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RECYCLING AND MELTING PROCESS OF THE ZIRCONIUM ALLOY CHIPS

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ABSTRACT

Pressurized water reactors (PWR) commonly use U235 enriched uranium dioxide pellets as a nuclear fuel, these are assembled and stacked in zirconium alloy tubes and end caps (M5, Zirlo, Zircaloy). During the machining of these components large amounts of chips are generated which are contaminated with cutting fluid. Its storage presents safety and environmental risks due to its pyrophoric and reactive nature. Recycling industry shown interest in its recycling due to its strategic importance. This paper presents a study on the recycling process and the results aiming the efficiency in the cleaning process; the quality control; the obtaining of the pressed electrodes and finally the melting in a Vacuum Arc Remelting furnace (VAR). The recycling process begins with magnetic separation of possible ferrous alloys chips contaminant, the washing of the cutting fluid that is soluble in water, washing with an industrial degreaser, followed by a rinse with continuous flow of water under high pressure and drying with hot air. The first evaluation of the process was done by an Energy Dispersive X-rays Fluorescence Spectrometry (EDXRFS) showed the presence of 10 wt. % to 17 wt. % of impurities due the mixing with stainless steel machining chips. The chips were then pressed in a custom-made matrix of square section (40 x 40 mm - 500 mm in length), resulting in electrodes with 20% of apparent density of the original alloy. The electrode was then melted in a laboratory scale VAR furnace at the CCTM-IPEN, producing a massive ingot with 0.8 kg. It was observed that the samples obtained from *Indústrias Nucleares do Brasil* (INB) are supposed to be secondary scrap and it is suggested careful separation in the generation of this material. The melting of the chips is possible and feasible in a VAR furnace which reduces the storage volume by up to 40 times of this material, however, it is necessary to correct the composition of the alloy for the melting of these ingots.

1. INTRODUCTION

The fuel element used in nuclear reactors of the PWR type is generally composed of uranium dioxide pellets (UO_2), packaged in zirconium alloys tubes, due to the transparent nature of the zirconium to the PWR thermal neutrons. These tubes are called fuel rods and are arranged in matrix sets of 14 x 14 to 17 x 17 tubes to form the fuel element (Fig. 1). The extremities of the fuel rods are sealed with end plugs that can be eventually made of a less restrictive composition zirconium alloy. The zirconium alloys commonly used in the tubes and end plugs are known as Zircaloys but others are also used (Table 1) [1]. Currently these alloys are imported to Brazil and its reuse represents a challenge for the recycling industry [2]. The lathe machining of these parts generates large amounts of chip scraps contaminated with cutting fluid and oil.

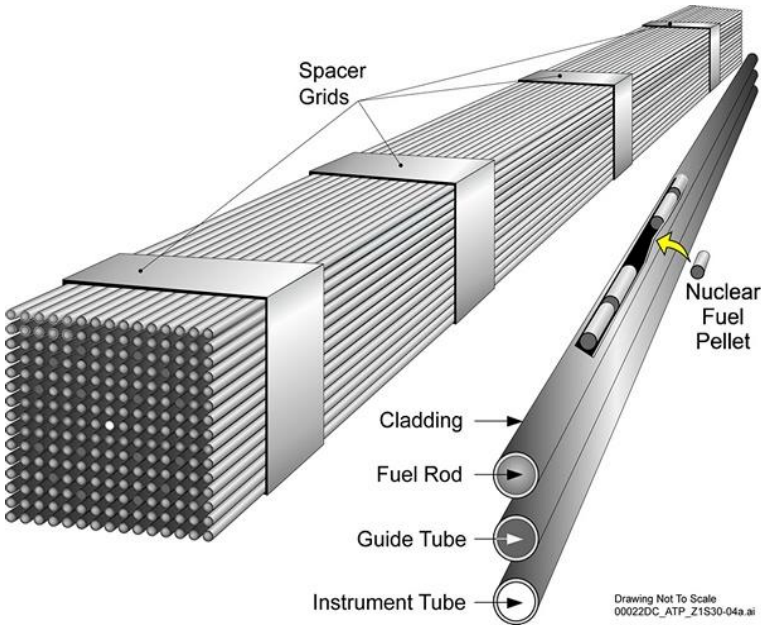


Figure 1: Fuel rod arrangement description [3].

