

# STUDY OF THERMOMECHANICAL TREATMENT FOR MANUFACTURING $UAl_x/Al$ DISPERSION TARGETS

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## Abstract

Uranium aluminide/aluminum ( $UAl_x-Al$ ) targets are widely used in research reactors to produce  $^{99}Mo$  radioisotopes as a fission product of  $^{235}U$ . The  $^{99}Mo$  decays into  $^{99m}Tc$ , which is the most suitable radionuclide for single-photon emission computed tomography image technique. The  $UAl_x-Al$  targets were fabricated according to the picture frame technique, which employs hot rolling of such dispersion. The  $UAl_2$  is the starting uranium compound used as fissile material in the dispersion. During the manufacturing of targets some solid state reactions take place between  $UAl_2$  and Al matrix producing  $UAl_3$  and  $UAl_4$ . The specification claims that the finished target must be free of  $UAl_2$  in its composition, because  $UAl_2$  is harder to dissolve in radiochemical processing. This work aims to develop a thermomechanical treatment that can consume all  $UAl_2$  initially presented in the dispersion. The dilatometry and x-ray diffraction with Rietveld refinement were used to obtain a final optimized thermomechanical treatment for the  $UAl_x/Al$  dispersion targets.

## 1. Introduction

The use of radioisotopes in nuclear medicine has been increasingly contributing to the practice of modern medicine. Among them, the Technetium-99m ( $Tc-99m$ ) is the most widely used radionuclide in diagnostic imaging in nuclear medicine and is employed in approximately 30 million medical procedures annually worldwide [1]. Considering a domestic demand, in 2014 Brazil utilized roughly 450 Ci/week coming from  $Mo-99/Tc-99m$  generators and this consumption corresponds to 4% of the total global consumption of  $Mo-99$ . The  $Tc-99m$  stems from radioactive decay of the  $Mo-99$  which is commercially produced in Materials Test Reactors (MTR) by means of irradiation of  $U-235$  targets. It is important to mention that continuous supplying of  $Mo99$  has decreased over the last decade, mainly due to shutdowns that have occurred in the main research reactors that produce radioisotopes [2]. To deal with this scenario, Brazil has decided to build up a multipurpose reactor which among other functions will irradiate uranium targets to produce enough  $Mo-99$  to supply domestic demand.

Currently, there are two technologies available to produce low enriched uranium (LEU) targets. The first one is based on a uranium-aluminum intermetallic compound ( $UAl_x$ ) dispersed into an aluminum matrix (dispersion targets) and the other one is based on metallic uranium thin foils.

Dispersion targets are produced using a well-known technology called picture-frame technique with certain particularities depending on the manufacturer [3,4]. Generally in this

technology a fissile meat (dispersion of  $UAl_x$  and Al) is clad in an aluminum structure and rolled up until it reaches the desired thickness.

The value of  $x$  in  $UAl_x$  varies depending on the fabrication parameters such as hot rolling temperature and thermal treatment. In this work  $UAl_2$  was used as a starting material, and during the hot rolling process and thermal treatment the uranium dialuminide reacts with Al from the matrix to form higher aluminides ( $UAl_3$  and  $UAl_4$ ). So the  $x$  in this formula denotes a mixture of such higher aluminides.

There is a concern about the presence of  $UAl_2$  in the finishing target. Cols *et. al.* [5] pointed out that during the radiochemical process that takes place in the post irradiation step, the  $UAl_2$  is harder to be dissolved in alkaline solution and must be transformed into higher aluminides at the time of the thermo-mechanical processing or even after the irradiation process. In this manner, the specification claims that the finished target must be free of  $UAl_2$  in its composition.

*Mustaq et. al.* [6] describes the development of  $UAl_2$ -Al targets in Pakistan and presents the specification of the miniplate and how these plates were produced considering many aspects of manufacturing. However, the paper does not give much detail about the timing of the  $UAl_2$  transformation.

Since studies with more details about the conversion of  $UAl_2$  into higher aluminides in targets have not been identified in the open-literature the present work aims to develop a thermo-mechanical treatment that can consume all  $UAl_2$  initially present in the dispersion. In order to obtain an optimized time and temperature for thermo-mechanical processing, this investigation was performed with aid of dilatometry and X-ray diffraction technic.

