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STUDIES ON HOT ROLLED INTERDIFFUSION PAIR U-10Mo/AA1050

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ABSTRACT

The U-Mo alloys are investigated with the goal of becoming nuclear material to fabricate high-density fuel elements for high performance research reactors. This enrichment level suggests that the U-Mo alloys should be between 6 to 10wt%, which can give up to 9gU/cm^3 as fuel density. Nevertheless, the U-Mo alloys are very reactive with Al. Interdiffusion reaction products are formed since nuclear fission promotes chemical interaction layer during operation, leading to potential structural failure. Present studies were made with treated hot rolled diffusion couples of U-10Mo inserted in Al (AA1050). The U-10Mo/AA1050 pairs were treated at 550°C during three soaking times (5h, 40h and 80h). From microstructure analyses, rapid diffusion of Al happened inside U-10Mo during heating for hot rolling at 540°C during 15 min, reaching approx. 8 at%Al in a range of 200 µm towards U-10Mo. Longer times (5, 40, 80h) at 550°C maintained this level of Al-content up to 1000 µm inside U-10Mo. A minor depth (approx. 1 µm) near the interdiffusion contact had higher Al-content, but not sufficient to form identifiable (U,Mo)Al$_x$ structures. Probably, residual elements in raw materials, probably only Si, reduced drastically the interdiffusion phenomena between U-10Mo and AA1050, maybe due to silicon presence. The phase Al3.21U0.47 is suggested as the interdiffusion blocker.

INTRODUCTION

The conversion need of HEU research reactors to LEU fronts opened goals to seek alternative fuel elements of high density. The developing of a denser core in uranium leads to higher intensity in the neutron flux and smaller amounts of spent fuel to be stored in repositories. The U-Mo alloy has been investigated with the purpose of becoming a nuclear material for making high-density fuel elements for research reactors of high performance. This alloy could have high density in fuel core up to around 9 gU/cm^3 and offers advantages in the reprocessing uranium spent fuels, since they are more easily recovered if compared to current fuels (1) (2) (3) (4).

During fabrication of fuel plates, the U-Mo alloy could employ the technology for the current geometry of LEU fuel. The MTR fuel type plate dispersion of nuclear alloy particles could have volume load up to 55% (5). The fuel element plates are made from cermets (U-Mo powder + Al) encapsulated in welded aluminum plates and hot rolled. U-Mo alloy is very reactive in aluminum presence in thermal cycling process and under neutron irradiation. The reaction products are undesirable from the standpoint of nuclear power because they help increasing the chemical interaction layer, since it has low thermal conductivity. This situation may cause structural failure (swelling) in the fuel element in operation (3).

This interaction in the system U-Mo/Al is due to interdiffusion between Al and the region of U-Mo, forming reaction products (6). This interaction is prone to happen at in-pile experiments in research reactors (7). The thermal experiments are normally carried out below γ-phase temperature formation to simulate the interdiffusion and phases formation in U-Mo-Al (8). The more frequently observed phases have been $(U,Mo)Al_2$, $(U,Mo)Al_3$ $(U,Mo)AL_4$ (6).

Ryu et al (9) simulated heat-treated growth-layer interaction in U-10Mo/Al fuel dispersion and found that the growth rate of these layers had activation energy for the constituent UAl_3 in the range of 277-316 kJ/mol. With treatments of 550°C during 40h, the interdiffusion pair showed 3 levels and range of interaction layer, building up in aluminum towards the U-10Mo alloy. This layer had a depth of approximately 500 µm, displaying the UAl_3 (exper. 77.5 at%Al) as the most structured one (>400 µm) towards the center of U-10Mo alloy. Near the contact region, there were 2 other layers (~50 µm each), having 81.6 at%Al (UAl_4) and 88.3 at%Al respectively.

Figure 1 – Uranium ingot, Molybdenum cylinders and Zirconia crucible.

Figure 2 – U-10Mo alloy

Mirandou et al. (10) studied thermal treatments at 580°C in couples of U-7Mo/Al using optical microscopy and SEM. The thermal interdiffusion at 580°C promoted the formation of $(U,Mo)Al_3$, $(U, Mo)AL_4$ reaction products. It was also observed a very thin layer near the side of Al as $Al_{20}UMo_2$, which might be the contact phase (3rd layer) of RYU's work commented above. During decomposition of γ (U, Mo), XRD revealed phases in reaction layer as being (U, Mo)Al_3, $U_6Mo_4Al_{43}$, γ (U, Mo) and α (U), Mirandou et al. (11) (10), studying pairs U-7Mo/Al-6061 and U-7Mo/Al-A356 at 550°C and 340°C, confirmed the presence of Si-phases (U_3Si_5). The interaction layer depth in this work had just few micrometers accounted to a probable participation with Si diffusion. Al-Si stable alloys are formed and hindered substantially the evolution of aluminum interdiffusion into the U-Mo structure.

In the present study, it was chosen the U-10Mo alloy to have most of the structure made of γ-phase, since this phase has low α-phase formation, with metastable γ-phase quite stabilized by Mo-content (3). The main aim was to use the aluminum alloy AA1050, which is one of the possibilities to fabricate MTR fuel plates. In this way, preparing the interdifusion pair by encapsulation and hot rolling of U-10Mo/AA1050, using hot rolling process temperature (540-550°C). In this context, it is feasible to check how far the chemical interaction would happen in practical fuel fabrication.