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

Alloy	Sn (wt. %)	Fe (wt. %)	Cr (wt. %)	Ni (wt. %)	Nb (wt. %)	Hf (μg.g^{-1})	Zr (wt. %)
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

- Not specified

This work present the development and the viability study of a process for the recycling of zirconium alloys chip scraps by melting in VAR furnace. These scraps are usually discarded by the industry because of their high surface to volume ratio, one of the characteristics of a fire hazardous material, and their elastic nature, rendering it difficult to die press in a usable VAR electrode.

Due to historical developments of the fuel elements by the *Indústrias Nucleares do Brasil* (INB), the received material to perform this project is a non-controlled mix of zirconium alloys. The chips generated are stored in plastic drums, which are kept in an exclusive and recluded building due the pyrophoric nature of the zirconium alloys and the large surface to volume ratio of their chips. This situation impose the need of extra safety care within the INB facilities and is one of the original reasons of this project. No special care is taken with the cutting fluid contamination of the chips, so a cleaning process is required prior to the consolidation by vacuum arc melting. Usually the recycling industry have some practices to clean the cutting fluid out of ordinary industrial scraps (e.g. Aluminum alloys and steels). Commercially available treatments of scraps include centrifugation or pressing in order to remove large quantities of fluid to be recycled as well as the metal itself [4]. The use of the afore mentioned techniques for cleaning of the chips generated by INB is not adequate to this project due to the specific quality and quantities involved, when contamination with ordinary metals may lead to the failure of the fuel components eventually made from recycled material.

VAR furnaces are known as the only technology accepted by the nuclear industry for production of alloys used in the nuclear fuel parts [5]. The nature of VAR furnace imposes that the density of the electrodes very close to the massive ones 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 presented in this paper.

2. EXPERIMENTAL

Three cleaning routes are proposed for zirconium alloy chips, followed by route 3, for which a cleaning station (Fig. 2) 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.

Figure 2: Cleaning station for washing of zirconium alloy chips.

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 melted in an electric arc furnace under non-consumable electrode vacuum (MRC – Fig. 3).

Figure 3: Samples placed in the oven, from left to right: material as received; washed with magnetic separation and washed without magnetic separation.

It was developed a matrix of square section 40 x 40 mm by 500 mm in length for preparation of the electrode. For this process, it was necessary to collect aproximately 1 kg of 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. The Fig. 4 shows the developed matrix and the electrode produced.

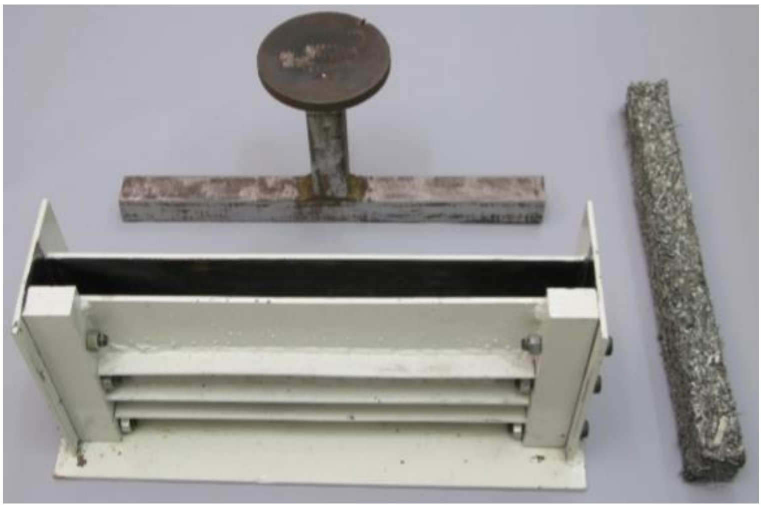


Figure 4: Developed matrix and compressed electrode.