## **2. Experimental**

### **2.1. Synthesis and Characterization of $UAl_2$ button/powder**

The intermetallic  $UAl_2$  was prepared from a mixture of metallic uranium and metallic aluminum in stoichiometric proportions to obtain  $UAl_2$  (81.5 wt% U). The starting materials were charged into a zirconia crucible and melted using a 15 kW induction furnace. Prior to melting, the furnace was purged three times with argon after vacuum of  $5 \times 10^{-2}$  mbar and the melting was performed under argon atmosphere. The  $UAl_2$  ingot was manually ground in a mortar under argon atmosphere.

### **2.2. Thermal Mechanical Processing**

The roll billet consisted of a picture frame, two cover and a briquette. These components were assembled and joined by Tungsten Inert Gas (TIG) welding and then rolled to form the targets, as per the picture-frame technique. Prior to the rolling operation, the briquettes were degassed at 250 °C for 3 hours under a vacuum of  $0.8 \times 10^{-3}$  mbar. The assemblies were hot-rolled at 540 °C in 6 rolling passes. After the hot rolling passes the plates were heated in the furnace for different periods of time (annealing). The final specified thickness for the target was reached with two cold-rolling passes. For each specific period one plate was withdrawn for x-ray diffraction analysis.

### **2.3. Dilatometry Measurements.**

A mixture of aluminum and  $UAl_2$  powders corresponding to 57 and 35 in volume respectively was compacted to produce specimens for dilatometric analysis. The nominal particle size distribution of the  $UAl_2$  powder in the specimen was 80 wt. % in range of 44 to 150  $\mu\text{m}$  and 20 wt. % of particles smaller than 44  $\mu\text{m}$ . This proportion is the same used to manufacture the targets. The analysis were done either in a continuous mode using heating rate

10°C/min, varying the temperature from 25°C until 610°C or in isothermal mode at 540°C for 40 hours.

## 2.4. X-Ray Diffraction

X-ray diffraction data were collected from samples in powder form as well as in rolled target meats by a Bruker D8 Advance diffractometer, operating with Cu-K $\alpha$  radiation at 40 kV and 30 mA, with a step size of 0.02° and 10 s per step. The reference information was obtained from the ICDD files 58195, 58196 and 24233. The crystalline phases were quantified using the Rietveld method with software TOPAS for data processing.

## 2. Results and Discussion

The phase composition obtained by X-ray diffraction with Rietveld refinement for the UAl<sub>2</sub> ingot is presented in Table 1. Figure 1 shows the experimental and simulated diffraction pattern by applying the Rietveld method where it is noted that the main peaks belongs to UAl<sub>2</sub> phase with some small reflexes form UAl<sub>3</sub>. The value of  $\chi^2$  resulting from the refinement was 1.82, showing a good agreement between the experimental and the theoretical values. In the diffraction pattern an identification of some peaks from UO<sub>2</sub> was omitted in order to facilitate the visualization of main peaks and keep clear the graphic. In the Table 1 it is possible to access the weight fraction of UO<sub>2</sub> calculated by the refinement.

Phase	Rietveld (%)
UAl <sub>2</sub>	91.7 ± 0.3
UAl <sub>3</sub>	5.5 ± 0.2
Oxides (UO, UO <sub>2</sub> )	2.8 ± 0.2
Empirical formula	UAl <sub>1.97</sub>

Table 1 – Phase composition on the UAl<sub>2</sub> powder.

