Am phases in the matrix of a U-Pu-Zr alloy with Np, Am, and rare-earth elements

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Abstract

Phases and microstructures in the matrix of an as-cast U-Pu-Zr alloy with 3 wt% Am, 2% Np, and 8% rare-earth elements were characterized by scanning and transmission electron microscopy. The matrix consists primarily of two phases, both of which contain Am: ζ -(U, Np, Pu, Am) (~70 at% U, 5% Np, 14% Pu, 1% Am, and 10% Zr) and δ -(U, Np, Pu, Am)Zr₂ (~25% U, 2% Np, 10-15% Pu, 1-2% Am, and 55-60 at% Zr). These phases are similar to those in U-Pu-Zr alloys, although the Zr content in ζ -(U, Np, Pu, Am) is higher than that in ζ -(U, Pu) and the Zr content in δ -(U, Np, Pu, Am)Zr₂ is lower than that in δ -UZr₂. Nanocrystalline actinide oxides with structures similar to UO₂ occurred in some areas, but may have formed by reactions with the atmosphere during sample handling.

Planar features consisting of a central zone of ζ -(U, Np, Pu, Am) bracketed by zones of δ -(U, Np, Pu, Am)Zr₂ bound irregular polygons ranging in size from a few micrometers to a few tens of micrometers across. The rest of the matrix consists of elongated domains of ζ -(U, Np, Pu, Am) and δ -(U, Np, Pu, Am)Zr₂. Each of these domains is a few tens of nanometers across and a few hundred nanometers long. The domains display strong preferred orientations involving areas a few hundred nanometers to a few micrometers across.

1. Introduction

Minor actinides (Np, Am, and Cm) formed during irradiation of nuclear fuels are important contributors to the long-term hazards of nuclear waste. The FCRD and METAPHIX projects are currently pursuing one possible approach to decreasing long-term radiotoxicity from the minor actinides by incorporating them into U-Pu-Zr alloy fuels for transmutation (e.g., [1-9]). The transmutation fuels are intended for reprocessing using a molten salt electrochemical process, which may leave low concentrations of rare-earth (RE) fission products in the recycled fuels (e.g., [10, 11]).

Understanding irradiation-induced changes in U-Pu-Zr transmutation fuels requires accurate knowledge of the phases and microstructures in un-irradiated fuels. Characterizing Am-bearing phases is particularly important because Am is easily lost during high-temperature processing (e.g., [12, 13]). Am-RE inclusions have been identified in a variety of alloys (e.g., [14-16]). X-ray maps showing variations in concentrations of Am adjacent to RE inclusions in as-cast U-Np-Pu-Am-Zr-RE alloys [17] suggest that the matrix may contain Am-bearing phases that do not have REs.

Previous attempts to characterize phases and microstructures in the matrix of as-cast U-Pu-Zr alloys using scanning electron microscope (SEM) analysis (e.g., [15, 17-19]) were unsuccessful because the alloys are too fine-grained. This paper uses transmission electron microscope (TEM) analysis to obtain images, single-crystal electron-diffraction patterns, and microchemical data from areas a few tens of nanometers to a few micrometers across from an alloy whose nominal composition is U-20Pu-3Am-2Np-8RE-15Zr (where RE is a rare-earth alloy of 6% La, 16% Pr, 25% Ce, and 53% Nd and all proportions are specified by weight). The concentration of minor actinides in this alloy is comparable to that in fuels from the METAPHIX project (e.g., [2-5]) and to the alloys in which variations in concentrations of Am in the matrix

were observed [17]. The concentration of REs is intended to approximate a transmutation fuel that has been previously reprocessed and irradiated to high burnup levels. Although techniques used to cast the sample are similar to those for fuel pins, no irradiation testing of this material was planned.

Because of the high spatial resolution of the TEM data, it was possible to identify and characterize individual matrix phases. Although TEM characterization techniques are commonly used in a wide variety of materials (e.g.,[20]), we believe this is the first time they have been applied to any Am alloy.

2. Samples

Approximately 10 grams of starting materials (U, Pu, previously prepared Pu-18Am alloy, Np, Zr, and previously prepared RE alloy) were arc-melted in an argon-atmosphere glovebox. The alloy was homogenized by melting it twice, inverting it before each melting. It was arc-melted a final time and cast in a fused silica tube with a nominal 4 mm inner diameter that had been previously prepared by applying a commercially available zirconia mold wash (suspension of zirconia in ethanol) to the inner surface of the mold with a swab. After casting, the alloy was allowed to cool rapidly to ambient temperature.

