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Recycling of Zircaloy machining chips by VAR remelting and powder metallurgy techniques

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Abstract

In the fabrication of nuclear reactor core parts, machining chips of Zircaloy are generated. These alloys are strategic for nuclear technology and cannot be discarded. In the present work are presented two methods for recycling of Zircaloy chips. One of the methods is by melting in VAR furnace and the other by powder metallurgy method. By this method the Zircaloy was submitted to hydriding process and milled in a high-energy ball mill. The powder was cold isostatically pressed and vacuum sintered. The elemental composition of the samples obtained by both ways was determined by XRF and compared to the specifications. The phase composition was determined by XRD. The microstructures resulting of both processing methods, before and after rolling were characterized using optical and scanning electron microscopy. The good results of the powder metallurgy method suggest the possibility of producing small parts, like cladding cap-ends, using near net shape sintering.

Introduction

The nuclear fuel of PWR reactors is composed of uranium dioxide pellets - UO_2, assembled in metallic tubes called cladding. These tubes arranged in sets of 14x14 to 17x17 tubes form the fuel element. The retention of fission products is done, primarily, in the UO_2 ceramic pellets that accommodate part of the products of uranium fission. The second barrier is the cladding wall, which insulates the fuel from the water of the reactor primary circuit, which has moderator and coolant role. The cladding and structural components of the fuel elements are exposed to this water environment at high pressure and high temperature, besides high flux of energetic neutrons. This leads to extreme requirements of mechanical strength and corrosion behavior for these materials. Additionally, the nuclear cladding materials must present low absorption cross section for neutrons. The materials that best meet these requirements are known as Zircaloys. The Zircaloys are zirconium alloys that present excellent mechanical and corrosion properties and low absorption cross section for thermal neutrons. For low neutron absorption the zirconium has to be absent from hafnium, since this element has high absorption cross section for neutrons. The mechanical and corrosion properties are closely related to appropriate chemical compositions [1]. The zirconium alloys known as Zircaloy-2, Zircaloy-4 and Zirlo® are used in the manufacture of some reactor core parts, as claddings, coolant tubes tube guides and spacer grids [1-3]. Table 1 shows typical elemental compositions of Zircaloys [4, 5]. The advantage of Zircaloy-4 compared to Zircaloy-2 is its lower hydrogen absorption under water corrosion for PWR reactors [6]. Nuclear grade zirconium alloys are considered strategic materials and, therefore, beyond its high cost, are not freely commercialized. Thus, the production of zirconium alloys is a requirement for the autonomous domain of the process of nuclear power generation.

Table 1 - Typical composition of Zircaloy-2, Zircaloy-4 and Zirlo (mass %) [1, 4-6].

Element	**Sn** (%)	**Fe** (%)	**Cr** (%)	**Ni** (%)	**O** (%)	**Hf**	**Zr**	**Nb** (%)
Zircaloy-2	1.2-1.7	0.07-0.20	0.05-0.15	0.03-0.08	0.12	<100 ppm	bal.	-
Zircaloy-4	1.2-1.7	0.18-0.24	0.07-0.13	-	0.12	<100 ppm	bal.	-
Zirlo®	0-0.99	0.11	-	-	0.11	40 ppm	bal.	0.98

Zirlo® is a trade-mark from Westinghouse Electric Company. – Not specified.

Brazil has the technology for the production of nuclear fuel from uranium mining to manufacturing and assembly of fuel elements, including the isotopic enrichment process. However, the production of zirconium alloys is not carried out in the country at industrial scale and, therefore, the Zircaloy used in its nuclear power plants is imported.

In the fabrication of nuclear fuel elements parts, a great amount of Zircaloy residues like machining chips and scraps are generated and, as this material cannot be discarded as ordinary metallic waste, the recycling of this material presents a strategic role for the Brazilian Nuclear Policy due to economic and environmental aspects. In this work are described two methods that are being developed to recycle Zircaloy chips.

