

## REFINING U-ZR-NB ALLOYS BY REMELTING

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### Abstract

The high density U-Zr-Nb and U-Nb uranium-based alloys can be employed as nuclear fuel in a PWR reactor due to their high density and nuclear properties. These alloys can stabilize the gamma phase, however, according to TTT diagrams, at the working temperature of a PWR reactor, all gamma phase transforms to  $\alpha''$  phase in a few hours. To avoid this kind of transformation during the nuclear reactor operation, the U-Zr-Nb alloy and U-Nb are used in  $\alpha''$  phase. The stability of  $\alpha''$  phase depends on the alloy composition and cooling rate. The alloy homogenization has to be very effective to eliminate precipitates rich in Zr and Nb to avoid changes in the alloying elements contents in the matrix. The homogenization was obtained by remelting the alloy and keeping it in the liquid state for enough time to promote floating of the precipitates (usually carbides, less dense) and leaving the matrix free of precipitates. However, this floating by density difference may result in segregation between the alloying elements (Nb and Zr, at the top) and uranium (at the bottom). The homogenized alloys were characterized in terms of metallographic techniques, optical microscopy, scanning electronic microscopy, EDS and X-ray diffraction. In this paper, it is shown that the contents of Zr and Nb at the bottom and at the top of the matrix are constant.

### Introduction

Uranium and its alloys are employed in various applications due to their high density and nuclear properties. The metals Nb, Ti, Zr, Hf and Re have high solubility in gamma uranium and they do not form any intermetallic compound. However, Zr and Nb have a special advantage because of their low capture cross section for thermal neutrons (1).

The U-Zr-Nb alloys can stabilize the gamma phase (cubic), however, some different martensitic transformations have been found to occur, depending upon composition and cooling rate. The martensite phases identified with orthorhombic phases having non-equilibrium lattice parameters are called  $\alpha'$ , and monoclinic modifications, which occurs at even higher alloys contents, are called  $\alpha''$  (2). According some time-temperature-transformation diagrams for these alloys (3), at the working coolant temperature of a PWR reactor (about 300°C), all the gamma phase transforms to alpha phase in a few hours. To avoid this kind of transformation during the nuclear reactor operation, and differently of U-Mo alloys, the U-Zr-Nb alloys are used in  $\alpha''$  phase (2) (1).

The stability of  $\alpha''$  phase depends on the alloy composition (4). So, it's necessary to homogenize the alloy to obtain the desirable composition in the matrix and, consequently, obtain the required phase. Heat treatment at 1050°C for 72h under argon flux was showed to be effective to eliminate the microsegregation, however, this thermal treatment was not able to remove the precipitates (probably carbides, with are very stable). Furthermore, in some samples, the content of Zr and Nb in the precipitates increased, depleting even more the matrix (5).

One solution to remove these precipitates is remelting the alloy and to leave in liquid state for a sufficient time to allow the precipitates to float by density differences. After this process, the upper part of the ingot can be removed. This remelting process cannot be done in an induction furnace because the electrical currents and magnetic fields generated in the metal agitates the liquid metal, not allowing the precipitates (less dense) to float. For this reason, the remelting process was made in a resistance furnace under argon atmosphere (6). However, this floating by density difference may result in segregation between the alloying elements (Nb and Zr, less dense, at the top) and uranium (more dense, at the bottom), changing again the composition of the matrix, making it richer in alloying elements on the top and richer in uranium at the bottom. It is necessary to verify if this type of segregation occurs after the remelting process.

## Experimental

For this work, the U-Zr-Nb and U-Nb alloys (all compositions are reported in weight percent) were obtained by melting cubic pieces of uranium, zirconium sponge and niobium sheets in an induction furnace with the use of graphite crucible under argon atmosphere. The materials stays melted during 10 to 12 minutes and subsequently it was casted into a copper cylindrical mould of 2,5 cm diameter and 15 cm length dimensions. Further, the ingot was cut in samples with thickness of approximately 2mm and whose mass is approximately 5 grams each.

