Zr inclusions in actinide-Zr alloys: new data and ideas about how they form

Dawn E. Janney, Thomas P. O'Holleran^a

Idaho National Laboratory, Idaho Falls, ID 83415 USA

^aRetired

Corresponding author:

Dawn E. Janney

Idaho National Laboratory, Mail Stop 6188

Idaho Falls, ID 83415-6188

USA

Phone: 208-533-7478

Fax: 208-533-7863

E-mail: dawn.janney@inl.gov

Contact information for Dr. O'Holleran: dr.tpoh@hotmail.com

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Zr inclusions in actinide-Zr alloys: new data and ideas about how they form

Dawn E. Janney*, Thomas P. O'Holleran^a

Idaho National Laboratory, Idaho Falls, ID 83415 USA

*To whom correspondence should be addressed. Phone 208-533-7478, fax: 208-533-7863,

dawn.janney@inl.gov

^aRetired

1. Introduction

High-Zr inclusions are common in actinide-Zr alloys (e.g., [1-4]), despite phase diagrams indicating that these alloys should not contain a high-Zr phase. The inclusions may contain enough Zr to cause significant differences between bulk compositions and those of inclusion-free areas [1, 3, 5], leading to possible errors in interpreting data if the inclusions are not considered. Previous researchers noted a correlation between the oxygen concentration during casting and the volume fraction of high-Zr inclusions in U-Pu-Zr alloys [4], suggesting that the inclusions might be oxygen-stabilized Zr. Other researchers suggested that the inclusions might be stabilized by other impurities such as C, N, and Si, or might represent a previously unknown high-Zr phase [1, 5, 6]. However, little is known about the inclusions, and previous researchers attempting to explain them have concluded that further investigation is required. This letter presents detailed microstructural and microchemical data from individual inclusions, leading to new ideas about how the inclusions form.

2. Material and methods

Data in this paper are from an as-cast alloy whose nominal composition is 52 wt.% U, 20% Pu, 3% Am, 2% Np, 15% Zr, and 8% rare-earth (RE) alloy consisting of 6 wt.% La, 16% Pr, 25% Ce, and 53% Nd. Casting, sample preparation, and electron-microscope analysis were described in previous publications involving the same sample [7-9]. Phases and microstructures in this sample do not represent room-temperature equilibrium [7, 8], consistent with the

prolonged annealing times required to achieve equilibrium in other U-Pu-Zr alloys at temperatures below 600 °C (e.g., [4, 10]).

3. Results

The sample consists primarily of an actinide-Zr matrix surrounding high-Zr inclusions and two kinds of RE inclusions with different actinide concentrations (Figures 1a and b) [7, 8]. The high-Zr inclusions have straight edges and regular shapes, and occur adjacent to rounded or irregularly shaped areas of high-actinide RE material. Most of the high-Zr inclusions are less than 10 micrometers across, although individuals up to ~20 micrometers long were observed. Small areas of material whose contrast suggests a high concentration of actinides are commonly visible inside the high-Zr inclusions in SEM images.

TEM images of several of the high-Zr inclusions (Figures 1c-f) show continuous, gently curving Bragg fringes or planar defects, suggesting that each inclusion consists of a small number of relatively strain-free crystals. The TEM images also show numerous nanometer-scale sub-inclusions inside the high-Zr inclusions.

TEM-EDX spectra from high-Zr inclusions (Table 1) show Zr with ~1-2 at.% actinides. Spectra from the nanometer-scale sub-inclusions and from areas with large numbers of sub-inclusions show higher concentrations of actinides than spectra from other areas. Several of the spectra have small peaks that might be C or N; however, it is not clear whether these elements are surface layers or part of the alloy. None of the spectra have detectable concentrations of REs.

4. Discussion

This paper presents microchemical and microstructural data on high-Zr inclusions in a complex actinide-Zr-RE alloy. Compositions of these inclusions are similar to those reported from other actinide-Zr alloys (e.g., [4, 6]). The shapes of the high-Zr inclusions in the present data differ from the “globular” shapes reported in other publications (e.g., [5, 11]) but resemble those in U-Pu-Zr alloys with similar concentrations of minor actinides and lower concentrations of REs [12]. Shapes of high-Zr inclusions are sensitive to small variations in concentrations of

impurities and local conditions during casting [11, 13], and it seems likely that the high-Zr inclusions studied here are comparable to those reported by previous researchers.

