Materials Science Forum Vol. 805 (2015) pp 700-705
Online available since 2014/Sep/12 at www.scientific.net
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doi:10.4028/www.scientific.net/MSF.805.700

CHARACTERIZATION OF METALLIC ZIRCONIUM SPONGE

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Keywords: Zirconium alloy, Metallic zirconium sponge, PWR, BWR.

Abstract: When used commercially, the zirconium alloys are utilized in the shape of tubes to encapsulate the UO2 pellets in the PWR and BWR Power reactors. The metallic zirconium is an essential metallic element for the types of alloys in which the obtainment route rests in the ore opening for the production of zirconium oxide followed by the processes of pelletizing, chlorination, purification, reduction and distillation. Through the technique of X-Ray Diffraction the present phases were identified. Using the Fluorescence of an X ray it was possible to determined the chemical composition of the zirconium sponge. The mechanical properties of Vickers microhardness were obtained using a microdurometer. As a result, it was established that it is possible to define a methodology for the preparation of a sample of metallic zirconium for the microstructure analysis, as well as that its chemical purity is 97,265% linked to the microhardness of approximately 51 HV.

INTRODUCTION

Zirconium was discovered accidentally by Klaproth in 1789 and isolated in its impure metallic form in 1824 by Berzelius [1]. The zirconium blades in their ductile form were made by Lesly and Hamburger in 1910. In 1925, the researchers Van Arkel and de Boer discovered a method to refine zirconium using a thermal dissociation of zirconium iodide in an incandescent tungsten filament, achieving a pure and ductile metal [2,3]. In 1946, William J. Kroll and his staff developed a process to obtain zirconium on a large scale using his past experience from developing technology to obtain metallic titanium. They obtained a sponge of metallic zirconium from the reaction of zirconium chloride in the presence of a reducing agent [2,3]. In Brazil, the achievement of zirconium sponge was highlighted during the 1980´s when Monzani [4] reproduced the Kroll process using zirconium tetrachloride that was supplied by *Western Zirconium* as well as tetrachloride that was produced at the Nuclear and Energy Research Institute, IPEN-CNEN/SP.

There are many ways to produce metallic zirconium according to the classification of Lehr *et al.*, quoted by Monzani [4], being: reduction of zirconium tetrachloride by Na, Ca, Mg or Al; reduction of zirconium tetrafluoride by Ca or Mg; reduction of alkaline double fluorides by Na or Al; reduction of zirconium oxide by alkali metals or alkaline earth metals; reduction of zirconium oxide by carbon or carbide and electrolytic processes. More recently, in 2002 the Brazilian author Lobo [5] studied the microestruture of zircaloy-4 under different thermo-mechanical treatments. The zirconium alloys are commercially known as zircaloy and they are used in the shape of tubes to encapsulate the UO2 pellets in power reactors of PWR and BWR types. The importance of zirconium in nuclear technology is related to its low thermal neutron absorption cross-section (0,19 barn) which is linked to certain properties such as high melting point, good mechanical strength and corrosion resistance [6]. Its applicability in the chemical industries is due to its high resistance to various acids. It's used in manufacturing equipment such as heat exchangers, pumps, piping, valves, etc.. [7].

In Brazil, there are only a few studies published about the characterization of zirconium sponge. In this context, this paper intends to contribute by presenting the chemical composition, structural phases, the vickers microhardness and microstructural analyzes of zirconium sponge produced in IPEN-CNEN/SP through the Kroll process.

The process to obtain zirconium sponge consists of subjecting the ceramic or nuclear grade zirconium oxide to the pelletizing, chlorination, purification, distillation and reduction, as shown in Figure 1.

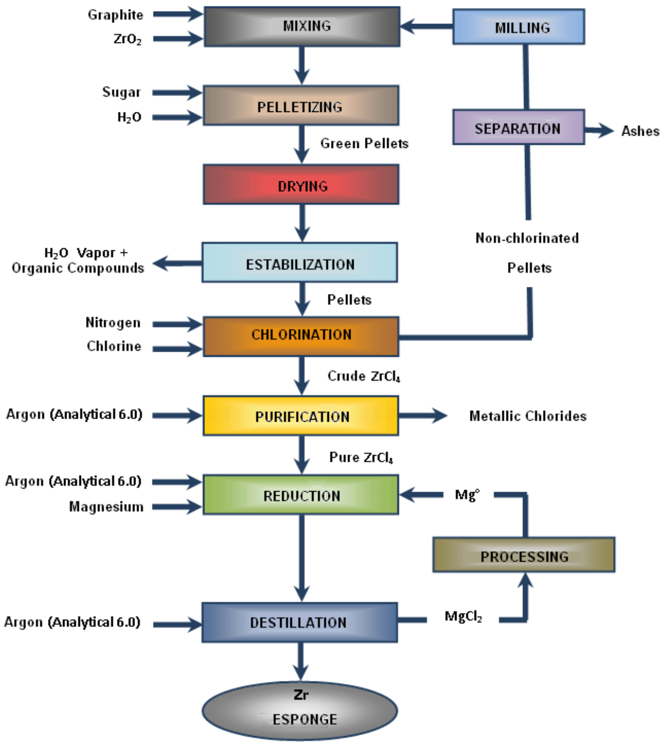

Fig. 1 - Flowchart of the process to obtain zirconium sponge.