The remelting procedure was made in a resistance furnace under argon flux, employing yttria stabilized zirconia crucible. The remelting steps were:

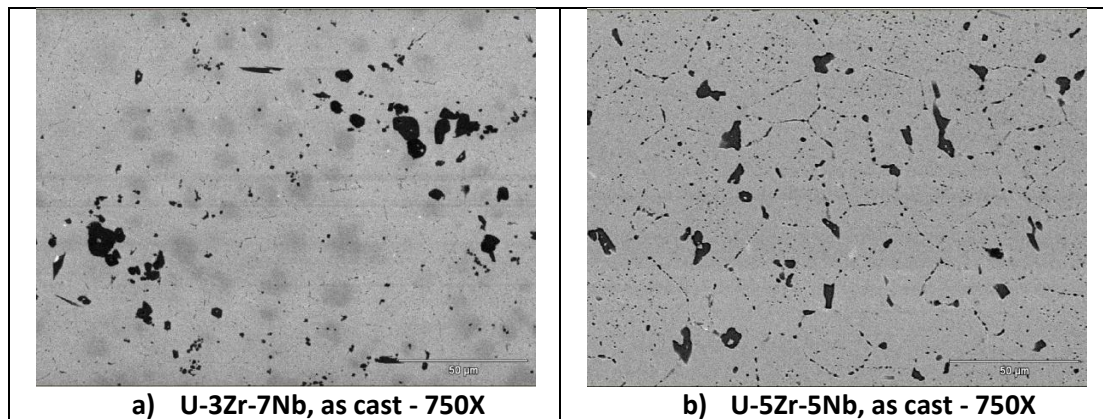
- a) Heat the sample from room temperature up to 1.570°C, at a rate of 10°C/min, and stay at this temperature for 15 minutes
- b) Cooled from 1.570°C to 1250°C at a rate of 0,2°C/min (or 0,3°C/min)
- c) Cooled from 1250°C to 900°C, at a rate of 5°C/min
- d) Then, water quenching.

The temperature of 1570°C was chosen because all U-Zr-Nb alloys melts in a lower temperature and the temperature of 1250°C was selected to ensure that all alloys will solidify at this temperature. The cooling from 1250°C to 900°C was used to avoid a thermal stress in the oven's ceramic tube during the quenching .

For all the optic and electron microscopy examinations, samples were resin mounted into 2,5 cm diameter mould and they were mechanically ground, polished down to 3 µm diamond and 1 µm colloidal silica. Scanning electron microscopy was performed on a JEOL instrument model JSM-5310 equipped with the energy dispersive X-ray spectroscopy system (EDS).

## Results and discussions

In this work, samples of U-6Nb, U-2.5Zr-7.5Nb (Mulberry Alloy) and U-5Zr-5Nb were homogenized by remelting process. Figure 1 shows a typical backscattered electrons micrograph examinations of as cast U-5Zr-Nb (left) and as cast U-3Zr-7Nb (right) alloys.



**Figure 1** Backscattered electrons micrographs of as-cast alloys  
(a) U-3Zr-7Nb (b) U-5Zr-5Nb

The precipitates showed on the figure 1 are found equally distributed in the sample and there is no region free of them. The U-3Zr-7Nb micrograph shows three different regions of the as-cast alloys (matrix, microsegregation shown in the micrographs as gray spots and precipitates as dark spots) and Table 1 shows the microanalysis of each region. These values are the mean values of several measurements and the value in brackets are the standard deviation. In the matrix, there is a segregation of zirconium and, most intensively, niobium. The precipitates have a very high content of zirconium (63.37%), niobium (33.13%) and a little amount of uranium (3.5%).

