

Evaluation of As-Cast U-Mo Alloys Processed in Graphite Crucible Coated with Boron Nitride

Kleiner Marques Marra, Tércio Pedrosa

Abstract—This paper reports the production of uranium-molybdenum alloys, which have been considered promising fuel for test and research nuclear reactors. U-Mo alloys were produced in three molybdenum contents: 5 wt.%, 7 wt.%, and 10 wt.%, using an electric vacuum induction furnace. A boron nitride-coated graphite crucible was employed in the production of the alloys and, after melting, the material was immediately poured into a boron nitride-coated graphite mold. The incorporation of carbon was observed, but it happened in a lower intensity than in the case of the non-coated crucible/mold. It is observed that the carbon incorporation increased and alloys density decreased with Mo addition. It was also noticed that the increase in the carbon or molybdenum content did not seem to change the as-cast structure in terms of granulation. The three alloys presented body-centered cubic crystal structure (γ phase), after solidification, besides a seeming negative microsegregation of molybdenum, from the center to the periphery of the grains. There were signs of macrosegregation, from the base to the top of the ingots.

Keywords—Incorporation of carbon, macrosegregation and microsegregation, solidification, uranium-molybdenum alloys.

I. INTRODUCTION

IN the last decades, a great deal of research effort has been put into the development of new nuclear materials (fuel elements) for pilot reactors destined to research and tests. Such new fuels have been characterized by a low isotopic enrichment in relation to the previous ones (isotope ^{235}U lower than 20%), high uranium density and good behavior during service, evaluated in terms of reduced susceptibility to the phenomenon termed “swelling”, which results from the generation and intense coalescence of fission gas bubbles [1], [2]. This phenomenon leads to mechanical failures of the structure of the fuel element when irradiated.

The fissile uranium concentration reduction results from an international agreement (the RERTR program - Reduced Enrichment for Research and Test Reactors), proposed by the US Department of Energy and signed at the end of the 1970's. This agreement was established with the aim of preventing the use of high enriched fissile uranium fuels, since this kind of material could be diverted to unpeaceful activities.¹

Since then, development researches have focused on uranium metal alloys that present higher density and good thermal conductivity, and therefore best performance in comparison to the traditional ceramic fuels (oxides and

silicates of uranium) [3]. Moreover, the metal alloys provide the stabilization of the uranium body-centered cubic structure (γ -phase), which is considered to present low susceptibility to swelling. Swelling is strongly determined by some crystalline phases present in the fuels' microstructure, notably by α -phase (orthorhombic).

Pure uranium metal, natural candidate in the search for the maximum density, is inadequate because of the intensity swelling observed during its nuclear irradiation. Such a behavior is related to the presence of α -phase stable at room-temperature. This solid solution phase also has as disadvantages in relation to the γ -phase low corrosion resistance and worse mechanical proprieties (low ductility) [4]. Therefore, transition metals such as Mo, Nb, Ti, V, Zr, and Cr have been added to the production of uranium alloys because they stabilize γ -phase, in a condition that is metastable to room temperature. Among the aforementioned elements, the main uranium alloys that show the tendency to stabilize the cubic phase are U-Mo, U-Nb, U-Re, U-Ti, U-Zr, and U-Zr-Nb. Among these alloying elements, molybdenum is the most attractive [4], [5].

Fuel elements can be produced with a homogenous core (monolithic form) or as composites obtained from powder metallurgy, in this case with the uranium alloy uniformly dispersed within a matrix of non-fissile good thermal-conductor material (usually aluminum alloys). Fuel elements dispersed in aluminum have reached densities of 8-9 g-U/cm³, while in monolithic form, the densities are around 16 g-U/cm³ [4], [5]. Hence, the knowledge of phase transitions in uranium alloys destined to research and test reactors is paramount to a predict ability about the behavior of such alloys during irradiation in the reactors and decisive to make them feasible as fuel elements. This paper is part of a broader study in which the structural stability of U-Mo alloys will be assessed in different molybdenum solute concentrations. Firstly, three alloys were fabricated with molybdenum contents of 5 wt. %, 7 wt.%, and 10 wt.%. An electric vacuum induction fusion furnace was used for this purpose. From the author's previous experiences, it is known that the use of graphite crucible and mold in that kind of furnace caused intense incorporation of carbon to the uranium alloys and that, on the contrary case, when yttria stabilized zirconia recipients are used, the contamination is negligible. Therefore, this investigation aimed at producing U-Mo alloys with boron nitride-coated graphite crucible and mold, which, according to literature, produce an efficient barrier against carbon contamination of the uranium alloys [6], [7]. With the alloys produced, the efficiency of BN coating and the as-cast

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structure of produced material were studied.

