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Chemical and microstructural characterization of remelted Zircaloy by X-ray fluorescence techniques and metallographic analysis

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Abstract Brazilian nuclear power reactor (PWR type) use, as nuclear fuel, sintered UO_2 pellets with Zircaloy cladding. The cladding material has to present high mechanical strength and corrosion resistance, which are related to the material chemical composition and microstructural characteristics. Zircaloy machining scraps were remelted using VAR process, resulting in a billet, and its elemental composition was determined. The major elements Zr, Sn, Fe, Cr and Ni were determined by EDXRFS; Hf and contaminants were determined by WDXRFS. The chemical analysis did not show changes in the alloy elemental composition, except for Fe and Cr, which their out-off content can be attributed to contamination from steel scraps. The found Cu contamination may be related to the contact of the melted Zircaloy droplets with copper crucible. The billet microstructure was evaluated using optical and scanning electron microscopy and showed the typical zirconium alloy microstructures (needle and plates) resulting from the high cooling rate and thermal gradients, present during the solidification.

Keywords X-ray fluorescence analysis · Zircaloy chemical characterization · Zircaloy scraps recycling · Microstructural and optical characterization

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Introduction

The nuclear fuel used in the power water reactor (PWR) type nuclear reactor is sintered uranium dioxide pellets (UO_2), with Zircaloy cladding. Brazil is self-sufficient in the nuclear fuel production since mining, enrichment and nuclear fuel manufacture processes, excluding the production of Zircaloy, which is imported. Usually, Zircaloy scraps from nuclear fuel parts fabrication cannot be discarded and are disposed in drums, without any treatment, contaminated by machining fluids and other metal scraps. The recycling of this material is important for the Brazilian Nuclear Policy, which targets the reprocess of Zircaloy residues for economic and environmental aspects.

The alloys, so-called Zircaloy-2, Zircaloy-4 plus Zirlo® are used in nuclear fuel manufacture as claddings and refrigerator pipes [1]. The properties of Zircaloys are related with chemical composition and microstructural characteristics; where, in Table 1, their chemical compositions are presented [2, 3].

Vacuum arc remelting (VAR) is a melting process for production of metal ingots with elevated chemical and mechanical homogeneity for highly demanding applications. The use of this technique allows the production of ingots of reactive metals, that cannot be melted in open air furnaces and presents some other advantages, like a high degree of control over the microstructure, the ability to minimize segregation and the elimination of gases dissolved in the melted metal, generally detrimental to properties, that can escape from liquid metal to the vacuum chamber. Additionally, elements with high vapor pressure such as oxygen, carbon, sulfur, and magnesium (frequently contaminants) are lowered in concentration.

Zirconium, hafnium and titanium are reactive metals due to their facility to react in presence of oxygen and/or

Table 1 Zircaloy-2, Zircaloy-4 and Zirlo® chemical composition [2, 3]

Alloy	Sn (%)	Fe (%)	Cr (%)	Ni (%)	Hf (µg g^{-1})
Zircaloy-2	1.2–1.7	0.07–0.20	0.05–0.15	0.03–0.08	<100
Zircaloy-4	1.2–1.7	0.18–0.24	0.07–0.13	–	<100
Zirlo®	0–0.99	0.11	–	–	<40

nitrogen and they are known as refractory compounds [4]. Their alloys are very resistant to inorganic acid attack making the dissolution process for sample preparation difficult, so their determination from rock, minerals and metallurgic materials has been a challenge for analysts. In metallurgical areas, the sample preparation, mainly in the quality control of the production processes, should be simple, rapid and reproducible.

X-ray fluorescence spectrometry (XRFS) has developed into a well-established multi-elemental analytical technique, with a wide field of practical applications (mineralogy, biology, archeology, micro-electronics, forensic and materials) [5, 6]. One of the major areas of application is the analysis of mixtures which are difficult to separate chemically, once chemical separation is often unnecessary, since spectra of the individual elements may be clearly differentiated [7]. Also, the direct analysis of metals and alloys has been one of the main applications, on account of its rapidity and satisfactory accuracy. Moreover, the technique is non-destructive, hence the same samples can be used for further analyses. Therefore, the XRFS is a fast, precise and low-priced method, when compared to other multi-elemental analytical techniques such as AAS (Atomic Absorption Spectrometry) and ICPOES (Inductively Coupled Plasma Optic Emission Spectrometry.

