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STUDY OF METHODS FOR PHASE CHARACTERIZATION IN INTERMETALLIC UAl_x

Giovanni Contubia, Rafael H. L. Garcia, Adonis M. Saliba-Silva, Elita F. Urano de Carvalho, and Michelangelo Durazzo

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
gconturbia@ipen.br

ABSTRACT

The UAl_x is an intermetallic compound used in the manufacture of irradiation targets for molybdenum-99 production. The fissionable uranium-235 is presented in the form of intermetallic UAl_x powder, which is dispersed in an aluminum matrix. This paper aims at studying methods for phase characterization of the intermetallic. The index x identifies the phase composition of the compound, usually a mixture of UAl_2, UAl_3 and UAl_4. The phase composition was quantified in the UAl_x powder and UAl_x-Al dispersion by means of image analysis and x-ray diffraction, applying the Rietiveld method. Both methods allowed the quantification of the presented phases . The results from the two methods differed from each other with respect to the concentration determination. Possible error sources are discussed in this paper. The quantification method based on x-ray diffraction showed potential to be applied to the RMB Project for phase quantification in UAl_x-Al dispersion targets, which is required by specification.

1. INTRODUCTION

Every year the world demands more than 30 million medical imaging procedures that use technetium-99m radioisotope (Tc^{99m}), which correspond to approximately 80% of all nuclear medicine diagnoses. [1] This radiopharmaceutical product derives from the radioactive decay of molybdenum-99 (Mo^{99}), which is commercially produced in research reactors by irradiation targets that contain uranium-235. However, continuous supplying of Mo^{99} 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 meet domestic demand.

There are currently two technologies available to produce uranium targets. One is based on metallic uranium thin foils [3] and the other one is based on a uranium-aluminum alloy dispersed in an aluminum matrix [4].

The binary system, uranium and aluminum, forms a phase diagram which shows the existence of intermetallic compounds consisting of three phases, UAl_2, UAl_3 and UAl_4. The mixture of these phases is known in the literature as UAl_x [5]. Because of its experience acquired over the years in the manufacturing technology based on dispersion fuels, IPEN has decided to adopt this technology for fabricating UAl_x-Al dispersion targets for future Mo^{99} production in Brazil.

Characterizing the phase composition in UAl_x powder used as raw material for target fabrication is important because the maximum uranium concentration depends on the phase composition presented in the starting powder. Furthermore, it is important to mention that the UAl_3 and UAl_4 are more easily dissolved in alkaline solutions than the UAl_2, which defines, ultimately, the radiochemical processing throughput after the irradiation [6]. So, the presence of UAl_2 in the UAl_x-Al dispersions target also must be quantified.

This paper aims at investigating methods to quantify the phases present in UAl_x powder and UAl_x-Al dispersions. Two possible methods were investigated: image analysis and x-ray diffraction.

2. MATERIALS AND METHODS

The intermetallic was prepared from a mixture of metallic uranium and metallic aluminum metal in stoichiometric proportions to obtain UAl_2 (81.5 wt% U). The starting materials were charged into a zirconium crucible and melted using a 15 kW induction furnace. Prior the melting, the furnace was purged with argon after vacuum of 2.6×10^{-3} mbar. The UAl_x ingot was ground in a mortar under argon atmosphere.

A mixture of aluminum and UAl_x powders corresponding to 50 and 45 vol% respectively has been pressed to form the target meet, which is called briquette. It contains UAl_x particles dispersed in an aluminum matrix. The particle size distribution of the UAl_x powder in the briquette was 80 wt% of 44 to 150 μm particles and 20 wt% of particles smaller than 44 μm.

The roll billet consists of a picture frame, two cover and a briquette. This compoments were assembled and joined by Tungsten Inert Gas (TIG) welding and then rolled to form the targets, according to the picture-frame technique [7-9]. Prior the rolling operation, the briquettes were degassed at 250 ^{o}C for 3 hours under vacuum of 0.8×10^{-3} mbar. The assemblies were hot-rolled at 450 ^{o}C in four rolling passes. The final specified thickness for the target was reached with two cold-rolling passes. Table 1 shows the typical rolling scheme adopted to manufacture UAl_x-Al dispersion targets.