**Table 1** - EDS microanalysis of U-3Zr-7Nb as-cast alloy.

<i>Region</i>	<i>% Zr (σ)</i>	<i>% Nb (σ)</i>	<i>% U (σ)</i>
<b>Matrix</b>	2,17 (0,66)	4,64 (0,89)	93,19 (1,47)
<b>Microsegregation</b>	3,94 (0,44)	12,56 (1,06)	83,5 (1,44)
<b>Precipitates</b>	63,37 (1,46)	33,13 (0,54)	3,5 (1,99)

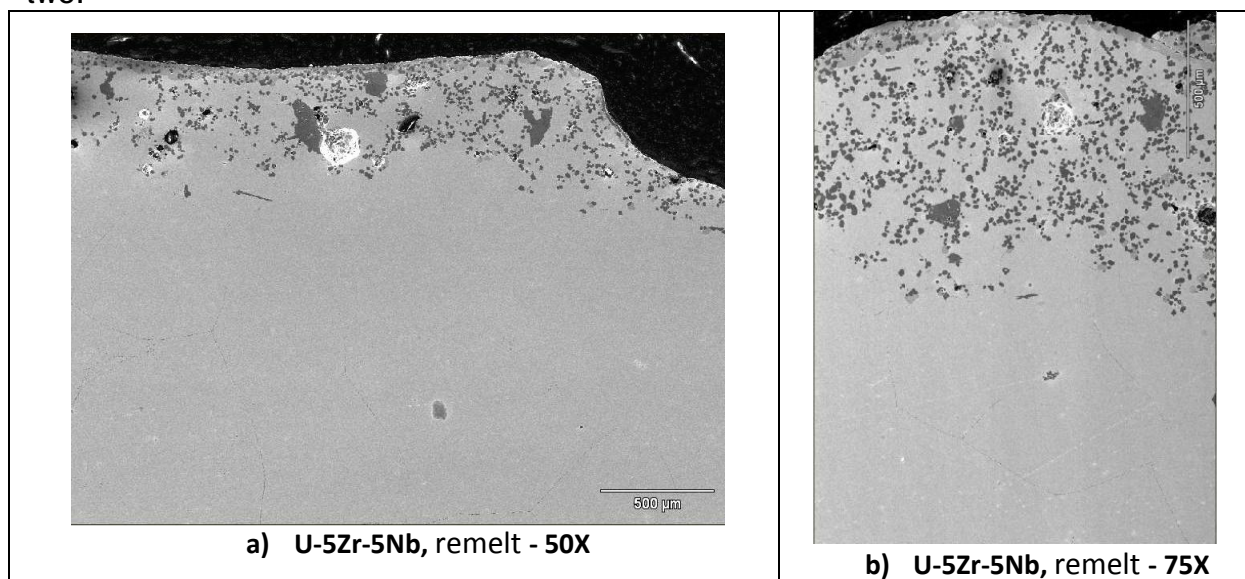
Table 2 shows the microanalysis of as-cast U-5Zr-5Nb. The microsegregation in the matrix area it is not as intense as in U-3Zr-7Nb, but it is possible to see the same

effect in higher magnification. The precipitates has a high zirconium segregation (90,66%) and a low content of niobium (3,95%) and uranium (5,39%).