In the present work, the chemical characterization of remelted Zircaloy billets, obtained by VAR process, was done. The major elements Sn, Fe, Cr and Ni were determined by EDXRF (Energy Dispersive X-Ray Fluorescence Spectrometry) and Hf determined by WDXRF (Wavelength Dispersive X-Ray Fluorescence Spectrometry). Also, is presented the billet micro-structural analysis by optical and scanning electron microscopies [8, 9].

Experimental

The Zircaloy scraps were received with contamination from machining fluids and were cleaned with commercial degreasing detergent and compacted in bar shape in a hydraulic press. The bars were remelted in a laboratory scale VAR furnace [10], resulting in billets of about 25 mm diameter and 120 mm long (Fig. 1). The central part of the billet was cut in two directions and named longitudinal (L) and transversal (T) samples.

Fig. 1 Ingot of remelted Zircaloy obtained by VAR process

Sample preparation

The L and T samples were encapsulated on polymeric cold resin and grounded up to grade 4000 SiC sandpaper, followed by polishing with 5 and 1 µm diamond and 0.5 µm alumina suspensions (Fig. 2). L and T samples plus BCR 98 standard sample (Certificated reference material, Zircaloy-4 from Commission of the European Communities) were analyzed by EDXRF for Cr, Fe, Sn and Ni determination. A fraction of the billet was dissolved in 25% (v/v) HF solution, where the elements were precipitated simultaneously and dried at 400 °C. This powder was ground and pelletized using an hydraulic press (B. Herzog, model HP HTP40) obtaining a 20 mm diameter and 0.1 mm thick pressed pellet for Hf determination by WDXRF.

XRF analysis

The EDXRF spectrometers operate at high tension (kV) and low current (µA); this configuration is very adequate for major and minor elements determination, achieving fast and precise analyses.

Cr, Fe, Sn and Ni were determined using EDXRF spectrometer (Shimadzu Co., model 720), using the following instrumental conditions: X-ray tube: Rh; excitation: 50 kV and 10.0 µA; detector: Si(Li); fixed counting time: 20 s; irradiation area: 1 mm^2. For each fluorescent characteristic line (CrKα, FeKα, NiKα and SnKα) six repetitions were obtained and their content were determined using the experimental sensitivity curve (Fig. 3), obtained by Fundamental Parameters method [6, 11].

The Fundamental Parameters method was evaluated using Zircaloy-4 certificated reference material (CRM BCR 098). The precision assess was carried out in relation

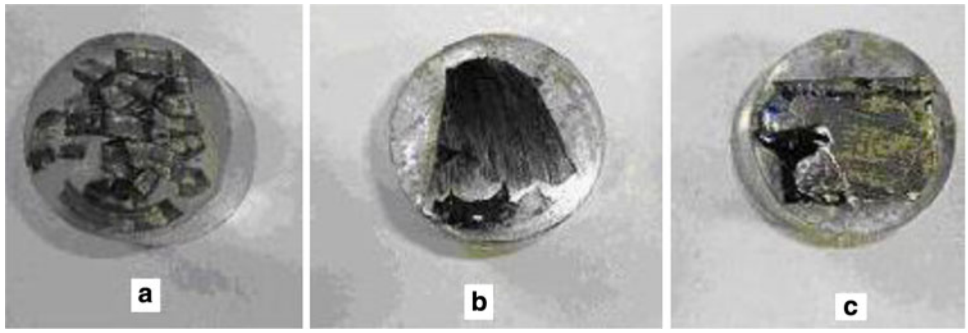

Fig. 2 Embedded samples **a** sample from the chips, **b** cross section of the ingot, and **c** longitudinal section of ingot

