

THE RECYCLING THROUGH MELTING MACHINING CHIPS, PRELIMINARY RESULTS

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ABSTRACT

PWR (Pressurized Water Reactor) reactors employ as nuclear fuel UO_2 pellets packed in zirconium alloy tubes, called cladding. In the manufacture of the tubes, machining chips are generated which cannot be discarded, since the recycling of this material is strategic in terms of nuclear technology, legislation, economics and the environment. These nuclear alloys are very expensive and are not produced in Brazil and are imported for the manufacture of nuclear fuel. In this work, it will be examined methods not yet studied to recycle Zircaloy chips using electron beam furnace in order to obtain ingots. In addition, it is intended to carry out the melting of new Zircaloy alloys, from the melting of zirconium sponge obtained in IPEN and imported and Zircaloy bars. The mechanical properties and the present phases of the material should be determined, as well as, the characterization of the microstructures by optical microscopy. This work, therefore, aims at the creation of a new line of research where methods will be approached to recycle the Zircaloy chips and to reduce in 30 times the volume by means of melting the enormous amount of material stored in the form of machining chips, being able to do other components for nuclear or chemical industry use, as well as conducting basic development research.

1. INTRODUCTION

Zirconium alloys have been used more extensively in the nuclear industry compared to other structural materials [1]. Among these alloys are those known as Zircaloy-4, being mainly applied in for fuel elements of the PWR (Pressurized Water Reactor), which are constituted by an organized set of tubes, where the UO_2 pellets are packaged. The tubes are also called cladding. Each one is closed at its ends by a plug, also made in Zircaloy, which is used as support during the assembly. These caps are known as end-caps. During the manufacture of these components large amounts of chips are generated, resulting from the machining of the parts on automatic mechanical lathes.

The zirconium-based alloys comply with nuclear requirements due to the excellent mechanical properties, corrosion resistance and low absorption cross-section for thermal neutrons [2]. 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 composition of Zircaloy-4 is shown in Table 1.

Table 1. Typical chemical composition of Zircaloy-4 [3,4].

Element (mass %)	Sn	Fe	Cr	O	Hf	Zr
Zircaloy-4	1.2-1.7	0.18-0.24	0.07-0.13	0.12	< 1000 ppm	balance

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 program of the process of nuclear power generation and the Zircaloy machining chips are a valuable source of nuclear grade zirconium. Zircaloy chips have a potential value estimated at US\$ 78/kg [4,5], since the Zr metal is the major constituent of Zircaloy (Zry-4 for short) alloy with the great advantage of being Hf free [6,7]. 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 [8]. However, the production of zirconium alloys is not carried out in the country at industrial scale and as consequence, the Zr alloys in its nuclear power plants is imported.

2. MATERIALS AND METHODS

The machining process employs a cooling fluid containing oil and it needs to be eliminated. For this, the chips were subjected to a cleaning step performed by pre washing for degreasing and pickling, followed by washing. Pickling was carried out in two steps of aqueous solutions: one with HCl (50% HCl: 50% H₂O) and one with HNO₃ (30% HNO₃: 70% H₂O). An electron beam melting (EB) was used to melt the Zircaloy chips. This equipment belongs to the IPT (Institute of Technological Research of São Paulo State) and a partnership was made with IPEN. After vacuuming, the electron beam (approximately 10 mm in diameter) was formed and a 220 g charge of Zry-4 chips was melted in a water-cooled copper crucible, forming a button with 66 mm in diameter and 14 mm thick.

The heat treatment was carried out in order to verify the influence of temperature on the Zircaloy-4 mechanical and microstructural properties, since several studies [9-11] show very important changes in mechanical strength, aiming to observe the presence and behavior of the phase beta in the microstructure. The heat treatments performed involved four treatment conditions: annealing, quenching, aging at 500 °C and at 700 °C.

Using the electrical erosion machining, cylindrical bars were taken from the molten button, as is shown in Fig. 1. Then the bars were machined to the dimensions of sub-size specimens for the mechanical testing according to ASTM [11].

In order to avoid specimen oxidation they were protected during the heat treatments by means of quartz encapsulation with argon atmosphere. The heat treatment was carried out in a muffle type furnace (EDG, model FI-1S). First, the encapsulated samples were subjected to heating at 950 °C, with a 2-hour level temperature with 3 samples, rapid cooled in water (quenching). The remaining specimen was kept inside the oven for slow cooling (annealing). After, one encapsulated sample was treated in the oven set at 500 °C and the other at 700 °C, with a 1-hour period and air-cooled.

