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CHARACTERIZATION OF OXIDATION PRODUCTS ON A $ZrFe_2$-TYPE LAVES INTERMETALLIC EXPOSED TO 200°C STEAM[1]

by

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ABSTRACT

The release of radioactive elements from the stainless steel-15 wt% zirconium (SS-15Zr) metal waste form will be governed by the corrosion behavior of $ZrFe_2$-type intermetallics phases present in the alloy. In this article, oxidation products that formed on a $ZrFe_2$-type intermetallic sample exposed to 200°C steam were characterized by Auger Electron Spectroscopy (AES) and Transmission Electron Microscopy (TEM). The data revealed two oxide layers on the sample surface: an outer crystalline iron-oxide layer and an inner amorphous zirconium-rich layer believed to be zirconium oxide. Thermodynamic considerations indicate that the zirconium-rich layer formed first. The iron-oxide layer appears to have resulted from the diffusion of iron through the zirconium-rich layer to the oxide-vapor interface.

Keywords: Intermetallic, Oxidation, Auger Spectroscopy, Transmission Electron Microscopy

INTRODUCTION

Laves intermetallics are prominent in the stainless steel–15 wt% zirconium (SS-15Zr) nuclear waste form that is being produced at Argonne National Laboratory for the disposal of metallic waste that results from the electrometallurgical treatment of Experimental Breeder Reactor-II (EBR-II) spent nuclear fuel[1]. In this treatment, uranium is electrorefined out of the metallic spent fuel in a LiCl-KCl-UCl_3 molten salt electrolyte at 550°C. The metallic remnants in the anode baskets of the electrorefiner, which include stainless steel cladding hulls, zirconium from the treated fuel, noble metal fission products (such as Tc, Ru, Rh, Pd), and actinide elements (mainly uranium), are consolidated by melting and then cast into ingots for eventual disposal in a geologic repository.

The microstructure of the baseline metal waste form, the SS-15Zr alloy, contains iron solid solution phases (ferrite and austenite) and $ZrFe_2$-type Laves intermetallics[2,3]. The fission product elements are contained in the alloy phases and do not form separate fission product-rich phases. Many fission products, such as Pd, Rh, and Ru, show a strong preference for the $ZrFe_2$–type intermetallics, whereas others such as Tc and Mo are present in all phases of the alloy. The actinide elements appear as locally enriched regions within the $ZrFe_2$ intermetallics. The release of fission products and actinide elements from the nuclear waste form during long-term geologic storage will be mainly governed by the corrosion behavior of the intermetallic phase. An understanding of intermetallic corrosion behavior is, therefore, necessary to develop mechanistic models of SS-15Zr alloy corrosion that can be used to predict release rates of radioactive elements from the nuclear waste form.

This article discusses the results of transmission electron microscopy (TEM) and Auger electron spectroscopy (AES) of oxidation products formed on a stainless steel-40 wt% zirconium (SS-40Zr) alloy that was tested for 56 days in a 200°C steam environment. The SS-40Zr composition yielded a microstructure that contained more than 95% of the Laves intermetallic compound. The TEM samples were prepared by ultramicrotomy in order to preserve the contents and spatial relationship of the corrosion products with the base metal. The AES samples were examined with a scanning Auger microprobe with ion-beam sputtering capability that allowed measurement of corrosion layer composition as a function of depth.

EXPERIMENTAL DETAILS

Alloy Fabrication, Microstructure And Corrosion Testing

Ingots of SS-40Zr alloy, each weighing ~20 g, were produced in a tungsten mesh furnace by mixing 304 stainless steel and high purity zirconium. The starting materials were placed in yttrium oxide crucibles and melted at 1650°C under an argon atmosphere for 2 h. Details of the experimental arrangement used to produce the ingots have been described elsewhere[2]. An X-ray diffraction (XRD) study showed that the as-cast ingots contained the C14 Laves intermetallic. Scanning electron microscopy of samples sectioned from the ingot revealed that the alloy mainly contained the Laves

intermetallic; small amounts of an unidentified phase (similar to the sigma phase observed in Fe-Cr alloys) were also observed.

Samples from the ingot were oxidized in a saturated steam environment. Monolith samples were suspended in a sealed stainless steel vessel that contained a small amount of deionized water. The water vaporized when the sealed reaction vessel was placed in a 200°C oven, resulting in 100% relative humidity at 16 atm. Corrosion products were formed on the metal surface by reaction with an adsorbed water layer. After 56 days of testing, the samples were removed from the test vessel for AES and TEM examination.