Table 1: Typical rolling scheme to manufacture UAl_x-Al dispersions targets

Target Number	Thickness (mm) (assembly starting thickness= 9.23 mm)					
	P1 (hot)	P2 (hot)	P3 (hot)	P4 (hot)	P5 (cold)	P6 (cold)
1	5.90	→ withdrawn for analysis (WA)				
2	5.98	3.91	→ WA			
3	6.03	3.90	2.66	→ WA		
4	6.00	3.90	2.65	1.77	→ WA	
5	6.02	3.89	2.64	1.77	1.63	→ WA
6	5.99	3.90	2.64	1.75	1.64	1.52

P = rolling pass

X-ray diffraction data were collected from samples of polished briquettes and rolled target meats by a Rigaku Multiflex diffractometer, operating with Cu-Kα radiation at 40 kV and 20 mA, with a scan of 0.02° and for 8 s counts. The reference information was obtained from the

ICDD files 58195, 58196 and 24233. The crystalline phases were quantified using the Rietiveld method with GSAS for data refinement.

The phase composition was also quantified by studying the microstructure of briquettes and rolled meats through scanning electron microscopy (backscattered electron image) and energy dispersive spectroscopy. A Philips XL30 microscope was used. Image analysis was used for quantifying the phases by using the software Omnimet Enterprise Buehler.

3. RESULTS AND DISCUSSION

Fig. 1 shows a scanning electron micrograph of the cross section of a UAl_x-Al briquette, where the UAl_x particles are homogeneously dispersed in the aluminum matrix. Because of the atomic number contrast obtained from the backscattered electrons, which is sensitive to the composition, it was possible to observe three shades of gray, which indicate the existence of three phases.

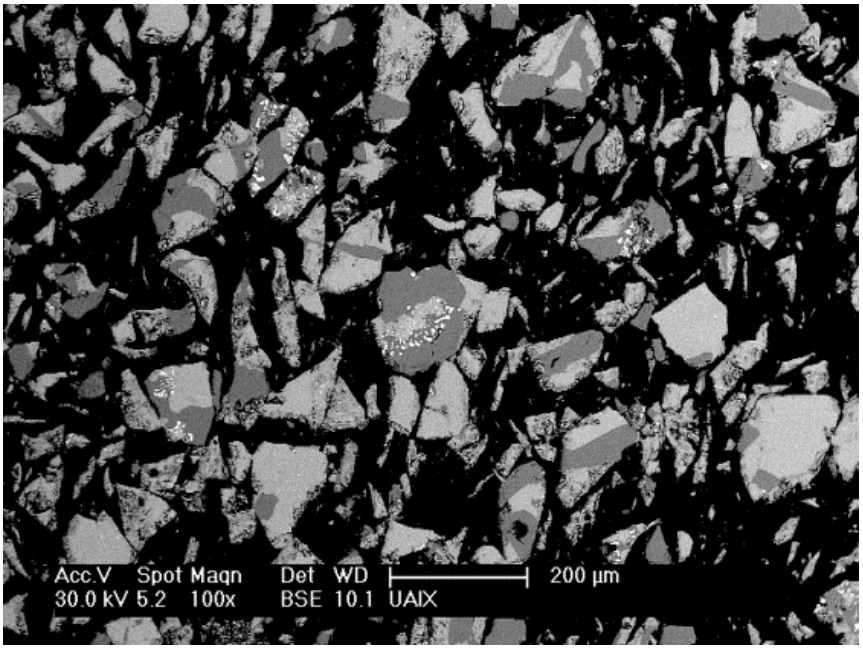

Figure 1: Scanning electron micrograph from a UAl_x-Al briquette cross-section illustrating the dispersion and the phases presented (backscattered electrons).

