

CORROSION BEHAVIOR OF STAINLESS STEEL-ZIRCONIUM ALLOY WASTE FORMS

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ABSTRACT

Stainless steel-zirconium (SS-Zr) alloys are being considered as waste forms for the disposal of metallic waste generated during the electrometallurgical treatment of spent nuclear fuel. The baseline waste form for spent fuels from the EBR-II reactor is a stainless steel-15 wt.% zirconium (SS-15Zr) alloy. This article briefly reviews the microstructures of various SS-Zr waste form alloys and presents results of immersion corrosion and electrochemical corrosion tests performed on these alloys. The electrochemical tests show that the corrosion behavior of SS-Zr alloys is comparable to those of other alloys being considered for the Yucca Mountain geologic repository. The immersion tests demonstrate that the SS-Zr alloys are resistant to selective leaching of fission product elements and, hence, suitable as candidates for high-level nuclear waste forms.

Keywords: nuclear waste, stainless steel, zirconium, corrosion, microstructure

INTRODUCTION

Stainless steel-zirconium alloys are being evaluated for the disposal of metallic waste generated during the electrometallurgical treatment of spent nuclear fuel [1, 2]. In the electrometallurgical process, chopped driver or blanket fuel segments are placed into the anode baskets of an electrorefiner. When a potential is applied, uranium, active fission products, and transuranic (TRU) elements dissolve at the anode into the molten salt electrolyte, while uranium is deposited onto a steel cathode [3]. The irradiated fuel cladding, assembly hardware, zirconium from the alloy fuel, noble metal¹ fission products (NMFP) (e.g., Tc, Rh, Ru, Pd, and Nb), and actinides left behind in the anodic dissolution baskets are melted together to make a metal waste form (MWF).

¹ The term "noble metal" means a metallic element that is inert or electrochemically noble during the electrometallurgical process.

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The baseline waste form for spent fuels from the Experimental Breeder Reactor-II (EBR-II), located at the Argonne National Laboratory site in Idaho, is a stainless steel-15 wt% zirconium (SS-15Zr) alloy. However, the zirconium content of MWF alloys may vary from 5 to 20 wt% Zr, depending on the composition of the starting fuel. The noble metal content of the waste forms depends on the burnup of the treated fuel; the actinide content depends on the efficiency of the electrorefining process. The waste forms may contain up to 4 wt% NMFP and up to 10 wt% actinides (mainly uranium).

To be acceptable in a geologic repository, waste forms must be chemically durable and be able to retain their radionuclide inventory [4]. The chemical durability of a waste form is dependent on various repository factors, which include solution composition, pH value, temperature, and radiolysis effects [5]. *In situ* studies are often conducted to identify phenomena associated with a specific repository environment. In addition, short-term laboratory experiments are used to identify corrosion mechanisms that could occur in a repository environment; this information may then be used to support material behavior models designed to evaluate long-term performance [4].

This article briefly describes the microstructures and some of the corrosion studies being conducted on representative, but non-radioactive, MWF alloys. Electrochemical corrosion measurements have been conducted at various pH values to obtain relative values of corrosion rate for various MWF compositions. Immersion tests in deionized water and in simulated J-13 groundwater² (representative of the proposed Yucca Mountain geologic repository in Nevada) have been performed to evaluate the release of fission products from the alloys. Corrosion tests on actinide-containing materials and on actual radioactive waste forms arising from the treatment of EBR-II fuels will be presented in future articles.

METAL WASTE FORM ALLOY MICROSTRUCTURES

Stainless steel-zirconium alloy ingots were prepared from Type 316 stainless steel, high-purity zirconium and representative noble metal elements. Small-scale alloy samples (20-40 g) were generated in a tungsten-element, resistance-heated furnace and larger samples (~ 2.5 kg) in an induction casting furnace. The starting materials were contained in yttrium oxide crucibles and heated to 1600°C under high-purity argon for ~ 1 to 2 h. The melt was allowed to cool and solidify within the yttrium oxide crucibles to produce the ingots. The microstructure of alloy ingots was studied using a combination of scanning electron microscopy (SEM) and diffraction (X-ray and neutron) techniques.