The study and development of the process to obtain a zirconium sponge (Fig. 1 Flowchart) was initiated at IPEN in 1986 and continued for nearly 15 years. The process was interrupted due to the priority of other institutional projects and was restarted recently in late 2010. The main objective was to optimize the production process of nuclear grade zirconium sponge, which is the basic raw material of special alloys. These alloys are used to manufacture the metallic components of the Nuclear Fuel Element.

The pelletizing step consists of blending the zirconium oxide, reducing agent and binding agent, using a blender like a rotating jar with vanes. After homogenization of these ingredients, the mixture is moistened and added to a pelletizing disc manufactured by Eirich. Water is added to the dry mixture alternately until pellets are obtained with a diameter of approximately 5 to 15 mm. These pellets are dried at 80 ° C and calcined at 600 ° C for 4 hours in an inert gas atmosphere.

During the chlorination process, the chlorinator reactor is initially heated by a furnace at 800-1000°C under an inert gas atmosphere. This is done in order to eliminate moisture throughout the chlorinator system. The chlorination reactor is then fed with pellets and these are subjected to a flow of chlorine gas at the working temperature of around 900 ° C. The zirconium tetrachloride is collected in two cooled condensers arranged in a row and kept at temperatures below 330^{o}C.

The purification step consists of the elimination of impurities from the zirconium tetrachloride that came from the chlorination process. This procedure also improves the product's characteristics by promoting its densification and thus making it easier to control in the subsequent steps.

In the reduction step, the purified zirconium tetrachloride is reduced with metallic magnesium according to the following chemical reaction:

$$ZrCl_{4(g)} + 2\ Mg_{(l)} \rightarrow Zr_{(s)} + 2\ MgCl_{2(l)}$$

In the distillation step, the reaction products and excess magnesium are separated. The zirconium sponge achieved by these processes has been subjected to characterization tests.

EXPERIMENTAL

The steps shown in Figure 1 achieved the following products: pellets, crude zirconium tetrachloride, pure zirconium tetrachloride and zirconium sponge, as shown in Figure 2 [4].

The procedure adopted for the preparation of samples for metallic zirconium characterizations consists of the following steps: cut the zirconium sponge using a "cut-off" with SiC disc in the transverse direction to the wall of the sponge contact with the crucible; A sample with approximate dimensions of 0.5 x 1.0 x 0.3 cm were selected for analysis of X-ray diffraction; Other samples of smaller dimensions were rinsed with acetone to remove the cutting fluid residues and then embedded in acrylic resin curing cold for metallographic preparation.

Among the procedures performed in metallographic sample is sanding with sandpaper grit sizes of 320, 400 and 600 mesh.

(a) **(b)** **(c)** **(d)**

Fig. 2 - Achieved products: (a) Green pellets; (b) Crude zirconium tetrachloride; (c) Pure zirconium tetrachloride; (d) Zirconium sponge [4].

Subsequently, these samples were polished using diamond suspensions with particle size of 9μm, 6μm, 3μm, and then colloidal silica for end polishing. These samples were analyzed by X-ray fluorescence and scanning electron microscopy.

RESULTS AND DISCUSSION

Table 1 presents the results of the chemical analysis from the zirconium sponge sample achieved at IPEN (average of three determinations).

Table 1 - Chemical composition of zirconium sponge.

Elements	1 (%at.)	2 (%at.)	3 (%at.)	Average (%at.)
Zr	97,446	96,986	97,362	**97,265±0,245**
Hf	1,976	2,016	2,174	**2,055±0,105**
Nd	0,397	0,437	0,366	**0,400±0,036**
Mn	0,113	0,214	0,034	**0,120±0,090**
Ni	0,027	0,107	0,011	**0,048±0,051**
Co	0,021	0,021	0,038	**0,027±0,010**
Fe	0,020	0,220	0,015	**0,085±0,117**

The presence of manganese is due to the type of reducing agent used in the reduction process which was the metallic magnesium. Hafnium is present due to the product being zirconium sponge achieved from ceramic grade zirconium oxide. The presence of iron is observed from the crucible used in the reduction and distillation processes since the sample was in contact with the wall of the crucible.

Similar results were obtained by Monzani [4] and by comparison with the chemical composition of ASTM (8,9), it has been discovered that the zirconium sponge achieved is adequate for commercial application with a purity very close to 98%, according to ASTM Grade R 60003.

Zirconium metal is difficult to achieve due to its properties, mainly for being pyrophoric material, and its quick reaction the gases of the atmosphere which makes it fragile.

In this context, was determined that the ductility of the material making up the Vickers hardness test with a hardness, Panambra brand, model MV1000B.