EDS analysis (Fig. 2) were used to quantify the levels of uranium and aluminum in the three phases. Region 1 (lighter gray tone, almost white) showed a composition of 99.0 wt% U and 1.0 wt% Al. As discussed later, this phase was identified by X-ray diffraction as UO. The grayscale observed on region 2 corresponded to the concentration of 82.5 wt% uranium and 17.5 wt% aluminium, while the darker gray tone related to the region 3 showed a composition of 76.6 wt% U and 23.4 wt% Al. Based on the stoichiometric composition, the compositions of the regions 2 and 3 characterize the UAl_2 and UAl_3, respectively

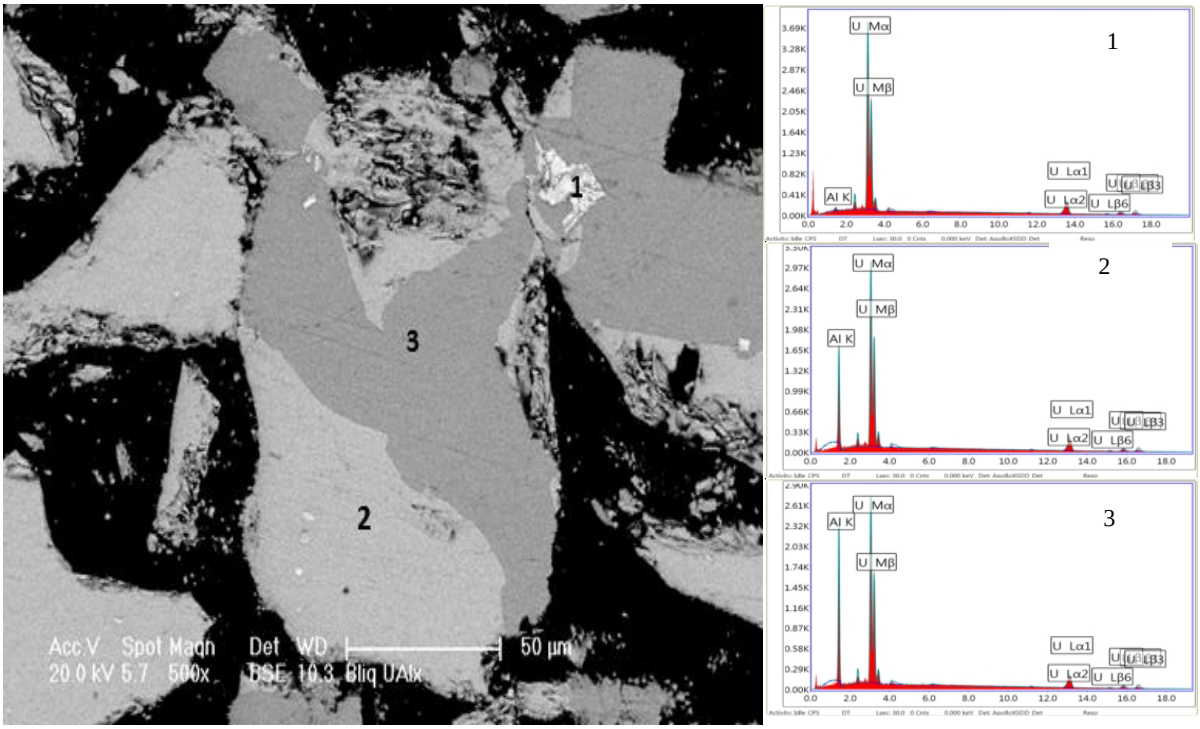

Figure 2: Scanning electron micrograph and EDS analysis of the regions designated by 1, 2 and 3. The compositions of regions 2 and 3 indicate the presence of UAl_2 and UAl_3, respectively (backscattered electrons).

The volumetric fractions of the three phases present were determined by using image analysis. Eight images were analyzed. Fig. 3 shows a typical image that was analyzed. The cyan color (light blue) was used to identify the UAl_2 phase, the yellow color was used to identify the UAl_3 phase and the dark blue color was used to identify the denser phase of UO. The red color was used to identify the aluminum matrix.