Auger Electron Spectroscopy

The AES data were obtained on a Physical Electronics model PHI 660 Scanning Auger Microprobe with PHI Multipak v.6 software. The samples were placed in an ultra-high vacuum (UHV) chamber with a base pressure of ~10^{-13} atm. The energy of the primary electron beam was set at 3 keV, and the diameter of the electron beam was adjusted to less than 1 μm. The samples were sputtered with argon ions to measure elemental composition as a function of depth. The argon ion beam energy was 3 keV, and the beam was rastered over an area of ~1.5 x 1.5 mm. The sputter rate for the instrument was calibrated for a SiO_2 layer on a Si substrate. Since sputter rates vary with oxide and metal composition, the oxide layer thicknesses obtained by the AES measurements are approximate.

The AES spectrum was obtained in the spot-mode of the scanning Auger microprobe. The elemental composition was determined by

$$C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \qquad (1)$$

where C_x is the concentration of element x, and I and S are the intensity and relative sensitivity factor, respectively. The peak intensities were determined with the "peak-to-peak height ratio" fitting routine, which measured the difference between the maximum and minimum values of the first derivative of the Auger intensity in the energy window expected for an individual element[4]. However, this method yielded inaccurate values for chromium in the oxide layer because of the overlap between the lower energy side of the Cr peak and the higher energy side of the O peak. The linear least squares fitting routine[5], which can resolve the intensity contributions of species with overlapping peaks was, hence, used to determine Cr peak intensity.

Transmission Electron Microscopy

The sample for TEM examination was coated with a low-viscosity epoxy to protect the surface corrosion products. After polymerization at 60°C for 24 hours, sample size was reduced by cutting the sample in half with a low-speed saw. One-half of the sample was then placed on a glass slide (surface-side down) and embedded in epoxy again. After polymerization, the glass slide was mounted on a polishing jig, and the sample was ground down as thin as possible. The goal was to thin the bulk metal as much as possible without breaking the sample or disturbing the oxidation layer/metal interface. This required several iterations of grinding, polishing, and re-embedding in the epoxy.

After the bulk metal was sufficiently thinned, small pieces of the sample, from different locations along the surface, were cut out by using a razor blade. These pieces were carefully oriented and embedded in epoxy blocks for ultramicrotomy. Thin sections were produced on the Leica Ultracut I Ultramicrotome. Sections ranged in thickness from 50-100 nm and were collected onto an electron transparent carbon substrate supported by a copper slotted grid. The sections were examined in a JEOL 2010 transmission electron microscope (TEM) using conventional bright field imaging. This was augmented by energy dispersive spectroscopy (EDS) for compositional analysis and electron diffraction (ED) for phase identification. The TEM results are based on the examination of thin sections taken from several regions along the sample surface.

RESULTS

Auger Electron Spectroscopy

The depth profile obtained from the $ZrFe_2$-type intermetallic sample at a sputter rate of 21 nm/min (SiO_2/Si) is shown in Fig. 1. The profile may be roughly divided into four regions.

- Region 1 (adjacent to the oxide-vapor interface) is between t=0 and 1 minute. This layer contains only Fe and O; the amount of Zr, Ni, and Cr in this region is at or below the noise level for the data. The presence of an oxide layer containing Fe and O agreed with XRD data that showed the presence of Fe_2O_3 (hematite) peaks on the sample surface[6].

- Region 2 (below Region 1) is between t=1 and 2.1 minutes. The oxygen content in this layer is about 60 at.% up to ~1.4 minute sputter and then decreases to about 50 at.%. The Fe content decreases sharply from 38 to 20 at.%. A corresponding increase is observed in the Zr content. The elements Cr and Ni appear in this layer after a sputter time of ~1.4 min and increase in content.

- Region 3 (adjacent to the metal) is between t=2.1 and 3.4 minutes. In this layer, the Fe content increases from 20 to 40 at.%, the Zr content from 20 to 26 at.%, and the Cr content from 9 to 13 at.%. The Ni content remains steady at ~6 at.%.

- The metal boundary was arbitrarily assigned at t=3.4 minutes. The oxygen content of this region decreases from 20 to ~3 at.% at t=5 minutes. This may be either a normal oxygen diffusion profile in the intermetallic or may be indicative of roughness in the oxide-metal boundary.

The redistribution of intermetallic elements due to oxide formation is evident in Fig. 2, which is a plot of the AES data normalized to exclude oxygen. The plot shows that the relative amount of Zr to Fe is higher in Region 3 than in the metal, which indicates a slight Zr enrichment in the vicinity of the metal-oxide interface. An enrichment in Cr relative to Fe is also observed. The sharp changes in the Fe, Zr, and Cr content of region 2, and the predominant concentration of Fe in region 1, are also clearly evident in the figure.