Chemical analyses were carried out to confirm the elemental composition of the alloy. Concentrations of Zr, La, Ce, Pr, Nd, Np, U, Pu-239, and Pu-240 were measured using inductively coupled plasma mass spectrometry (ICP-MS). Because the sample was not intended for irradiation, other Pu isotopes were not measured; however, Pu-239 and Pu-240 are estimated to represent about 90% of the total Pu based on analyses of other alloys using Pu from the same source. The concentration of Am was measured after chemical separation to eliminate possible isobaric effects from Pu-241.

The results of the chemical analyses are in Table 1. They confirm that actual concentrations of all elements except Pu are within 1 wt% of nominal compositions, and the actual concentration of Pu is ~80% of the nominal concentration. The analytical total is less than 100%, but is consistent with the estimated 5% measurement errors in individual analyses and the incomplete measurement of Pu. Some of the SEM and TEM data show locally significant concentrations of oxygen, which was not included in the chemical analyses; however, it is not clear whether the oxygen was part of the as-cast alloy or whether it was introduced during sample handling.

A sample was prepared for SEM analyses by embedding a transverse slice of the alloy in acrylic resin. Surface material was removed using progressively finer silicon-carbide papers (down to 1200 grit) with a water lubricant in an air-atmosphere glovebox. The sample was coated with a thin layer of sputtered metal before examination, but was not etched or electro-polished.

Three TEM samples, each approximately 10 μm square and 100 nm thick, were prepared from the SEM sample using a FEI Quanta 3D Dual Beam FEG Focused Ion Beam (FIB) instrument. Much of the material in each sample was too thick for optimum TEM analysis, and most of the data presented here are from thin areas a few micrometers across.

3. Analysis methods

SEM images were collected using a JEOL JSM 7000F field-emission SEM operating at a nominal accelerating voltage of 20 kV. Energy-dispersive X-ray (EDX) spectra were correlated with images to determine spatial distributions of elements. SEM-EDX spectra were not quantified because of limitations of the software in dealing with Am.

TEM analyses used a JEOL 2010 transmission electron microscope operating at a nominal voltage of 200 kV. Images and diffraction patterns were collected with Gatan Digital Micrograph software. TEM-EDX spectra were collected with a Bruker 133 silicon-drift detector and quantified using Bruker software. Spectra were collected from areas several hundred nanometers across for comparison with results of the ICP-MS analyses, and from areas 15-30 nm across to measure compositions in specific locations.

Phases that produced single-crystal diffraction patterns were identified by comparing the experimental TEM-EDX data to annealed U-Pu-Zr alloys [19]. Identifications were checked by comparing the experimental diffraction patterns to simulated patterns from published crystal structures [21, 22] produced using JEMS software [23]. Phases producing rings in diffraction patterns were identified by comparing the experimental diffraction and TEM-EDX data to the International Centre for Diffraction Data's PDF4+ 2012 database.

4.1 SEM and FIB data

SEM images (e.g., Figures 1a and 1b) show a light-contrast matrix surrounding high-Zr and high-RE inclusions. SEM-EDX spectra show that some of the high-RE inclusions also contain significant concentrations of Am, and that the matrix contains Zr and actinides but not REs. Contrast variations on a scale of tens of nanometers in FIB images (e.g., Figures 1c and 1d) suggest that the matrix is nanocrystalline and contains more than one phase. However, the microstructure is too fine-grained to provide detailed information about individual phases.

Some SEM and FIB images show elongated features consisting of a light-contrast central zone bracketed by darker zones (e.g., Figures 1b-1d). These features bound irregularly shaped polygons a few tens of micrometers across. Variations in the widths and sharpness of the edges of the dark and light zones suggest that the features are planar, and are tilted at different orientations relative to the sample surface.

4.2 TEM data

4.2.1 Images

TEM images (Figures 2 and 3) show that most of the matrix consists of dark and light domains a few tens of nanometers across and a few hundred nanometers long. Many of these domains are oriented approximately parallel to one of two perpendicular directions, forming strong local preferred orientation in areas that are hundreds of nanometers to micrometers across.