A set of electrodes with increasing compression loads was produced to find an ideal compression condition for the electrode fabrication. The results of the obtained apparent density are shown in Fig. 5 for electrodes produced from the clean chips in a 40 mm square section and 500 mm long die [6].

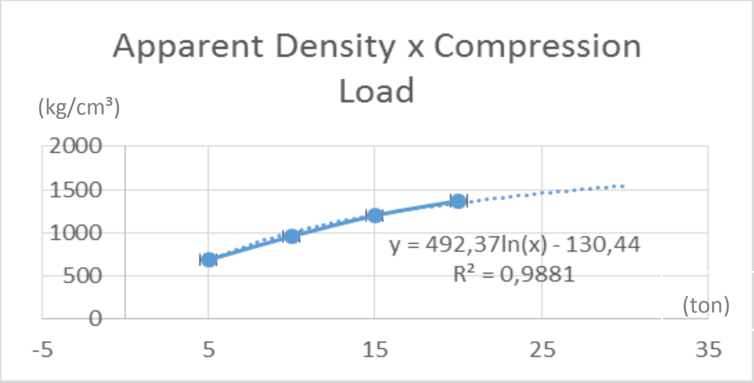


Figure 5: Plot of the apparent density against compression load for obtained electrodes.

Each electrode was melted in a modified VAR furnace locate at CCTM/IPEN exclude, and the assembly details of electrode is shown in Fig. 6. The original furnace allows the melting of massive electrodes 550 mm long (450 mm usable) with diameters ranging from 20 mm up to 35 mm in copper crucibles with 55 mm internal diameter. Maximum current available of 450 DCA provided by a rectified power source with 64 V open circuit voltage. The pressure in the furnace was obtained by two mechanical vacuum pumps reaching 1.10^{-2} mbar during the melting operation. A set of purge operations with argon were performed in order to diminish the quantities of oxygen, nitrogen and hydrogen to be present in the furnace atmosphere. The modified VAR furnace allows the melting of 40 mm square electrodes in a 30 mm internal diameter crucible [7].