Zirconium has very low solubility in iron. The addition of zirconium to 316 stainless steel results in the formation of ZrFe₂-type Laves and other intermetallic phases; the amount of these phases depends on the zirconium content of the alloy. For example, the intermetallic content of a stainless steel-5 wt% Zr (SS-5Zr) alloy (see Figure 1a) is ~ 10 vol% and that of a stainless steel-15 wt% Zr (SS-15Zr) alloy is ~ 50 vol% (see Figure 1b). The intermetallic phases are strong sinks for the austenite stabilizer, nickel. Intermetallic formation leads to nickel consumption from the austenite (γ) phase and, consequently, to austenite destabilization and ferrite (α)

² A representative composition of J-13 well water is (in mg/L): 11.5 Ca, 1.76 Mg, 45.0 Na, 5.3 K, 0.06 Li, 0.04 Fe, 0.001 Mn, 0.03 Al, 30.0 Si, 2.1 F, 6.4 Cl, 18.1 SO₄²⁻, 10.1 NO₃⁻, and 143.0 HCO₃⁻ [6].

formation. Figure 1a shows that ferrite, austenite and $Zr(Fe,Cr,Ni)_{2+x}$ are the major phases in SS-5Zr, whereas only ferrite and $Zr(Fe,Cr,Ni)_{2+x}$ are prominent in SS-15Zr.

The phases observed in the microstructure of SS-Zr alloys are summarized in Table 1. The intermetallic phases are the "preferred" location for several noble metal elements [7]. Fission product incorporation in SS-Zr alloy phases is strongly influenced by the volume fraction of the intermetallics, which is, in turn, influenced by the zirconium content of the waste form. The noble metals form discrete phases in a stainless steel alloy without Zr. Noble metal-rich phases are rarely observed in SS-Zr alloys with > 5 wt% Zr. The noble metal elements are dissolved in the major phases of the SS-15Zr and the stainless steel-20 wt% Zr (SS-20Zr) alloy. Niobium-rich areas are occasionally observed at the austenite-ferrite interfaces of SS-5Zr alloys containing this element.

CORROSION BEHAVIOR

Electrochemical Corrosion Testing

Electrochemical test methods provide a rapid means to estimate the corrosion behavior of metallic samples. The polarization resistance technique (based on ASTM G 59) was used to study the *relative* corrosion behavior of the various alloy compositions. The measurements were conducted in a corrosion cell consisting of a round-bottomed flask, graphite auxiliary electrodes, and a saturated calomel electrode which served as the reference electrode. The applied potential and resulting current were measured by a Versastat-II Potentiostat/Galvanostat and with SoftCorr III Corrosion Measurement software.³

Corrosion rates were measured in test solutions that ranged in pH from 2 to 10. The pH of our simulated J-13 composition was ~ 9 ; the acid and base solutions were prepared by adding hydrochloric acid and sodium hydroxide, respectively, to the J-13 composition. The pH = 2 solution represents an extreme condition that may not occur naturally in the repository environment, but is included as an aggressive test for the alloy samples.

Disk specimens (16-mm dia and 3-mm. thickness) were polished to a 600 grit finish and immersed in the test solutions. After equilibration for more than half hour, the sample potential was scanned ± 20 mV about the corrosion potential at a rate of 0.6 V/h (0.166 mV/s). The slope of the potential-current curve yielded the polarization resistance. The corrosion currents calculated from the polarization resistance (assuming anodic and cathodic Tafel constants to be 0.1 V) were converted into corrosion rates and are shown in Figure 2.

The corrosion rates for the various SS-Zr alloy samples were similar; the rates were not affected by additions of noble metal elements. In general, the corrosion rates in simulated J-13 solution (pH = 9) and pH = 10 solutions were comparable. The corrosion rates in the acidic solutions were higher; for most SS-Zr samples, the rates in pH = 2 solution were at least an order of magnitude larger than the rates in pH = 10 solution.

³ Electrochemical instrumentation and software were purchased from EG&G Instruments, Princeton, NJ.