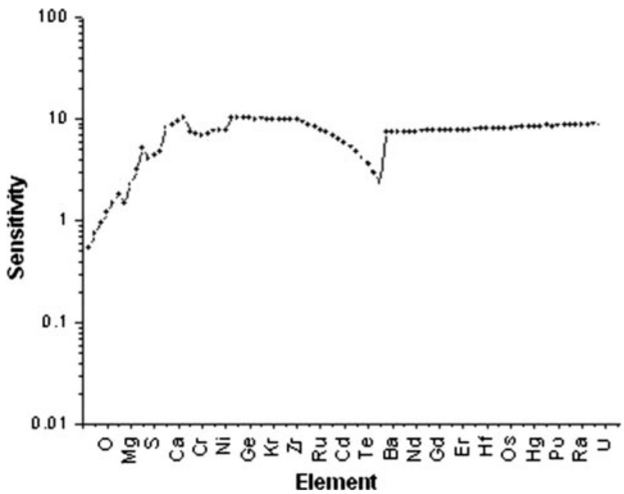

Fig. 3 Experimental sensitivity curve for EDXRF spectrometer (Shimadzu Co., model 720)

to relative standard deviation values (RSD%), and Z-score test was applied to evaluate the accuracy, according to EURACHEM/CITAC guide [13].

The WDXRF spectrometry is adequate for major, minor and trace elements determination, because this configuration, usually, operates with high voltage (kV) and high current (mA), allowing gain of fluorescent intensity counting rate. The HfLα line (1.569 nm) has overlapping effect with second order ZrKα line (0.786 nm $\times$ 2 = 1.572 nm). As the minimum voltage for ZrKα and HfLα lines emission are 18 and 12 kV, respectively [12], so Hf was determined using low voltage and high current excitation.

A WDXRF spectrometer from Rigaku Co, model RIX 3000 was used with Rh X-ray tube; 20 kV and 60 mA excitation; LiF(200) analyzing crystal; NaI(Tl) detector and 20 mm^2 irradiation area, as instrumental measurement conditions. Five measurements for HfLα line were obtained and peak decovolution was applied to separate overlapping effect between first order HfLα and second order ZrKα lines, using the spectrometer analysis software. The Hf content in T and L samples was determined by HfLα line integrated area related to BCR 98 value.

Microstructural analysis

The polished samples were examined at a Leica Q500 optical microscope and a Philips XL30 scanning electron microscope. After the chemical analysis by XRFS, the samples surfaces were etched with a solution of 45% HNO_3, 45% H_2O_2 and 10% HF and re-examined in order to reveal microstructure.

Results and discussion

The XRFS methodology was evaluated using certified reference material BCR 98 from Commission of the European Communities. According to EURACHEM/CITAC guide [13], the RSD% values <10% are considered satisfactory and values >10% are considered unsatisfactory. Cr, Fe and Sn determination presented 37.0, 21.7 and 21.4 RSD% values, respectively (Table 2). The low repeatability could be attributed to small irradiation area (1 mm^2), due to difficult selecting a flat and smooth surface in remelted samples.

The Z-score values evaluate the accuracy and precision of method [13]; accordingly values $|Z| < 2$ are considered satisfactory, values $2 < |Z| < 3$ are considered questionable and values $|Z| > 3$ are considered unsatisfactory. Cr, Fe and Sn determination presented $|Z| = 0.32$, 0.31 and 0.20, respectively, showing adequate accuracy for their determination (Table 2).

Cr, Fe, Ni, Cu, Sn and Hf determined values in L and T samples, plus specified compositions for Zircaloy-2 and Zircaloy-4 are presented in Table 3. The results showed contents of Fe (0.283 $\pm$ 0.06 and 0.0292 $\pm$ 0.06% for L and T samples, respectively) and Cr (0.240 $\pm$ 0.06 and 0.157 $\pm$ 0.04% for L and T samples, respectively) higher than specified values (Fe: 0.07–0.20 and 0.18–0.24% for Zircaloy-2 and Zircaloy-4, respectively; Cr: 0.05–0.15 and 0.07–0.13% for Zircaloy-2 and Zircaloy-4, respectively). As the VAR remelting process can be considered a clean route that do not modify the material composition, the higher content in Fe and Cr can be attributed to raw

Table 2 Certified and determined values, RSD% and Z-score values for CRM- BCR 98, Zircaloy-4

Element	Certified values (%)	Determined values (%)	RSD%[a]	Z-score values
Cr	0.0906 ± 0.009	0.081 ± 0.03	37.0	0.32
Fe	0.2143 ± 0.0020	0.23 ± 0.05	21.7	0.31
Sn	1.460 ± 0.009	1.4 ± 0.3	21.4	0.20

