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Development in corrosion resistance by microstructural refinement in Zr-16 SS 304 alloy using suction casting technique

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ABSTRACT

Zirconium (Zr)-stainless steel (SS) hybrid alloys are being considered as baseline alloys for developing metallic-waste-form (MWF) with the motivation of disposing of Zr and SS base nuclear metallic wastes. Zr–16 wt.% SS, a MWF alloy optimized from previous studies, exhibit significant grain refinement and changes in phase assemblages (soft phase: $Zr_2(Fe, Cr)/\alpha$-Zr vs. hard phase: $Zr_3(Fe, Ni)$) when prepared by suction casting (SC) technique in comparison to arc-cast-melt (AMC) route. Variation in Cr-distribution among different phases are found to be low in suction cast alloy, which along with grain refinement restricted Cr-depletion at the $Zr_2(Fe, Cr)$/Zr interfaces, prone to localized attack. Hence, SC alloy, compared to AMC alloy, showed lower current density, higher potential at the breakdown of passivity and higher corrosion potential during polarization experiments (carried out under possible geological repository environments, viz., pH 8, 5 and 1) indicating its superior corrosion resistance.

1. Introduction

About eleven percent of the world's electricity is contributed by nuclear energy (~376 GWe) generated by almost 437 reactors. More than 400 reactors [1] are thermal reactors which discard a large amount of radioactive Zr-base cladding hulls, spacer grids etc. [2], which are hazardous in nature and therefore merit immobilization and geological disposal [3,4]. Of late, an international consensus has been developed throughout the world to recognize the metallic waste as 'high level wastes' (HLW) when the radioactivity level is more than 3.7×10^{11} Bq/L or 100nCi per gram [2]. This is attributed to their association (due to their interaction with fuel either in the rector core or during their electro-metallurgical treatment) with radioactive activation products (Mn, Co, etc.), fission products (Ru, Sb, Cs, Sr, Ce, etc.) and alpha-emitters (U, Pu, Am, Cm, etc.). For geological disposal, prior conditioning of the waste [5] (i.e. minimization of waste volume into a solid form) is required for reducing the potential hazard during transportation, storage and final disposal. As a part of such conditioning treatments, there are several processes [2] followed all over the world for consolidation of metallic wastes into a solid form, which is known as metallic waste form (MWF). However, most of these processes, except melting route, lead to non-monolithic compacts, which are not suitable for long term disposal in geological repository due to faster bio-degradation, inferior mechanical properties and inadequate radiation stability (e.g. phase transformation) etc. [6–8]. Presently, cast Zr-SS alloys prepared by melting route are being investigated for the development of MWF alloys [9–21] with the motivation for immobilization of Zr and SS base nuclear metallic waste inventories produced during different activities at various stages of nuclear power program. Long term material performance of MWF necessitates desirable ductility to avoid disintegration of the form due to unavoidable impact (during handling or otherwise) and reliable corrosion resistance in order to ensure no or negligible leaching even in an aggressive environment of geological repository. Hence, vis-à-vis in-situ studies in specific environments, short-term laboratory experiments [2,15–21] were conducted to ensure suitable microstructure, desirable mechanical property and sustainable chemical durability of MWF alloys. In this context, numerous testing programs were reported in several studies [5,9–14,22–27]. However, most of these studies focus towards selection of SS-base suitable bulk compositions from SS-Zr alloys [9–18], whereas, only a few studies aim to develop Zr-base Zr-SS MWF alloy [19–21].

In our previous studies [20,21], a detailed micro-structural analysis and evaluation of corrosion resistance were carried out for six as-cast Zr-SS alloys, viz., Zr-5, 8, 12, 16, 20 and 25 wt.% SS (prepared by arc-melting route). Steam oxidation studies at elevated temperature have shown that among the aforementioned

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alloys, Zr–16 wt.% SS gained minimum weight or formed the thinnest (~3.7 μm) oxide layer (essentially Fe_2O_3) therefore indicating highest corrosion resistance [20]. Electrochemical studies at room temperature, under different simulated environmental conditions of possible geological repository, indicated that Zr-8SS is the most corrosion resistant against localized corrosion/ pitting among all the mentioned Zr-SS alloys and SS content in such alloys should not exceed 16 wt.%. Within this compositional limit, only Zr-16SS and Zr-8SS contain Laves phase, Zr_2(Fe, Cr), a potential host lattice for fixing radionuclides [14,25,28]. Zr-16SS, despite its lower corrosion resistance [21], was preferred over Zr-8SS, mainly attributed to higher distribution of the Laves phase in its microstructure and lower melting point (since, ^{137}Cs, ^{90}Sr etc. evaporate at moderate temperatures).

Keeping all these aspects in mind, an investigation has been carried out to look into a scope for improvement in the corrosion resistance of Zr-16SS alloy through microstructural modification. The alloy was prepared by suction casting method [29–31] and the microstructure, hardness and corrosion properties were compared with those obtained from arc-melt-cast (AMC) alloy. Details about experimental procedure and results are given below.