The corrosion rates for the SS-Zr alloys are one to two orders of magnitude lower than the rate for pure copper, and two to three orders of magnitude lower than the rate for mild steel. They are also comparable in magnitude to those for 316 stainless steel and Alloy C22, alloys that have been evaluated as candidates for nuclear waste canisters [8]. The results of electrochemical testing demonstrate that SS-Zr alloys are suitable for disposal of nuclear waste in a geologic repository.

Immersion Testing

Immersion tests provide information on the selective leaching of elements into representative test solutions. Our test procedure was based on MCC-1 (ASTM C 1220), a static leach test originally developed to evaluate the durability of glass-based waste forms. The test involves exposing the sample to a static solution for an extended duration at a fixed temperature. The outcome of the test is evaluated by measuring changes in specimen mass and solution composition and, if possible, examining the corrosion effects through metallographic analysis of the sample.

Immersion tests at 90°C in simulated J-13 solution were conducted on MWF samples of various compositions for durations up to 10,000 h (417 d). Disk-shaped specimens were polished to a 240 grit finish, then immersed in the test solution in sealed Teflon vessels. Minimal surface corrosion was observed on the test specimens even after 10,000 h; most samples retained their as-polished surfaces. The weight changes observed were very small and often within the resolution limit of the balance (± 0.0001 g). Negligible quantities of alloy constituents were present in the test solution, clearly indicating that the alloy samples were very corrosion resistant.

Immersion tests at 200°C were conducted to accelerate alloy corrosion and increase elemental dissolution into test solutions. Alloy disk specimens, 10 mm dia. and 2 mm thick, polished to a 240 grit finish were immersed in deionized water solution and sealed in titanium vessels for 28 days. The sample surfaces were examined after test completion. All specimens exhibited some degree of surface corrosion. The specimens containing 15 wt.% Zr and 20 wt.% Zr showed uniform corrosion, whereas the 5 wt.% Zr specimens showed localized attack. The weight changes for the samples were small and within ± 0.0001 g.

The test solutions were analyzed for the presence of elemental constituents from the alloys. The elements sorbed on the walls of the test vessel were removed by 1 wt% nitric acid; this "acid strip" solution was also analyzed. The elemental concentrations were obtained either by inductively coupled plasma-mass spectroscopy or inductively coupled plasma-atomic emission spectroscopy. The results showed that (1) elements such as Zr and Nb are often present in amounts below the detectability limits of the measuring instruments and (2) elements including Fe, Pd, Rh, Ru, and Mo may not be present in the test solutions but are often present in the acid strip solutions, i.e., they plate out on the test vessel walls.

In the literature on waste form studies, the relative leaching of elements is reported as a "normalized loss" which is defined as follows:

$$NL_i = \frac{(C_i - C_{is})V_s + (C_{i(as)} - C_{is(as)})V_{as}}{f_i A} \quad (1)$$

where

NL_i = normalized loss (g/m^2)

$C_i, C_{i(as)}$ = concentration (g/m^3) of i 'th element in test and acid strip solutions, respectively

$C_{is}, C_{is(as)}$ = starting concentration (g/m^3) of i 'th element in test and acid strip solutions, respectively

V_s, V_{as} = volume (m^3) of test and acid strip solution, respectively

f_i = fraction of i 'th element in sample

A = surface area of the sample (m^2)

The normalized loss data provide an indicator of the quantity of a given element that is released into solution, while accounting for (1) the weight fraction of the element in the alloy and (2) the surface area of the sample interacting with the test solution. Table 2 shows the normalized loss for various alloy compositions tested in deionized water at 200°C; the data are average values obtained from testing multiple specimens. Of the major elements, Ni leaches out the most followed by Cr, Mn, and Fe; the highest loss ($1.1 g/m^2$) was observed for Ni in the SS-5Zr-2Nb-1Ru-1Pd alloy. The NMFP elements show much smaller losses; the highest loss was observed for Mo ($0.09 g/m^2$) in the SS-20Zr-2Nb-1Ru-1Pd alloy. It is evident that all alloy compositions considered in our study display similar corrosion resistance and, more importantly, excellent retention of fission product elements.