[a] Number of repetitions: 6

Table 3 Chemical analysis results of L and T remelted Zircaloy samples

Element	L sample	T sample	Zr-2 chemical specification[a]	Zr-4 chemical specification[a]
Cr (%)	0.240 ± 0.06	0.157 ± 0.04	0.05–0.15	0.07–0.13
Fe (%)	0.283 ± 0.06	0.292 ± 0.06	0.07–0.20	0.18–0.24
Ni (%)	0.061 ± 0.02	0.052 ± 0.02	0.03–0.08	–
Cu (%)	0.043 ± 0.013	0.028 ± 0.011	–	–
Sn (%)	1.74 ± 0.35	1.60 ± 0.30	1.2–1.7	1.2–1.7
Hf (μg g^{-1})	94 ± 28	59 ± 18	<100	<100

[a] Zr-2, Zr-4 = Zircaloy-2 and Zircaloy-4, respectively

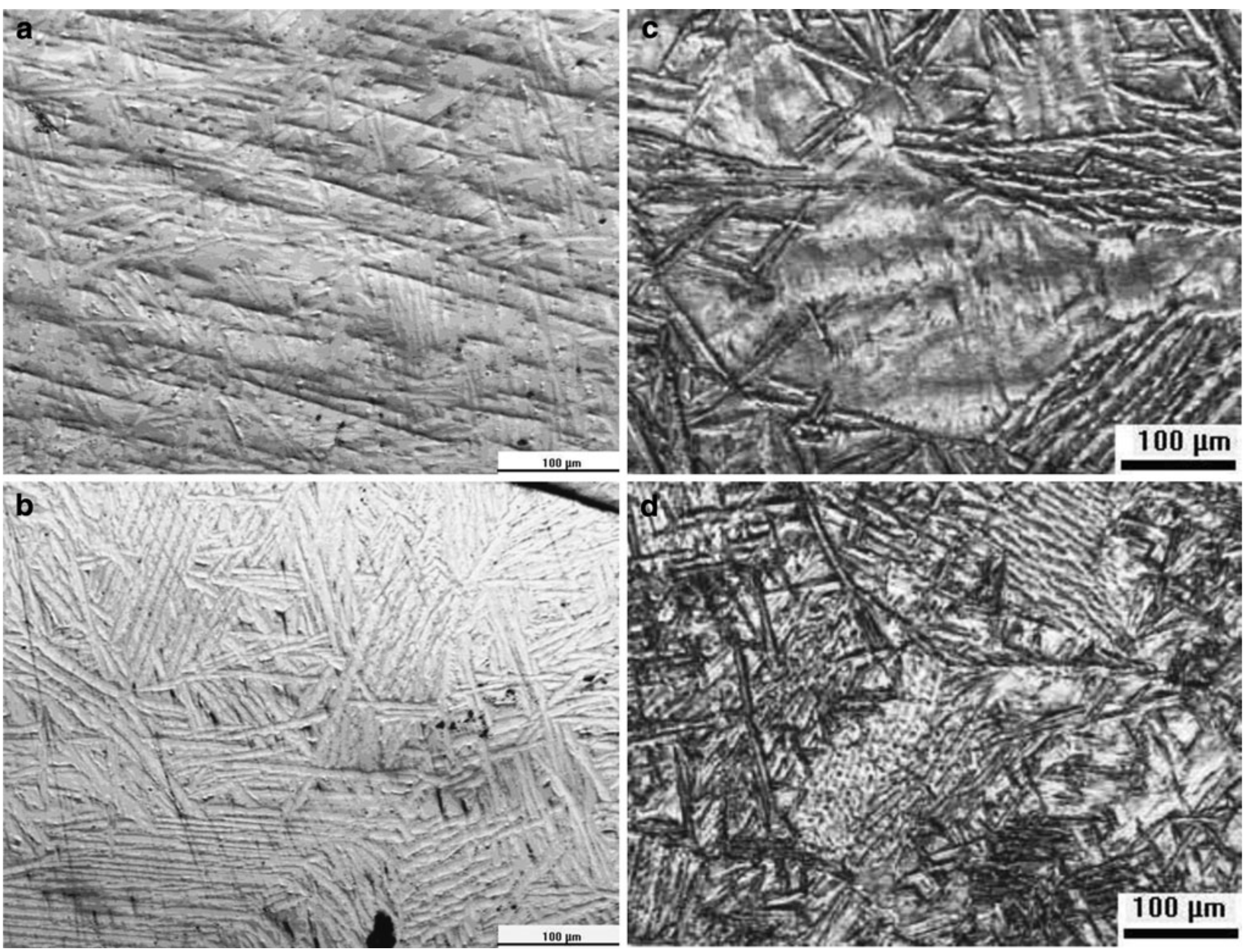

Fig. 4 Optical micrographs of polished samples without etching **a** longitudinal, **b** transversal and with etching, **c** longitudinal, and **d** transversal, revealing a typical cast Zircaloy microstructure