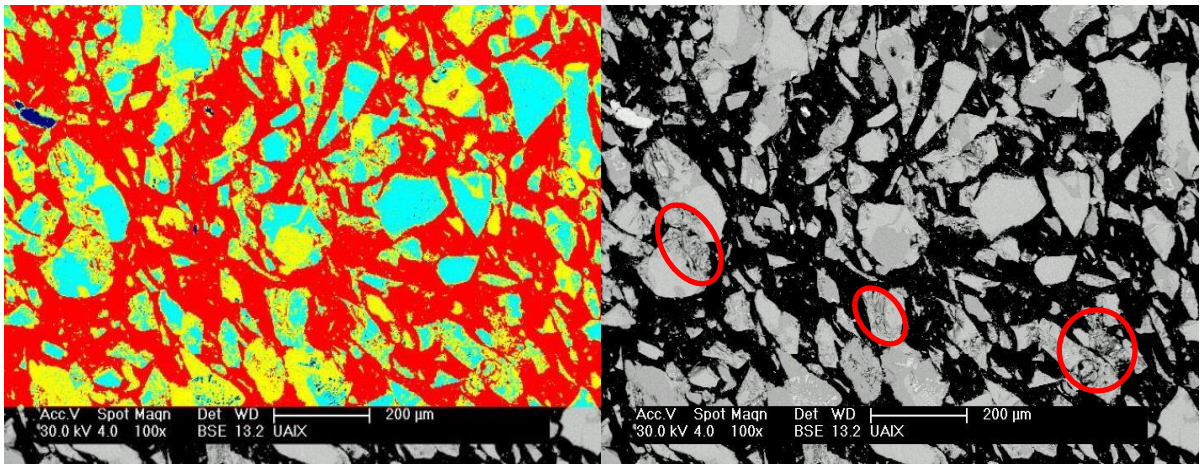

Figure 3: Left, image processed by the image analyze. Right, unprocessed image.

The red circles in Fig.3 (right) illustrate regions where fragmentation of UAl_2 (fragile phase) can be observed. The fragments of fragmented UAl_2 particles present a dark shade of gray that is confused with the shade of gray of UAl_3 particles. This is an important source of error, as discussed below.

The phase quantitation by image analysis resulted in 42.6 wt% for UAl_2, 56.26 wt% for UAl_3 and 1.2 wt% for UO. Chemical analysis determined the uranium content in the powder as 80.74 wt%, with a uranium loss of 0.76 wt% compared to the nominal uranium content of the starting composition of the charge of fusion (81.50 wt%). This loss can be attributed to the oxidation of uranium alloy during the melting process to form UO.

Considering that the uranium content was determined by chemical analysis and neglecting the presence of the oxidized phase remaining in the sample, from the U-Al equilibrium diagram [5] the expected phase composition in the powder would be about 89.4 wt% for the UAl_2 and 10.6 wt% for UAl_3. The composition resulted from the image analysis shows underestimated values for the UAl_2 concentration. This result can be explained by the fragmentation of the fragile UAl_2 particles, which occurs when pressing and rolling the UAl_x-Al dispersion. Differences in height (porosity) in the regions of fragmentation cause fewer backscattered electrons reaching the detector, which decrease the brightness in these regions and result in a darker shade of gray on the edges of the UAl_2 particles and fragments thereof. This darker shade of gray in the image is confused by the image analyzer as UAl_3, as illustrated by the regions marked with red circles in Fig 3. The image analyzer distinguishes the edges of the UAl_2 particles and its fragments as UAl_3. Thus, the processed image leads to a concentration underestimated for the UAl_2 fraction and overestimated for the UAl_3 fraction. This effect does not occur with the UAl_3 particles due to its greater ductility [7].