CONCLUSIONS

Stainless steel-zirconium waste form alloys are very resistant to the normal corrosion conditions envisioned at the Yucca Mountain geologic repository. Electrochemical corrosion tests have indicated that the corrosion resistance of the alloys is comparable to that of 316 stainless steel and Alloy C22. Immersion tests at 90°C in simulated J-13 solution and at 200°C in deionized water have shown that the selective leaching of fission products from the alloy samples is very small. The stainless steel-zirconium alloys have the capacity to immobilize and retain fission products and are, hence, suitable candidates for high-level nuclear waste forms.

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TABLE 1
PHASES OBSERVED IN THE MICROSTRUCTURE OF
STAINLESS STEEL-ZIRCONIUM ALLOYS

Alloy Composition	Major Phases	Minor Phases
SS316	γ	—
SS-5Zr	$\gamma + \alpha + \text{Zr(Fe,Cr,Ni)}_{2+x}$	—
SS-5Zr-2Nb-1Pd-1Ru	$\gamma + \alpha + \text{Zr(Fe,Cr,Ni)}_{2+x}$	Nb-rich regions at γ/α interface
SS-15Zr	$\alpha + \text{Zr(Fe,Cr,Ni)}_{2+x}$	γ , $\text{Fe}_{23}\text{Zr}_6$ -type intermetallic
SS-15Zr-1Nb-1Pd-1Rh-1Ru	$\alpha + \text{Zr(Fe,Cr,Ni)}_{2+x}$	γ , $\text{Fe}_{23}\text{Zr}_6$ -type intermetallic
SS-20Zr-2Nb-1Pd-1Ru	$\alpha + \text{Zr(Fe,Cr,Ni)}_{2+x}$	—

γ = Austenite, α = Ferrite, $\text{Zr(Fe,Cr,Ni)}_{2+x}$ = ZrFe_2 -type Laves intermetallic phase

TABLE 2
AVERAGE NORMALIZED LOSS (NL) FOR MWF SPECIMENS
IMMERSED IN 200°C DEIONIZED WATER FOR 28 DAYS

Alloy Composition	NL (Major Elements), g/m ²					NL (Fission Products), g/m ²				
	Fe	Cr	Ni	Zr	Mn	Mo	Nb	Pd	Rh	Ru
SS-5Zr-1Nb-0.5Ru-0.5Pd	^a	0.035	0.33	^a	0.056	0.02	^a	0.006	^b	0.0008
SS-5Zr-2Nb-1Ru-1Pd	0.014	0.53	1.13	^a	0.21	0.087	0.004	0.0039	^b	0.0018
SS-15Zr-1Nb-1Ru-1Pd-1Rh	0.31	0.073	0.58	^a	0.067	0.022	^a	0.0047	0.0005	0.0006
SS-20Zr-2Nb-1Ru-1Pd	0.0002	0.13	0.66	^a	0.055	0.092	^a	0.013	^b	0.0021