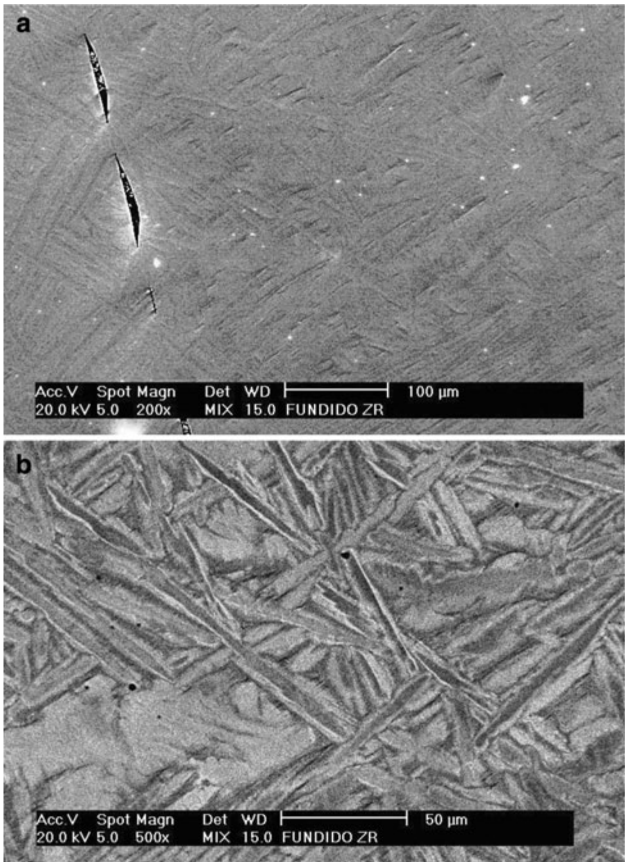

Fig. 5 Scanning electron micrographs **a** by secondary electrons showing a hole generated between two metal droplets (dark lens-shaped phase), **b** by backscattered electrons showing the typical needle-shaped structure

material (machining scraps), possibly contaminated by stainless steel and/or inconel residues. Otherwise, the Cu contamination could be attributed to the contact of high temperature melted droplets with copper crucible during the melting process. Sn, Ni and Hf determination presented values corresponding to Zircaloy-2 and Zircaloy-4 chemical specifications (Tables 1 and 3).

According to the ASTM and other authors [8, 9, 14], the microstructure of the cast billet is characterized by needles or platelets of α' martensite. Under slow cooling, the alpha phase nucleates on grain boundaries of β phase, forming a structure known as *Widmanstätten* type or also as basket-weave, which can be observed in the optical micrographs (Fig. 4) and scanning electron micrographs (Fig. 5). Otherwise, high cooling rates result in the formation of microstructures in the form of needles, similar to typical martensitic microstructure. The microstructures corresponding to longitudinal, sample L (Fig. 4a, c) and to transversal, sample T (Fig. 4b, d), cuts are similar, showing that the solidification process was isotropic for both directions. The scanning electron micrograph using secondary electrons (Fig. 5a) showed, also, a hole generated between two metal droplets (dark lens-shaped phase) and by backscattered electrons showed the typical needle-shaped structure (Fig. 5b).

Conclusions

The EDXRF analysis (Cr, Fe, Ni, and Sn determination) presented low precision due to small irradiation area, nevertheless rapidity and satisfactory accuracy was achieved, showing that the direct analysis in remelted samples from the VAR process is adequate.

This study demonstrated the effectiveness of VAR process for recycling of Zircaloy machining scraps, since Sn, Ni and Hf content correspond to nuclear grade zirconium alloys chemical specification, therefore the contamination of starting materials must be avoided. The billets microstructural analysis showed a characteristic microstructure of as-cast zirconium alloys.

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