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ACTINIDE-CONTAINING METAL DISPOSITION ALLOYS

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ACTINIDE-CONTAINING METAL DISPOSITION ALLOYS

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ABSTRACT

Argonne National Laboratory is currently developing an electro-metallurgical process for treating a wide array of spent nuclear fuels. As part of this process, two waste streams will be consolidated into waste forms; one will be a mineral and the other a metal alloy. The metal waste form is an alloy that contains cladding hulls, "noble" metal fission products, and Zr from alloy fuels. The nominal composition of the metal waste form alloys are stainless steel-15 wt.% Zr (SS-15Zr) for stainless steel clad fuel and Zircaloy-8 wt.% stainless steel (Zr-8SS) for Zircaloy clad fuel, with both alloys also containing up to 4 wt.% noble metal fission products. This paper investigates using the two nominal metal alloy compositions described above as a possible Pu and TRU disposition form.

I. INTRODUCTION

Argonne National Laboratory is currently developing an electrometallurgical process for treating a wide array of spent nuclear fuels [1]. As part of this process, two waste streams will be consolidated into waste forms; one will be a mineral and the other a metal alloy [2-5]. The metal waste form is an alloy that will contain cladding hulls, "noble" metal fission products (e.g., Pd, Ag, Tc,...), and Zr from alloy fuels. The nominal compositions of the metal waste form alloys are stainless steel - 15 wt.% zirconium (SS-15Zr¹) for stainless steel clad fuel and Zircaloy - 8 wt.% stainless steel (Zr-8SS) for Zircaloy clad fuel with both alloys also containing up to 4 wt.% noble metal fission products. The behavior of actinides (e.g., U, Pu, and Np) in the metal is of general interest since minor quantities (<0.1 wt.%) may be present in the metal waste stream or, alternatively, if the metal waste form is selected as a disposal form for actinide metals. It is important to identify whether or not the actinides tend to segregate or distribute homogeneously in the alloy. In terms of potentially using this alloy as a vehicle for disposing of excess Pu, it is of interest to determine what effects on alloy behavior result from adding large amounts of Pu (up to 10 wt.%).

To better understand the behavior of the metal alloy with incorporated actinides, alloys that comprise actinides

(U, Pu, or Np), Type 316 stainless steel² (316SS), and zirconium, or actinides, Type 304 stainless steel³ (304SS), and zirconium have been cast in an induction furnace; these cast alloys have been analyzed employing a scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX) to determine microstructure and phase development. This paper will discuss the results from these castings in terms of the developed microstructures and phase compositions and how they compare to alloys without added actinides. Comments will be made on the usefulness of these alloys for Pu disposition.

II. EXPERIMENTAL

Nine Pu-containing alloys were cast, as approximately 30 gram charges, in yttrium oxide ceramic crucibles (65 mm tall, 43 mm o.d., and 3 mm wall thickness) in an induction furnace. The alloy compositions included: Zr-8(304SS)-4Pu, Zr-8(304SS)-7Pu, Zr-8(304SS)-10Pu, 316SS-15Zr-0.5U-0.5Pu, 316SS-15Zr-2U-2Pu, 316SS-15Zr-2Np, 316SS-15Zr-6Pu-2Np, 316SS-15Zr-6Pu, and 316SS-15Zr-10Pu. The melting and solidification procedure involved heating the charged crucibles to 1600°C under flowing argon, holding for 2 hours, then cooling the ingots down to 1500°C, 1400°C, 1300°C, and 1200°C, and holding for 15 minutes at each of these temperatures. At 1200°C, the furnace was turned off. This cooling sequence lessened the chance of cracking the yttria crucibles, which have low thermal shock resistance.

Each solidified ingot was sliced longitudinally using a slow-speed diamond saw, mounted in epoxy exposing the sliced surface, polished through 1 µm diamond paste, and analyzed for microstructure and phase development with an ETEC Autoscan scanning electron microscope (SEM) equipped with a Kevex 8000 (Fisons Instruments) energy dispersive X-ray (EDX) analysis system. Secondary and backscatter electron micrographs were taken of each sample to determine the microstructure, and both

² The 316SS had a nominal composition of 16.3Cr- 10.5Ni- 2.1Mo-1.5Mn-0.7Si-0.05C-0.06N-0.008O-bal Fe.

³ A nominal composition for the added 304SS was, in wt.%, 18.3Cr-8.2Ni-1.5Mn-0.4Si-0.3Mo-0.3Cu-0.2Co-0.3P-0.02S-0.08N-0.08C-balFe.

¹ All alloy compositions are listed using wt.% compositions.

quantitative and qualitative SEM-EDX analysis were employed to determine phase compositions. Comparisons were made with microstructures of alloys of nominal composition without Pu or other actinides.