EXPERIMENTAL

To produce U-10wt% Mo, it was used natural uranium metal produced by IPEN’s magnesiothermic process (12). The uranium ingot, with the composition in Table 1, was pickled with nitric acid (65%). Stoichiometric amount of Mo was added as cylinders (3.175 x 3.175 mm) produced by Alpha Aesar (purity 99.95%). The mixture (U + Mo) was loaded in a zirconia crucible and the melting was performed in an induction furnace (ELATEC 15KW). The set of melting is shown in Figure 1. Before induction, 3-cycles of vacuum and purging argon (4.8) were made. Finally, the melting was made under 2.0x10^2 mbar (argon atmosphere). A U-10Mo ingot was produced with density of 16.80 g/cm^3, as shown in Figure 2. A homogenization heat treatment 1000°C during 72h was made in the U-10Mo alloy to ensure better compositional variation in metastable γ-phase in U-10Mo. This treatment was made inside a sealed retort of SS310 stainless steel with continuous 1 L/min flow of argon at 2.45 Bar. After annealing, the retort was removed from the oven and kept until reaching room temperature.

Table 1 - Raw Materials to prepare the interdiffusion pairs of U-Mo/AA1050

	Uranium	**U-10Mo**	**AA1050**
Elem.	**µg g^{-1}**	**µg g^{-1}**	**g g^{-1}**
Al	110 ± 3	90,5 ± 2,7	99,4 ± 0,1
B	< 0,4	< 0,4	
Ba	< 0,2	1,34 ± 0,16	
C	0.11%	0.09%	
Ca	6,0 ± 1,4	55,3 ± 5,6	
Cd	< 0,10	3,75 ± 0,01	
Co	0,60 ± 0,02	3,71 ± 0,02	
Cr	17,2 ± 0,5	43,5 ± 5,3	
Cu	20,3 ± 0,6	79,2 ± 0,2	0,033 ± 0,003
Fe	423 ± 17	579 ± 9	0,27 ± 0,03
Ga			< 0,01
Li	< 0,1	< 0,1	
Mg	5,17 ± 0,15	11,5 ± 1,6	< 0,01
Mn	196 ± 5	228 ± 7	< 0,01
Mo	< 3,0	9.74 g g-1	
Ni	73,0 ± 2,2	75,8 ± 1,4	< 0,01
Pb	< 6,0	< 6,0	
S			0,031 ± 0,002
Si	36,4 ± 1,9	500 ± 10	0,20 ± 0,07
Sn	11,1 ± 2,5	216 ± 18	
Ti			< 0,01
U	Balance	Balance	
V	0,80 ± 0,21	10,1 ± 0,2	
Zn	1,64 ± 0,28	<1,0	< 0,01

Table 2 - Sample heat treatments to simulate IL formation

Samples Id	**Time (min)**	**Temperature (^{0}C)**
PL (1A)	4800	550
PL (1B)	2400	550
PL (2A)	300	550
PL (2B)	2400	150
PL (3)	15	540

To prepare the diffusion pairs of U-10Mo/AA1050, the samples U-10Mo were cut in tablet format using diamond wheel cutter, followed by metallographic preparation of interfaces for contact with the aluminum in the diffusion couples. The tablets were polished by diamond paste of 3 μm.

To accommodate the tablets inside AA1050 matrix, a square hole was milled to contain the tablet. Possible oxide formation was avoided by pickling with nitric acid (65%). AA1050 was blasted and pickled with NaOH, followed by passivation with nitric acid. The sets were welded and received a first cold rolling pass to guarantee a proper contact between the tablet and AA1050 set. Then, a full welding around of aluminum set was made before hot rolling. The set was then heated at 540°C during 15 minutes before being hot rolled. The hot rolling reduced the set thickness by 38% with a single pass. Then, the interdiffusion pair has been formed. The final thickness of the plate was 7.35 ± 0.01 mm. The samples were identified and cut by guillotine. X-ray images were taken to guide the pairs positioning. The hot rolling fabrication had no losses. The SEM in Figure 6 (a) shows how perfect was the interdiffusion line formed.

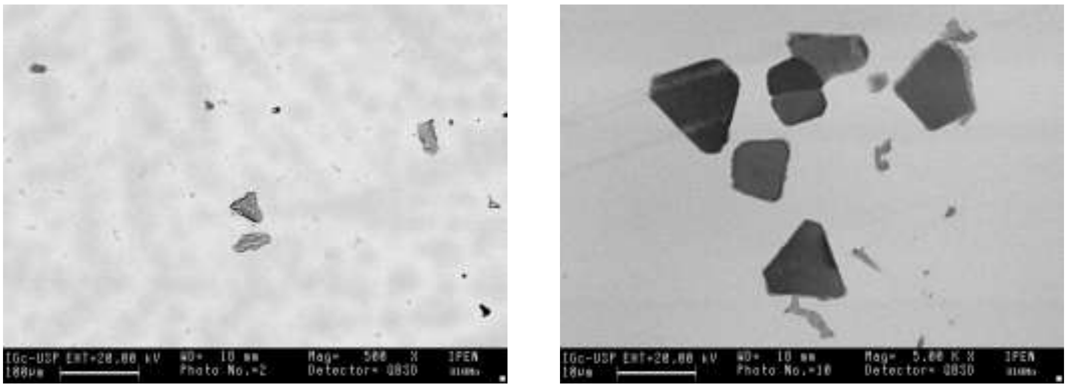
The heat treatment of diffusion couples was made in a resistance furnace with no atmosphere conditioning. These treatments are listed in Table 2. The cooling of the samples were performed placing the sets outside the oven and let them reach room temperature.

The microstructures of the samples were observed with optical microscopy (OM) and scanning electron microscopy (SEM JXA system Jedle 6400). Chemical microanalysis was performed by energy dispersive spectroscopy (EDS) device attached to the SEM. The diffraction of X-rays was analyzed in a Rigato Multiflex diffractometer (CuKα 1.54056 Å). The raw materials and the U-10Mo sample were characterized by chemical analysis, by infrared techniques, ICP-OES, X-ray fluorescence spectrometry and gravimetry.