II. MATERIALS AND METHODS

In order to produce the U-Mo alloys, a Leybold-Heraeus electric induction fusion furnace, model IW-7P, was used. In this equipment, the graphite crucible that contains the metal charge is involved by an induction coil through which a high-frequency electric current circulates (4.8 kHz), under a maximum power output of 50 kW. After the metal charge is melted, a bottom bore in the crucible is open so that the molten material flows inside a mold, in lower level, also made of graphite, in a way to produce rectangular section prismatic ingots. The dimensions of the crucible and of the mold are presented in Table I. Both the crucible and the mold are put inside the induction furnace. It is worth noticing that before the alloy was melted, the furnace was submitted to three purge cycles with high-purity argon (a 400 torr), followed by vacuum (a 0.1 torr). The vacuum was kept after the third cycle, and then the alloys were melted and made flow.

Three U-Mo alloys compositions were made, aiming at different Mo concentrations, that is, 5 wt. %, 7 wt. %, and 10 wt.%. The uranium metal source used to produce the alloys had 99 wt. % uranium purity, while the molybdenum source presented a Mo concentration of 99.8 wt. %. Both materials present carbon content lower than 500 ppm and were loaded into the graphite crucible under the form of small chips, with dimensions smaller than 2 mm. That was done to make the melting and mixture of the materials easy, since molybdenum has a melting point around 2620 °C, much higher than that of uranium (around 1130 °C), and also above the maximum temperature reached during melting (around 1400 °C). The uranium chips were deoxidized with dilute solution of nitric acid (50%), and the two metal materials were degreased with acetone before the production of the alloys.

TABLE I
DIMENSIONS OF GRAPHITE CRUCIBLE AND MOLD USED TO PRODUCE THE U-MO ALLOYS

Crucible	Inner diameter (mm)	62,5
	Wall thickness (mm)	7
	Height (mm)	147
	Bore diameter in the bottom (mm)	10
Mold	Inner dimensions (mm)	15x35
	Wall thickness(mm)	38 (bottom wall) & 31 (lateral wall)
	Height (mm)	152

The crucible and the mold were coated with a ceramic material (boron nitride) in liquid suspension by cold spraying. The BN spray was provided by a brazilian supplier: Lubrifilm Co. According to the literature this kind of coating can result in a barrier, preventing the direct contact of the uranium alloys bath with the graphite and hence attenuate the incorporation of carbon to the alloys, even at temperatures higher than 1.000 °C [6], [7].

Fig. 1 shows, as an example, the crucible internally coated with boron nitrite (in white color) and Table II presents the used parameters of the induction furnace for the production of

each alloy, as well as the quantity of metallic inputs used.



Fig. 1 Graphite crucible coated with boron nitrite

TABLE II
ELECTRICAL POWER, FUSION TIME AND QUANTITY OF METAL MATERIALS USED TO PRODUCE THE U-MO ALLOYS (ELECTRICAL POWER= 20kW)

Alloy	Melting Time (minute)	Mass of Uranium and Molybdenum (g)
U-Mo5w%	13	438,0 and 25,3
U-Mo7w%	15	390,4 and 32,0
U-Mo10w%	13	475,9 and 55,5

The metallographic preparation of the alloys samples for microstructure observation in an optic microscope - OM (Leica, model DMG M) and in a scanning electron microscope - SEM (Zeiss, model Sigma VP), was done by grinding (up to abrasive sheet #1000) and mechanical polishing (with diamond paste, 3µm), followed by electrochemical polishing and etching with a phosphoric acid solution [8].

The carbon content of the U-Mo alloys was obtained in Leco analyzer, model CS 230, and the other chemical elements were evaluated through X-ray fluorescence spectroscopy, in Shimatzu EDX-720 equipment.

The alloys' density was measured through Archimedes' method, following the standard test method ASTM C 373-88 (1999).

In order to identify crystallography phases, a Rigaku diffractometer, model D\MAX Ultima, was used, and being applied a tension of 40 kV and a filament current of 30mA (copper anode).

The QuantiKov software was used to analyze the digital microstructure images generated in the SEM, aiming at determining the area fraction of the uranium carbides in the metal matrix.

As to the evaluation of the grain size, the intercept method was applied, following the ASTM E 112 (1996).