Some TEM images also show elongated features ~100-200 nm across and several micrometers long (e.g., Figures 2d, 3a-3c). Each of these features has a dark central zone bracketed by light zones. Images of the same areas produced by different instruments confirm that the large elongated features in the FIB, SEM, and TEM images are the same. (Mechanisms for forming image contrast differ between the instruments, and the light central stripes and dark edges of the linear features in the SEM and FIB images are consistent with dark central stripes and light edges in TEM images.)

RE inclusions located on the elongated features are associated with discontinuities in the dark central stripes of the features (Figures 3a, 3b). There is no obvious relationship between matrix microstructures and RE inclusions not located on elongated features (Figures 2b, 2c). High-Zr inclusions are commonly bordered by paired zones of dark and light matrix material, whether or not the inclusions are on elongated features (Figures 3c, 3d).

4.2.2 TEM-EDX spectra

Proportions of actinides and Zr in all but one of the TEM-EDX spectra from areas several hundred nanometers across (Figure 2, Table 2) are similar to those in the bulk sample (Table 1, atomic percentages without REs). None of the TEM-EDX spectra show RE elements or Si. One of the spectra shows a significant concentration of oxygen.

TEM-EDX spectra from individual dark and light areas (Figure 3, Table 3) show that all four actinides are in both materials. Light areas have more Am than dark areas, and more Zr than U. With the exception of spectra from Area 1C3 (which have lower concentrations of actinides and Zr because of their high concentrations of O), all of the spectra from the light material show similar compositions. In contrast, dark areas have more U, Pu, Np, and Zr than light areas, and also have more U than Zr and wider variations in relative proportions of U and Zr.

4.2.3 TEM electron-diffraction data

Figure 4 shows experimental and simulated electron-diffraction patterns from an unusually large single crystal of dark material. These patterns are consistent with ζ -(U, Pu). Closely spaced reflections correspond to large d-spacings that do not occur in δ -UZr₂.

Unfortunately, no comparable crystal of the light material could be found, although it is likely that diffraction patterns from the dark material also include reflections from adjacent light material. The reflections shown by the arrows in Figure 4g are significantly more intense than those in the corresponding simulated ζ -(U, Pu) diffraction pattern (Figure 4f), suggesting that these reflections may include diffracted intensity from both the dark and the light phases. The unusually intense reflections are consistent with δ -UZr₂ (Figure 4h).

In addition to sharp reflections, the experimental diffraction patterns have diffuse, discontinuous rings whose d-spacings correspond to high-intensity reflections from face-centered-cubic actinide oxides such as UO₂, NpO₂, PuO₂, and AmO₂.

5. Discussion

5.1 Phase identification and characterization

Three crystal structures were distinguished using electron-diffraction data, and TEM-EDX spectra were collected from two materials identified in images. In combination, these data represent at least three phases: a dark phase with a structure similar to that of ζ -(U, Pu), a light

phase with a structure that is probably similar to that of $\delta\text{-UZr}_2$, and at least one nanocrystalline actinide oxide with a structure similar to that of UO_2 . All four of the actinides are present in the dark and light phases, which can be identified as $\zeta\text{-(U, Np, Pu, Am)}$ and $\delta\text{-(U, Np, Pu, Am)Zr}_2$ respectively. As there is no single-phase microchemical data from the nanocrystalline oxide, it is not possible to determine which actinides it contains.

Because of the fine-grained microstructure, the areas included in some of the individual TEM-EDX spectra are comparable to the widths of the dark and light domains. Variations in proportions of U and Zr in these spectra may indicate that each spectrum includes both dark and light materials, in different proportions. Only spectra from relatively large areas of dark material (1A2-6, 1A2-12, 1C3-7, 1C3-8, 1C3-10, and 1C3-DP) are likely to represent single phases, and all but one of these spectra (1C3-DP) is from the central stripe of an elongated feature. If it is assumed that all of the oxygen and a proportional amount of U are in UO_2 , the composition shown by these spectra is ~70 at% U, 5% Np, 14% Pu, 1% Am, and 10% Zr. (The assumption that the oxygen is in UO_2 is for convenience; however, substituting other actinides in proportions similar to those in the bulk composition of the sample does not change the composition shown by spectra from the dark material significantly. ZrO_2 is not considered here because there is no evidence for it in the diffraction patterns.)