RESULTS AND DISCUSSION

The chemical analyses of the uranium and the aluminum alloy AA1050 brought many constituents to the system of interdiffusion analysis. Since the literature cogitates that silicon hinders the interdiffusion between aluminum and U-Mo pairs, it was the most studied in this work.

Microstructures of U-10Mo alloy prior to heat treatment are shown in Figure 3(a) and (b).



(a) (b)

Figure 3 – (a) U-10Mo as cast (b) Region magnification with α-phase

In these micrographs, there are punctual regions rich in α-phase. As noted in SEM/EDS, these regions have higher content of U and absence of Mo. This rich region of α-phase probably was found to be associated with carbides and oxides of uranium. The surrounding material is γ-phase (U, Mo) (light area). This phase, as seen in Figure 3(a), revealed a dendritic formation during peritectic solidification of γ-phase. The difference in composition of (U, Mo), estimated qualitatively by EDS, was approximately 1 at% U inside this structure. Trying to homogenize this phase, it was performed a heat treatment at 1000°C during 72h.

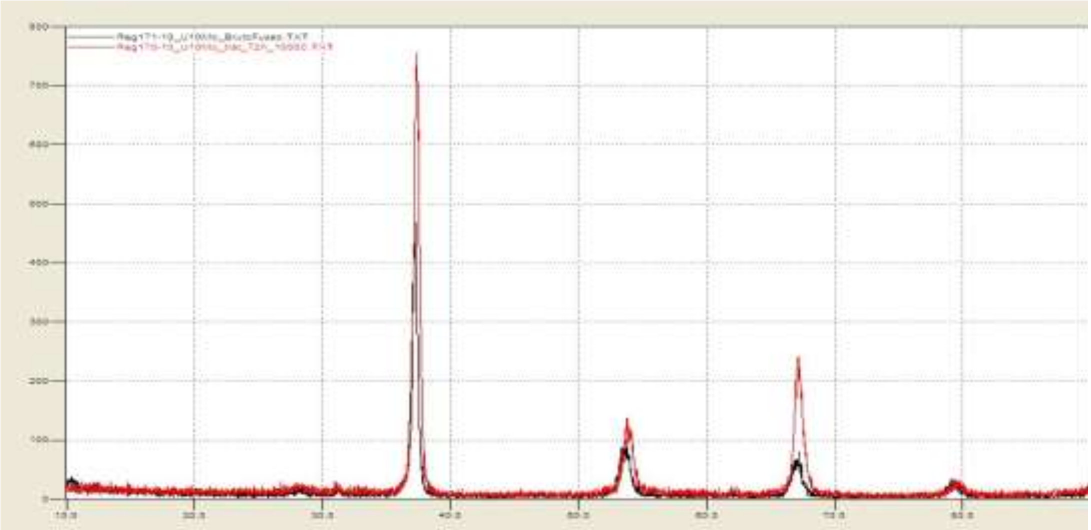


Figure 4 – Xray diffraction pattern showing the as cast (black shaded) U-10Mo and the treated one at 1000°C during 72h (line)

The XRD showed a better definition for the treated U-10Mo peaks, as shown in Figure 4 . As could be seen, the main diffraction peaks became narrower and moved to the right revealing a better defined interplanar structure. It is reasonable to say that there was an atomic rearrangement in U-10Mo structure reducing crystalline imperfections. Seong et al. (13) suggested, by means of neutron diffraction, that the formed phase in U-10Mo is metastable ordered structure U_3Mo with characteristics of the space group P-4m2 (115 *tetragonal*: a = b = 4.8305 Å, c = 3.418 Å). Nevertheless, Sinha et al. (14) showed recently a XRD studies suggesting this phase as being cubic. The presented XRD peaks at Figure 4 were much closed to the diffractogram for U-10Mo.

The analysis of heat treated samples allowed preliminary evaluation of the interdiffusion of Al in the area of U-10Mo alloy. The resulting structure revealed a layer of chemical interaction between the phases and AA1050/γ (U, Mo), but different from the expected one described in the literature.