**Table 2** - EDS microanalysis of U-5Zr-5Nb alloy as cast.

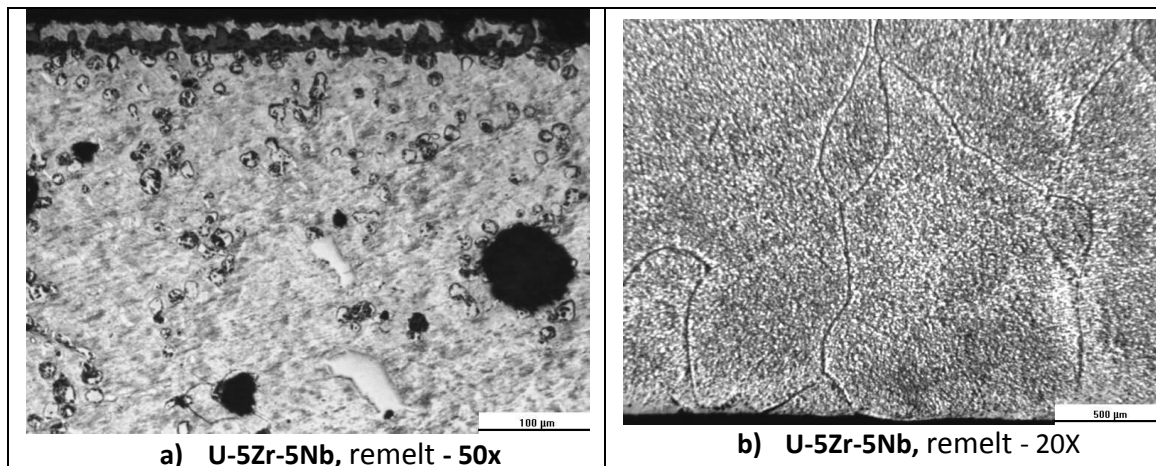
<i>Region</i>	<i>% Zr (<math>\sigma</math>)</i>	<i>% Nb (<math>\sigma</math>)</i>	<i>% U(<math>\sigma</math>)</i>
<b>Matrix</b>	3,31 (0,32)	4,34 (0,32)	92,35 (0,38)
<b>Precipitates</b>	90,66 (2,34)	3,95 (0,98)	5,39 (2,89)

Figure 2 shows the backscattered electrons micrograph examinations of U-5Zr-5Nb alloy after it was remelted. The upper part is rich in precipitates and the bottom part is practically free of them. The same result was obtained for U-6Nb and U-2.5Zr-7.5Nb. It can be observed also that the grain boundary is denoted as almost imperceptible thin line and do not contain precipitates, as shown in figures one and two.



**Figure 2** - Backscattered electrons micrographs of remelted U-5Zr-5Nb a)50x; b)75x

Figure 3 shows the optical micrograph examinations of U-5Zr-5Nb alloy after remelting process. In the micrograph on the left, it's shown the precipitates at the upper part of the sample. The micrograph on the right shows the absence of precipitates and in the grains boundary at the bottom part of the sample.



**Figure 3** - Optical micrographs of remelted U-5Zr-5Nb a)50x; b)75x

Figure 3 shows the optical micrograph examinations of U-6Nb alloy after the remelting process. The micrograph on the left shows the precipitates at the upper part of the sample. The micrograph in the right shows the absence of precipitates bottom of the sample.