Transmission Electron Microscopy

The TEM micrographs (e.g., Fig. 3) of oxidation products formed on the alloy surface showed the presence of at least three distinct layers. Average compositions measured by EDS from the various layers are also shown in Fig. 3. The thickness of the top layer (Layer 1) ranged from 10 to 40 nm. The EDS analysis showed that this layer consisted mainly of Fe and O, which agrees with the AES data (region 1 in Fig. 1). Electron diffraction identified the layer as hematite (Fe_2O_3), which agreed with prior X-ray diffraction data.

Beneath the iron oxide was a ~20 nm thick, adherent layer (Layer 2) that contained Zr and O and varying amounts of Fe and Cr. This layer corresponds to Regions 2 and 3 in Figs. 1 and 2. The Fe content showed a local minimum, similar to that seen in the AES data. A microdiffraction pattern obtained from the layer showed diffuse rings, which indicated that the structure was amorphous. This layer is probably a substoichiometric Zr oxide, ZrO_{2-x}, similar to that observed on $ZrFe_2$–type intermetallic precipitates in oxidized Zircaloys[7-9]. The elements Fe, Cr, and Ni may be present as small metal crystallites in the ZrO_{2-x} matrix. Microdiffraction would not detect these crystallites if they were widely dispersed throughout the ZrO_{2-x} layer.

Below the zirconium-oxide layer was a very thin (~2 nm) layer that is seen as a dark line in Fig. 4. The EDS analysis indicated that this layer contained little oxygen. The Ni:Cr ratio in this layer was ~1, whereas the Ni:Cr ratio in the adjacent metal and the overlying oxide was <1. Diffraction patterns could not be obtained because of the thinness of the layer; however, the Ni:Cr ratio suggests that the layer may be the C36 Laves polytype[10]. The outward diffusion of nickel from the base metal (C14 intermetallic) during the corrosion process could have resulted in C36 polytype formation at the metal-oxide interface.

DISCUSSION

The AES and TEM results show that two distinct oxide layers are formed on the $ZrFe_2$–type intermetallic: (1) an inner, amorphous, adherent zirconium-rich phase believed to be ZrO_{2-x}, with varying amounts of Fe, Cr, and Ni, and (2) an outer, crystalline, porous iron-oxide layer with trace amounts of Zr and Cr. Our observations are similar to those reported by investigators studying the oxidation of $Zr(Fe,Cr)_2$ intermetallic particles within Zircaloys[7-9]. These studies have shown that a thin film of ZrO_2 forms immediately when the particles are exposed to steam at temperatures from 400-600°C. The elements Fe and Cr then diffuse through this layer to the oxide-vapor interface where they form iron and chromium oxides.

In a similar manner, a ZrO_{2-x} layer is expected to form rapidly when the $ZrFe_2$–type intermetallic is exposed to the 200°C steam environment. The effective oxygen partial pressure for zirconium oxidation at the oxide-metal interface has been estimated to be $\sim 10^{-112}$ atm at 200°C, which is far too low for the oxidation of Fe, Cr, and Ni in the intermetallic (see Fig. 4). These elements will oxidize only when the oxygen partial pressure exceeds their equilibrium partial pressures. The Fe, Cr, and Ni may be present either as metals or as oxides within the ZrO_{2-x} layer.

The presence of Fe_2O_3 at the oxide-vapor interface suggests that Fe diffuses outward through the ZrO_{2-x} layer. It is not clear if Fe is metallic or oxidized during this migration. The minimum in Fe content observed in Layer 2 suggests that the diffusion of Fe from the ZrO_{2-x} layer to the oxide-vapor interface is faster than the diffusion of Fe from the metal into the ZrO_{2-x} layer. Since Cr (or Ni) was not observed at or near the oxide-vapor interface, it is apparent that Cr does not diffuse outward through the ZrO_{2-x} layer. The reasons for the non-migration of Cr (or Ni) are not known at this time. However, the absence of Cr (and Ni) in the top layer agrees with studies indicating that only Fe migrates out of the intermetallics at the lower temperatures (400°C); Cr (and Ni) migration out of the particles occurs only at the higher temperatures (600°C)[7].

SUMMARY

A multi-layered oxide was formed on a $ZrFe_2$-type intermetallic exposed to 200°C saturated steam. The layer adjacent to the metal was dense, adherent, and amorphous. This layer is most likely a substoichiometric Zr oxide containing varying amounts of Fe, Cr, and Ni, either as metals or as oxides. Above the Zr oxide was a porous, crystalline iron-oxide (hematite) layer. This layer appears to have formed by Fe diffusion through the Zr-oxide layer to the oxide-vapor interface. The complementary nature of the AES and TEM techniques to study nanometer-size oxide layers is clearly evident in this work. An understanding of intermetallic corrosion mechanisms is crucial to the development of a corrosion model that will be used to model metal waste form behavior in a geologic repository.