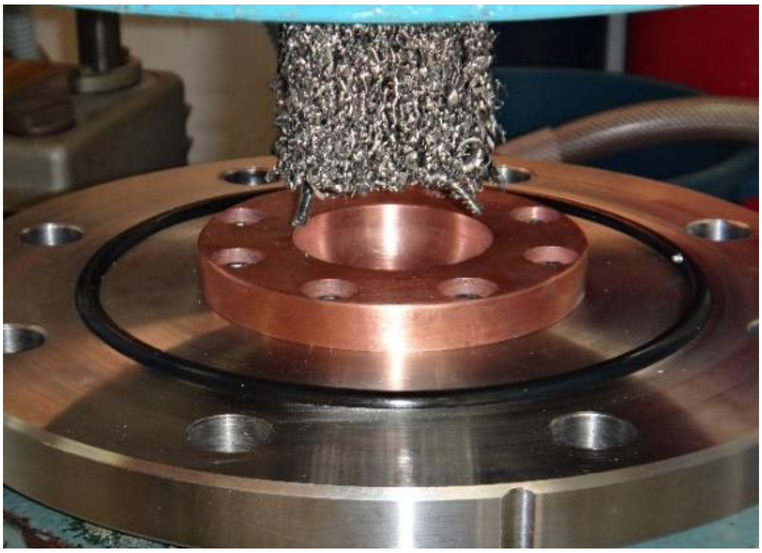
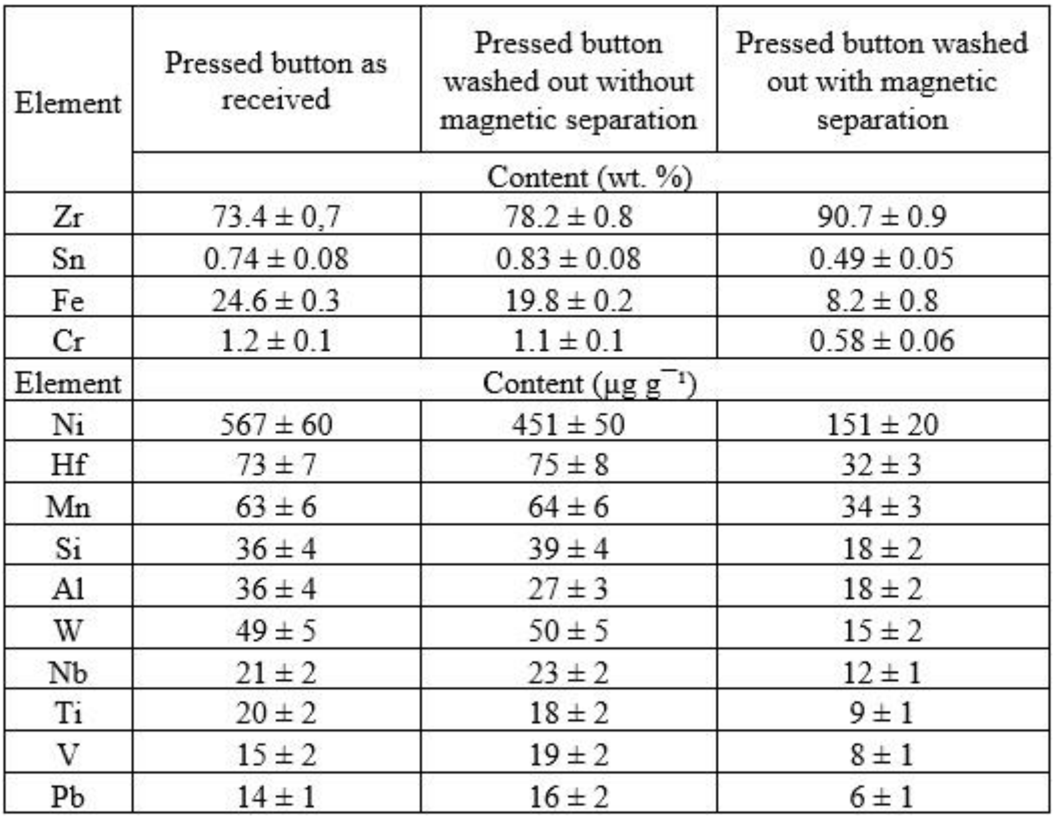


Figure 6: Detail of the modification made on the CCTM VAR furnace.

3. RESULTS AND DISCUSSION

The EDXRFS analysis results of the samples collected from different locations in the drums suggested the presence of iron alloys as a contamination of the batch received from INB, and this evaluation was also performed for washed samples with magnetic separation and washed samples without magnetic separation [8] (Table 2). Since this paper dealt with the chip batch of only one drum then nothing can be assert about be total of the stored scraps. The magnetic separation performed after the cleaning of the chips resulted in amounts from 11% up to 17% weight of ferrous materials in the drum. This quantity is important since it will affect the alloy composition after melting, and it will be discussed further.

Table 2: EDXRFS analysis results.



Element	Pressed button as received	Pressed button washed out without magnetic separation	Pressed button washed out with magnetic separation
	Content (wt. %)		
Zr	73.4 ± 0,7	78.2 ± 0.8	90.7 ± 0.9
Sn	0.74 ± 0.08	0.83 ± 0.08	0.49 ± 0.05
Fe	24.6 ± 0.3	19.8 ± 0.2	8.2 ± 0.8
Cr	1.2 ± 0.1	1.1 ± 0.1	0.58 ± 0.06
Element	Content (µg g^{-1})		
Ni	567 ± 60	451 ± 50	151 ± 20
Hf	73 ± 7	75 ± 8	32 ± 3
Mn	63 ± 6	64 ± 6	34 ± 3
Si	36 ± 4	39 ± 4	18 ± 2
Al	36 ± 4	27 ± 3	18 ± 2
W	49 ± 5	50 ± 5	15 ± 2
Nb	21 ± 2	23 ± 2	12 ± 1
Ti	20 ± 2	18 ± 2	9 ± 1
V	15 ± 2	19 ± 2	8 ± 1
Pb	14 ± 1	16 ± 2	6 ± 1

