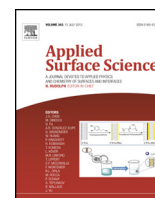




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Electrochemical properties of the passive film on bulk Zr–Fe–Cr intermetallic fabricated by spark plasma sintering

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ABSTRACT

Although Zr-based second phase particles (SPPs) are important factors influencing corrosion resistance of zircaloy cladding materials, the corrosion behavior of SPPs has not been investigated by means of electrochemical method so far. In order to clarify the role of SPPs commonly existed in zircaloy, bulk Zr-based intermetallics were firstly fabricated by spark plasma sintering (SPS) at temperatures 1373 K and an applied pressure of 60 MPa in this work. Both the natural passive film on surface and oxidation behavior of intermetallic has been investigated in this work. X-ray diffraction (XRD) pattern showed that as-prepared intermetallic of crystal structure belongs to Laves phase with AB₂ type. Electrochemical measurement of passive film on surface of bulk Zr-based intermetallic exhibited significant difference with that of zirconium. Potentiodynamic measurements results revealed that intermetallic exhibited higher corrosion potential and lower corrosion current density than that of pure zirconium, implying that Zr-based second phase will act as cathode when they are included in zirconium matrix. Meanwhile, significant improvement of Zr–Fe–Cr intermetallic on the water chemistry corrosion resistance was demonstrated comparing with Zr–Fe and Zr–Cr binary intermetallics.

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1. Introduction

For the past five decades, zirconium alloys are extensively applied as cladding tubes in fuel assemblies due to low thermal neutron cross-section, proper corrosion resistance and adequate mechanical properties. Recently, the pursuit of high burn-up and zero damage of fuel components have prompted the development of new zircaloy by alloying with improved adequate mechanical properties and resistance to long-term corrosion. Most of alloying elements except sternum existed in solid solution have a very low solid solubility in α -Zr matrix, such as iron, chromium and niobium, which precipitant as second phase particles (SPPs) with size of tens of nanometer to submicron since they are poorly soluble in zirconium matrix. Recently, it has been revealed that numerical relationship between corrosion resistance of zircaloy cladding materials and SPPs with uniformly distribution in zircaloy was almost important, and the crystallographic structure and the

chemical stoichiometry of SPPs precipitated in these alloys have been well established [1,2].

The two most common SPPs are the ternary Zr(Fe,Cr)₂ (in Zircaloy-4) and Zr₂(Fe,Ni) (in Zircaloy-2) [3–5]. The main metallurgical factors related to corrosion characteristics of zircaloy include the size and distribution of SPPs precipitates such as Zr(Fe,Cr)₂ [6–8], these Zr-based Laves phase displayed several potential properties at elevated temperatures, such as better oxidation resistance and higher mechanical strength than polycrystalline zircaloy. SPPs residing at the oxide–metal interface were reported to oxidized more slowly than the surrounding Zr matrix [9,10]. Hydrothermal oxidation of the Zr-based Laves phase Zr(Fe,Cr)₂ is an important issue when considering zircaloy corrosion resistance. Investigating of passivation behavior for Zr-based intermetallic is an effective approach to corrosion resistance of SPPs in zircaloy.

The SPPs distributed in zircaloy was quite difficult investigated due to the small volume fraction and sizes in massive alloys by conventional analysis methods. It has been an urgent need for independent research of SPPs to extract SPPs from zircaloy matrix. Several efforts have been devoted in past few decades to conducting the study of single Zr-based Laves phase. One of these was to extract SPP from Zircaloy-4 with electrochemical extraction method [11]. Another way was to isolate SPPs from α -Zr matrix through anodic

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dissolution procedure, giving access to a precise determination of the crystallographic structure and lattice parameters of SPPs [12]. The existing methods emphasized in characterizing chemical composition of SPPs in different zircaloy, and lack of corrosion property restricted the comprehensive understanding of SPPs. Despite previous numerous studies, one cannot easily get a full picture of the electrochemical behavior of passive film without bulk Zr-based intermetallic.

Spark plasma sintering (SPS) was developed based on the idea of employ a pulsed DC current on electric discharge machine for sintering near-full density compacts since the early 1960s [13]. Afterwards SPS was widely used in fabricating ceramics, metals, hard materials and composite materials on account of many advantages over conventional powder metallurgy methods, including high reproducibility, accurate control of sintering energy, as well as high sintering speed, safety, and reliability [14–17].

In this paper, we employed SPS for the first time to prepare highly compact Zr-based intermetallics commonly existed in zircaloy. Though binary phases do not tend to form in zircaloy, an investigation of the binary intermetallic was also important to understand the role that individual alloying elements play in the interaction between corrosion resistance and the phase of intermetallic. Consequently, this allows us to determine which kind of SPPs were likely to behave as hindering factors for hydrochemistry corrosion. Therefore, electrochemical properties of binary and ternary intermetallics were compared to commercial pure zirconium. The microstructure of intermetallics was studied by electron microscopy and X-ray diffraction and electrochemical properties were investigated by potentiodynamic and electrochemical impedance spectroscopy in water chemical medium. The objective of our study is to clarify the passive properties on Zr-based intermetallic and attempt to interpret the role of SPPs on the hydrothermal corrosion behavior of zircaloy.