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Fig. 2 Aspect of U-5wt.%MO ingot

III. RESULTS AND DISCUSSION

The superficial aspect of the ingots was considered good, with discrete presence of shallow cavities and with little shrinkage on the top. For the analyses purpose, cross-sections transversal to the major axis (height) were taken 5 mm from the bottom and 5 mm below the surface on the top of the ingots. The analyses were always made in the central regions of such sections. It must be observed that the small ingots presented a thickness of 15 mm and a width of 35 mm, with a variation of height from 43 to 53 mm.

Fig. 2 shows, as an illustration, the ingot obtained for the U-5%Mo composition. Table III presents the ingots' final mass and the respective efficiency obtained in relation to the mass of the metallic inputs. The lower efficiency of the U-7w%Mo alloy is related to a problem that happened during the elaboration of that alloy, when the crucible's sealing pin got stuck at the end of the molten metal flow, no allowing its final fraction to be poured into the mold.

The chemical composition obtained in the ingots base is shown in Table IV. It can be observed that there was a deviation in relation to the concentration planned for the molybdenum element. Attention must be called to the fact that there was also detection of the elements Zr, P, Fe, Ni, and Zn, but the sum of

those elements contents always ranged from 0.4 wt.% to 0.6 wt.%.

TABLE III
INFORMATION ABOUT U-MO INGOTS PRODUCTION

Alloy	Mass (g)	Casting efficiency (%)
U-5%Mo	449.0	96.9
U-57%Mo	356.4	84.3
U-10%Mo	491.6	92.5

TABLE IV
CHEMICAL COMPOSITION OF THE U-MO INGOTS (w%)

Alloy	Mo	C	Other elements
U-5%Mo	5.80	0.117	0.420
U-7%Mo	8.15	0.146	0.495
U-10%Mo	9.03	0.192	0.573

Note: U content: balanced.

It can also be observed in Table IV that there was a noteworthy carbon contamination, resulting from the graphite crucible and mold besides an increase in that element concentration with the raise of the molybdenum content. Such an effect is certainly related to the increase of the solubility of carbon in uranium with the raise of the molybdenum content, which can be seen in phase diagram of the ternary alloy U-Mo-C [9]. In Fig. 3, it can be inferred that the BN coating was partially effective since a much higher level of contamination was verified when uncoated (bare) crucible and mold were used. A deterioration of the BN coating layer must have happened because of the high temperature of the molten metal and the convection currents (and resulting erosion) caused by the oscillating magnetic field.

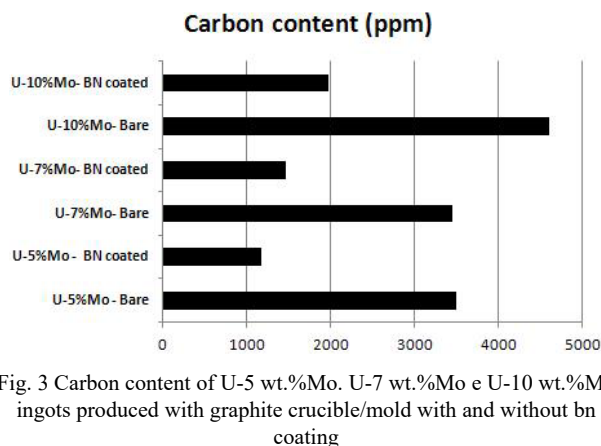


Fig. 3 Carbon content of U-5 wt.%Mo, U-7 wt.%Mo e U-10 wt.%Mo ingots produced with graphite crucible/mold with and without bn coating

The increase of the Mo content caused a decrease of alloys' density as showed in Fig. 4. This effect is due to the fact that Mo is "lighter" than uranium. The mathematical adjustment equation obtained by linear regression predicts, as Fig. 4 shows, a pure uranium density (Mo=0 content) of 18.60 g/cm³ lower than that informed in the literature [10] which is of 19.07 g/cm³. Such a difference is certainly related to the contaminating chemical elements present in the alloys produced ("other elements" in table IV) and to carbon itself.