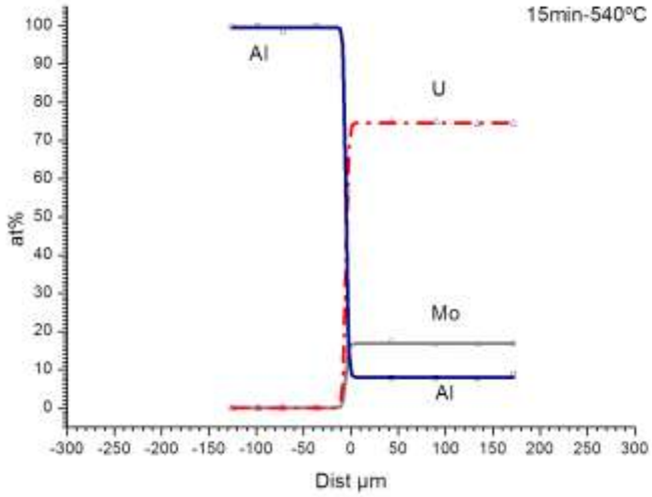
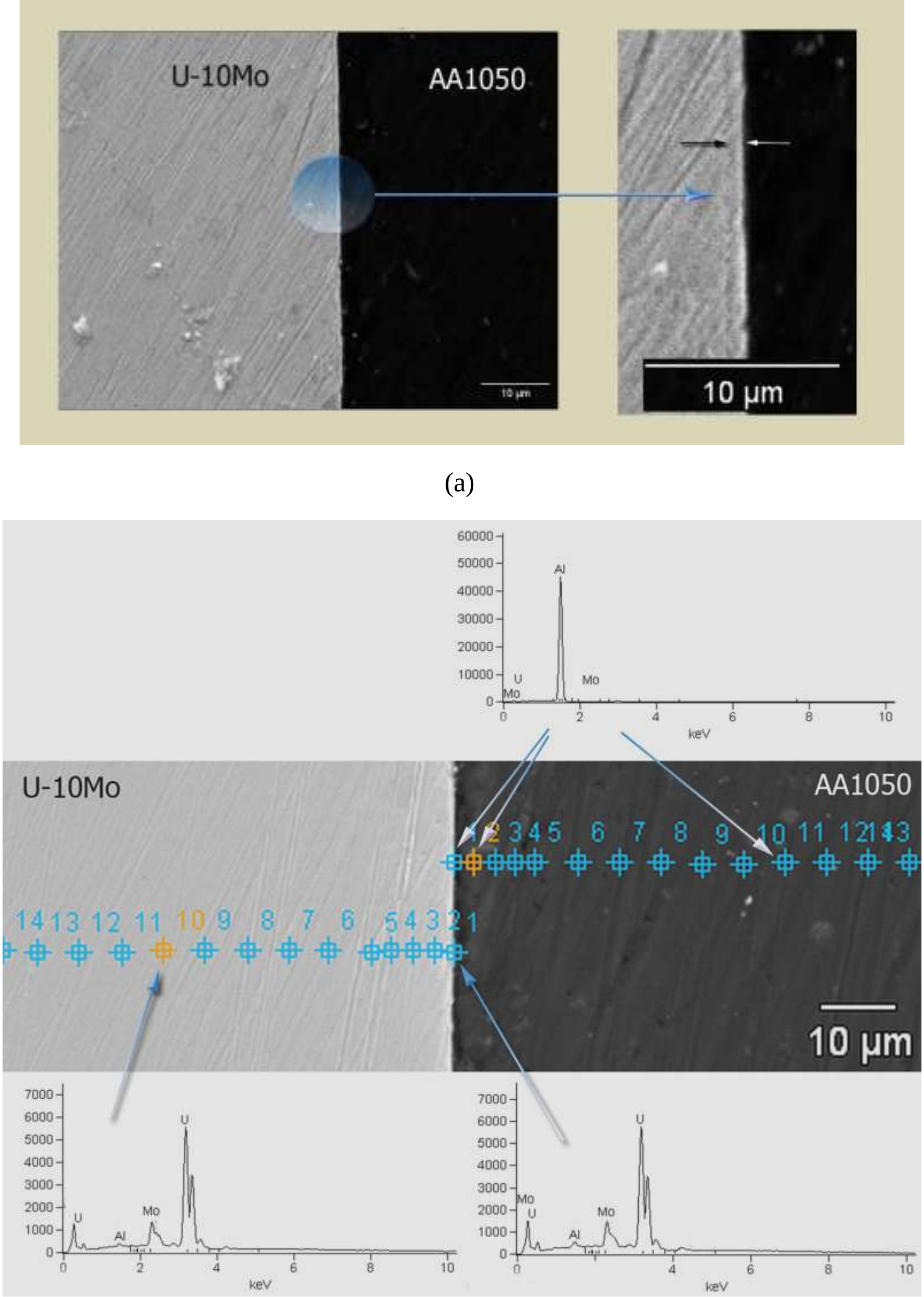


Figure 5 – Interdiffusion curves for U, Al and Si after soaking for 15min at 540°C

The heating of 15min at 540°C for hot rolling the samples showed to be very significant. This sample preparation was sufficient to promote a rapid evolution in aluminum diffusion inside U-10Mo, as shown in Figure 5. In this short soaking time, the aluminum diffusion towards the alloy reached a fixed amount of ~8 at% Al until approx. 200 µm inside U-10Mo region. Probably, Al easily formed solid solution inside the U-Mo, occupying the structure sites very swiftly, with no major structure changes. EDS analysis detected that the Al content, within this soaking time, reached 2at%Al at sample center (approx.1000 µm from interface). By the way, this hot rolled sample preparation roughly simulated the first reduction pass in hot rolling of fuel plate. A complete set of rolling passes for MTR plate would require 10 passes of hot rolling that would be equivalent to approx. 150 min of soaking at 540°C, allowing more exposition for happening the interdiffusion phenomena.

Nevertheless, the heating treatments at 550°C and higher heating time (5h, 40h and 80h) did not reproduced a similar continuous raise of Al contents as would be forecast. With longer periods of soaking, it was observed that the level of aluminum did not surpass the level of 8 at% reached at few minutes of high temperature heating. The apparent change was the thickness increasing of this fixed Al amount towards the U-Mo region bulk.

The only real difference in aluminum concentration occurred very near to the interdiffusion interface that separated the U-Mo from the matrix. After 80 hours soaking, the interdiffusion sample at 550°C, as could be seen in Figure 6, showed a very thin region (~ 1 µm), where Al reached an amount of 11 at% in average by means of qualitative EDS measurements. This amount is not far beyond the 8 at%Al found just ahead of it in the same sample, which stayed constant until the sample center.



(a)

(b)

Figure 6 – Interdiffusion pair U-10Mo/AA1050 after heat treatment of 80h at 550°C. (a) General view and magnification at right side showing the interaction layer; (b) EDS analisys of the same sample.

