

Thermal Interdiffusion Products of U-10Mo in Al Matrix

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Abstract. New nuclear fuel material with high density in uranium is envisaged for intense irradiation research reactors. The alloy U-Mo has been researched as a feasible candidate to be used in such reactors. This nuclear fuel is conceived to be used encapsulated in aluminum matrix. Nevertheless, there are interaction products of U-Mo/Al which form porosity during irradiation, leading to routine operation harms in research reactors. This interaction is due to solid solution interdiffusion of species, mainly of Al towards U-Mo region forming reaction products. This interaction could be studied by on-pile method, observing the occurrence of formed products during irradiation, but this method is costly and used only for long term experiments in very few reactors in the world. For this, several out-of-pile studies using heat treatments of diffusion pairs are carried out at adequate temperatures and times, just below the γ -phase eutectoid temperature to simulating the interdiffusion and formation U-Mo-Al phases. In the present study, it was employed a new developed assembling method to prepare interdiffusion pairs by immersing sliced U-10Mo sticks inside molten Al. These samples are made by induction furnace, in temperature range ~660-670 °C, under controlled argon atmosphere, in order to entrap molten Al around U-Mo sticks and so keeping this entangled structure after solidification. The interdiffusion pairs are then cut and prepared for treatments. This novel sample preparation guarantees full contact between the U-Mo and Al without oxidation contact, creating so, the ideal conditions for interdiffusion investigation of the interfaces of Al/U-Mo. Preliminary results to study interaction products were achieved by heat treatments during 5h at 550°C. Observations and calculations from SEM/EDS microstructures and XRD diffractograms revealed few microns interaction layer between the matrix and the fuel material, resembling phases reported in the literature for the interaction products between U-Mo-Al. This layer is mainly composed by Al and U, Mo phases, probably (U, Mo)Al₃ and phases containing Si, as U₃Si₅ and a proposed one Al₂Si₃U₃ that fits better to XRD spectrum of experimented diffusion pairs.

Introduction

Since the years 80's, the program RERTR of USA-DOE has encouraged the use of low enriched uranium (LEU, ²³⁵U < 20 at%) in fuels for research reactor worldwide. The necessity to use lower ²³⁵U enrichment on conversion to LEU imposed the increasing of the total density of uranium atoms in the fuel consequently [1,2]. A possible route for reactor conversion from higher enrichment to LEU fuel is to use standard fabrication technology and the fuel geometry already

being used in commercial fabrication processes to make LEU fuel in the same external configuration as used for the fuels being fabricated. The rolling process, used to make plate-type fuel, has been shown to be suitable for producing dispersions with fuel particle volume loading up to approximately 55 vol.% [3]. Other methods, such as extrusion, would be limited to lower volume levels [4].

Metallic uranium alloys are the only possible materials having potentiality to be used as fuel phase in high-density LEU dispersion fuels for high power research reactors. In order to meet fissile atom density requirements at a fuel particle volume fraction, many studies have been carried out with uranium alloys, as U_xMe , where Me could be Fe, Mn, Mo, Zr, etc [1]. These studies showed that γ -stable (cubic crystal structure) metallic fuels are more resistant to swelling than α -uranium-based (orthorhombic crystal structure) fuels under low burn-up, at high-temperature irradiation conditions. The phase γ U is not thermodynamically stable under the fabrication and aimed irradiation conditions, however some alloys of uranium can remain in the γ -phase in a metastable state indefinitely at room temperature, and for long periods of time at elevated temperature. Of particular interest are the alloys U–Mo and U–Zr–Nb. Aluminum-clad dispersion fuels in some reactors routinely attain 80% peak ^{235}U burn-up. Peak fuel temperature in these applications is generally less than 523 K.

Meyer et al. [1] found, during irradiation at maximum burn-up of 70% ^{235}U at a temperature of approximately 65°C, that fuels with 6 wt% Mo or more performed well during irradiation, exhibiting low to moderate fuel/matrix interaction layer (IL) and stable fission gas bubble. Nevertheless, the swelling of fuel particles due to fission gas decreased as alloy content increased from 6 to 10 wt%Mo. The rate of fuel–matrix interaction increased when the molybdenum content was less than 8 wt%. The increasing rate of interaction layer thickness was approximately the same for both U–10Mo atomized as for the mechanical powder of the same composition. On the other side, fuel particles containing 4 wt% Mo reacted extensively with the matrix aluminum during fuel fabrication and irradiation. U–4Mo showed the growth of large fission gas bubbles by interlinking the smaller bubbles formed with the extensive fuel–matrix interaction leading to inter-particle contact. These behaviors increased the likelihood for the occurrence of breakaway swelling.