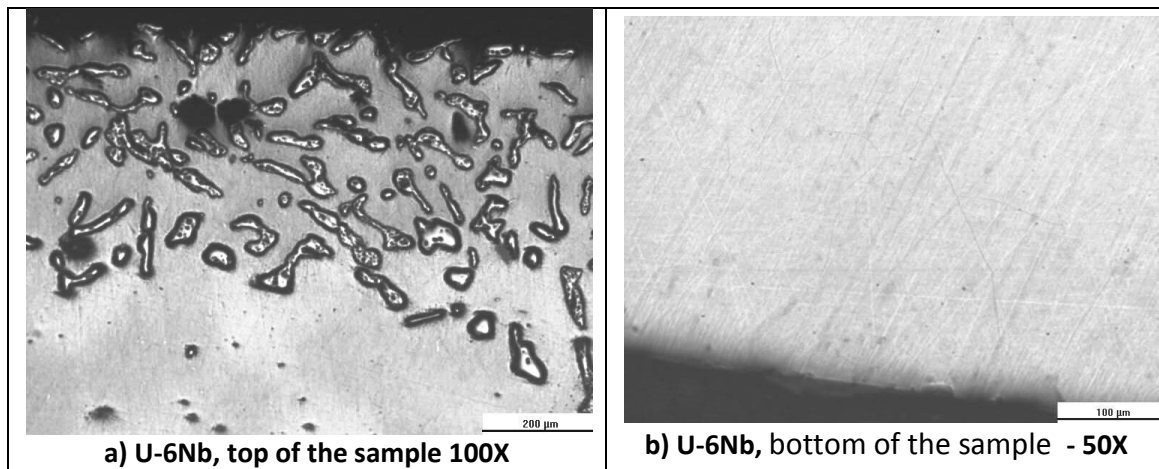


Figure 4 - Optical micrographs of remelted U-6Nb a)100x; b)50x

Table 4 shows the punctual EDS microanalysis of U-6Nb, U-5Zr-5Nb and U-2.5Zr-7.5Nb alloys after the remelting process. The values found in Table 4 were calculated by taking the average of several punctual analysis in all over the sample, i.e., in the upper part and in the bottom part of the sample. For the U-5Zr-5Nb, the amount of zirconium and niobium increased and the uranium content was decreased in the matrix. For the U-5Zr-5Nb and U-2.5Zr-7.5Nb alloys, the precipitates are richer in zirconium and poor in niobium and uranium. In the U-6Nb alloy the precipitates are almost pure niobium.

Table 4 - EDS microanalysis of U-6Nb, U-5Zr-5Nb and U-2,5Zr-7,5Nb alloy after remelting process.

		%Zr ( $\sigma$ )	%Nb ( $\sigma$ )	%U ( $\sigma$ )
U-6nb	Matrix	-	4,50(0,70)	95,50(0,70)
	Precipitate	-	99,41(0,63)	0,59(0,63)
U-5Zr-5Nb	Matrix	4,05 (0,13)	4,36 (0,15)	91,59 (0,24)
	Precipitate	95,31 (2,69)	2,79 (2,37)	1,9 (0,61)
U-2,5Zr-7,5Nb	Matrix	1,65 (0,12)	6,85(0,11)	91,49 (0,21)
	Precipitate	83,05(10,63)	2,57 (0,37)	14,38 (11,01)

Table 5 shows the punctual EDS microanalysis of the upper and the bottom part of the matrix for the U-6Nb and U-5Zr-5Nb samples, after the remelting process. The values for these two measures (upper and bottom parts) are practically the same, showing no segregation of alloying elements due to density difference.

**Table 5** - EDS microanalysis of U-6Nb and U-5Zr-5Nb after remelting process.

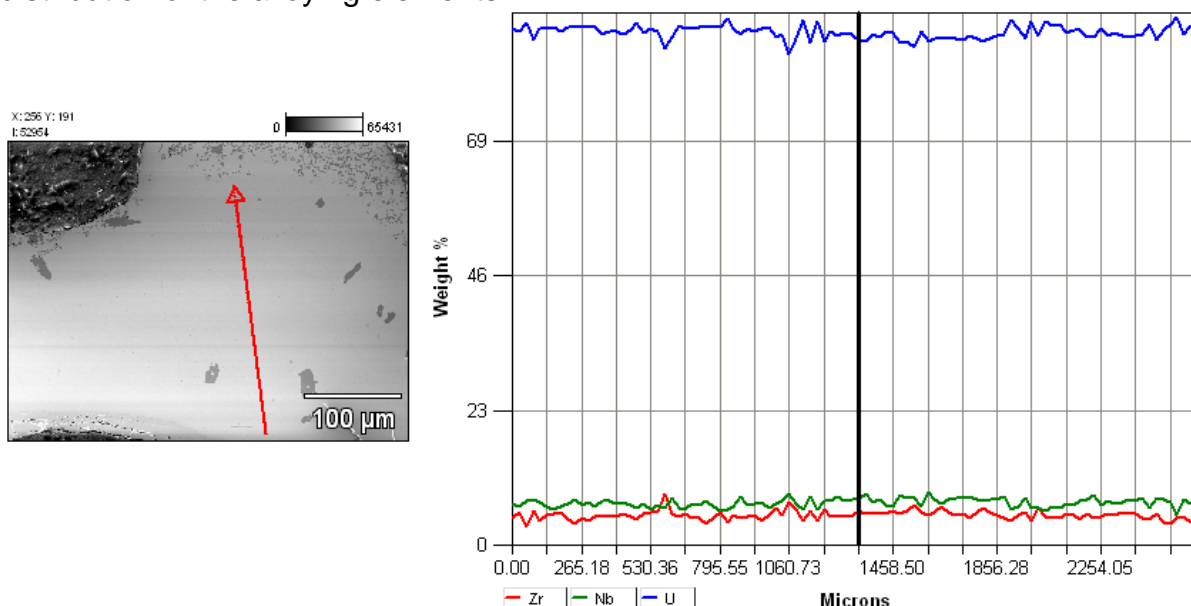
		%Zr ( $\sigma$ )	%Nb ( $\sigma$ )	%U ( $\sigma$ )
U-6nb	Upper Part	-	4,57(0,07)	95,47(0,07)
	Bottom Part	-	4,43(0,97)	95,57(0,97)
U-5Zr-5Nb	Upper Part	4,05 (0,11)	4,55 (0,12)	91,39 (0,28)
	Bottom Part	4,35 (0,13)	4,76 (0,01)	90,89 (0,11)

