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# Study on the Viability of the Recycling by Electric Arc Melting of Zirconium Alloys Scraps Aiming the Scalability of the Process

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**Abstract.** Turning chips of zirconium alloys are produced in large quantities during the machining of alloy rods for the fabrication of the end plugs for the Pressurized Water Reactor (PWR) fuel elements parts of Angra II nuclear reactor (Brazil – Rio de Janeiro). This paper presents a study on the search for an efficient way for the cleaning, quality control and Vacuum Arc Remelting (VAR) of pressed zirconium alloys chips to produce a material viable to be used in the production of the fuel rod end plugs. The process starts with cutting oil clean out. The first step in this process consists in soaking a bunch of chips in clean water, to remove soluble cutting oils, followed by an alkaline degreasing bath and a wash with a high-pressure flow of water. Drying is performed by a flux of warm air. The oil free chips are then subjected to a magnet in order to detect and collect any magnetic material, essentially ferrous, that may be present in the original chips. Samples of the material are collected and then melted in a small non consumable electrode vacuum arc furnace for evaluation by Energy Dispersive X-ray Fluorescence Spectrometry (EDXRFS) in order to define the quality of the chips. The next step consists in the 15 ton hydraulic pressing the chips in a die with 40 mm square section and 500 mm long, producing an electrode with 20% of the Zircaloy bulk density. The electrode was finally melted in a laboratory scale modified VAR furnace located at the CCTM–IPEN, producing 0.8 kg ingots. The authors conclude that the samples obtained from the fuel element industry can be melting in a VAR furnace, modified to accommodate low density electrodes, allowing a reduction up to 40 times the original storage volume, however, it is necessary to remelt the ingots to correct their composition in order to recycle the original zirconium alloys chips. in a process to reduce volume and allow the reutilization of valuable Zircaloy scraps.

## Introduction

The fuel element used in nuclear reactors of the PWR type is, generally, composed of uranium dioxide pellets ($UO_2$), packaged in tubes made of zirconium alloys, 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 14x14 a 17x17 tubes to form the fuel element (Fig. 1). The extremities of the fuel rods (Fig. 2), are sealed with end plugs, that can be eventually made out of a less restrictive composition zirconium alloy – personal communications. 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 into 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.

Fig. 1 – Typical actual fuel rod sectioned for visualization of the internal parts. At the left side one can see the end plug whose the lathe machining generates chips like the ones used in this paper.

Fig. 2 – Extremity of a fuel element where one can see a set of 17x17 fuel rod arrangement, produced by INB.

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

| Alloy | Sn (%) | Fe (%) | Cr (%) | Ni (%) | Nb (%) | Hf ($\mu g.g^{-1}$) | 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 |

This work present the development of the viability of a process for the recycling by melting of zirconium alloys chip scraps. These scraps are usually discarded by the industry because of its high surface to volume ratio, one of the characteristics of a fire hazardous material, and its springy 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 material received 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 secluded building due the pyrophoric nature of the zirconium and the large surface to volume ratio of the 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 and steels). The scraps may be centrifuged or pressed in order to remove large quantities of fluid to be recycled as well as the metal itself [3]. The use of the afore mentioned techniques for the cleaning of the chips generated by the 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 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.

## Experimental Procedure

The turn lathe chip scraps are received from INB packaged in plastic bags inside 200 liters plastic drums. Small quantities of original the material were collected from diverse apart places in the drums, then, pressed in a 20 millimeters of diameter die. The pressed briquette were arc melted in 50 mbar argon atmosphere in order to provide a homogenous samples. The sample obtained was submitted to a X ray fluorescence analysis in order to determine the presence of impurities, as a procedure to quality control original batch.

The authors evaluate 3 routes for the cleaning of the chips. Firstly an evaluation route, with the use of an organic solvent, toluene, and drying with a hot air. A second route is based a process that uses limonene as a grease solvent and HF as a surface deoxidizing agent [5]. Finally, a third route developed in the laboratory, that uses a alkaline industrial soap: dissolution of the machining fluid with water; degrease with an alkaline industrial degreaser; rinse with water; drying (small quantities per cycle); magnetic separation of ferrous alloys.

A set of electrodes with increasing press loads was produced to find an ideal press condition for the electrode fabrication. The results are shown in Fig. 3 for electrodes produced from the clean chips in a 40 $mm^2$ square section and 500 mm long die Fig. 4 [6].

The electrode was melted in a modified VAR furnace locate at CCTM/IPEN. The 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 inner 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 $1.10^{-3}$ mbar during the melting operation. A set of purge operations were performed in order to diminish the quantities of oxygen, nitrogen and hydrogen to be present in the furnace atmosphere. The modification of the furnace allows the melting of 40 mm square electrode in a 30 mm inner diameter crucible. The configuration is shown in Fig. 5a and Fig. 5b. The melting of the electrode was carried out under standard VAR conditions, most of the melt was conducted at 450 A, allowing low amperage periods for the warm up and ingot hot topping.