Ryu et al [5] simulated thermally the growing of U–10Mo/Al IL in dispersion fuels and found that the growth rate of these layers had activation energy to grow UAl_3 alloys as the 277 to 316 kJ/mol. It was shown that the concentration profiles of reaction layers in U–10Mo displayed three layers of intermediate phase, which have an integrated interdiffusion coefficient for Al and for U in UAl_3 phase, which were larger than those for other phases and this diffusion coefficient increased with annealing time. An exothermic heat resulting from the reaction between U–Mo and Al was then observed. UAl_3 structured phase was characterized as a predominant phase during this heating at 700°C. Mirandou et al. [6] studied thermal treatments at 580°C of the reaction layer in couples U–7wt%Mo/Al using optical and scanning electron microscopy. It was found that when the U–7 wt%Mo alloy was previously homogenized at 1000°C had the $\gamma(\text{U}, \text{Mo})$ phase retained at room temperature. The further thermal treatments at 580°C promoted the formation of $(\text{U}, \text{Mo})\text{Al}_3$ and $(\text{U}, \text{Mo})\text{Al}_4$ were present in the interaction layer. It was also observed a very thin band near the Al side as a ternary compound $\text{Al}_{20}\text{UMo}_2$. When the decomposition of the $\gamma(\text{U}, \text{Mo})$ took place, a drastic change in the diffusion behavior was observed. The XRD analysis indicated the presence of phases of the following structures in the reaction layer: $(\text{U}, \text{Mo})\text{Al}_3$, $\text{Al}_{43}\text{U}_6\text{Mo}_4$, $\gamma(\text{U}, \text{Mo})$ and $\alpha(\text{U})$. Mirandou et al. [7, 8] studying the interaction layer of U-7%Mo and Al 6061 and Al A356 at 550°C and at 340°C found that a IL band confirmed the presence of phases as identified before, but with some differences accounted by silicon presence. The $\text{U}(\text{Al}, \text{Si})_3$ phase forms basically the IL, but when the decomposition of $\gamma(\text{U}, \text{Mo})$ occurs, then the formation of UAl_3 and $\text{Al}_{43}\text{U}_6\text{Mo}_4$ occurs. The existence of a defective U_3Si_5 seems to be important seed for the formed interaction.

In the present work, it is verified the necessity of annealing the raw material U-10Mo, just after casting, in order to prepare the diffusion pairs and also to identify the presence of possible compounds formed during heat treatment of U-10Mo with Al alloy containing 0.25%Si (Al 1050)

heated during 5h at 550°C, simulating so, the on-pile irradiation in intense neutronic bombarding conditions, as used in high performance research reactors.

Experimental Methods

U-10Mo Fabrication. To produce U-10wt%Mo, it was used metallic uranium produced by IPEN's magnesiothermic process [9]. The raw material was blended with stoichiometric quantities of molybdenum slug Alpha Aesar 99.95% (3.175 x 6.15mm pieces). The blend (U+Mo) was loaded in a zirconium crucible to produce the alloy U-10Mo. The melting was carried out in an induction furnace (ELATEC 15KW). Before inducting the charge, a 3-times cycle of Argon purge+vacuum was made, varying the pressure from 2.6×10^{-3} (max. vacuum) to 2.0×10^2 mbar. This final pressure was used during induction melting of the charge.

Interdiffusion Pairs. The alloy U-10Mo was removed from the furnace and treated in a soaking pit furnace at 1000°C for a period of 9 hours, inside a SS310 sealed tube, with continuous Ar flux (2.45 Bar; 1 Lmin^{-1}). The retort was then taken out of the furnace and the temperature drop was made by fluxing argon during 16 h until reaching the room temperature. All these treatments were carried out in order to establish more homogeneous phase $\gamma(\text{U, Mo})$. The piece of U-10Mo was then segmented in small sticks (2mm x 2mm x 20 mm) to prepare the diffusion pairs. The diffusion pairs were made by melting aluminum cuts (5mm x 10mm x 70mm) around 2 sticks of U-10Mo inside an alumina crucible. Both materials, aluminum and U-Mo sticks were pickled in nitric acid (65 vol%) for 2 min before loading the charge. The used aluminum was the alloy Al-1050 (99.08%Al, 0.40%Fe, 0.25%Si and other impurities less than 0.30%). The preparation of the furnace followed the same procedure was cited above. The melting temperature in the induction furnace was around 660°C. Once the molten aluminum was achieved, then the furnace was immediately switched off and the inductor was kept circulating water to speed up the cooling. The samples of the interdiffusion pairs were made by transversal cuttings (10mm x 10mm) of the ingot piece of Al+U-Mo sticks. In this work, two basic techniques to prepare the diffusion pairs are discussed: induction fusion of Al with prismatic sticks of U-Mo; introduction of U-Mo sticks into beveled Al piece by thermal interference method. All these materials were manipulated under controlled atmosphere with vacuum sealed ampoules containing the pairs. As expected, no visual alteration of the U-Mo sticks was observed by optical observation. This happened since the temperature to melt U-Mo alloys is much higher and the residence time of U-Mo sticks and Al melting was less than 15min until the Al got solidified and relatively cold ($< 150^\circ\text{C}$). After this, the diffusion pairs were cut from the ingot and encapsulated in glass tubes under argon atmosphere and treated during 5h at 550°C in a conventional reheating furnace.