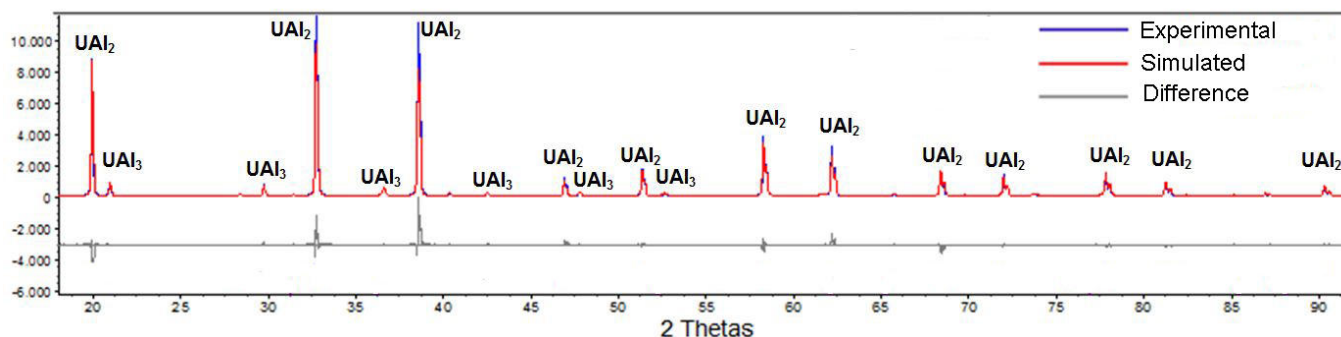


Figure 1: X-ray diffraction pattern of UAl<sub>2</sub> powder.

A sample from the button was scanned by electronic microscopy as shown in Figure 2. Due to atomic number contrast obtained from the backscattered electrons, which is sensitive to the composition, it was possible to observe three shades of gray, which indicates the existence of three phases. The EDS analysis was carried out to shed light on these existing

phases. So, the phases of the button are composed mainly by  $\text{UAl}_2$  with a small fraction of  $\text{UAl}_3$  that was solidified from residual melt at the grain boundaries. Some inclusions were observed, mostly by uranium oxide (lighter gray tone, almost white). These results are in accordance with diffraction analysis.

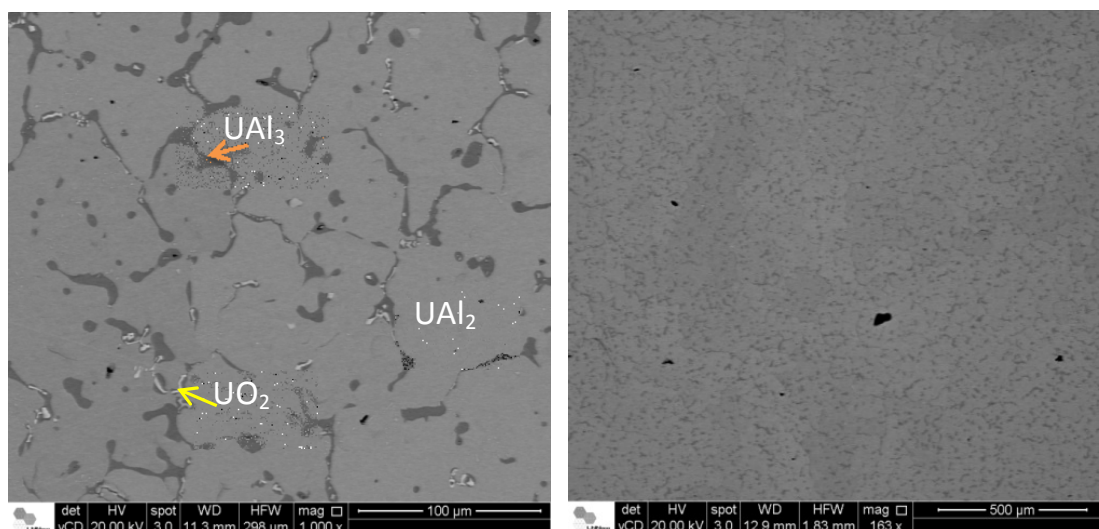


Figure 2:  $\text{UAl}_2$  button; (a) Backscattered image in high magnification demonstrating the microstructure composed majority of  $\text{UAl}_2$  with minority quantity of  $\text{UAl}_3$ . (b) Backscattered image in low magnification showing the homogeneity of the button.

Dilatometric measurements were taken to extract the preliminary information about the temperature and time necessary to consume all  $\text{UAl}_2$  during the thermo-mechanical processing.