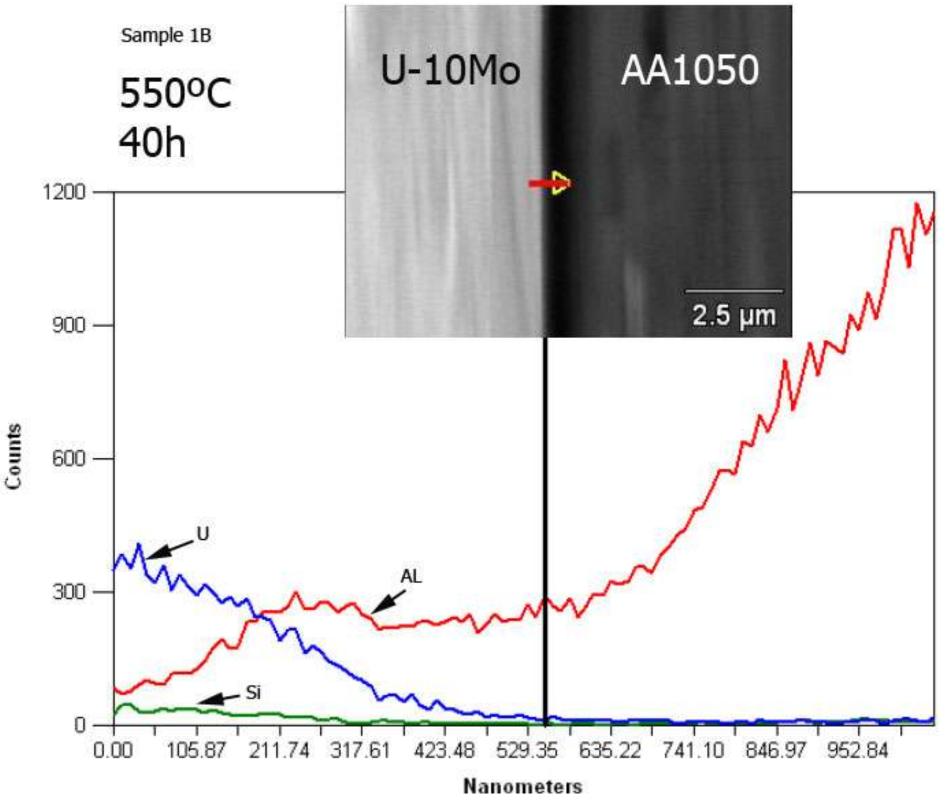


Figure 7 – EDS profile line showing U, Al and Si lines

To understand better this area around the interface, it was made an EDS line profile, as shown in Figure 7. The curves, in the range of 1 µm, showed the evolution of Al, U, Si contents after heat treatment of the couple at 40h at 550°C. They displayed an evolution that confirms qualitatively the EDS data in Figure 6. A smaller IL of with 400-500 nanometers presented a plateau of Al-content. This IL, if compared to heat treatment of 80h at 550°C, had an IL thickness roughly doubled.

Comparing these results with Ryu's (9), it is possible to say that the present study did not show an intense Al-interdiffusion inside U-10Mo, as expected. A probable explanation for this, it would be an interference of another solid solution element, since the Ryu's Al-matrix dealt with pure aluminum and in the present case it was used AA1050.

As an evidence for this, it may be noticed that Si-content consistently increased from the interface towards U-10Mo bulk, as shown in Figure 7. In the graph, there was a clear plateau of Al-content in a region of 500 nanometers, which decreased while Si and U-content increased. This raise could be associated with a barrier formation creating difficulty to Al-diffusion. Mirandou's results (11) emphasized Al diffusion difficulty with silicon presence with the happening of its solid state reactions. Nevertheless, no proper U-Al or (U,Mo)-Al could be suggested, since the IL formation was found to be very insipient in Al-content for the formation of any known phase.

XRD spectra was collimated inside U-10Mo region near the interface plane and showed relevant results, as presented in Figure 8. It could be noticed a possible evolution of the original spectrum (Figure 4) towards some disturbance in the diffractograms after being treated for diffusion. It is clear the appearance of Al peaks and a possible product containing Si. Exploring the PDF cards, a potential candidate appeared as an Al-Si intermetallic product $Al_{3.21}Si_{0.47}$ (PDF#41-1222). Figure 8(e) shows a detail of Figure 8(d) illustrating the evidence of the 100% intensity peak of $Al_{3.21}Si_{0.47}$ beside the pure Al peak. Figure 8(f) presents the XRD peaks Al-Si phase, which are very close to Al peaks, but always displaced rightwards. Comparing the 2θ angles with the XRD spectra of treated pairs, it may be seen that this phase appeared to reveal its participation during all stages of heat treatment.