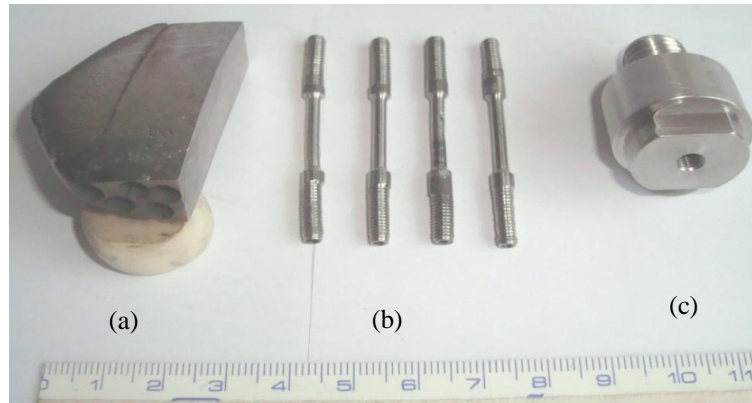


Figure 1. a) molten button; b) specimens for tensile testing; c) specimens adapter to the testing machine.

The samples for microstructural analysis were removed from the cast materials by precision diamond cutting and embedded in cold curing polyester resin and subjected to grinding on SiC with 400, 600, 1200, 2400 and 4000 grit. The preparation was sequenced with 6 μm diamond paste metallographic polishing, followed by 1 μm diamond paste and finally with 0.06 μm colloidal silica. The etching was performed with a solution of 50% H_2O_2 + 25% HNO_3 + 25% ethyl alcohol + 2 HF drops [12].

The Zircaloy microstructural analyzes was carried out in either in the as melted and heat treated samples and were carried out by optical microscopy (Olympus BX51M) with image analysis software.

3. RESULTS

It is shown in Fig. 2 (a, b) the Zry-4 melted button using the electron beam melting method.

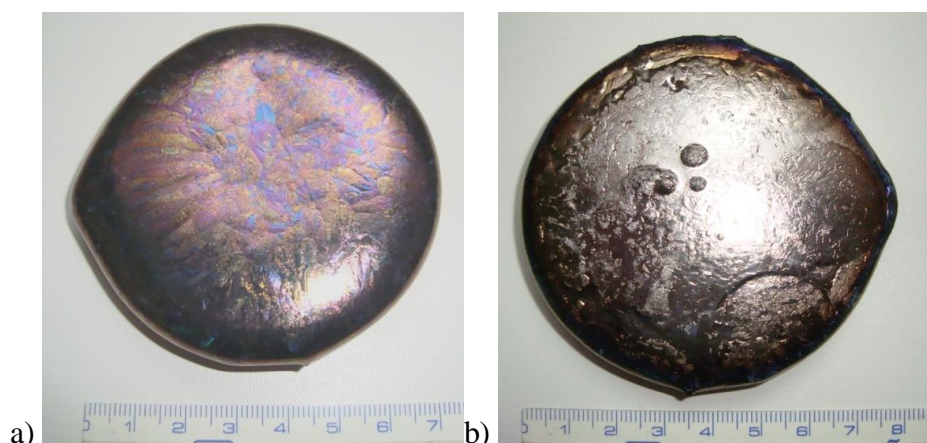


Figure 2. a) Upper face; b) lower face of the Zry-4 melted button.

In Figs.3 and 4 are shown the stress x strain curves of the heat treated samples and in the Tab. 2 it is possible to verify the values obtained of the mechanical properties of the Zry-4 obtained by the electron beam melting.

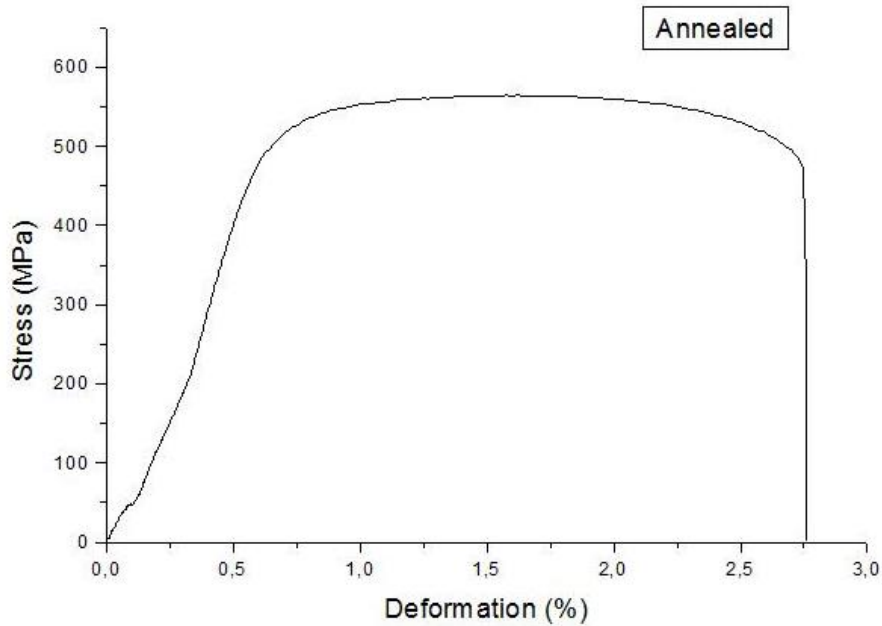


Figure 3. Stress x engineering deformation curve of annealed sample.