Figure 3 shows the change in length of  $\text{UAl}_2$ -Al pellets during the heating and its derivative curve (red curve). There is no substantial change in length below  $540^\circ\text{C}$ . However, the displacement increases drastically around  $540^\circ\text{C}$  (onset of the curve) due to the solid state reactions that take place between  $\text{UAl}_2$  and Al, forming less dense  $\text{UAl}_3$  as well as  $\text{UAl}_4$ . Moreover, it is possible to note that around  $570^\circ\text{C}$  the derivative curve reaches a maximum rate and decreases over the high temperature. From Figure 3 it was inferred that the optimized temperature for hot rolling process should be between  $540$ - $570^\circ\text{C}$ . These results are in agreement with the ones reported by S. Nazaré *et. al.*[7] that showed that the reaction rate between  $\text{UAl}_2$ -Al starts to show some progress only above  $500^\circ\text{C}$ . Below  $500^\circ\text{C}$  these reactions are too slow to observe any progress through metallographic and dilatometric analysis.

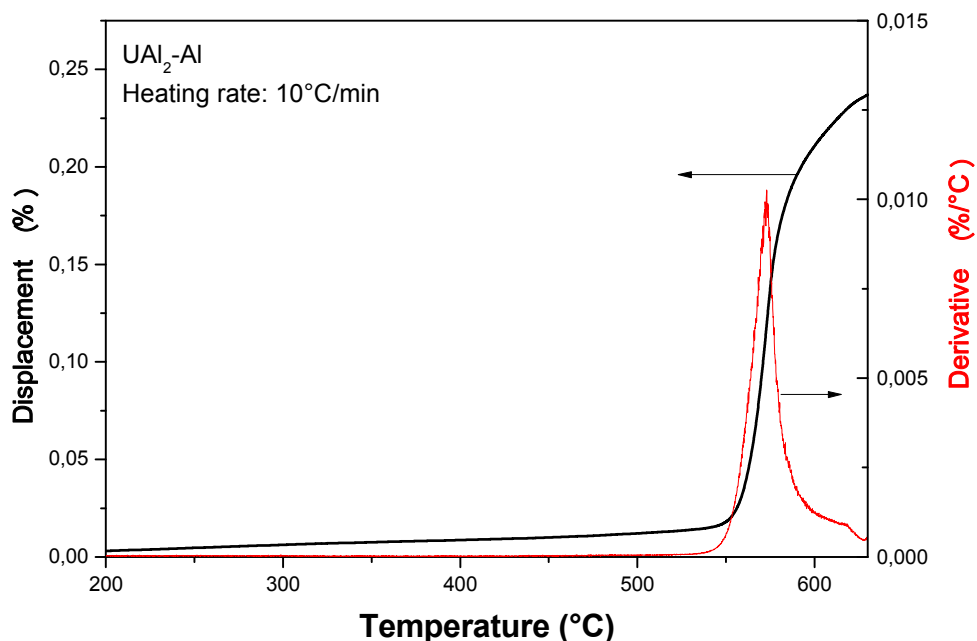


Figure 4: Dilatometric curve of UAl<sub>2</sub>-Al pellet

In order to evaluate the annealing time, an isothermal dilatometry was carried out at 540°C for 40 h. In Figure 3 it is shown an isothermal curve of UAl<sub>2</sub>-Al pellet. In general this curve can be fitted using a power function law that was a common function used to describing an interdiffusion behavior between uranium and aluminum pair [8].

Considering that in the UAl<sub>2</sub>-Al system occur two solid state reactions (i.e. UAl<sub>2</sub> + Al → UAl<sub>3</sub> and UAl<sub>3</sub> + Al → UAl<sub>4</sub>) with different rates, for instance, it is reported that the formation of UAl<sub>3</sub> is much faster than the formation of UAl<sub>4</sub> [7,9]. Shekar *et. al.* [10] described that the solid state reaction between UAl<sub>3</sub>-Al to form UAl<sub>4</sub> can take as long as 6 weeks at 677 °C. Based on these reports it was proposed that due to its very different rates these reactions could appear separately in the isothermal measurements