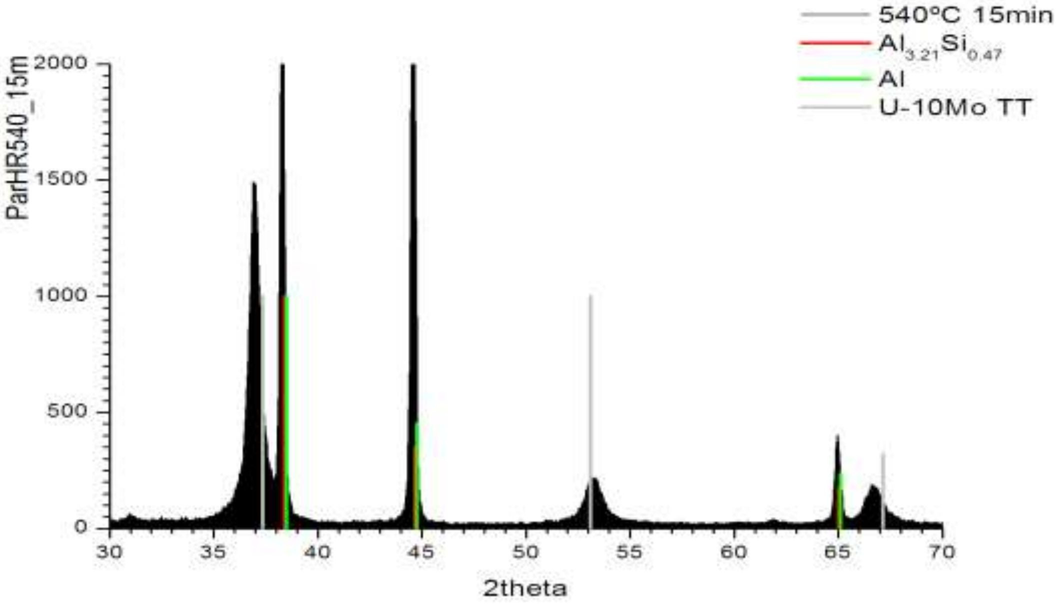


Figure 8(a) Hot Rolling Sample Preparation 540°C for 15min

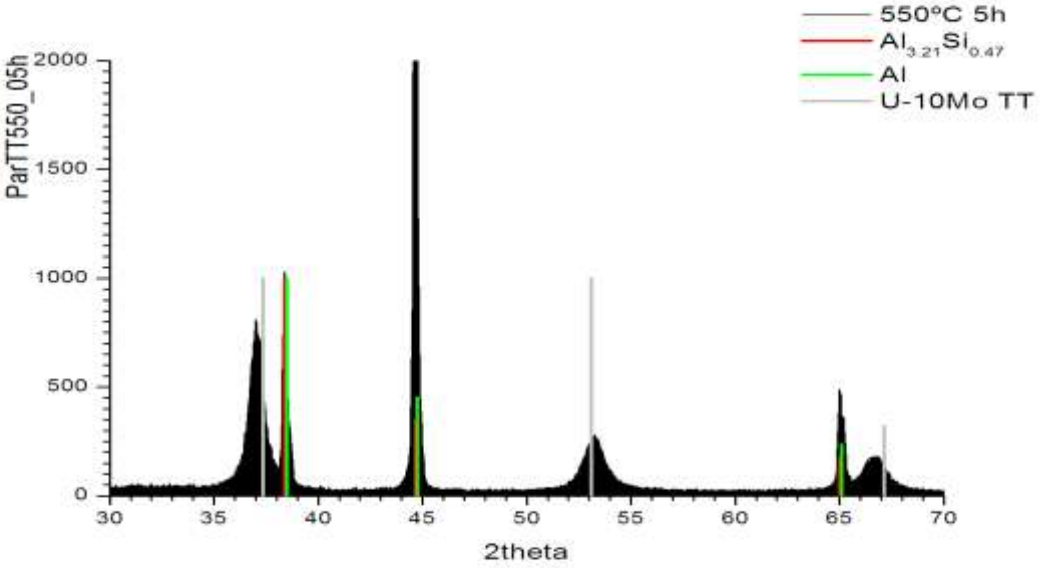


Figure 8 (b) Heating Treatment at 550°C for 5 h

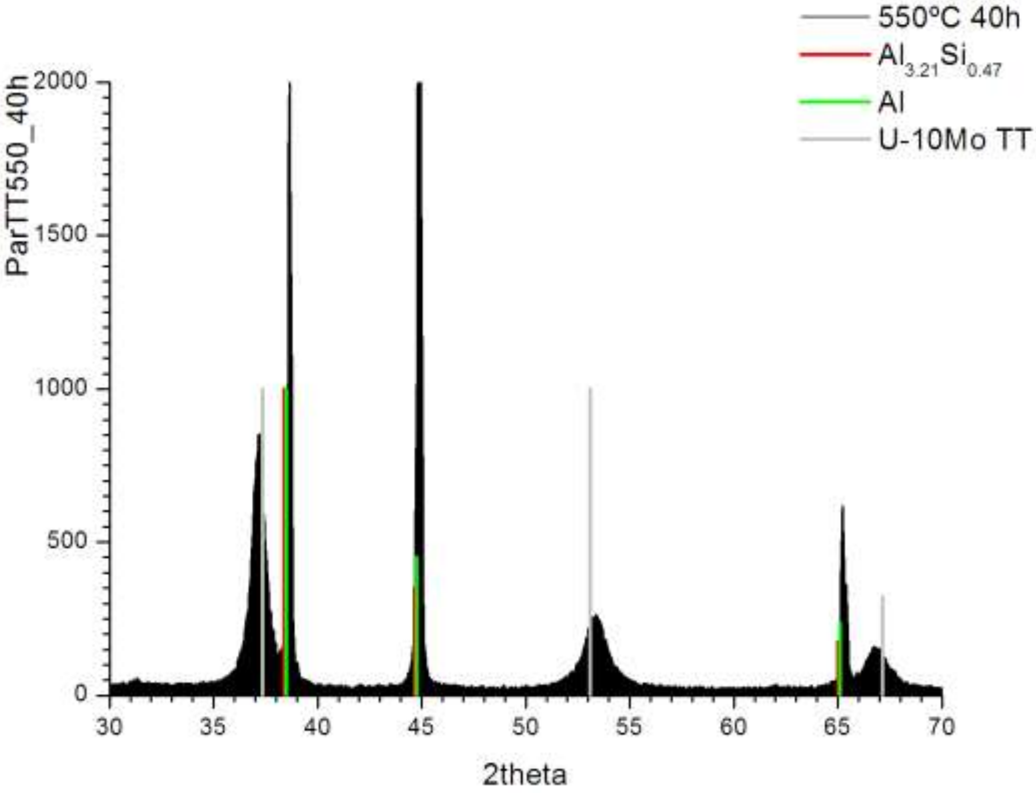