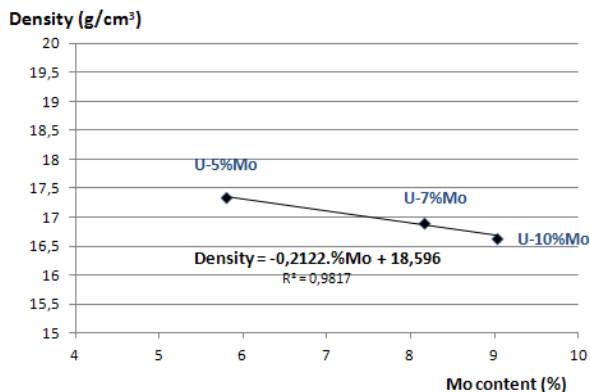


Fig. 4 Density variation with Mo content

It was also observed that there was a chemical composition variation between the top and the base of the ingots, which indicates the occurrence of macrosegregation in the solidification of the ingots. This was reinforced by the difference between the density values between the top and the base (lower density on the top because of the segregation). For example, the Mo content, the carbon concentration, and the density are presented in Table V for the base and top of the U-10 wt.%Mo alloy ingot.

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The result of the X-rays diffraction analysis indicated that the three U-Mo alloys basically presented body-centered cubic metastable structure (γ -phase). as metal matrix. with the occurrence of uranium carbides (UC) precipitated in the matrix. as showed in Fig. 5. The observation of the microstructure under optic microscopy confirmed the presence of a matrix with a big quantity of carbides. besides a not so coarse granulation. ranging from 30 to 45 μm (Figs. 6 and 7). A difference between the microstructure of the ingots top and base was observed as well with a coarser granulation on the top. Therefore, the cooling rate imposed to the ingots by the mold was able to generate a granulation that was not so coarse and sufficient to guarantee the presence of uranium under metastable γ -phase since there was not decomposition of this phase in others more thermodynamically stable at room temperature: α and γ' [8]. The coarser granulation on the top was certainly due to a slower local cooling rate.

Attention must be called to the grains appearance with a characteristic of cellular dendritic substructure (observed in MO). This kind of substructure is common in U-Mo alloys in as-cast state and results in the occurrence of negative segregation of molybdenum (microsegregation) in a way that the grain contours present a more reduced concentration of this element [8].

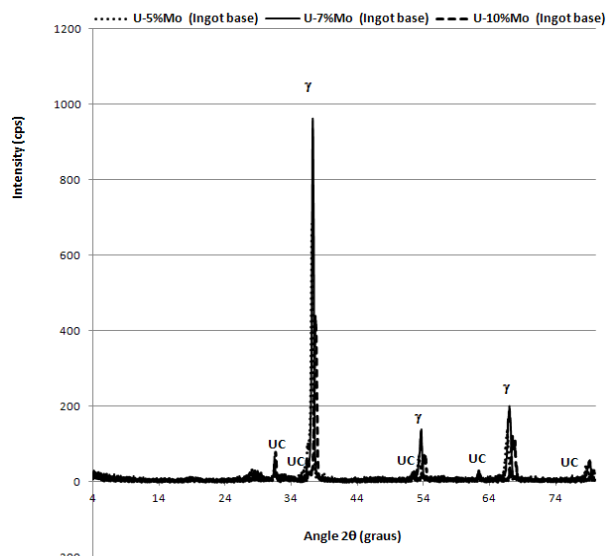


Fig. 5 X-ray diffraction patterns of the U-Mo alloys

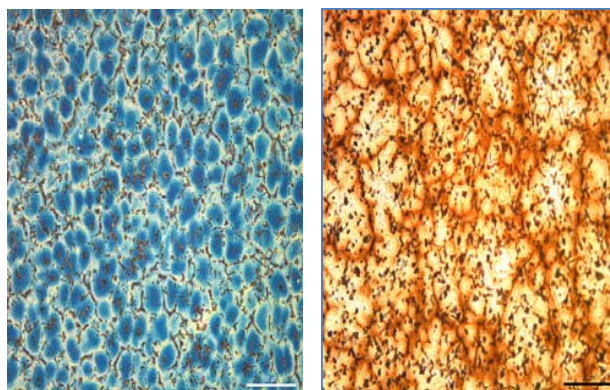
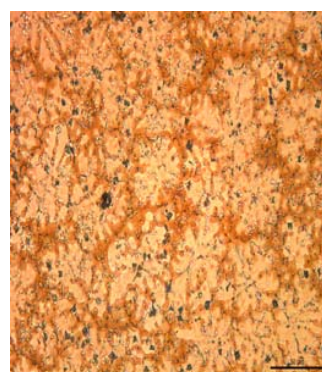
(a) Grain Size: $30.3 \pm 3.5 \mu\text{m}$ (b) Grain Size: $37.6 \pm 5.9 \mu\text{m}$ (c) Grain Size: $2.4 \pm 3.7 \mu\text{m}$