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List of Figure Captions

Fig. 1. The AES data from a $ZrFe_2$-type intermetallic sample oxidized in 200°C steam for 56 days. The sputter rate was 21 nm/min (SiO_2 on Si), and data were acquired every 0.1 minute.

Fig. 2. Same as Figure 1, but data normalized to exclude oxygen.

Fig. 3. Bright-field TEM image of corrosion layers formed on a $ZrFe_2$-type intermetallic (C14 polytype) tested in 200°C steam. The EDS analysis indicated that Layer 1 was an iron oxide, and Layer 2 was an amorphous zirconium oxide. Layer 3 was metallic and may be a C36 Laves polytype.

Fig. 4. Schematic diagram illustrating the partial pressures for oxidation of Zr, Cr, Fe, and Ni present in the $ZrFe_2$-type intermetallic in 200°C steam.

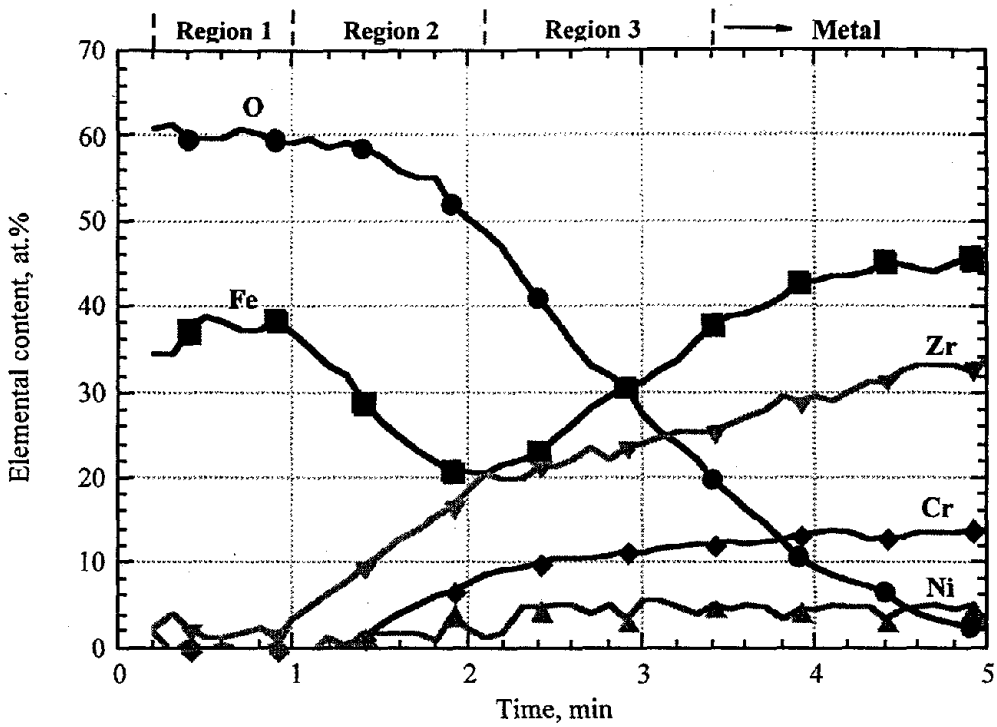


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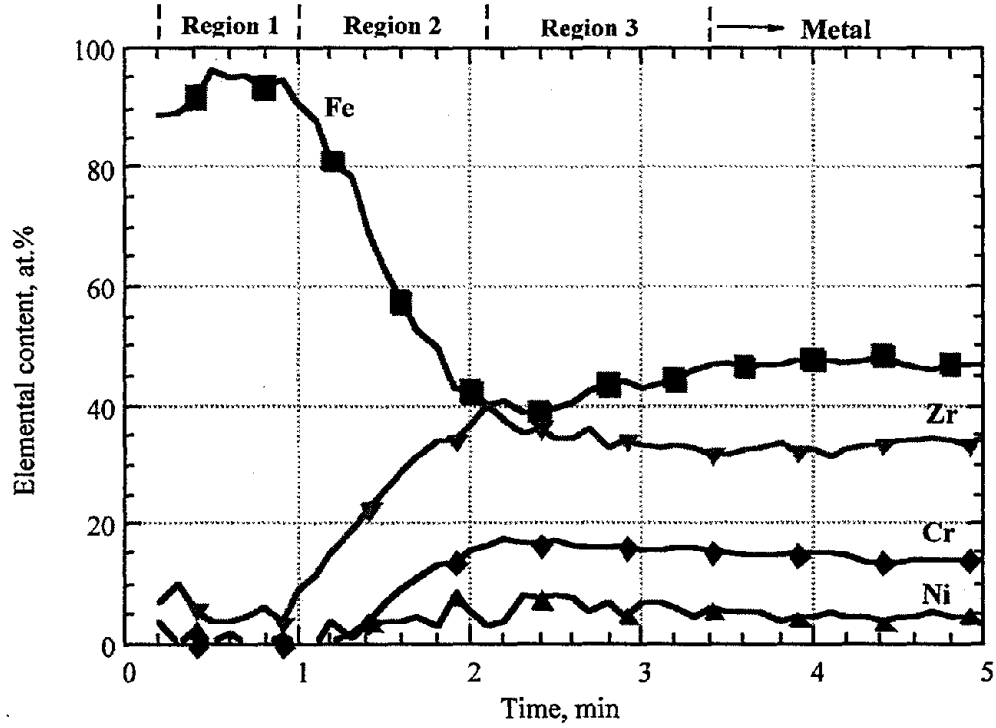


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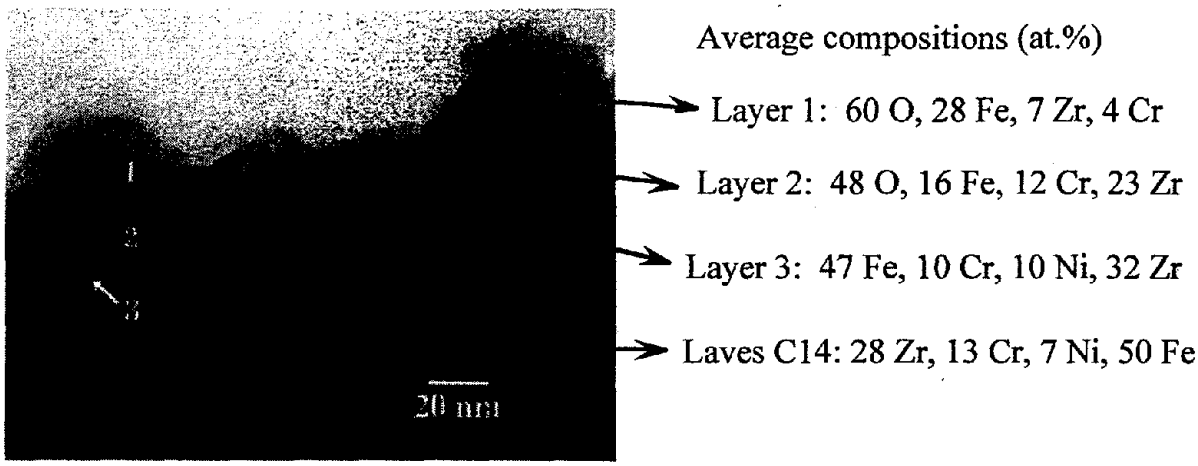


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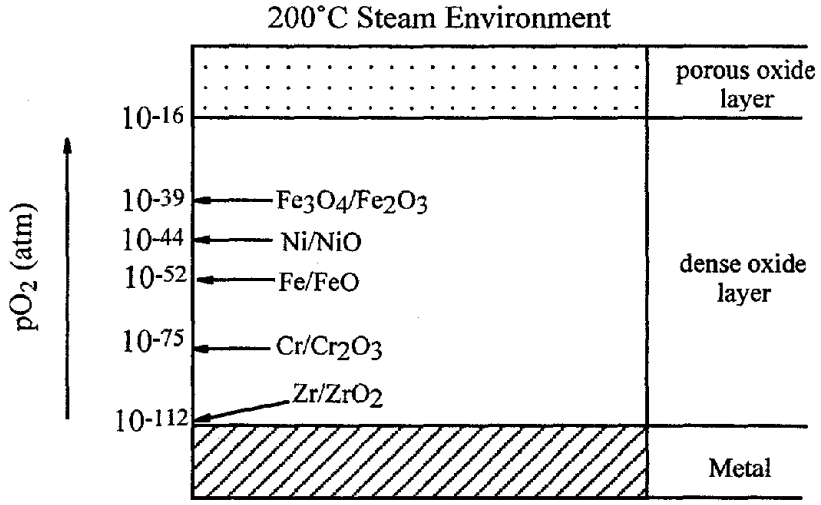


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