Compared to the production of new alloys the recycling of Zircaloy chips has advantages, once the starting material is already free of hafnium and has the specified composition. It is estimated that the economic savings in recovery of Zircaloy chips by electric arc furnaces is of US$ 78/kg [7]. In addition, the chips are generated in large quantities during the production of nuclear core parts, like the caps of the cladding tubes [8]. The caps of the tubes, also known as end-caps, shown schematically in Figure 1, are made by the machining of bars of Zircaloy. The machining chips generated by this process is contaminated by machining lubricants and surface oxides, must be long term stored in adequate conditions, once zirconium is pyrophoric and, also, nuclear grade Zircaloy is a controlled material. Thus, the recycling of this material gives, additionally, a destination to the stored material and may represent an economical advantage.

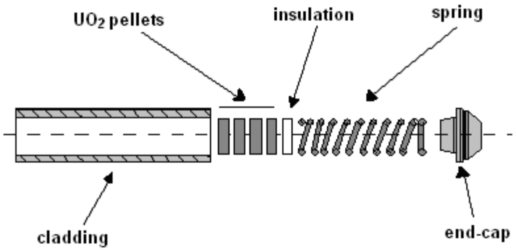


Figure 1 - Schematic drawing of the components of PWR rod fuel [8].

Experimental

Preparation of the material

The machining process of Zircaloy parts for fuel elements employs cutting oil, which impregnates the material. In order to remove the impurities, the chips were washed with a degreasing detergent and acid etched. It was, also, performed a manual magnetic separation of possible iron or steel particles. The washing procedure was repeated three times, 20 minutes each, using commercial neutral detergent and water in ultrasonic bath and then washed in deionized water. After the last washing, the material was dried with ethylic alcohol under a stream of heated air. The etching was done in two steps, firstly with HCl (50 HCl: 50 H_2O), followed by a second etch with HNO_3 (30 HNO_3 : 70 H_2O), 20 minutes each. The etched chips were washed using deionized water and dried using ethylic alcohol and heated air. The aspect of the cleaned material is shown in Figure 2 (a).

In order to accommodate the machining chips in the cavities of the furnace copper crucible and avoid dispersion of the electric arc, the material was compacted using two types of compaction dies; a circular (14 mm internal diameter) and a rectangular (13 x 32 mm). It was employed a hydraulic manual press and loads of 0.5 t (circular) and 1.5 t (rectangular). In Figure 2 (a) are shown examples of cleaned chips and two compacted briquettes and in Figure 2 (b) is show the rectangular die.

(a) (b)

Figure 2 - Zirconium machining chips after cleaning and compaction (a). Rectangular press die (b).

Powder metallurgy process

Zirconium is one of the most suitable metals for powder metallurgy. Zirconium powder can be compacted and sintered close to its theoretical density. The sintered Zr is ductile and can be rolled, drawn and extruded. It is known [9] that hydrogen must be absorbed up to, at least, 50 % (atomic %) in zirconium, making the material brittle and adequate for its comminution. According to reaction kinetics studies of Zr and H_2, the significant absorption of hydrogen by zirconium occurs from 235° C and has a maximum between 300° C and 375° C. After grinding, the material can be dehydrated during the sintering process under vacuum. The complete removal of hydrogen occurs at low pressure (10^{-5} mbar) and temperatures above 800° C [10].

The hydriding was carried out in a system composed by a stainless steel retort and a resistive tubular furnace. A circular compacted sample was placed in an alumina crucible and placed in the retort connected to an H_2 line and to the high vacuum system. Initially the system was evacuated to 0.3 mbar, purged with H_2 and then heated to 500° C. After temperature stabilization H_2 was injected for 5 minutes and then the retort was placed outside the furnace to be cooled at air. The hydride material was ground preliminary in an agate mortar and then in a high-energy planetary ball mill (zirconia balls diameter = 5 mm; proportion of powder 1 g: 10 g balls) with cyclohexane and grinded at 200 rpm for 30 min. The milled powder was dried under vacuum for 45 min and isostatically pressed at 200 MPa in a rubber mold (12 mm internal diameter). Part of the powder was reserved for determination of particle size distribution and X-ray diffraction measurements.