Figure 8 (c) Heating Treatment at 550°C for 40 h

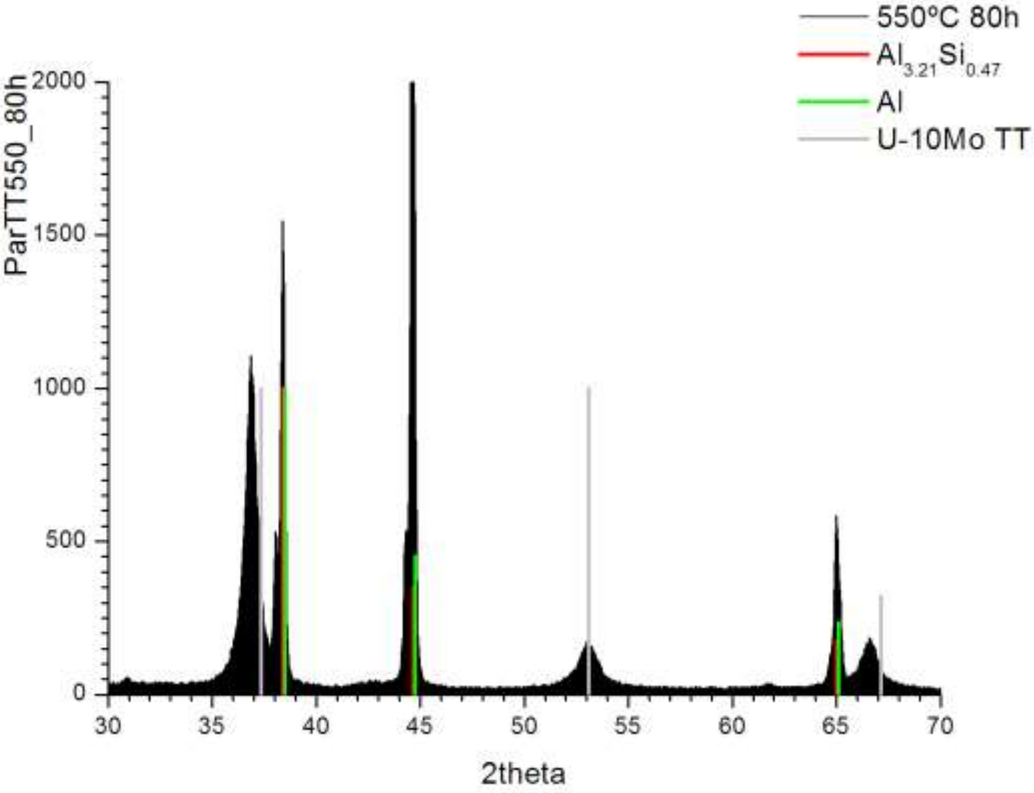


Figure 8 (d) Heat Treatment at 550°C for 80h

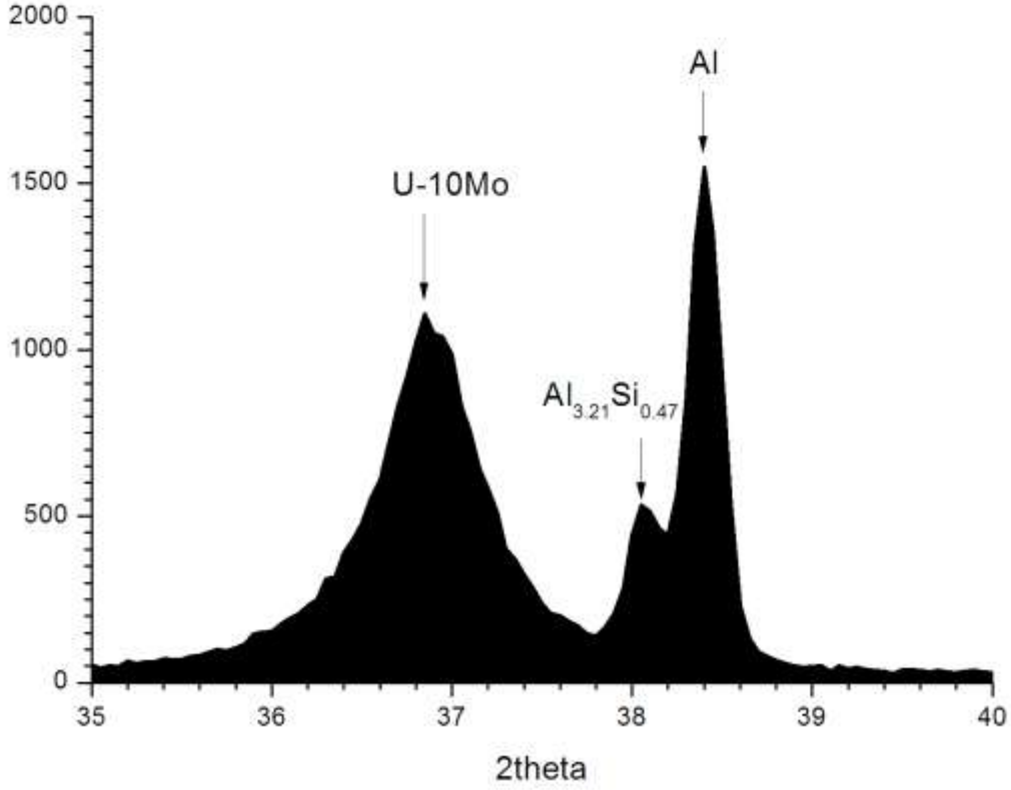
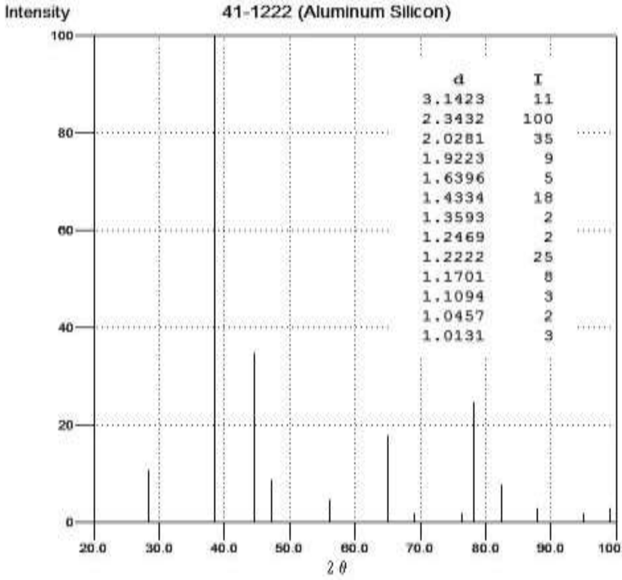