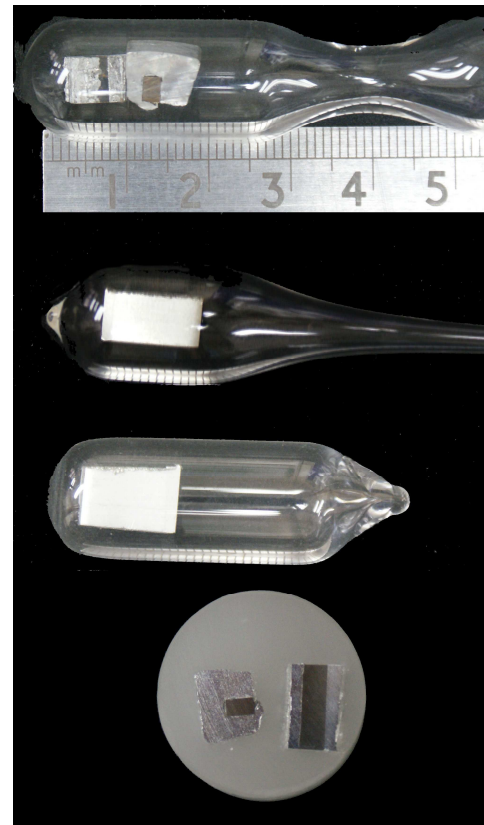


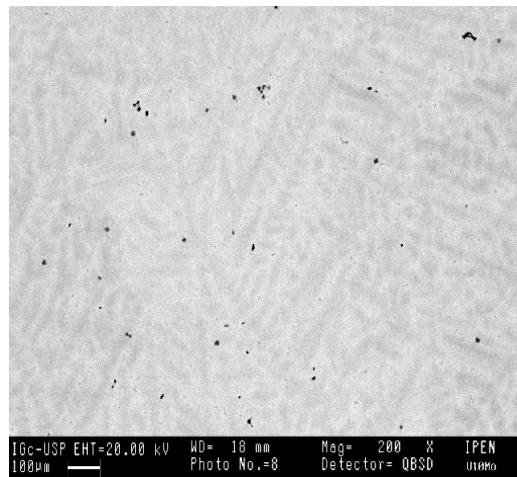
Figure 1 - Assemblings of interdiffusion pairs produced by Al-melting and by thermal interference methods

Metallographic and XRD Analysis. The samples microstructures were observed with optical (OM) and scanning electron microscopes, a SEM/EDS System JXA 6400 JEDL. The chemical analysis was performed by an energy dispersion spectroscopy (EDS) device attached to the SEM. X-ray

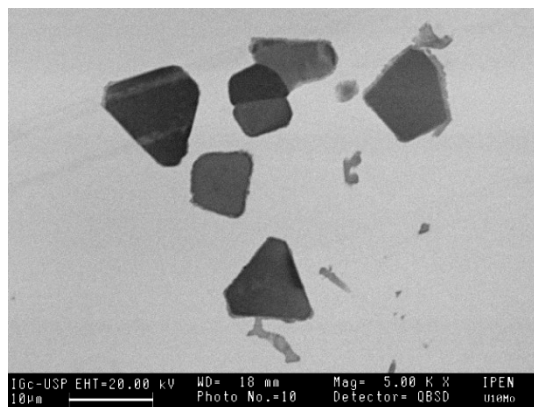
diffraction analysis, made over the treated and untreated surfaces of the samples, were performed with $\text{CuK}\alpha$ ($\lambda=1.54056 \text{ \AA}$) radiation in a monochromatic Rigato Multiflex. This technique was used to identify and roughly qualify the phases present in each state.

