Study of recycling process viability of zirconium alloys chips for melting in VAR furnace

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Resumo

Cavacos de ligas de zircônio (M5, Zirlo, Zircaloy) são gerados em elevadas quantidades na confecção de tubos e tampões das varetas que compõem o elemento combustível de reatores de potência refrigerados a água pressurizada (PWR). Essas são ligas importadas e por isso é mostrado interesse pela indústria de reciclagem na sua reutilização. Este trabalho apresenta os estudos de um processo de reciclagem e a obtenção de eletrodos prensados para serem fundidos em um forno VAR (*Vacuum Arc Remelting*). O processo se inicia com uma separação magnética, lavagem do fluido de corte que é solúvel em água, utilização de um desengraxante industrial, seguido por um enxágue com fluxo contínuo de água em alta pressão e secagem por fluxo de ar quente. Para a obtenção de eletrodos, os cavacos foram prensados em uma matriz de seção quadrada 40x40 mm² com 500 mm de comprimento, resultando num eletrodo com 20% da densidade aparente da liga. A fusão foi feita um forno VAR de laboratório no CCTM-IPEN, gerando um lingote maciço de 0,8 kg. A fusão dos cavacos é possível e viável em um forno VAR o que reduz em até 40 vezes o volume de armazenamento desse material.

Abstract

Zirconium alloy chips (M5, Zirlo, and Zircaloy) are generated in high quantities in the manufacture of tubes and end caps of the rods that form the fuel element of pressurized water reactors (PWR). These are imported alloys and so it is shown interest by the recycling industry in its reuse. This work presents the studies of a recycling process and the obtaining of electrodes pressed to be melted in a Vacuum Arc Remelting (VAR) furnace. The process begins with a magnetic separation, washing of the water-soluble cutting fluid, use of an industrial degreaser, followed by a rinse with continuous high-pressure water flow and drying by hot air flow. To obtain electrodes, the chips were pressed in a square section die 40x40 mm² with 500 mm in length resulting in an electrode with 20% of the apparent density of the alloy. The melting was done a laboratory VAR furnace in the CCTM-IPEN, generating a massive ingot of 0.8 kg. The melting of the chips is possible and viable in a VAR furnace that reduces the storage volume of this material by up to 40 times.

Keywords: Zirconium alloy, Recycling, VAR furnace.

1. Introduction

The nuclear fuel used in PWR (Pressurized Water Reactor) power reactors is typically composed of uranium dioxide pellets (UO_2), packaged in tubes made of zirconium alloys, called casing or cladding. These tubes form the fuel rod that, arranged in sets of 14x14 to 17x17 tubes forming the fuel element, as can be seen in Figure 1.

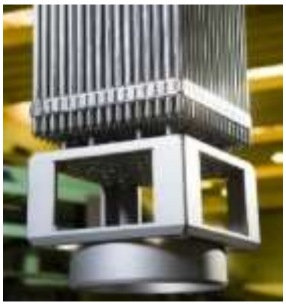

Figure 1: Part of a fuel element of a PWR reactor.

Zirconium alloys are used due to the natural resistance of the zirconium to the PWR thermal neutrons, resistance to corrosion in the high temperature water and low cross section [1]. The composition of these alloys is shown in Table 1.

Table 1 – Chemical composition of Zircaloy 2, Zircaloy 4, Zirlo and M5.

Alloy	Sn (%)	Fe (%)	Cr (%)	Ni (%)	Nb (%)	Hf (μg g⁻¹)	Zr (%)
Zircaloy-2	1.2-1.7	0.07-0.20	0.05-0.15	0.03-0.08	-	<100	Balance
Zircaloy-4	1.2-1.7	0.18-0.24	0.07-0.13	-	-	<100	Balance
Zirlo	0-0.99	0.11	-	-	0.9-1.13	<40	Balance
M5	<0.003	0.0273	<0.004	-	0.8-1.2	-	Balance

The machining of these tubes generate chips contaminated with machining oil and cutting fluid. Zirconium alloys chips are produced in large quantities during the machining of rods for the PWR fuel elements parts. Actually, zirconium alloys are imported into Brazil and the machining chips scraps poses a challenge to the recycling industry. This paper presents the first steps on the recycling processes and the results for the search of an efficient way on the cleaning, quality control and electrode fabrication to be melted in the Vacuum Arc Remelting (VAR) furnace [2].

The process starts with the cutting fluid washout and is followed by the die pressing of the clean chips. Process evaluation was first made by means the X-ray fluorescence tests in order to define the quality of the scraps. Results indicate the need of the inclusion of a magnetic separation step in the process to remove the ferrous alloy present in the scraps. The die pressing of the scraps yields process adequate 1 kg electrodes to be melted in the CCTM prototype scale VAR furnace [3].

VAR furnaces are known to be the only technology accepted by the nuclear industry for the production of the alloys used in the nuclear fuel parts [4]. The nature of the VAR furnace imposes that the density of the electrodes be very close to that of the massive in order to yield useful and economical ingots. The pressing of springy chips render an electrode with low relative densities close to 20% of the bulk material. A modification of the VAR furnace was proposed to overtake this difficulty and the first results are present in this paper.