III. RESULTS

A. Zr-8(304SS) Alloys With Added Actinides

The microstructure for the Zr-8(304SS)-10Pu alloy is presented in Figure 1a. It is representative of the microstructures observed for the Zr-8(304SS)-based alloys with added Pu. The compositions of the main phases for this alloy and the Zr-8(304SS)-4Pu and Zr-8(304SS)-7Pu alloys are listed in Table 1. Also included in this table are the phase compositions observed in a Zr-8(304SS) alloy without Pu [5].

The Zr-8(304SS)-based alloy exhibits a microstructure that comprises a dominant α -Zr phase and Zr-Fe-Cr and Zr-Fe-Ni intermetallic phases. Three main phases were identified by composition, viz. $Zr_2(Fe,Ni)$ (the sum of Fe and Ni ratioed to Zr is approximately 33 at.%), $Zr(Fe,Cr)_{2+x}$, and α -Zr. An X-ray diffraction analysis of a Zr-8(304SS) alloy has confirmed the existence of these three phases [4,5]. A minor phase is detected along the edges of the α -Zr islands that contains Zr, Fe, and Cr; it has an approximate composition of 60 at.% Zr-26 at.% Fe-14 at.% Cr. The added Pu segregates along the lath-like (platelet-like) α -Zr phase boundaries. Increasing the amount of Pu added to the alloy results in a higher solubility of Pu in the α -Zr phase matrix along with more Pu residing at the α -Zr lath boundaries (up to 3 at.% Pu is observed in the α -Zr lath boundaries in the alloy with 4 wt.% added Pu and up to 12 at.% Pu is observed in the α -Zr lath boundaries in the alloy with 10 wt.% added Pu); the Pu does not segregate into discrete phases when added in increasing amounts to

Zr-8(304SS)-based alloys.

B. 316-15Zr Alloys With Added Actinides

The nominal microstructure seen for the 316SS-15Zr-based alloys with added U, Pu, or Np (in this case for the 316-15Zr-10Pu alloy) is shown in Figure 1b. The phase compositions for all the cast alloys are enumerated in Table 2 (except for alloy 316SS-15Zr-0.5U-0.5Pu whose phase compositions are nearly identical to 316SS-15Zr-2U-2Pu). Also included are the phase compositions for a 316-15Zr alloy without actinides cast in an induction furnace.

The eutectic alloy microstructure comprises three phases: an Fe solid solution phase, a $Zr(Fe,Cr,Ni)_{2+x}$ phase, and a high-Pu region in the $Zr(Fe,Cr,Ni)_{2+x}$ phase that appears bright in a SEM micrograph. This microstructure is observed for all 316-15Zr-based alloys irrespective of the added actinide or group of actinides. Increasing the amount of actinides in the 316SS-15Zr alloy results in a higher volume fraction of the high-contrast, high-actinide regions in the $Zr(Fe,Cr,Ni)_{2+x}$ phase. No mass segregation of actinides into discrete phases is observed when U, Pu, or Np is added in increasing amounts to a 316SS-15Zr-based alloy.

IV. DISCUSSION

Adding Pu to Zr-8(304SS) or 316SS-15Zr alloys does not drastically alter the observed microstructures from what is observed in the nominal alloys. In Zr-8(304SS) alloys, the additions of 4, 7, and 10 wt.% Pu result in some changes in the Zr concentration of the $Zr(Fe,Cr)_{2+x}$ phase as a function of Pu concentration (see Table 1), but this phase is known to have a large range in composition, based on the Fe-Zr binary phase diagram [6], so this result is not unexpected. Little change in concentration is

Table 1. Approximate Phase Compositions for As-cast Alloys Zr-8(304SS), Zr-8(304SS)-4Pu, Zr-8(304SS)-7Pu, and Zr-8(304SS)-10Pu.

Alloy (wt.%)	Phase	Composition (at.%)				
		Fe	Cr	Ni	Zr	Pu
Zr-8(304SS)	$Zr(Fe,Cr)_{2+x}$	42	21	0.7	34	0
	$Zr_2(Fe,Ni)$	28	0.4	6	66	0
	α -Zr	3	2	1	93	0
Zr-8(304SS)-4Pu	$Zr(Fe,Cr)_{2+x}$	36	17	0.3	47	0.2
	$Zr_2(Fe,Ni)$	25	0.7	5	69	0.3
	α -Zr	1	1	0.1	96	1.5
Zr-8(304SS)-7Pu	$Zr(Fe,Cr)_{2+x}$	39	18	0.1	42	0
	$Zr_2(Fe,Ni)$	26	0.5	6	66	0.7
	α -Zr	1	1	0.2	95	2.5
Zr-8(304SS)-10Pu	$Zr(Fe,Cr)_{2+x}$	40	20	1	38	0.5
	$Zr_2(Fe,Ni)$	25	0.5	5	67	1.6
	α -Zr	0.4	0	0.4	93	5

Table 2. Approximate Phase Compositions for As-cast Alloys 316SS-15Zr, 316SS-15Zr-2U-2Pu, 316SS-15Zr-6Pu, 316SS-15Zr-10Pu, 316SS-15Zr-2Np, and 316SS-15Zr-6Pu-2Np.

