurgy and Ceramics, 1957, USAEC Report.
18 L. S. Castleman, J. Nucl. Mater, 3 Nº1 (1961), p. 1-15.
19 P. Villars et al, Pearson's Handbook of Crystallographic Data For Intermetallic Phases 2; 1989, American Society for Metals, New York.
20 N. Saunders et al, CALPHAD, Pergamon Materials Series **1**, Cahn, R.W. (Ed.), 1998, Elsevier Science, Oxford.
21. B. Sundman et al, CALPHAD 9 (1985), 153-190.
22 M. E. Kassner et al, J. Nucl. Mater. 167 (1989) p. 160-168
23 L. Kniznik et al, Proc. of the 9º Congreso Int. de Met. y Mat. SAM – CONAMET 2009 y Primeras Jornadas Int. de Mat. Nucl., Bs As, Argentina, accepted after peer review
24 Software for Computational Thermodynamics and for Diffusion Controlled Simulations, developed and distributed by the Division of Physical Metallurgy, The Royal Institute of Technology, Stockholm, Sweden.
25 H. J. Ryu et al, J. Nucl. Mater, 321 (2003), p. 210-220.
26 A. Borgenstam et al, Journal of Phase Equilibria, **21**, Nº3 (2000), p. 269, 280.
27 Y. Du et al, Metallurgical and Materials Transactions A, 32A (2001), p. 2396-2400.
28 H. Meher, "Numerical data and functional relationships in science and technology, Vol. 26, Diffusion in Solid Metals and Alloys"; 1990, Landolt-Börnstein, Springer-Verlag, Berlin.
29 A. Soba et al, J. Nucl. Mater, 360 (2007), p. 231-241.
30 P.C. Tortorici et al; Metallurgical and Materials Transactions A, 30A (1999), p. 545-550.