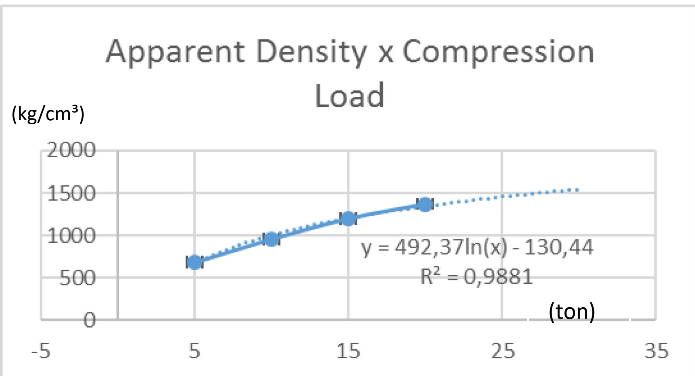


Fig. 3 – Plot of the apparent density against compression load.

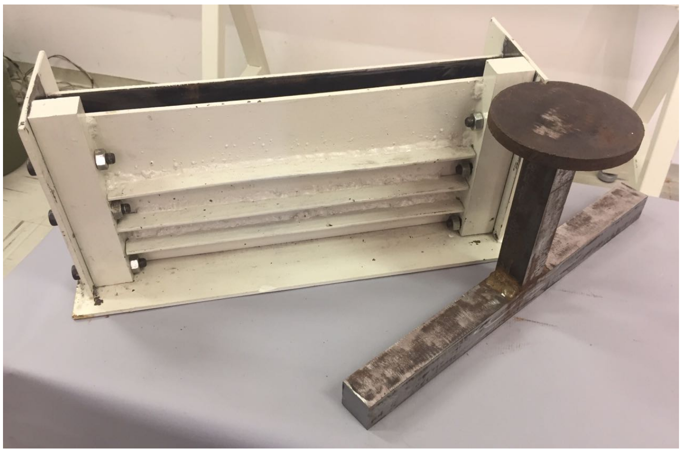

Fig. 4 – The pressing die developed to produce the VAR electrode.

Fig. 5a – Actual image of the modified CCTM VAR Furnace.

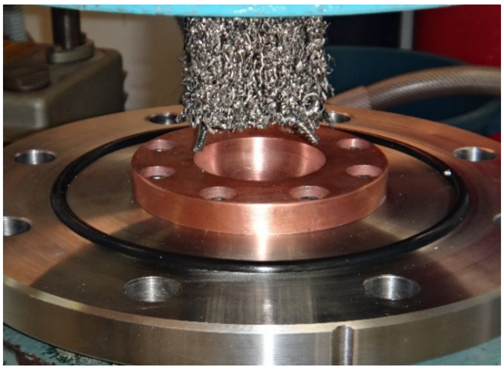

Fig. 5b – Detail of the modification made on the CCTM VAR furnace.

**Results and Discussion**

The results from X-ray fluorescence analysis of the samples collected in different apart locations in the drums suggest the presence of iron alloys as a contamination of the batch received from INB [7], Tab.2. Since this paper deals 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 results in amounts from 11% up to 17% weight of ferrous materials present in the drum. This is a quantity to care about since it will affect the alloy composition after melting. The authors suggest a quality control procedure for the scraps handling in order to avoid this kind of contamination as well as the recovery of different zirconium alloys to be done at the milling station

Table 2 – Summarized result of the X-ray Fluorescence Spectrometry.

| Element | Weight Content (%) |
|---|---|
| Zr | $78.2 \pm 0.8$ |
| Sn | $0.83 \pm 0.08$ |
| Fe | $19.8 \pm 0.2$ |
| Cr | $1.1 \pm 0.1$ |

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, namely the material of interest to recycling comes mixed with other materials.

The chips used in this paper are constituted mainly of the continuous type and a very small amount of the segmented ones [8]. The ratio or segmented to the total was evaluated given a result of 5%.of the total. The segmented chips are a source of loss for the process efficiency for they fall loose 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 allows the authors to estimate an increase in the apparent density up to 1544 kg/m3 to 300 kN compressing load. 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 ram movement. The transversal resistance is severely impaired so the electrode presents a very high flexibility. The mechanical resistance of the electrode is strongly anisotropic being the axis along the length the more resistant. 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 for a careful storage to avoid geometrical degradation.

After melting of the electrode (Fig. 6) 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 if electrode is melt to the designed length.

Fig. 6 – Result of the melting of the electrode described in this paper.

## Conclusions

The chips from the INB seems 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, 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 Skill 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 pyrophoric accidents.

Considering the facts that the zirconium alloys chips can be melt by the modified VAR process with good apparent results and 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.

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