Results and Analysis

The microstructures before heat treatment are displayed in figure 2a and b. As could be seen in raw structure in figure 2a, it contains spots of α -phase, as U was the major element found in EDS and no Mo was found at this spots. This phase, as evaluated by quantitative metallography, was present in less than 1% in volume. A better displayed of α -phase rich region is seen in figure 2b. The surrounding material is $\gamma(\text{U, Mo})$ phase (lighter area). This phase was also properly identified by SEM/EDS. Inside the broader light area, it can be noticed a fading gray structure revealing dendrite formation, that shows the remaining liquid, during cooling. The difference in composition inside $\gamma(\text{U, Mo})$ area is around 1 at% of U. To avoid this composition difference at the same phase, it was carried out a 9-hour heat treatment at 1000°C , which showed effective changes as presented in the XRD diffractogram shown in figure 3. This spectrum displays the results of raw molten material and the treated one, side by side, and the comparison of the spectra of UMo_2 (tetragonal $I4/mmm - a=3.437; c=9.834; Z=2$) and γU (cubic $Im-3m - a=3.5420\text{\AA}; Z=2$). These 2 structures represent references of possible extreme structures of the potential microstructure that was produced during the annealing at 1000°C for 9 hours.



(a)



(b)

Figura 2 (a) Non treated microstructure of U-10Mo (b) α -phase magnified

RXD of this material before and after heat treatment is indicated in figure 3 and showed that the material did not differ much in phases. Nevertheless, the shape of peaks revealed relevant changes. It may be noticed that the wider peaks of raw U-10Mo after the treatment became thinner and higher and moved towards the right direction, probably due to the incorporation of Mo-atoms in the cubic lattice of γ (U, Mo) phase. This indicates that the interspaces between the crystallization planes approached to a more defined and stable structure. It is fair to say that U-Mo atoms reduced the crystal imperfections and vacancies due to a probable short distance interdiffusion, which finally homogenized the final structure.

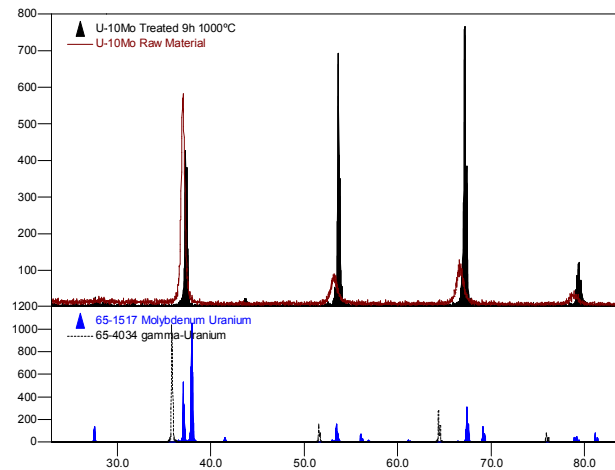


Figure 3 - Diffractogram of raw molten U-10Mo and treated at 1000°C during 9h. UMo₂ and γ -U are also shown as references.

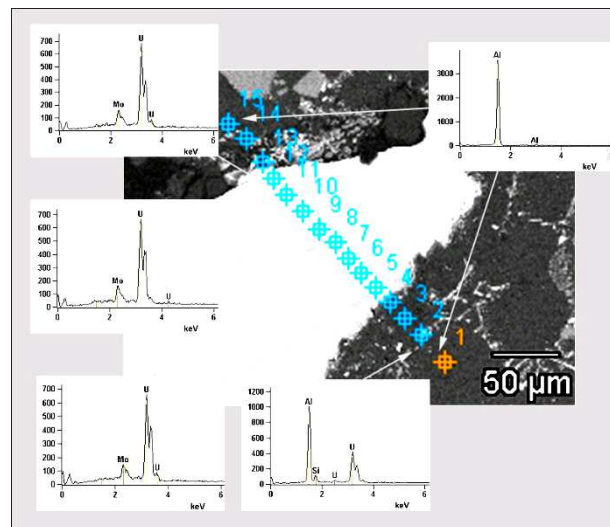


Figure 4 - SEM and EDS measurements of U-10Mo surrounded by Al and Al-(U,Mo) subproducts forming the interaction layer. Between the marks 2 and 4 presumably is the region of subproducts in a band around 50 μ m

When the diffusion pair was subject to 5h annealing at 550°C, the resulting structure displayed an image revealing the interaction layer between Al and (U, Mo) phases as could be seen in figure 4. It is interesting to notice the presence of Si in the IL region. This presence is accounted as originated from the alloy Al-1050 that has 0.25%Si. This influence has been apparent and communicated in the literature [7], that Al containing Si, as Al-6061 (0.6wt%Si) could lead to the formation of silicide in the IL at Al-side limit during diffusion of Al inside γ (U, Mo) phase. The suggested phase was U₃Si₅, but other phases were said that could be possible in an open range of U(Al,Si)₃.