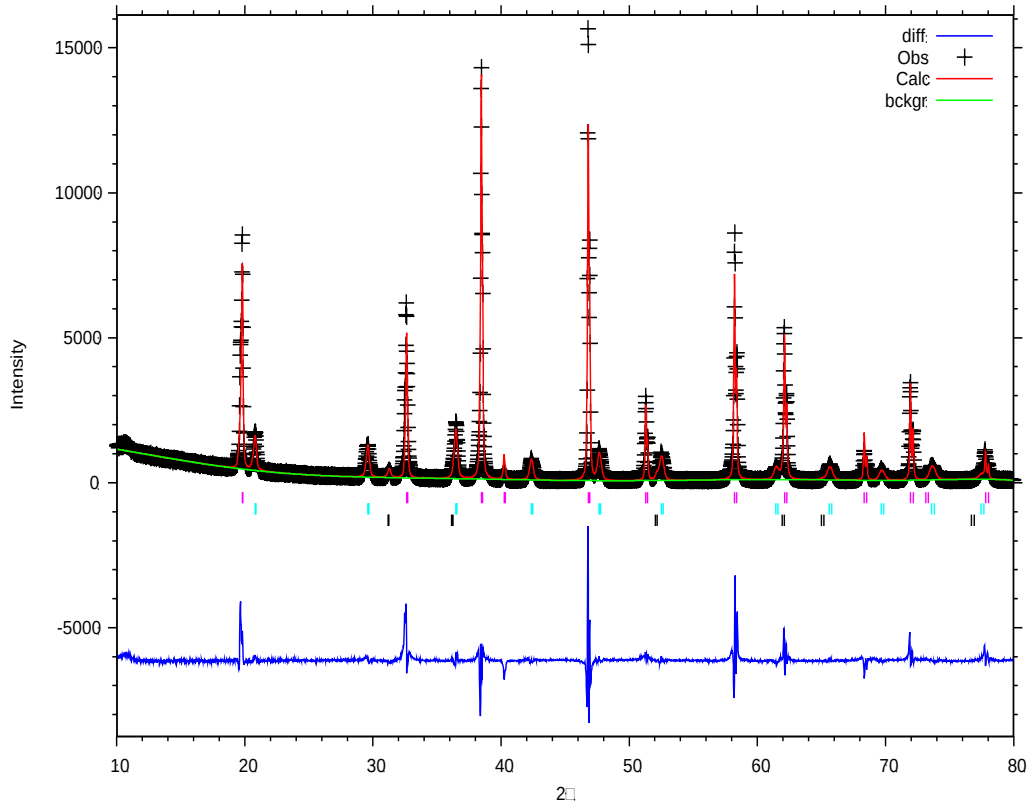

Figure 4: Experimental and calculated diffractograms for the UAl_x powder. The peaks marked with purple bars are from UAl_2, cyan bars from UAl_3 and black bars from UO.

The phase composition obtained by X-ray diffraction for the same UAl_x-Al briquette analyzed by image analysis is presented in Fig. 4, which shows the experimental and

calculated diffraction pattern by Rietveld method. The value of $\chi 2$ resulting from the simulation was 66, showing a reasonable agreement between the experimental and the theoretical values.
As mentioned before, the compositional analysis of the phases obtained by SEM-EDS indicated the existence of UAl_2, UAl_3 and a third phase rich in uranium (lighter gray tone, almost white, region 1 in Fig. 2). This observation was confirmed by X-ray diffraction, which shows that the uranium-rich phase is UO. The results for the phase measurement from the Rietveld method showed 85.4 wt% for UAl_2, 11.4 wt% for UAl_3 and 3.2 wt% for UO.

By Analyzing the results, it can be observed that they who? are extremely different with respect to the phase quantification. Table 2 summarizes the results obtained by image analysis and X-ray diffraction with Rietiveld refinement.

Table 2: Results for phase quantitation in UAl_x powder (wt%)

Phase	Rietiveld	Image Analysis	Expected Composition (chemical analysis)
UAl_2	85.4	42.6	89.4
UAl_3	11.4	56.2	10.6
UO	3.2	1.2	0

The UAl_2 content determined from Rietiveld refinement is below the one expected according to the chemical analysis. This indicates low fit between the experimental and calculated data by the method, which could be attributed to the impossibility of rotating the sample during the X-ray diffraction analysis, since it was not possible to use the "spinner" during the analysis to avoid preferred orientation. Anyway, the approximation can be considered good, with a deviation of around 5 %.

In order to verify the feasibility of the method for following the phase composition during the UAl_x-Al dispersion target manufacturing process, core samples were analyzed by the x-ray diffraction with Rietveld refinement after each rolling pass, as showed in Table 1. The aim was to follow the phase composition evolution during the rolling process for target fabrication. This aspect is important, since the maximum UAl_2 phase concentration presented in the target must be determined by specification request. Polished specimens of the targets meat were analyzed by X-ray diffraction applying Rietveld refinement. The results are presented in Table 3.

