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STUDY OF THE PROCESSES FOR OF REMELTING ZIRCONIUM ALLOYS IN AN ELECTRIC ARC FURNACE

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ABSTRACT

Zirconium alloy tubes are used as cladding for fuel elements of PWR nuclear reactors, which contains the UO_2 pellets. In the manufacture of these fuel element parts, machining chips from the nuclear grade zirconium alloys are generated. Hence, these machining chips cannot be discarded, as ordinary metallic waste. Thus, the recycling of this material is a strategic aspect for the nuclear technology, both for economic and environmental issues. The main reason is that nuclear grade alloys have very high cost, are not commercially produced in Brazil and has to be imported for the manufacture of the nuclear fuels. This work discusses a method to melt and recycle Zircaloy chips, using an electric-arc furnace to obtain small laboratory ingots. The chemical composition of the ingots was determined using X-ray fluorescence spectroscopy and was compared to the specifications of nuclear grade Zircaloy and to the chemical composition of the received machining chips. The ingots were annealed in high vacuum, as well as were hot rolled in a mill. The microstructures were characterized by optical microscopy. The hardness was evaluated using the Rockwell B scale hardness. The results showed that the compositions of the recycled Zircaloy comply with the chemical specifications and a suitable microstructure has been obtained for nuclear use.

1. INTRODUCTION

The UO_2 pellets of nuclear fuel in the PWR reactors are usually encased in zirconium alloy tubes. This material is used as fuel-rod cladding in all water-cooled nuclear reactors, which constitute more than 90 percent of the world's power reactors. Both the cladding and other structural components of the fuel elements are exposed to water environments at high pressure and high temperature. Furthermore, to be used at the reactor core it is necessary that these materials have a low absorption cross-section for thermal neutrons. The zirconium-based alloys comply with nuclear requirements due to the excellent mechanical properties, corrosion resistance and low absorption cross-section for thermal neutrons. These properties are obtained due to the low hafnium content in the alloys and appropriate chemical compositions and microstructures. The most common alloys are called Zircaloy-2, Zircaloy-4, Zirlo® and M5®, whose elemental compositions are shown in TAB. 1.

TABLE 1. Typical nominal compositions of Zircaloy-2, Zircaloy-4, Zirlo® and M5® alloys [1-4]

Element (mass %)	Sn	Fe	Cr	Ni	O	Hf	Zr	Nb
Zircaloy-2	1.2 - 1.7	0.07 - 0.20	0.05 - 0.15	0.03 - 0.08	0.12	< 1000 ppm	balance	-
Zircaloy-4	1.2 - 1.7	0.18 - 0.24	0.07 - 0.13	-	0.12	< 1000 ppm	balance	-
Zirlo®	0 - 0.99	0.11	-	-	0.11	40 ppm	balance	0.98
M5®	< 30 ppm	0.03	40 ppm	-	0.14 - 0.15	-	balance	1.00

Each rod is closed at its ends by a plug also made of Zr alloy, which is produced from solid metal bars. During manufacture of this component, large amounts of chips resulting from machining of parts in automatic lathes are generated. Nuclear grade zirconium alloys are considered strategic materials. Therefore, besides its high cost, it is not freely commercialized. Consequently, the production of Zr alloys is a requirement for the autonomous domain of the process of nuclear power generation and the Zircaloy machining chips are a valuable source of nuclear zirconium. Recent work by Collins et al. with the Zr recovery of spent fuel elements evaluates the zirconium in these conditions between $ 40-80 / kg [5], since the Zr metal is the major constituent of Zircaloy (Zry-4 for short) alloy with the great advantage of being Hf free [1].

Brazil has the technology for the production of nuclear fuel from the uranium mining to manufacturing and assembling of fuel elements, including the isotopic enrichment process. However, the production of zirconium alloys is not carried out in the country at industrial scale and as consequence, the used Zr alloys in its nuclear power plants is imported.

2. MATERIALS AND METHODS

The Zry-4 raw material used in this work was provided in the form of machining chips contaminated with cutting oil. The conditioning treatment consisted of an initial step of material cleaning, followed by compaction of the chips [6]. Initially a manual magnetic separation was undertaken in order to remove undesirable ferrous alloys chip contaminations. After, it was used a degreasing with household neutral detergent and water rinsing, followed by acid pickling with HCl (50 HCl : 50 H_2O) and HNO_3 (30 HNO_3 : 70 H_2O) during 30 min, this to remove other possible non-magnetic impurities containing Fe. The chemical composition of the samples was determined by the technique of energy dispersive X ray fluorescence spectrometry (EDXRFS). The determination of the elements was performed by the method of fundamental parameters, where the sensitivity curve was obtained using standards and certified materials [7,8]. Certificates and measured values for CRM 098 standard were used for calibration.