2. Experimental details

2.1. Synthesis

A mixture of commercial metallic powders of zirconium (purity >99.9%, particle size <50 μm), ferrum (purity >99.9%, particle size <50 μm) and chromium (purity >99.9%, particle size <50 μm) were used as starting materials for fabricating Zr-based intermetallics. Powders were mixed with a desired molar ratio of alloying elements in intermetallic and subsequently loaded in a stainless steel vial under argon atmosphere. Mechanical milling was carried out in a wet ball-milling for 10 h at a low rotation speed of 180 r/min to thoroughly mix the powders and the milling media were zirconia balls. Absolute ethanol was added as a process control agent (PCA) to prevent the agglomeration of powders during milling. After milling, the mixed powders were dried in vacuum.

The as-milled powder was firstly cold pre-pressed into a pellet at the load of 10 MPa and then inserted into a graphite mold with diameter of 14 mm. A layer of aluminum-foil paper (~0.1 mm thickness) was put into the inner part of mold to reduce the carbon contamination, and boron nitride was applied onto inner surface of the mold. Then the pellet with the die was consolidated into a bulk composite in a spark plasma sintering furnace (SPS-1050T system, Sumitomo Coal Mining, Japan) at 1373 K and total sintering time was fixed to 40 min. The heating rate was controlled as high as 75 °C/min. Prior to the SPS process, the SPS furnace was evacuated and filled with argon for three times, and then evacuated to a vacuum of 10^{-1} Pa. A compressive pressure of 60 MPa was applied in the whole process after sintering. The sample was naturally cooled down to ambient temperature

and take out after compressive pressure being released. The aluminum and carbon contamination on surface of samples were finally removed by polishing.

2.2. Characterization

All as-prepared samples were ground with 400# to 5000# waterproof abrasive paper (Starke GmbH, Germany) followed by polishing to a mirror finish with 0.5 μm diamond paste. The specimens were rinsed in deionized (DI) water and subsequently degreased in absolute ethyl alcohol and acetone for 10 min in an ultrasonic bath respectively. The phases of starting powder and as-sintered intermetallics were characterized by X-ray diffraction (XRD) with Cu K α radiation of $\lambda = 1.5418 \text{ \AA}$ at 200 mA and 40 kV (Rigaku D/Max 2500 v/pc, Japan). Field-emission scanning electron microscopy (FESEM) (JSM-7001F, JEOL, Japan) equipped with an energy dispersive spectroscopy (EDS) system was used to characterize morphologies of surface. For metallographic observation, the polished surfaces of as-sintered samples were etched with etching solution (35% HNO₃ + 5% HF + 40% H₂O). The chemical state on surface of sample was measured by means of X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi X-ray Photoelectron Spectrometer, ThermoFisher Scientific, USA). Due to exposure of sample to mechanical-pumping oil during XPS measurement, the energy position should be adjusted by comparing the surface energy of the absorbed carbon on surface of the specimen with that of the standard binding energy, 285.0 eV.

Hydrothermal oxidation of as-prepared intermetallics was carried out in homemade static experimental autoclave filled with aqueous solution simulating water chemistry medium in primary loops of PWR (a deoxygenated aqueous B-Li solution consist of 0.01 mol/L LiOH and 0.1 mol/L H₃BO₃ (pH=9.4), the same below), 300 °C for 24 h. The dissolved oxygen (DO) in aqueous solution was removed by a steam of pure argon and controlled to be below 10 ppm before the autoclave hydrothermal oxidation.

For electrochemical measurement, machined and cleaned samples with opening section of 100 mm² were prepared by connected to conductive rods and sealed within acrylic-based resin as working electrode. Electrochemical measurements were performed in a conventional three-electrode cell with a platinum as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Electrochemical measurement was conducted in a deoxygenated solution of 0.01 mol/L LiOH and 0.1 mol/L H₃BO₃ at room temperature using Im6e electrochemical workstation (ZAHNER-elektrik GmbH & Co. KG, Germany) before and after hydrothermal oxidation.

The electrochemical behavior of intermetallics before and after hydrothermal oxidation was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization curve was measured from -100 mV to +100 mV of open circuit potential with a sweep rate of 0.1667 mV/s. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined from polarization curves by Tafel extrapolation method, respectively. Electrochemical impedance spectroscopy (EIS) was carried out over a frequency range of 100 kHz–0.01 Hz with at an applied AC disturbance signal of 10 mV sinusoidal around open circuit potential. Mott-Schottky measurements were carried out through a single frequency at 1 kHz in the potential range of relative to SCE with a voltage scan rate of 50 mV/s. Each measurement was repeated at least three times to check the reproducibility. The results obtained were reproducible and no significant variation was found for the same system.

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