The treated material in the present work had a rather complex structure and many possibilities have shown up. An XRD was made from this region, shown in the figure 5. This panel is a rough tentative to suggest sub-products in this region, which are shown in the diagram. Initially, it should be said that the diagram displayed a large background (detached from the presented XRD), but suggesting that some amorphous material is present in the region, probably glassy material. It also reveals higher degree of defective arrangement in atomic scale, due to displacement of peaks. Doing some searches in XDR-files, some compositions could be seen as present in this interaction layer as UAl_4 or $U_6Mo_4Al_{43}$ as already suggested by Mirandou et al. [6-9]. Additionally, it was also suggested that the formed phase containing Si could be present as U_3Si_5 , but searching the files to fit in XDR spectrum of figure 4, it can be seen that U_3Si_5 fits in some peaks, but not so intensively.

It was also found that the phase $Al_2Si_3U_3$ fitted better than U_3Si_5 . It is fair to say that Al and Si being neighbor atoms in periodic table and have close atomic radii. So, they are atoms easily interchangeable in an Al-Si structure and could make better links with either sides of the diffusion pair, to Al-side and (U,Mo)-side. So, as whole, it is possible to think that $(Al,Si)_xU_3$ phases are feasible to be present in this type of structure. As stated in the Mirandou's works [6-9] the U_3Si_5 was found precisely defined in treatments during more than >600h at 340°C. Compared to this work, the presented tested material has just 5h at 550°C, accounted to be in an intermediate stage, with a rather complex structure.

Conclusions

The alloy U-10Mo is basically $\gamma(U, Mo)$ with less than 1% in volume of α -phase rich region. As shown in the XRD of raw and treated material, the as-cast alloy should undergo a heat treatment at γ -phase temperature 1000°C, during several hours in order to establish a more defined structure for $\gamma(U, Mo)$ to be used as diffusion pair for studies of interaction layer. From the annealing experiment with a U-10Mo/Al treated during 5h at 550°C, it is noticeable the formation of several products of (U,Mo), Al, Si due to diffusion and solid state reaction in the interaction layer in a still ongoing structure formation. Nevertheless, the formed interaction layer is mainly composed of phases with Al and U,Mo, probably $(U,Mo)Al_3$ and phases containing Si, such as U_3Si_5 . Additionally, it was proposed the presence of $Al_2Si_3U_3$, not yet cited in the literature since it fitted well to XRD spectrum of experienced diffusion pair.

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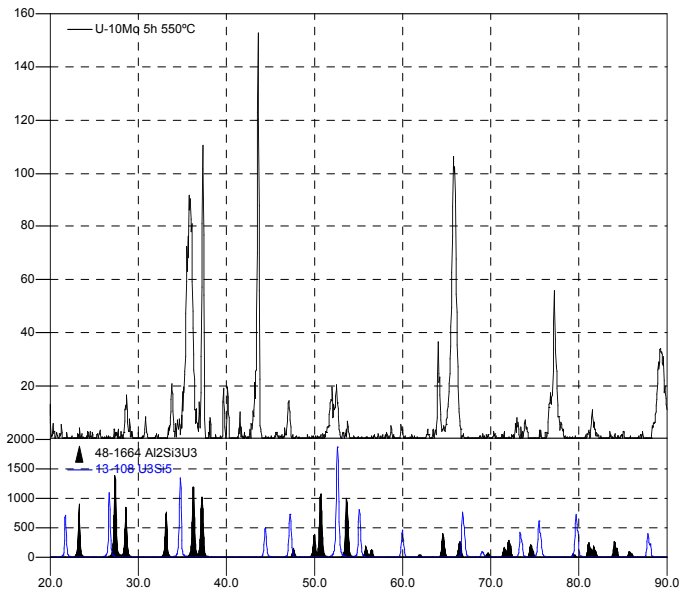


Figure 5 - XRD of diffusion pair of U-10Mo and Al treated at 1000°C during 5 hours. The lower peaks filled in black color represent the phase $Al_2Si_3U_3$, the other U_3Si_5

present research and to CTM/SP (Centro Tecnológico da Marinha) for providing SEM/EDS analysis to this experiment.

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