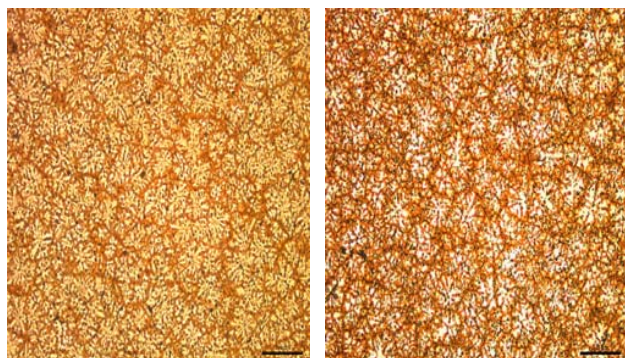
Fig. 6 Microstructure (om) and average grain size (gs) for the three studied alloys (ingot base). (a) U-5 wt.%Mo. (b) U-7 wt.%Mo. (c) U-10 wt.%Mo. (500x)

In respect of uranium carbides, two types of precipitate were observed: one of “quadrilateral” morphology (type 1) and the other in elliptic or rounded form (type 2). The type 1

shows bigger dimension almost always occurred inside the grains and might have been formed in the liquid phase of the alloy [11]. The type 2, on the other hand, tended to occur next to and around the grain boundary supposedly formed during solidification or in solid phase (Fig. 8).

TABLE V
MO AND C AVERAGE CONTENT AND DENSITY FOR THE U-10W%MO ALLOY
(BASE AND TOP)

Alloy	Ingot base	Ingot top
Mo content(%w)	9.03	9.98
Carbon content (ppm)	1978.7	2011.1
Density (g/cm ³)	16.64	16.54



(a) GS=32.4±3.7μm (b) GS=45.2±7.4μm

Fig. 7 Microstructure (OM) and average grain size (GS) for the U-10%-MO Alloy (A) base. (B) top. (200x)

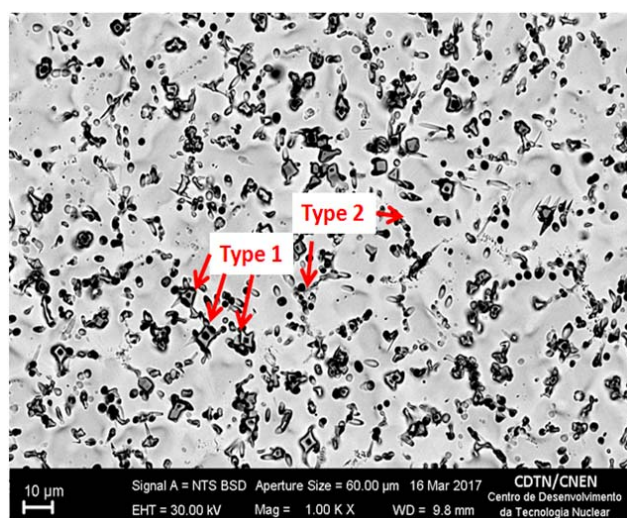


Fig. 8 Uranium carbide aspect (SEM) U-10wt. %MO alloy (Ingot top)

Microstructure images under high magnification in SEM combined with concentration maps obtained by Energy Dispersive Spectroscopy (EDS) show that the particles in the metal matrix are really uranium carbides as Fig. 9 demonstrates.