Table 6 shows the EDS microanalysis of an area (about 100 $\mu$ m x 100  $\mu$ m) of the U-6Nb, U-2.5Zr-7.5Nb and U-5Zr-5Nb samples, after the remelting process. For the U-6Nb , U-5Zr-5Nb and U-2.5Zr-7.5Nb alloys, this area analysis was made in the bottom part, in an area without precipitates. For the U-5Zr-5Nb, it was included an analysis on the upper part, in an area with precipitates. The precipitates are responsible for the high concentration of zirconium in the measurements made at the top of the sample. This demonstrates a preferential segregation of zirconium in relation to niobium.

**Table 5** - EDS microanalysis of U-6Nb and U-5Zr-5Nb after remelting process.

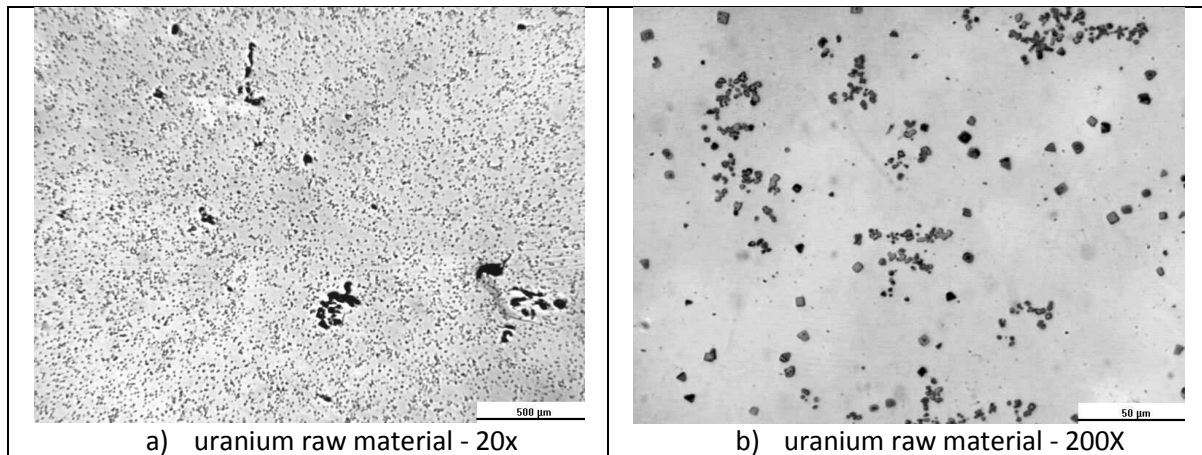
		%Zr ( $\sigma$ )	%Nb ( $\sigma$ )	%U ( $\sigma$ )
U-6nb	Bottom part, without precipitates	-	4,58	95,42
U-5Zr-5Nb	Upper Part	24,61 (1,62)	4,81 (0,09)	70,67 (1,53)
	Bottom Part	4,19 (0,33)	4,26 (0,59)	91,55 (0,82)
U-2,5Zr-7,5Nb	Bottom part, without precipitates	1,62	7,32	91,06

Figure 5 shows the EDS line scan profile for the U-5Zr-5Nb alloy. This analysis was made from the bottom to the upper part, in a line free of precipitates. The contents of zirconium and niobium are practically constant in all the line, showing a uniform distribution of the alloying elements.