In the plot showed in Figure 3 the curve was interpreted as presenting two features in its shape, one of them has a power growth (fast reaction) and it was fitted using power function  $y = 2.41x^{0.69}$  giving an adjusted R-squared = 0,98. This power profile was attributed to first solid state reaction which is the consumption of UAl<sub>2</sub> and formation of UAl<sub>3</sub>. It worth pointing out that in the first 1,5 hour the derivative curve increased abruptly and this behavior was ascribed to UAl<sub>2</sub>-Al reaction between very fine particles. From the second hour the displacement increased in power growth profile and extended for approximately 9-10 h where the derivative curves become almost constant.

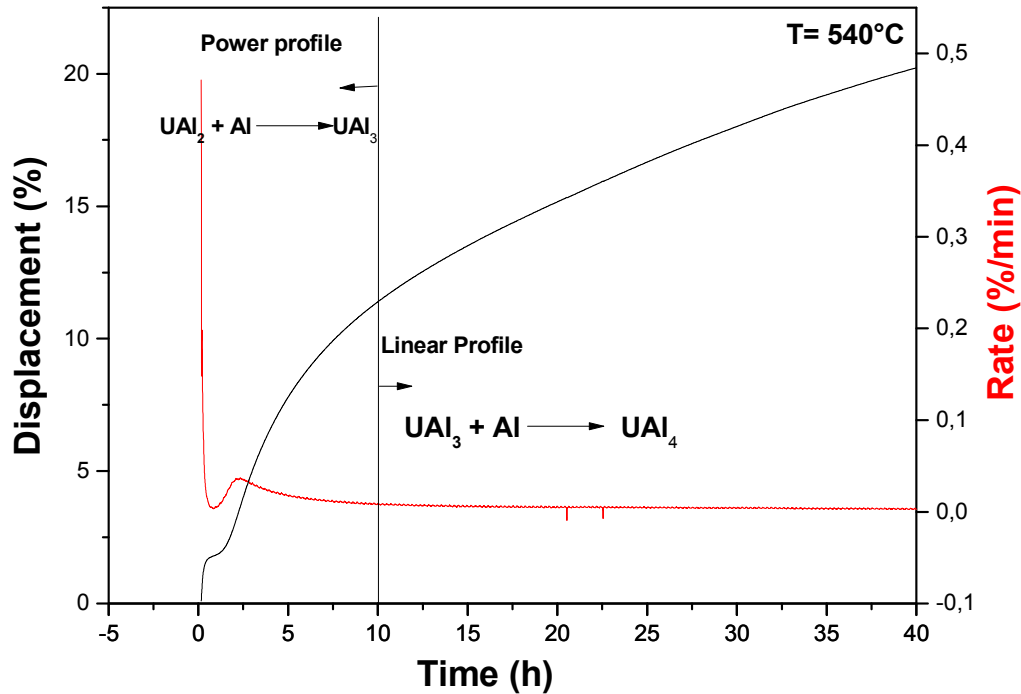


Figure 5: Isothermal displacement at 540 °C for UAl<sub>2</sub>-Al pellets.

The other part of the above-mentioned curve extends approximately from 10 h until 40 h and it was attributed to second solid state reaction which is a formation of UAl<sub>4</sub> and presented a linear growth profile (slow reaction), This profile was fitted using a linear function  $y = 0.28x + 9.24$  giving an adjusted R-squared = 0.99. This assumption is in accordance with results published by A. K, Chakraborty *et. al.* [11] that showed the reaction between UAl<sub>3</sub> and Al presents a linear displacement profile. Moreover, it is important to mention that the isothermal measurement was carried out until 40 hour and the reaction had not finished yet. This behavior confirms that the reaction between UAl<sub>3</sub> and aluminum is very sluggish when compared with the reaction between UAl<sub>2</sub> and Al. These results are consistent with those published in literature [7,9,10]. From this isothermal curve it is possible to estimate that the annealing time might last around 10 hour to consume all UAl<sub>2</sub>.