2. Experimental

2.1. Alloy preparation using vacuum arc melting and suction cast techniques

About 50 g buttons of Zr-16SS alloys were produced from pure zirconium metal and 304L SS in an arc melting furnace. The furnace was operated at around 25–28 V potential and 800–900 A current and was evacuated and refilled with high purity Ar of about 400 mm Hg (0.53 atmosphere). After furnace cooling, cast alloys were obtained in the form of pan cake. The alloy was homogenized through repetitive melting and casting for several times.

Alloy button prepared in arc-melting process was cut into small pieces. These cast alloy pieces were again re-melted in an arc-melting unit attached to a suction casting unit, where, the melt was cast into a small rod shape (3.9 mm dia and 71 mm long) in a copper casting block which is surrounded by a cooling arrangement for water circulation. In order to achieve higher cooling of the casting, water was cooled with dry-ice before its circulation. Such suction-casting technique is frequently used for processing bulk glassy alloys of various systems in a form of rod/tube samples [29–31].

2.2. Microstructural characterization of suction cast specimens

2.2.1. Characterization by X-ray diffraction technique

X-ray diffraction (XRD) analyses for SC and AMC samples were carried out in a Bruker X-ray powder diffractometer (Model D8 Discover) using CuKα radiation (wavelength: 1.5406 Å), 40 kV acceleration voltage and 30 mA tube current. Samples were prepared in the form of small blocks and the scanning was carried over a range of 10–70° (2θ), using a four circle Goniometer with an increment of 0.01° per step at a rate of 1° per minute. The phase analyses were done comparing the diffraction patterns with Joint Committee on Powder Diffraction Standards (JCPDS) files.

2.2.2. Characterization by SEM and EPMA

Both the specimens were investigated by Scanning Electron Microscope (SEM) and Electron Probe Micro-Analyser (EPMA) to reveal their morphological as well as micro-chemical information. The SEM images were taken using an acceleration voltage of 20 and 30 kV in 'back scattered electron (BSE)' image detection mode. The microstructural and micro-chemical analyses of these samples were done by means of CAMECA SX-100 EPMA using an acceleration voltage of 20 keV and stabilized beam current of 4 nA and 20 nA for 'back scattered electron (BSE)' imaging and quantitative analyses respectively. The beam size was kept at ≤1 μm to reduce the convolution effect so as to achieve the near most correct estimation of the phase compositions. Pure metallic standards were used for quantitative analyses and the raw data were corrected for atomic number (Z), absorption (A) and fluorescence (F) following Pouchou and Pichoir (PAP) methods [32].

2.3. Characterization by micro-hardness test

The hardness measurements of the alloys were carried out using MICROHARDNESSTESTER FM (Japan). The micro-hardness value was reported taking an average of five readings measured at a load of 200 gf and dwell time of 15 s.

2.4. Corrosion studies

2.4.1. Sample preparation for electrochemical test

The arc-melt-cast (AMC) specimens with dimension of 10 mm (length, l) × 10 mm (width, w) × 5 mm (thickness, t) and suction-cast (SC) specimens with dimension of 50 mm (t) × 3.9 mm (dia.) were prepared for electrochemical study. For electrical connection, stainless steel wires were attached to one side of these specimens. Mounting of these samples was done in such a way so that the surface attached with stainless steel wire got fully covered with epoxy resin and the other surface remained exposed for experiment. These exposed surfaces were ground with successively finer grades of SiC emery papers up to 1000 grit and were subsequently metallographically polished using 1 micron diamond paste. These specimens were then cleaned ultrasonically with soap solution and water. Prior to electrochemical test, the sample-mount interface at the exposed surface of the specimen was covered by corrosion resistant lacquer to avoid crevice corrosion.

2.4.2. Potentiodynamic polarization and surface characterization

Corrosion behavior of the aforementioned AMC and SC Zr–16 wt.% SS specimens were evaluated by potentiodynamic polarization study. The polarization studies were carried out in distilled water at three different pH levels, such as, pH 8, pH 5 and pH 1 simulating mild basic, mild acidic and highly aggressive environments of repository respectively. The different pH of the test solutions were prepared by adding appropriate concentrations of HCl and NH_4OH in distilled water. All the potentiodynamic polarization experiments were carried out at room temperature (26 °C), in open to air and non-stirred conditions, using the Greene cell consisting of three electrodes; reference electrode (saturated calomel electrode, SCE), counter electrode (Pt) and working electrode (specimen). Using an GESP electrochemical interface, the polarization studies were conducted at 20 mV/min scan rate and were continued till break down of passive potential. The studies were repeated for 2–3 times for each specimen to verify reproducibility of the results.

After electrochemical studies, each specimen was examined under an optical microscope. Whereas, the specimens subjected to polarization studies at pH 1 were investigated by SEM (and EPMA) to establish if any localized attack had taken place.

3. Results

3.1. X-ray diffraction and electron probe micro-analysis

Fig. 1 shows XRD patterns of SC and AMC Zr-16SS specimens. In addition to the peaks related to the phases, such as, α-Zr, Zr_2(Fe, Cr) and Zr_3(Fe, Ni) present in the AMC specimen (see Fig. 2a), XRD pattern of SC specimen also contained additional peaks which were indexed with β-Zr and ω-Zr (Fig. 1). Lower and higher