With the aim of obtaining an average hardness of zirconium sponge, five indentations were performed in the sample with a diamond cone and test force of 300gf and subsequently used to calculate the average and standard deviation 51.08HV ±4,92, respectively.

The studied material has a low hardness value, approximately 51HV as achieved in the distillation furnace.

The hardness of this material can be increased by treating it in an electric furnace with impure gas argon atmosphere. This is because the metallic zirconium has high reactivity with gases, particularly oxygen and nitrogen.

According to Monzani [4], the atmosphere of the furnace influences the value of Vickers hardness of metallic zirconium, reaching values of about 500HV in an impure argon gas atmosphere (Ar S type) and 190 HV in a pure argon gas environment (Air type U). During their research in 1947, Kroll and his staff produced metallic zirconium ingots with a hardness of 156HV [10].

In figure 3 the standard X-ray diffractogram of metallic zirconium in comparison with an X-ray diffractogram of the zirconium sponge sample is shown.

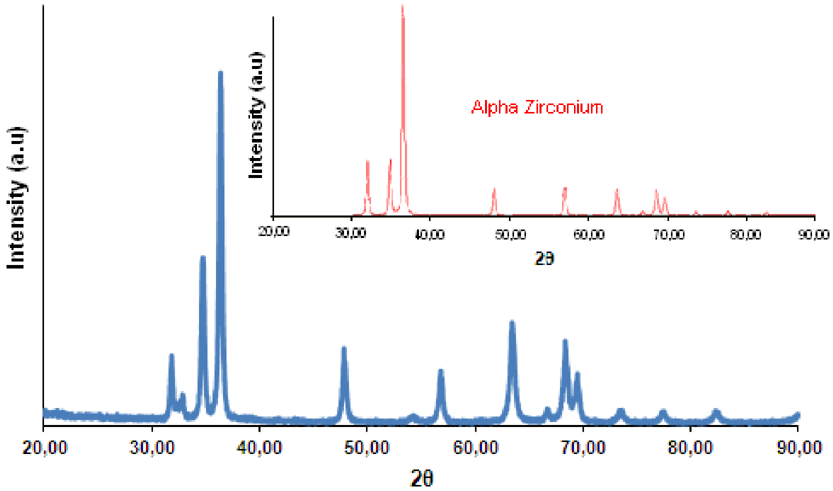

Fig. 3 – X-ray diffractograms of the zirconium sponge sample.

Comparing the result of the X-ray diffractogram of zirconium sponge with the standard of metallic zirconium by using Crystallographica Search Match Software, it was possible to verify that the material presents Zr alpha phase stable until 862°C with hexagonal structure compact, according to Miller [3].

The microstructural analysis of different sections of the zirconium sponge sample was performed using a scanning electron microscope - SEM. The preparation the zirconium sponge sample is extremely difficult and has been developed according to the experimental procedure shown.

In Figure 4 (a) and (b) the micrographs of the zirconium sponge sample achieved at IPEN are shown.

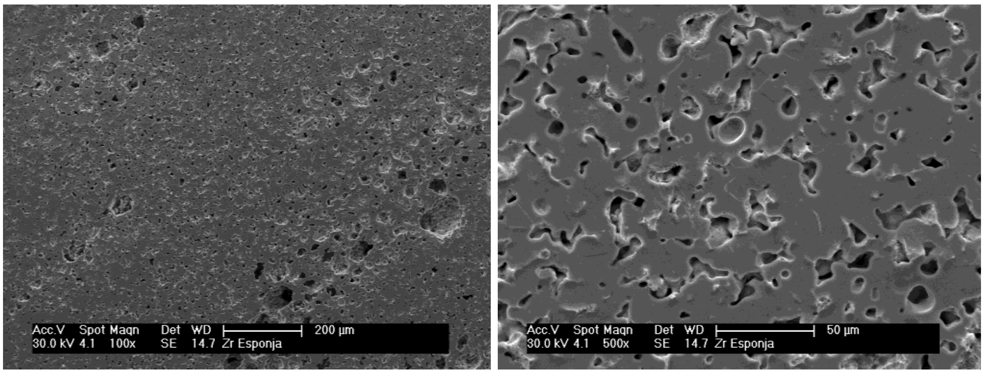

Fig.4 – Electron micrographs of zirconium sponge: (a) Mag. 100x, (b) 500x Mag.

Figures 4 (a) and (b) show a non homogeneous distribution of pores in the sponge, with dimensions reaching approximately 30 microns, without inclusions or precipitates.

CONCLUSIONS

The following conclusions are established in this work:

- The zirconium sponge can be used for commercial applications due to its purity close to 98% at.;

- It was possible to define a methodology for the preparation of zirconium sponge samples for metallographic tests;
- The sponge zirconium has the Zr alpha phase, stable up to 862 ° C with a compact hexagonal structure;
- The hardness of achieved material can be increased by treating it in a melting furnace with inert gas atmosphere;
- There is a possibility of increasing the purity of the sponge and as well as increase its ductility, optimizing the process parameters.

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