The fact that the material is a mixture of different alloys is critical to the development of the recycling process and rendering to the material the status of secondary scraps.

The chips used in this paper are constituted mainly of the continuous type and very small amount of the segmented ones [9]. The segmented chips are a source of decreasing for the process efficiency as they can loosen when in the surface of the electrode. Care must be taken to mix the segmented chips in the continuous chips to keep then in the electrode, in order to enhance process efficiency.

The apparent density obtained for the electrodes ranges from 685 kg/m³ to 1370 kg/m³. The tendency curve plotted on the experimental data allowed to estimate an increase in the apparent density up to 1544 kg/m^3 for compressing load of 300 kN. This increase in density may lead to an increase of 28% the furnace capacity.

As the pressing movement occurs in one direction only and due to the springy nature of the chips, the electrode presents a kind of layered feature perpendicular to the press direction. The transversal resistance is severely impaired so the electrode presented a very high flexibility. The mechanical resistance of the electrode is strongly anisotropic being the more resistant direction along the length. This feature shows that it is perfectly adequate for the melting in the VAR furnace whereas that during the melting operation the electrode is subjected only to the axial load of its own weight, then, production of the electrode for the VAR laboratory furnace is viable and possible, despite the need of careful storage to avoid geometrical degradation.

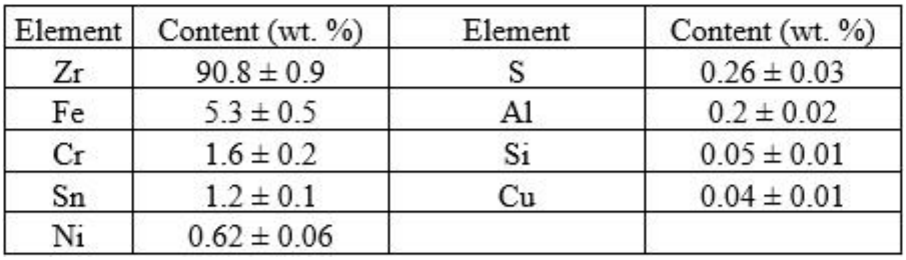
After melting of the electrode (Fig. 7), it was obtained two pieces of massive material with solid metallic appearance. The weight of starting electrode 914 g and the combined weight of the solids summed 555 g or 60% of the mass of the electrode. The fusion operation was deliberately stopped before the total consuming of electrode, so the above efficiency does not represent the overall process. It is expected the efficiency to rise up to the planned level of 80% when electrode is melted in the designed length. This is being considered an evolution of the funnel presented in Fig. 6 [10].

Figure 7: 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 Table 3.

Even when a magnetic separation was performed, the amount of chips required for the melt is that of the entangled state, was not sufficient to reach the iron composition specified in the alloy, and it is necessary to add procedures that would make the process unfeasible.

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



Element	Content (wt. %)	Element	Content (wt. %)
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		

4. CONCLUSIONS

The zirconium alloy chips from the INB seems to present a contamination with ferrous metals. This contamination confer to these chips the denomination of secondary type of scrap. This poses some difficulties for recycling process, requiring extra process steps and energy consumption (e.g. magnetic separation). This problem can be overcomed by careful separation and storage of the material during and after its production, eventually enhancing the quality of the final ingots. The solid products presented a metallic aspect and are very massive. This kind of metallic material can be remelted, either by an industrial scale VAR furnace or in a Induction Skull Melting (ISM).

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 as pyrophoric accidents.

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

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