The sintering was carried out in a tubular resistive furnace under vacuum. The treatment started at room temperature until reaching a vacuum of 7 x 10^{-5} mbar, when the heating started at the rate of 8° C/min up to 1070º C. After 2 h at this temperature the pressure was stabilized at 4.8 x 10^{-6} mbar and the hydrogen was removed. The sintering was carried out at 1070° C for 20 h. The systems employed for hydriding and sintering are shown in Figure 5.

After sintering the sample was weighed and measured for determination of its apparent density, which was compared to the theoretical density of Zircaloy-4 (6.6 g cm^{-3}).

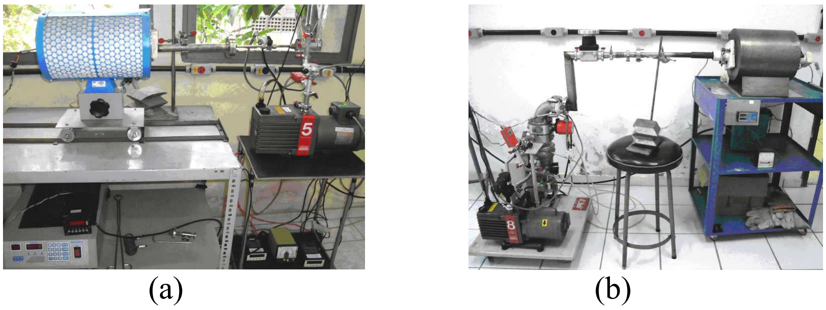

(a) (b)

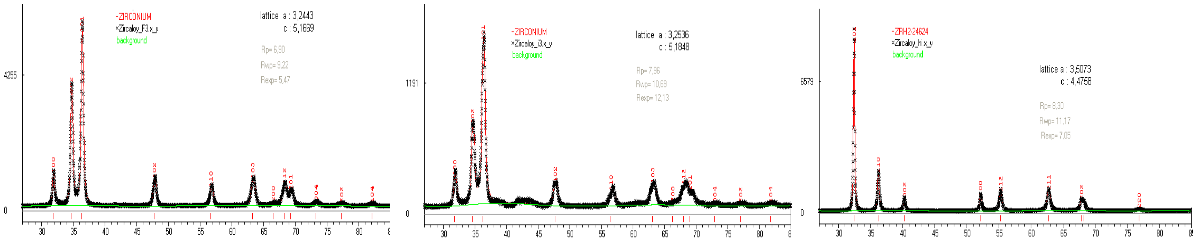
Figure 3 - Hydriding system (a) and vacuum sintering system (b).

Characterization

The hardness was measured using a hardness tester with 1/16" diameter steel ball tip and a 100 kg load, using the Brinell hardness scale. Measurements were made in three regions along the flat section of the samples, maintaining a standard distance between them. The X-ray diffraction measurements were performed in a Rigaku diffractometer (model Ultima-IV) using Cu-K_α radiation.

The elemental composition of the samples was determined using X-Ray Fluorescence Spectrometry (XRFS), using a Shimadzu EDXRF spectrometer (model 720) and a Rigaku WDXRF spectrometer (model RIX 3000). The determination of elements Sn, Fe, Cr, Ni and Hf was performed using the fundamental parameters method and the sensitivity curve was obtained using standard and certified materials. The methodologies for sample preparation and data analysis were described elsewhere by Sato et al [11].

Results and discussion



(a) (b) (c)

Figure 4 – Full profile refinements of X-ray diffraction data (Cu-kα) for samples: (a) Zircaloy obtained by arc melting; (b) Zircaloy obtained by sintering; (c) Zircaloy hydride powder. The refined cell parameters and refinement residues are show in the figures.