Figure 8 **(e) Detail of $Al_{3.21}Si_{0.47}$ Peak from diffractogram 8d**



d	I
3.1423	11
2.3432	100
2.0281	35
1.9223	9
1.6396	5
1.4334	18
1.3593	2
1.2469	2
1.2222	25
1.1701	8
1.1094	3
1.0457	2
1.0131	3

Figure 8 **(f) [PDF 41-1222] Peaks of $Al_{3.21}Si_{0.47}$**

Figure 8 – XRD spectra inside U-10Mo area near interface plane for original alloy and the heat treated: (a) Heating at 540°C during 15min; (b)-(d) Heat Treatment at 550°C during 5h, 40h and 80h (e) XRD peaks for the intermetallic $Al_{3.21}Si_{0.47}$

A possible evolution of the participation during heat treatment soaking time is shown in Figure 9. As could be seen, there is a movement around the 2θ=38.40°, which is the characteristic angle with maximum intensity in the XR-spectrum of $Al_{3.21}Si_{0.47}$. It should be emphasized that this angle did not appear in the original U-10Mo before the pairs were treated.

In Figure 9, the displayed intensities are probably only due to Al + Al-Si products. The 15 min treatment peak showed Al+Al-Si structure as having the largest cell parameter (higher interplanar distance). This peak moved rightwards as the residence time became 5h and moved further with 40h treatment. Between 40h and 80h the movement was backwards and displaying a “shoulder” in the left side of the curve, accounted to be a settling of $Al_{3.21}Si_{0.47}$ structure. This phase formation probably made a potential coherent arrangement with U-10Mo structure. We impute this Al-Si phase formation as the blocking agent impeding futher aluminum diffusion towards U-10Mo bulk.

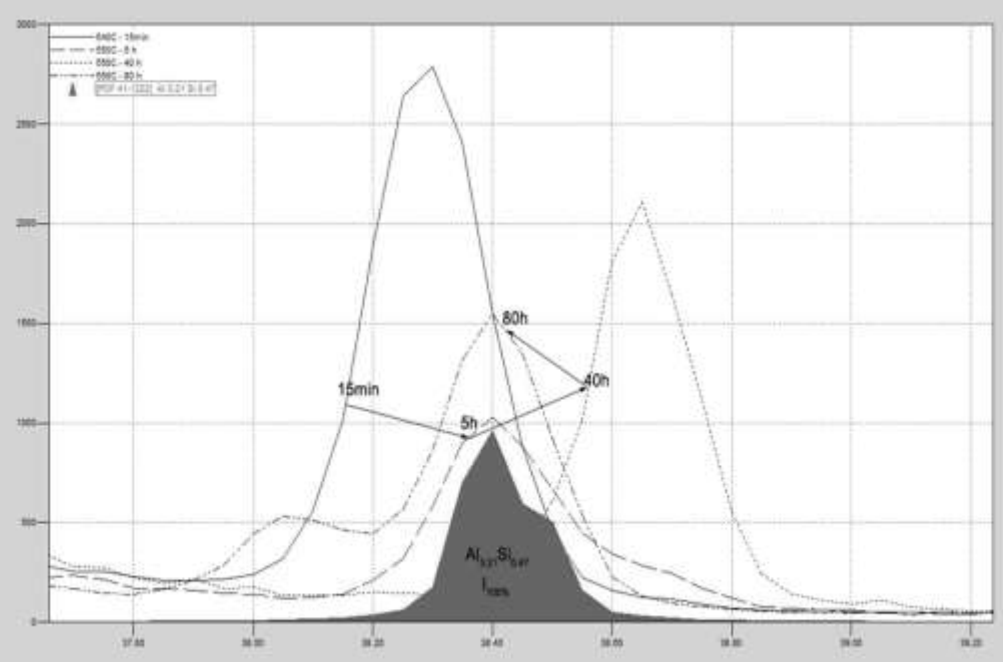


Figure 9 - Evolution of 2θ=38.40° (simulated 100% intensity peak for $Al_{3.21}Si_{0.47}$) in heat treated pairs during the several soaking times at 550°C

CONCLUSIONS

The produced alloy was basically U-10Mo, with cubic structure γ (U, Mo) with less than 1 vol% of α-phase. The structure changed slightly after heat treatment 1000°C during 72h.

The technique of assembling interdiffusion pair by hot rolling method produced good and regular interface for interdiffusion studies. It also simulated adequately a hot rolling pass in production of monolithic MTR fuel using U-10Mo with AA1050 as matrix .

The sample preparation by hot rolling had 15 minutes of soaking time at 540°C. This conditioning was enough for a rapid Al-diffusion inside U-10Mo structure, sufficient to reach steadily 8at% Al until 200 µm from interdiffusion interface and 2 at% Al at

1000 µm. Longer soaking time of interdiffusion pairs, up to 80h at 550°C revealed some composition variation of U, Mo, Al in approx. 1 µm region close to interface plane. No proper phases of U-Mo/Al were identified. As AA1050 have 0.25wt%Si, probably, there was only Al solid solution inside U-10Mo within U-Mo bulk. This experimentation showed that interaction layer between U-10Mo/AA1050 was highly hindered. Silicon had co-diffusion with Al, limited to few micrometers near the diffusion interface. XRD spectra suggested that in this area might have formed an intermetallic $Al_{3.21}Si_{0.47}$ structure, associated with insipient Al diffusion, inside the U-10Mo, which may explain the hindrance of further Al-interdiffusion in the pair U-10Mo/AA1050.

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