The equipment used for melting the chips was a VAR (vacuum arc remelting) furnace fitted with non-consumable electrode (W-2%ThO_2) under inert gas atmosphere (Ar: 99.998%

purity). The VAR operating conditions are shown in TAB. 2. The machining chips were compacted into small briquettes aimed for a properly accommodation of the charge in the grooves of the melting floor of VAR, in turn to avoid scattering of the electric arc during melting. Six small briquettes of compacted machining chips were placed inside a 10 mm width groove to be melted altogether, resulting in bars with approximately 50 x 10 x 10 mm^3 dimensions, as shown in FIG. 1. These bars were used for the characterization studies. Altogether, 10 melting charges were carried out.

TABLE 2. Operating parameters related to the VAR preparation, current and atmosphere during melting of the samples

Conditions	Melt
Furnace purging (before melting)	3 times in 150 mmHg vacuum alternated with Ar injection at 760 mmHg
Current (A)	110
Atmosphere and pressure during melting (mmHg)	Ar/760

From the 10 ingots, two of them, in this work named samples 1, 2 and 3 were subjected to a thermo-mechanical treatment, which consisted of annealing at 850 °C and 950 °C, respectively, followed by hot rolling in a two-high-four-high mill at 30% thickness reduction. In order to avoid oxidation of the Zr alloy during furnace heating, these samples were encapsulated in copper tubes. The samples were cut with a diamond precision disk and embedded in cold-cure polyester resin, and subjected to grinding with SiC paper 400 to 4000 mesh. This was followed by polishing in 6 μm and 1 μm diamond paste, with final polishing in colloidal silica. The etching was carried out with a solution of H_2O_2 50% + 25% HNO_3 + 25% ethanol + 2 drops HF [9]. The metallographic analysis was performed in an optical microscope.

The hardness measurement was made with the Rockwell hardness scale B (HR_B). For samples 1 and 2, the hardness measurements were performed along the transverse and longitudinal section after hot rolling. This was carried out to verify the occurrence of the anisotropy hardness due to mechanical working. The X-ray diffraction measurements were carried out in a diffractometer with goniometer set-up in the theta-theta geometry with 285 mm radius and fitted with pyrolytic graphite monochromator, scintillation detector, CuK_α radiation, 40 kV voltage and 30 mA current. The samples used for X-ray diffraction analysis were prepared through grinding the surfaces up the 1200 mesh [10].

3. RESULTS AND DISCUSSION

TAB. 3 shows a comparison of the chemical specification values for Zry-4, CRM 098 standard certified values [7], CRM 098 measured values and the Zry-4 chips. As it can be seen, the chemical composition of the machining chips and the measured values in CRM 098 are in agreement with the certified values within the measurement accuracy, validating the analysis methodology. In addition, the analysis showed that the composition of the chips meets the specification as seen in TAB. 1.

The TAB. 4 presents the results of chemical composition measured by X-ray fluorescence of the samples obtained after melting the Zry-4 machining chips. The chemical analysis of the samples contained in this table showed that all the alloy elements content are as specification, except for Fe which is above the specified value, indicating that there was still contamination of the machining chips that was not removed during the cleaning treatment.

TABLE 3. Chemical analysis of CRM 098 standard and Zry-4 chips by X-ray fluorescence spectroscopy

Element (mass %)	**CRM 098** certified values [7]	**CRM 098** measured values M±U - (N=3)	**Zry-4 chips** measured values M±U - (N=3**)**
Cr	0.0906±0.009	0.088±0.003	0.080±0.010
Fe	0.2143±0.002	0.210±0.006	0.213±0.036
Sn	1.460±0.009	1.42±0.15	1.246±0.102
Zr	balance	98.30±0.15	98.43±0.06

Note: M - average; U - uncertain; N - repetitions number.

TABLE 4. X-ray fluorescence chemical analysis of Zr alloy obtained after melting the Zry-4 machining chips and the specification values for the Zry-4 alloy

Element (mass %)	**Melted sample**	**Zry-4 specif.** [2]
Cr	0.066±0.003	0.07-0.13
Fe	0.340±0.030	0.18–0.24
Sn	1.110±0.030	1.2–1.7
Zr	98.45±0.010	balance

FIG. 1a shows the appearance and size of the as melted ingots of Zry-4 and the same samples after hot rolling and after encapsulation removal. The hot-rolled ingots had a section area reduction percentage of 27% and 32% in the samples 1 and 2, respectively, as it can be observed in FIG. 1b. It is noted that the encapsulation was effective in avoiding the oxidation on the sample during the hot rolling.

a) b)

FIGURE 1. a) Ingots obtained in VAR furnace after melting Zry-4 machining chips. b) Samples 1 and 2 after hot-rolling and encapsulation removal.