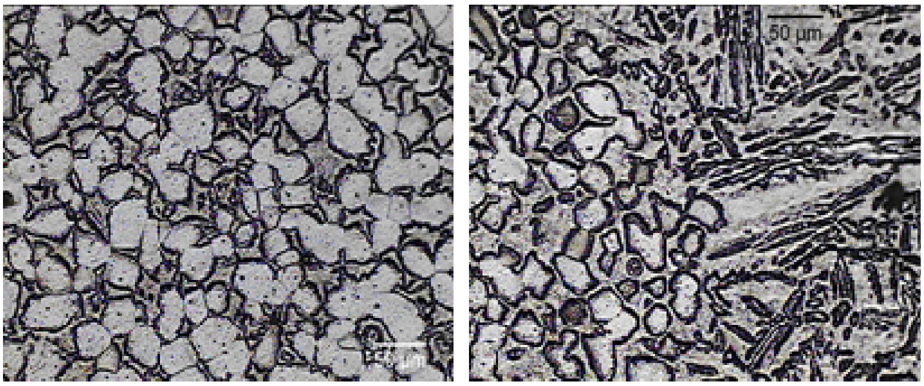


Figure 5 – Optical micrographs from two regions of the sintered sample at different magnification.

Table 2 – Results for elemental composition determined by energy dispersive X-ray fluorescence analysis (mass %): certified and determined composition for CRM-098 standard; specifications for Zry-2 and Zry-4; determined values for sintered sample and for VAR-fused samples (fusion 1 and 2).

	Cr (%)	Fe (%)	Sn (%)	Hf (μg g^{-1})
CRM 098 (certified)	0.0906±0.009	0.2143±0.002	1.460±0.009	77.6±3.0
CRM 098 (determined)	0.091±0.003	0.218±0.012	1.489±0.028	75.7±2.0
Zry-4 (specification)	0.07 - 0.13	0.18 - 0.24	1.2 - 1.7	< 100
Zry-2 (specification)	0.05 - 0.15	0.07 - 0.20	1.2 - 1.7	< 100
Zry-SINT	0.070±0.002	0.293±0.012	1.295±0.043	58.5±2.7
Zry-VAR (fusion 1)	0.111±0.002	0.535±0.010	1.332±0.027	55.6±5.7
Zry-VAR (fusion 2)	0.397±0.005	5.516±0.043	1.224±0.032	60.0±5.7

CRM 098: *Certified Reference Material BCR, Commission of the European Communities, Brussels, Belgium;* ***Zr-4****: Zircaloy 4;* ***Zr-2****: Zircaloy 2;* ***Zry-SINT****: Sintered sample;* ***Zry-VAR****: VAR melted samples.*

Table 3 – Results for Full Profile Refinements of X-ray diffraction data for melted and sintered Zircaloy.

Sample	Space Group	Cell Param.a (Å)	Cell Param. c (Å)
Zry-VAR	P63/mmc	3.2443	5.1669
Zry-SINT	P63/mmc	3.2536	5.1848

The particle size determination for Zry hydride powder by LASER scattering presented an average particle diameter of 5.06 μm for the first grinding and 3,17 μm for the second. The sintered material presented an apparent density of 6.4 g.cm^{-3}, which corresponds to 95% of the theoretical density of Zr. A new sintering using the second grinding hydride and new sintering parameters is under run and, probably, will improve the density and microstructure of the material. Both the melted and sintered Zircaloy presented hexagonal α-zirconium structure whit small difference in the cell parameters, as shown in Figure 4 and Table 3. The microstructure for sintered Zry is more homogeneous and isotropic than for the fused material. The chemical analysis showed contents of Fe and Cr (for fused samples) higher than the specified values due to contamination of the starting Zry chips by steel in the storage. The contents of Sn and other elements comply the specifications for Zry but the sintered sample is more homogeneous.

Conclusions

It was demonstrated the effectiveness of the powder metallurgy processes for recycling of Zircaloy machining chips. It was established and evaluated a methodology for the determination of the chemical composition of recycled Zircaloy by X-ray fluorescence spectrometry. The X-ray diffraction analysis shows that both, the melted and the sintered Zircaloy, presented α (hexagonal) zirconium structure. The sintered material presents more chemical homogeneity and better microstructure than the fused material. The starting Zry chips must be free of contamination of other alloys. The sintering process must be improved in order to obtain higher densities, aiming the production of nuclear core parts by near net shape powder metallurgy process.

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