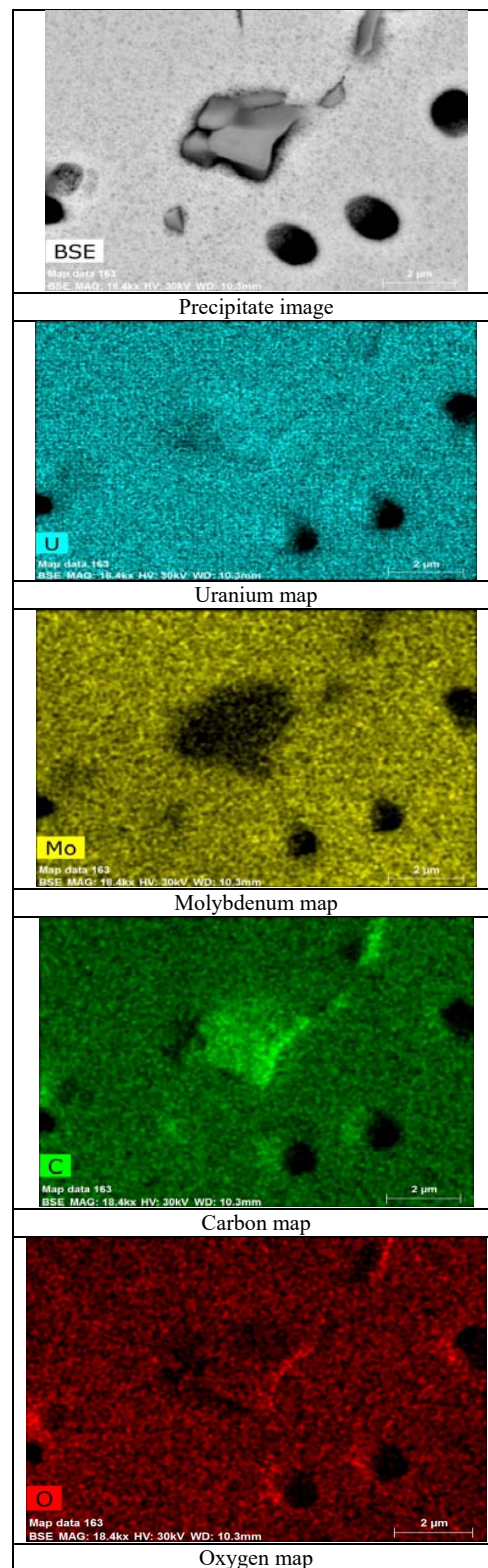


Fig. 9 Image and concentration map via EDS/SEM of a UC particle in metallic matrix of the U-5wt.%MO alloy (ingot base)

An attempt to correlate the carbon content of the U-Mo

alloys with the area fraction of the carbides was made. In order to do so, the carbides concentration was obtained by processing the microstructure images obtained in SEM (generated by backscattered electrons) with the use of a renowned image analysis software: QuantiKov. Nevertheless, as Table VI shows, there was overestimation of the area fraction when results were compared to values predicted by the mathematic model developed by the researcher Devaraj and collaborators [12]. Such a model is based on the carbon content and density of the uranium alloys. The observation of images obtained in SEM under high amplification showed the origin of this difference. The solution of phosphoric acid was used to reveal the microstructure caused severe corrosion, dissolving a big part of carbides and causing cavities that were bigger than the dimension of these particles. This effect can be seen in Fig. 8, where cavities previously occupied by carbides can be seen as well as a partial separation between the particle showed and the matrix. certainly caused by the chemical reagent.

It was also observed that there is no apparent relation between the carbon content (or Mo content) and the granulation resulting from as-cast structure as indicated by Fig. 10.

TABLE VI
AREA FRACTION (A_f) OF URANIUM CARBIDES AND CARBON CONTENT FOR THE U-Mo ALLOYS

Alloy	Carbon content (ppm)	QuantiKov (%)	Devaraj (%)
U-5%wMo (base)	1165	11.6	3.8
U-7%wMo (base)	1464	5.5	4.8
U-10%wMo (base)	1979	22.9	6.4
U-10%wMo (top)	2011	22.3	6.5

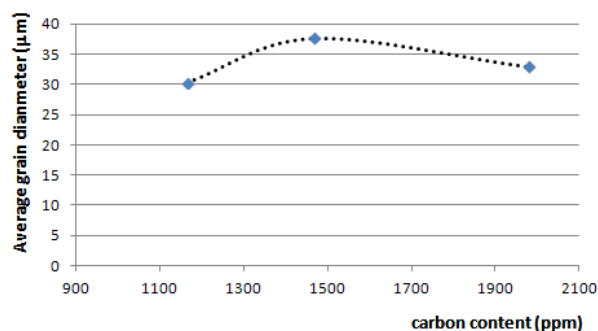


Fig. 10 Carbon content related to grain size for the U-Mo alloys (ingot base)

IV. CONCLUSION

This paper approaches the production of U-Mo alloys in electric vacuum fusion furnace in three molybdenum contents: 5 wt.%, 7 wt. %, and 10 wt. %. In the alloys production, a graphite crucible and a mold internally coated with boron nitride were used. This coating did not prove to be totally effective.

The carbon content of the alloys increased with the concentration of molybdenum, reaching up to 2000 ppm for the most Mo-loaded alloy. It was also verified that the Mo

increasing reduced the alloys density.

The granulation of as-cast structure was not very coarse, ranging from 30 to 45 micrometers without showing clear dependence on the carbon or on the molybdenum content.

The microstructure presented characteristic of occurrence of molybdenum microsegregation. The granulation appeared to be coarser on the ingots top certainly because of a softer local cooling rate.

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