Fig. 5 presents the phase composition evolution inside the target meat during the target manufacturing process. After the first hot-rolling pass it occurs remarkable transformation of UAl_2 to UAl_3 due to the solid state reaction with aluminum from the dispersion matrix. This reaction results from the heat treatment performed before the first hot-rolling (1 hour at 450 ^oC). In the subsequent hot-rolling passes does not occurs significant transformation, keeping the composition stable, within the error of the Rietveld method. After the last hot-rolling pass a new thermal treatment is accomplished with duration of 1 hour at 450 ^oC (blister test). The objective of this new heat treatment is to verify the bonding quality. After this new heat treatment, a significant transformation from UAl_2 to UAl_3 and the starting UAl_4 formation occur again, which is formed by the reaction of UAl3 with the aluminum matrix of the dispersion. The oxide concentration keeps unchanged within the error of the method.

Table 3: Results for phase quantitation in UAl_x target meats (wt%)

Rolling Pass	UAl_2	UAl_3	UAl_4	UO
Briquette	85.4	11.4	0	3.2
P1 (hot)	74.3	24.3	0	1.4
P2 (hot)	71.7	27.2	0	1.1
P3 (hot)	75.5	22.7	0	1.8
P4 (hot)	73.1	24.7	0	2.2
P5 (cold)	47.6	47.1	4.6	0.7
P6 (cold)	48.1	45.6	5.3	1.0

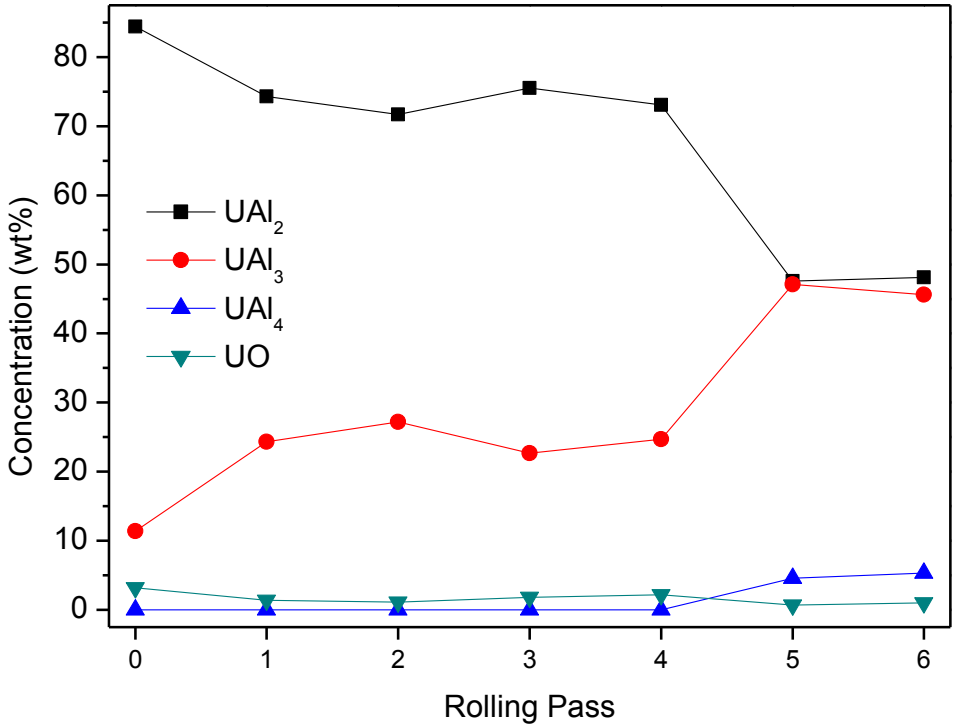

Figure 5: Phase composition evolution during the target manufacturing process.

3. CONCLUSIONS

Two possible methods for phase quantification in dispersion based UAlx-Al irradiation targets were successfully studied.

The method based on scanning electron microscopy and image analysis proved to be inapplicable due to some errors related to the fragmentation of UAl_2 particles.
The method based on X-ray diffraction with Rietveld refinement proved to be applicable, with an estimated error of 5 %. By applying this method, it was possible to follow the

evolution of the phase composition during the target manufacturing process. However, additional work on these methods is necessary to determine the error of the method.

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