^aElement below detectability limits of measuring instrument

^bElement not present in alloy

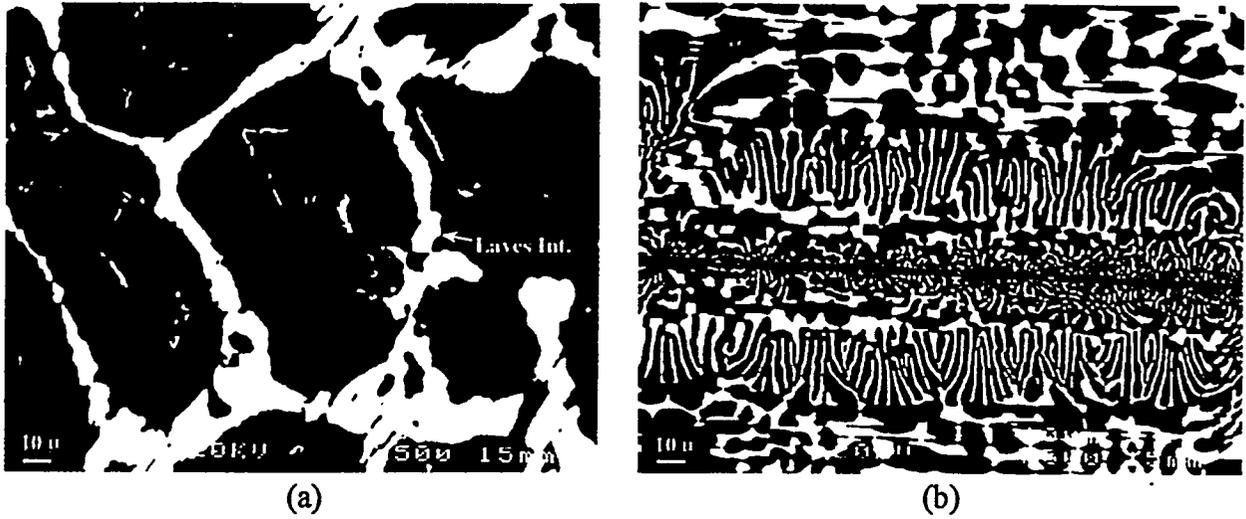


Figure 1. (a) Typical microstructure in a stainless steel-5 wt% Zr alloy. The dark phase is α (ferrite), the gray phase is γ (austenite) and the bright regions are $Zr(Fe,Cr,Ni)_{2+x}$. (b) Typical microstructure in a stainless steel-15 wt% Zr alloy. The dark regions are ferrite, and the bright regions are $ZrFe_2$ -type intermetallics.

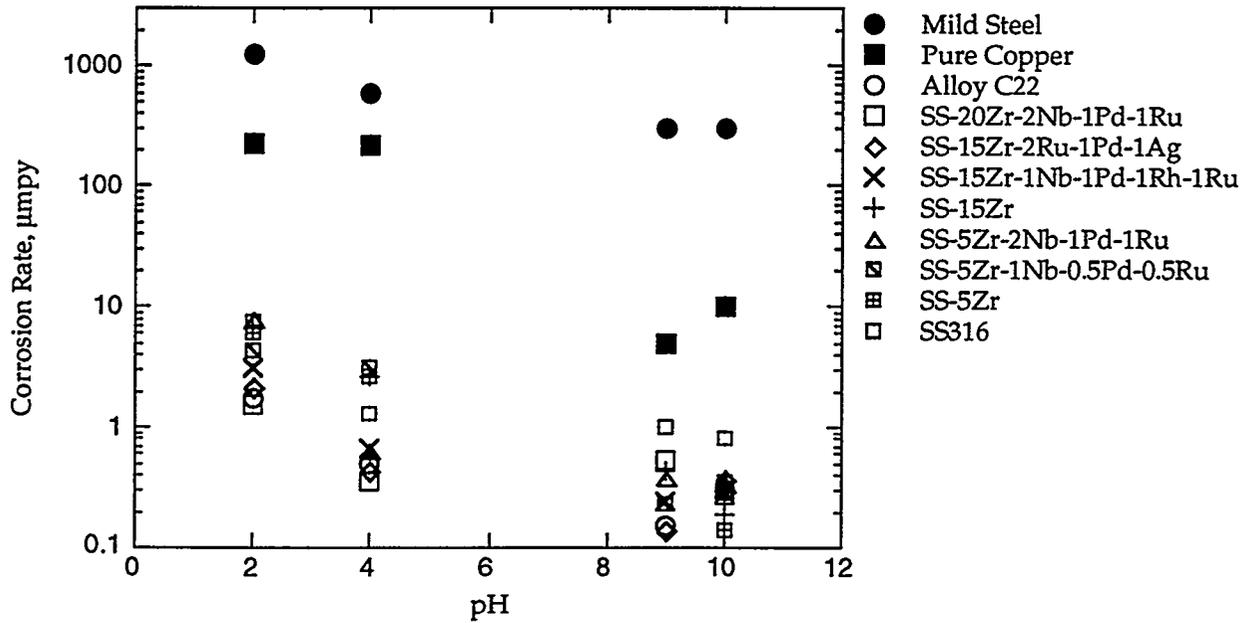


Figure 2. Graphical representation of corrosion rates (μmpy = micrometers per year) measured for various alloy samples in different test solutions.

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