Alloy (wt.%)	Phase	Composition (at.%)						
		Fe	Cr	Ni	Zr	U	Pu	Np
316SS-15Zr	Zr(Fe,Cr,Ni) _{2+x}	55	9	12	23	-	-	-
	Fe solid solution	71	20	8	0	-	-	-
	etched-out	68	26	4	0	-	-	-
316SS-15Zr-2U-2Pu	Zr(Fe,Cr,Ni) _{2+x}	57	7	13	22	0.5	0.5	-
	Fe solid solution	74	21	3	1	0.2	0.2	-
	High-contrast	49	3	22	12	9	5	-
316SS-15Zr-6Pu	Zr(Fe,Cr,Ni) _{2+x}	55	8	14	22	-	1	-
	Fe solid solution	71	24	4	1	-	0.2	-
	High-contrast	38	3	34	8	-	17	-
316SS-15Zr-10Pu	Zr(Fe,Cr,Ni) _{2+x}	55	7	14	22	-	2	-
	Fe solid solution	70	25	3	1	-	0.5	-
	High-contrast	35	2	34	7	-	20	-
316SS-15Zr-2Np	Zr(Fe,Cr,Ni) _{2+x}	58	7	21	13	-	-	0.5
	Fe solid solution	71	23	5	0.4	-	-	0.5
	High-contrast	42	3	34	6	-	-	15
316SS-15Zr-6Pu-2Np	Zr(Fe,Cr,Ni) _{2+x}	60	8	17	13	-	1	0.5
	Fe solid solution	70	24	5	0.5	-	0.4	0.1
	High-contrast	46	3	30	6	-	10	5

observed for the Zr₂(Fe,Ni) phase as more Pu is added to the Zr-8(304SS) alloy. In the α -Zr phase, the Pu concentration increases (from 1.5 to 5 at.% Pu, respectively, as shown in Table 1) as more Pu is added to the alloy, and an increase is observed in the Pu concentration at the α -Zr lath boundaries (up to 12 at.% for the Zr-8(304SS)-10Pu alloy).

The Pu distribution in Zr-8(304SS) alloys with added Pu is favorable, since no discrete, high-Pu phases develop as more and more Pu is added. In terms of repository performance of a Zr-8(304SS) alloy with added Pu, the presence of discrete, very-high-Pu phases may degrade the leaching and corrosion performance of the alloy. With the microstructure of the nominal alloy remaining intact in Pu-containing alloys, such a degradation is not to be expected.

For the 316SS-15Zr alloys little change in microstructure is observed as more Pu, or actinides, is added. The main result of adding any actinide is the appearance of a high-actinide, high-contrast regions in the Zr(Fe,Cr,Ni)_{2+x} phase; and, the result of adding up to 10 wt.% Pu, as shown in Table 2, is an increase in the Pu-content of the high-contrast phase region (up to 20 at.%). Based on SEM micrographs, an increase in the volume percent of this phase region in the alloy is also observed. In cases where multiple actinides are added, up to 15 at.% actinide is observed in the high-contrast phase region. Furthermore, changes in the Zr concentration of the Zr(Fe,Cr,Ni)_{2+x} phase itself occur as more Pu and actinides are added to the 316SS-15Zr alloy. The Zr content in Zr(Fe,Cr,Ni)_{2+x} phase drops from 23 at.% in

the nominal 316SS-15Zr alloy to as low as 13 at.% in the alloy with 2 at.% added Np. In the alloys with added U or Pu and no Np, the Zr content in the Zr(Fe,Cr,Ni)_{2+x} phase is 22 at.%. Therefore, there are subtle differences in the phases that develop depending on the type of actinide added. The Fe solid solution phase in these alloys does not exhibit changes in concentration due to additions of actinides to the nominal alloy.

Like the Zr-8(304SS) alloy, the 316SS-15Zr alloy does not develop discrete, very-high-Pu phases in its microstructure as higher concentrations of Pu are added. In terms of repository performance, either one of these alloys with added Pu should behave favorably. It has been demonstrated with immersion tests in J13 well water and electrochemical corrosion tests [4] that both Zr-8(304SS) and 316SS-15Zr alloys exhibit superior corrosion properties and an eminent tendency to retain constituents, like noble metal fission products, when exposed to liquids; and since adding Pu to Zr-8(304SS) and 316SS-15Zr alloys has little effect on the alloy microstructure and phase development, the performance of the alloys should remain intact. Consequently, based on the results of this study, Zr-8(304SS) and 316SS-15Zr alloys are viable for Pu disposition.

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Figure 1. A backscatter electron SEM micrograph of the as-cast microstructure (a) for alloy Zr-8(304SS) with 10 wt.% added Pu and (b) for alloy 316SS-15Zr with 10 wt.% added Pu.