**Figure 5** - EDS line scan profile for the U-5Zr-5Nb alloy

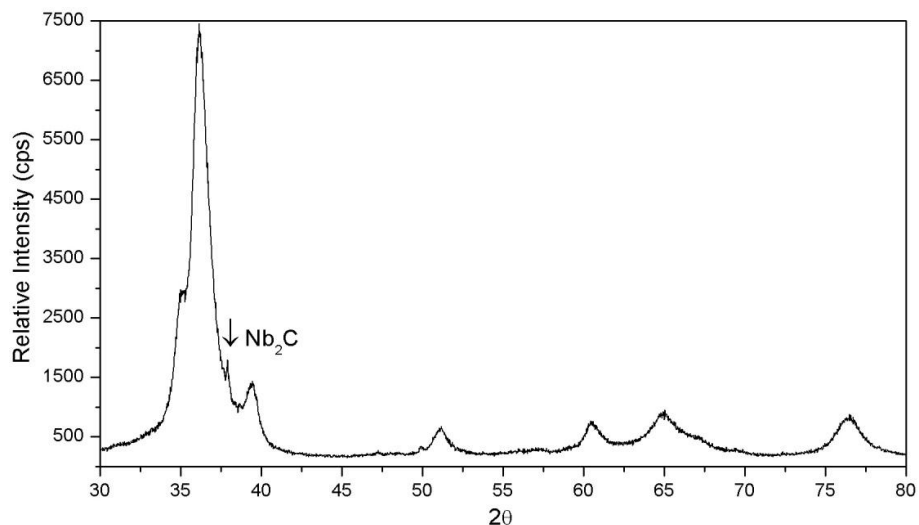
About the precipitates, it can be speculated that they are carbides of the types UC or Nb<sub>2</sub>C formed from C impurities contained in the uranium raw material. The formation of such carbide precipitates is thermodynamically favored due the very low solubility of C in uranium. Figure 6 shows a micrograph of the raw uranium. It can be observed several precipitates, distributed throughout the sample. It was not make any EDS analysis to confirm the presence of carbon in these precipitates in the raw uranium because the EDS equipment used in this investigation is unable to identify carbon.



**Figure 6** - Optical micrographs of uranium raw material - a)20x; b)200x

Figure 7 shows the X-ray diffraction of U-6Nb alloy. In this figure, it can be observed, besides the typical pattern of monoclinic α'' phase, the peak at about 36°, that clear indicates the presence of Nb<sub>2</sub>C precipitates, supporting the assumption that the precipitates of the alloys are very stable carbides stable even at high temperature.

These precipitates could not be vanished even after extensive homogeneous thermal treatments, but only by remelting process proposed at this work. Finally, it could be said that, regardless of the structures of these rich in Zr and Nb precipitates, they deplete the matrix in those elements, altering in this way the properties in relation to the nominal alloy.



**Figure 7** - X-ray diffraction scan of U-6Nb sample.

An alternative to compensate for the depletion of alloying elements in the matrix would put an excess of zirconium and niobium during melting or during the refinement of the alloy, reaching the desired composition of the matrix. Thus, the refining technique could homogenize the matrix and remove some of the carbon in the form of zirconium and niobium carbides.

## Conclusions

The refining technique presented in this paper was very effective to homogenate the matrix of U-Zr-Nb and U-Nb alloys and it was capable to restrict the precipitates in a thin layer on the top and it can be easily removed, leaving a matrix almost free of precipitates. There was no evidence of segregation of alloying elements by density difference. The contents of zirconium and niobium found at the top and bottom of the matrix were the same.

The formation of stable precipitates deplete significantly the content of alloying elements in the matrix of the U-Zr-Nb and U-Nb samples. The precipitates have higher content of zirconium than niobium, usually above 80%, and this causes a more pronounced depletion in the content of zirconium when compared with niobium.

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