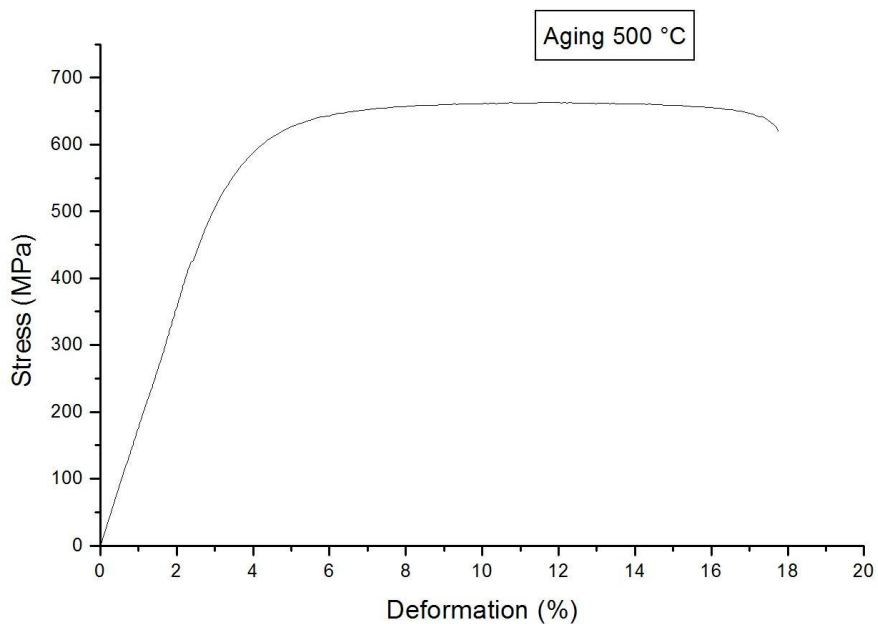


Figure 4. Stress curve x engineering deformation curve of the sample subjected to aging treatment at 500 °C.

The image of Fig. 5 is related to a section of the sample of the Zircaloy-4 molten button obtained by the electron beam method, and the typical microstructure of the material in the raw state of melting can be observed. In the Figs. 6 and 7 it can be observed the microstructure of the samples that were submitted to the heat treatments mentioned previously.

Table 2. Mechanical properties of Zircaloy-04 (tensile strength and deformation) obtained by the electron-beam melting method and the nominal strength according to ASTM [10].

Heat treatment	Tensile strength (MPa)	Deformation (%)	Tensile strength ASTM (MPa)	Deformation ASTM (%)
Annealed	562	12.9	385	18
Aging 500 °C	662	14.2	-	-
Aging 700 °C	357	0	-	-



Figure 5. Zircaloy-4 microstructure obtained by the electron-beam melting method (raw state) with a Widmanstätten structure characteristic of the basketweave morphology. Etched.

Regarding the mechanical properties, the strength limit is above the ASTM specification, while the deformation is in the same range and can be considered satisfactory. It can be observed that there was an increase of the tensile strength when the material is in the aged state.

The microstructures analyzed by optical microscopy have the characteristic aspect of those found in the literature [13], however it is interesting to confirm by means of EDS scanning electron microscopy the present phases and to identify some found precipitates, such as those that appear in the microstructures of the sample aged at 500 °C (Fig. 7). The appearance of these microstructures is consistent with the heat treatments, that is, the annealing has led to the thickening of the Widmanstätten slats in the microstructure and the aging has led to the phases coalescence.



Figure 6. Zircaloy-4 microstructure sample treated with annealing showing characteristic morphology of Widmanstätten structure of basketweave form.



Figure 7. Zircaloy-4 microstructure sample aged at 500 °C with the same previous morphology but different arrangement.

4. CONCLUSION

The methods selected for the melting through the electron beam (EB) were effective to obtain a homogenous material with characteristics considered appropriate and was fast as a function of the amount of charge placed which took approximately 5 min to melt, besides an efficient vacuum system, causing little oxidation to the material.

The preliminary results up to the present moment of the project have shown positive in function of the obtained properties.

ACKNOWLEDGMENTS

The authors thank: INB (Nuclear Industries of Brazil S.A.) for providing the machining chips and to the CNPq for awarding a post doctorate scholarship to the author. To Daniel Leal and Eduardo J. Nogueira for the melting in electron beam and sample preparation, respectively.

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