In FIG. 2 is shown a typical microstructure of the samples before heat treatment and in FIGs. 3 and 4 are shown the optical micrographs of the samples heated according to the temperature and rolling mills schemes mentioned before. In the optical micrograph of the rolled sample at 850 °C shown in FIG. 3, it is observed Widmanstätten microstructure features. Before the rolling, the fibers have a parallel-type arrangement, with lengths between 80 μm and 100 μm, as shown in FIG. 3. After the rolling, the fibers have taken the Widmanstätten basket weave configuration with smaller and finer fibers, measuring between 40 and 60 μm and approximately 5 μm thick. In the optical micrograph of the rolled sample to 950 °C, as shown in FIG. 4, there is a morphology similar to the previous, i.e., Widmanstätten basket weave type, but appearing thickening of the fibers, having 5 μm to 10 μm in the thickness and 30 μm to 40 μm in the length.

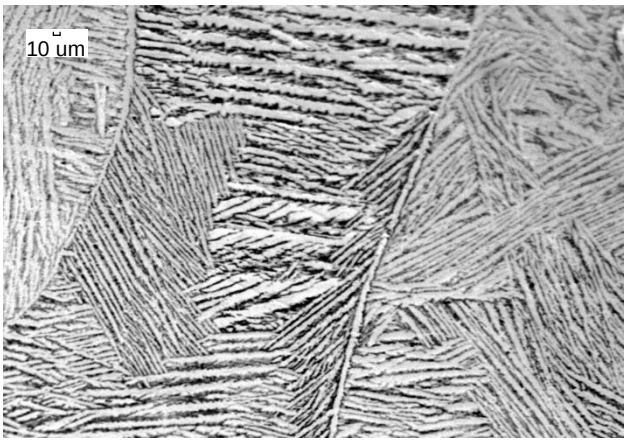

FIGURE 2. Optical micrograph sample 1 of before heat treatment, where it can be observed parallel slats of the α phase.

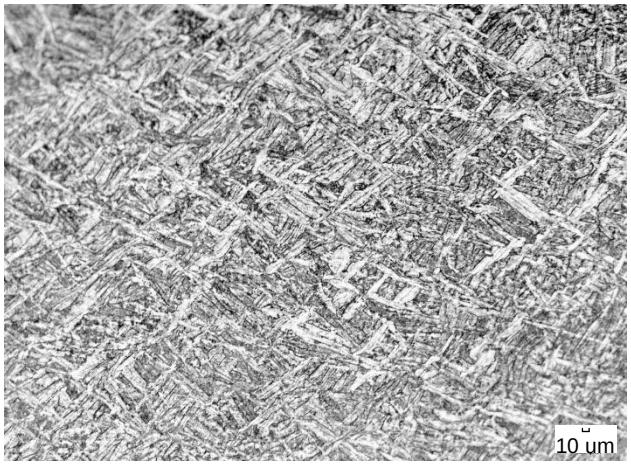

FIGURE 3. Optical micrograph sample 1 after the annealing at 850 °C and hot rolling, with characteristic morphology of Widmanstätten structure of basket weave form[11]**.**

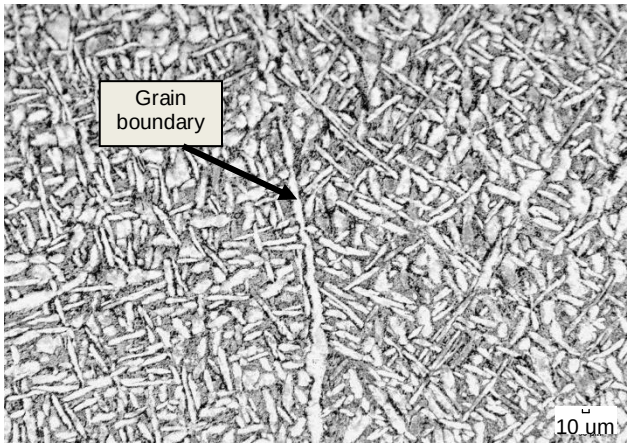

FIGURE 4. Optical micrograph of the sample 1 after annealing at 950 °C and hot rolling.

The TAB. 5 lists the Rockwell B hardness values measured in the samples 1, 2 and 3, after the thermo-mechanical treatment. In order to know the evolution of the hardness with the thermo-mechanical treatment, it was measured the hardness of the sample 3 prior to hot rolling and was used as reference to compare with the samples 1 and 2.