The present data show that high-Zr material characteristically occurs adjacent to high-actinide RE material, although high-actinide RE inclusions commonly occur without adjacent high-Zr material [7, 8]. The large sizes of the high-Zr and high-actinide RE areas and wide variations in the proportions of adjacent high-Zr and high-actinide RE materials indicate that the two materials originally crystallized as separate phases. Microstructural relationships and consideration of phase diagrams suggest that the high-Zr inclusions nucleated at interfaces between immiscible liquids that later crystallized to form the matrix and RE inclusions.

The areas of high-actinide material appearing inside high-Zr inclusions in SEM images may have originated as small volumes of liquid that became surrounded by growing high-Zr crystals. However, the much smaller high-actinide sub-inclusions visible only in TEM images appear to have formed by solid-state diffusion. It seems likely that the high-Zr inclusions originally crystallized as actinide-Zr solid solutions that un-mixed during cooling.

Obviously, high-Zr inclusions cannot nucleate at interfaces with high-RE liquids in alloys that do not have REs. However, the present research suggests a possible mechanism by which trace impurities such as C, N, and O can lead to formation of high-Zr inclusions during casting: the impurities form small crystallites of high-temperature carbides, nitrides, or oxides, which serve as sites for nucleation of high-Zr inclusions.

5. Conclusions

High-Zr inclusions are commonly reported in actinide-Zr alloys with compositions where phase diagrams indicate that these inclusions should not occur. Previous researchers suggested that trace impurities such as C, N, and O from the original feedstock are involved in formation and stabilization of the inclusions but did not explain the mechanism by which these impurities contributed to formation of the inclusions.

This paper presents data from high-Zr inclusions in a complex U-Np-Pu-Am-Zr-RE alloy. It is suggested that the high-Zr inclusions nucleated as high-Zr solid solutions at interfaces

with high-actinide RE liquids, then unmixed to form nanometer-scale high-actinide sub-inclusions. In the absence of REs, the high-Zr inclusions in other actinide-Zr alloys may have nucleated at the edges of high-temperature impurity phases such as carbides, nitrides, and oxides, thereby causing the previously reported relationship between concentrations of oxygen and high-Zr inclusions.

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Figure 1: Images of high-Zr inclusions. Parts a and b) SEM images. Black arrows show high-Zr inclusions; white arrows show RE inclusions. Lighter-contrast RE inclusions have significant concentrations of actinides; darker ones do not. Small light-colored areas near tips of black arrows are high-actinide material inside high-Zr inclusions. White arrows in upper left of image b show small RE inclusions adjacent to elongated high-Zr inclusions. Parts c-f) TEM images showing high-Zr inclusions (light contrast), adjacent matrix (dark) and high-actinide RE material ("RE"). Numbers indicate locations of EDX spectra in the table. c) Two high-Zr inclusions surrounding small areas of RE material. "Hole" indicates the hole at the edge of the sample. d) Single white lines indicate a planar defect in a high-Zr crystal. Paired lines show edges of a zone with elongated dark sub-inclusions. e) Inclusion containing high-Zr and RE material. Arrows show dark sub-inclusions. f) Three high-Zr crystals and adjacent RE material. Black arrows show dark sub-inclusions. White lines show planar defects.

Table 1: Compositions from EDX spectra from high-Zr inclusions

Spectrum	Image (Figure 1)	At% (normalized to 100%)				
		Zr	U	Np	Pu	Am
1A1-1	a	99	1	0	0	0
1A1-4	a	99	1	0	0	0
1A7-38	a	99	1	0	0	0
1A5-25	b	98	1	0	0	0
1A5-26	b	98	1	0	1	0
1A5-29	b	96	3	0	1	0
1A5-34	b	98	2	0	0	0
1C5-14 ^a	c	91	7	1	2	0
1C5-15	c	99	1	0	0	0
1C7-28	e	95	3	0	1	0
1C7-29	e	98	1	0	0	0
1C7-31 ^a	e	46	38	3	12	1

^aCollected from a dark sub-inclusion, but may also include X-rays from superimposed high-Zr material