The thermomechanical processing was performed at 540°C in various different annealing times in order to evaluate how the uranium aluminides concentration varies. The concentration of all aluminides (UAl<sub>2</sub>, UAl<sub>3</sub> and UAl<sub>4</sub>) was assessed by X-ray diffraction/Rietveld refinements.

This result is also shown in Figure 3 where it is possible to note a decrease in UAl<sub>2</sub> concentration and an increasing of UAl<sub>3</sub> over the time. After 5 h the UAl<sub>3</sub> concentration reaches a maximum (90%) and start decreasing when UAl<sub>3</sub> was consumed to form UAl<sub>4</sub>. It is also worth pointing out that the formation of UAl<sub>4</sub> remains unaltered (less than 5 %) until UAl<sub>2</sub> be almost totally consumed (less than 10 %).

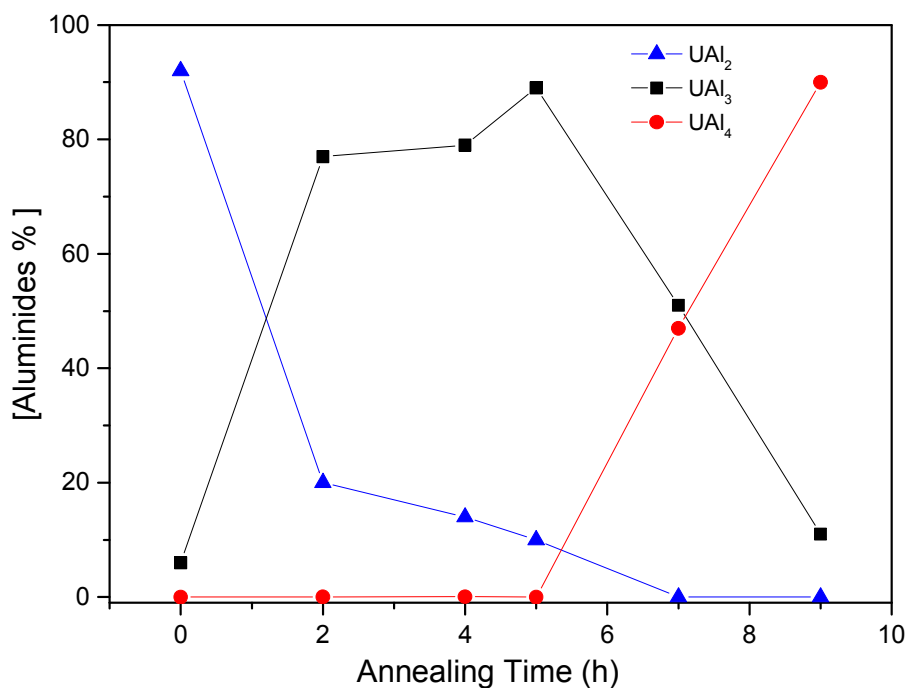


Figure 6: Uranium aluminides concentration versus annealing time after thermo mechanical processing. This curves shows that the minimum time to consume all UAl<sub>2</sub> is around 7 hours. At this time the meat composition is approximately 50% of UAl<sub>3</sub> and UAl<sub>4</sub>.

The minimum time to consume all UAl<sub>2</sub> during the annealing was lesser than to consume all UAl<sub>2</sub> during the isothermal measurement. This difference stems from the fact that during the thermo-mechanic processing fragmentation takes place in UAl<sub>2</sub> particles that are brittle, increasing the contact area between the reactants and then speeding up the rate of reactions.

## Conclusion

This work was intended to develop a thermal annealing to consume all the UAl<sub>2</sub> initially present into the dispersion. The use of dilatometric measurements was important to determine the temperature that needs to be applied into the thermo-mechanical processing. Moreover, this technic was also able to shed light on the duration of annealing even though the final length of time was precisely determined by thermo-mechanical experiment jointly with X-ray diffraction/Rietveld refinements. As a result, it was found out that the optimized annealing time should last 7 h at 540 °C in order to consume all UAl<sub>2</sub> and give an equivalent quantity of higher aluminides (UAl<sub>3</sub> and UAl<sub>4</sub>).

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