TABLE 5. HRB hardness of the samples measured before and after hot rolling in its transversal and longitudinal directions

Sample	1	2	3
Before rolling (HRB)	-	-	93.0 ± 0.5
Transversal section (HRB)	103.3 ± 0.4	89.7 ± 4.4	96.4 ± 2.3
Longitudinal section (HRB)	105.7 ± 0.5	92.8 ± 0.7	98.2 ± 0.2

The explanation for these values was found through the binary diagram Zr-Sn. It is noted that the samples 1 and 2 were at the time of rolling in α and β phases, respectively. According to this and from the deformation theory [10], the α phase is more difficult to deform, resulting in increased hardness, while sample 2 had a higher ductility due to be in β phase with lower hardness. Moreover, it can be seen from TAB. 5 that the hardness varies depending on the direction, that is, the hardness is different in the longitudinal and transverse directions of the sample that corresponds to the rolling direction. This is attributed to anisotropy of toughness [12,13].

In FIG. 5 is shown the X-ray diffraction pattern of the sample 4 plotted with the adjusted data using the Powder Cell program. Besides the identification phases, the adjustment also provides the indexes of diffracted plans and the values of the parameter settings in the network. FIG. 6 shows the X-ray diffraction of the samples 1, 2 and 3 with thermo-mechanical treatments plotted on the same graph for comparison.

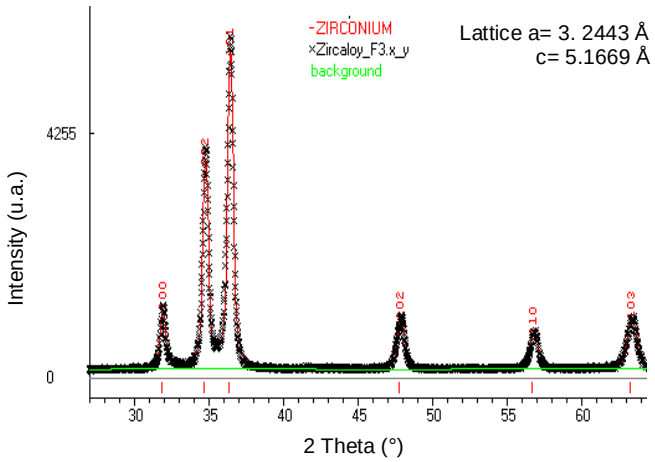

FIGURE 5. X-ray diffraction refinement of the Zyr-4 sample 4 after arc melting. The adjusted lattice parameters and the indexes are shown in the figure, indicating Zr.

The X-ray diffraction, as can be seen in FIG. 6 only revealed the presence of Zr, due to the fact the content of other chemical elements in the alloy is low and it was maintained the structure of the Zircaloy. In FIG. 6 it can also be noted that the different conditions of rolling did not interfere in the crystal structure of the samples.

Confronting each lattice parameters shown in FIG. 5 (a = 3.2443 Å, c = 5.1669 Å) with the values of zirconium HC structure found in the literature (a = 3.232 Å, c = 5.147 Å) [14][15], it is verified that the lattice parameters of Zircaloy samples are higher than those of pure Zr. The differences between the lattice parameters of Zr and Zircaloy samples are due to the different amounts of dissolved gases, alloying elements and microstructural conditions.

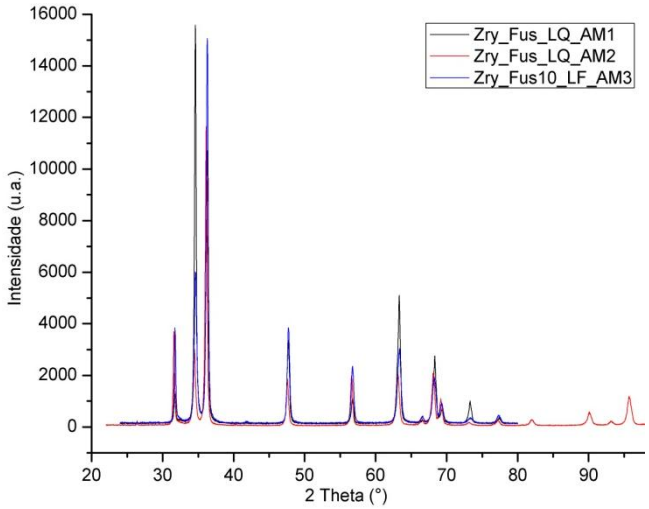

FIGURE 6. Superposition X-ray diffraction of the hot rolled samples of Zry-4.

4 CONCLUSION

Observing the chemical analyzes of samples after melting, it can be concluded that the original starting composition of Zircaloy alloy remained in the melted material. It is also

concluded that the supplied chips as raw material contained steel scraps, which increased Fe and Cr contents.

Through the microstructural analyzes of samples it can be concluded that the alloys showed the typical morphology of as cast Zircaloy. As for the rolling results it was found that the samples meet the conditions required for thermo-mechanical processing, although further studies needed to improve the ductility.

Finally, this study demonstrated the feasibility of recycling Zircaloy machining chips by remelting in electric arc furnaces in terms of suitable properties and thermo-mechanical processing.

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