2. Experimental

Three cleaning routes are proposed for zirconium alloy chips, followed by route 3, for which a cleaning station of the chips has been developed, consisting of:

- Magnetic separation
- Dissolution of the cutting fluid in a water tank;
- Cleaning with an industrial degreaser;
- Rinse with high pressure water flow
- Hot air continuous flow drying;

The procedure of process evaluation was performed using the EDXRFS analysis, three conditions were tested, materials as received, washed without magnetic separation and washed with magnetic separation. These samples were pressed into a 20 mm diameter die and cast in an electric arc furnace under non-consumable electrode vacuum (MRC – Fig. 2).

Figure 2: Samples placed in the oven, from left to right; material as received; washed with separation and washed without separation.

For the preparation of the electrode was developed a matrix of square section 40 x 40 mm by 500 mm in length. For this process, it is necessary to collect a bunch with 1 kg mass of the washed material. The electrode produced was pressed with a load of 20 ton force and has enough axial mechanical resistance to satisfy the fixation in the laboratory VAR furnace [3].

A set of electrodes with increasing press loads was produced to find an ideal press condition for the electrode fabrication. The results of the apparent density are shown in Fig. 3 for electrodes produced from the clean chips in a 40 mm square section and 500 mm long die.

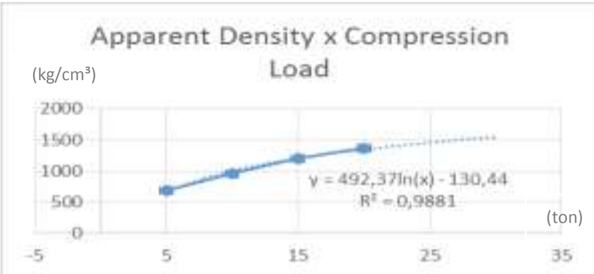

Figure 3: Plot of the apparent density against compression load.

The electrode was melted in a modified VAR furnace locates at CCTM/IPEN.

3. Results and Discussion

The EDXRFS analysis results of the samples collected from different apart locations in the drums suggest the presence of iron alloys as a contamination of the batch received from INB, for this evaluation we also analyzed washed samples with magnetic separation and washed samples without magnetic separation [5] (Tab.2).

Table 2: EDXRFS analysis results.

Element	Pressed button as received	Pressed button washed out with magnetic separation	Pressed button washed out without magnetic separation
	Content (wt. %)		
Zr	73.4 ± 0.7	90.7 ± 0.9	78.2 ± 0.8
Fe	24.6 ± 0.3	8.2 ± 0.8	19.8 ± 0.2
Cr	1.2 ± 0.1	0.58 ± 0.06	1.1 ± 0.1
Sn	0.74 ± 0.08	0.49 ± 0.05	0.83 ± 0.08

After melting of the electrode (Fig. 4), it was obtained two pieces of massive material with solid metallic appearance. The starting electrode weighted 914 grams and the combined weight of the solids sums 555 grams or 60% of the mass of the electrode. The fusion operation was deliberately ceased before the electrode being totally consumed, so the above efficiency doesn´t represent the overall process. The authors expect the efficiency to rise up to the planned 80% level when electrode is melt to the designed length.

Figure 4: Result of the melting of the electrode described in this paper.

In the product obtained from the melting process, a semi quantitative elemental characterization was also performed by EDXRFS analysis and the results are presented in Tab. 3.

Even if a magnetic separation is performed, the amount of chips necessary for melting and the tangled situation, is not sufficient to reach the iron composition specified in the alloy, and it is necessary to add procedures that would make the process unfeasible.

Element	Content (w.%)	Element	Content (w.%)
Zr	90.8 ± 0.9	S	0.26 ± 0.03
Fe	5.3 ± 0.5	Al	0.2 ± 0.02
Cr	1.6 ± 0.2	Si	0.05 ± 0.01
Sn	1.2 ± 0.1	Cu	0.04 ± 0.01
Ni	0.62 ± 0.06		

Table 3: Results of the EDXRFS analysis for the product obtained from the melting process.

4. Conclusions

The chips from the INB seem to present a contamination with ferrous metals. This contamination confer the chips the denomination of secondary type scrap. This poses some difficulties to the recycling, requiring extra process steps and energy consumption (e.g. magnetic separation). This problem can be overcome by careful separation and storage of the material during and after its production

The consolidation process of the zirconium alloy chips by melting in the VAR furnace would allow a 40-fold reduction in the inventory of INB chips, reducing environmental risks as well pyrophoric accidents.

Considering the facts that the zirconium alloys chips can be melt by the modified VAR process with good apparent results. It is possible to remelt them either by the VAR furnace or by ISM, the authors conclude that recycling process of zirconium alloys chips can be successfully performed in a laboratory scale and will further suggest the up scaling of the process.

5. Acknowledgments

The authors acknowledge Capes and CNPq for the scholarships to M. P. Gomes and L.A.M.dos Reis respectively, and FINEP for the financial support.

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