The minimum concentration of Zr in spectra from the dark material in areas other than 1C3 is significantly above the maximum 5 at% measured in $\zeta\text{-(U, Pu)}$ in U-Pu-Zr alloys annealed at 590 °C (the lowest temperature for which there is published experimental data [19]). If the concentration of Zr increases with temperature in $\zeta\text{-(U, Np, Pu, Am)}$ as it does in $\zeta\text{-(U, Pu)}$ [19], the concentration of Zr in the experimental data may indicate that the composition of the

dark matrix phase does not represent room-temperature equilibrium. Alternatively, it is possible that Np and Am increase the concentration of Zr in ζ -(U, Np, Pu, Am) relative to ζ -(U, Pu).

Spectra from the light phase in areas other than 1C3 consistently show ~55-60 at% Zr, 25% U, 2% Np, 10-15% Pu, and 1-2% Am. This concentration of Zr is somewhat lower than the ~65-80 at% in δ -UZr₂ (e.g., [22, 24-26]), suggesting that some of the sites that are occupied by Zr in δ -UZr₂ may be occupied by actinides in δ -(U, Np, Pu, Am)Zr₂.

5.2 Microstructure formation processes

The qualitative absence of REs in SEM-EDX and TEM-EDX spectra from the matrix is consistent with other studies of U-Pu-Zr alloys with minor actinides and REs [14-16]. Binary U-RE and Ce-Zr phase diagrams [27-31] suggest that the matrix formed from an actinide-Zr liquid that was immiscible with the liquid that formed the high-RE inclusions. There is no microstructural evidence for chemical reactions between the matrix and the high-RE inclusions at lower temperatures. Thus, it seems likely that microstructural evolution in the matrix was not influenced by the presence of the RE inclusions.

To our knowledge, there are no published phase diagrams that include U, Np, Pu, Am, and Zr. U-Pu-Zr phase diagrams (e.g., [19, 32]) indicate that the first phase to crystallize from a molten U-Pu-Zr alloy is a body-centered cubic solid solution commonly referred to as γ -U. Sub-solidus reactions lead to formation of ζ -(U, Pu) at grain boundaries, followed by transformation of the remaining γ -U to a fine-grained intergrowth of ζ -(U, Pu) and δ -(U, Pu)Zr₂ [33]. Microstructures in the present sample are consistent with a similar series of transformations, with the elongated features forming along prior γ -U grain boundaries. The narrow parallel domains in the rest of the matrix suggest crystallographic relationships between ζ -(U, Np, Pu, Am) and δ -(U, Np, Pu, Am)Zr₂.

The extent to which Np can be incorporated into γ -U solid solutions is controversial: some researchers report limited miscibility between γ -U solid solutions and (body-centered-cubic) γ -Np in binary Np-Zr alloys [34, 35], while others report complete miscibility [36]. Although understanding relationships between γ -(Np, Zr) and γ -(U, Pu, Zr) in room-temperature alloys is complicated by the likely existence of a solid solution between δ -NpZr₂ and δ -UZr₂ [34, 36-38], nothing in the present data suggests the formation of separate Np phases at any temperature.

6. Conclusions

This paper identifies and characterizes Am phases in the matrix of an alloy with nominal composition 52U-20Pu-3Am-2Np-8.0RE-15Zr (where RE is a rare-earth alloy consisting of 6% La, 16% Pr, 25% Ce, and 53% Nd and all proportions are by weight). The research combined SEM and FIB images with images, microchemical data, and single-crystal electron-diffraction data obtained using transmission electron microscopy. The high spatial resolution of the TEM data made it possible to determine the compositions and structures of individual phases for the first time.

The matrix consists primarily of two Am phases, which were identified as ζ -(U, Np, Pu, Am) and δ -(U, Np, Pu, Am)Zr₂ by analogy to U-Pu-Zr phase diagrams. Both phases occur in elongated domains a few tens of nanometers across and a few hundred nanometers long throughout most of the matrix. As a consequence of this geometry, excess free energies from phase boundaries are likely to be significantly larger than would be expected from randomly oriented isometric crystals. Individual domains display strong local preferred orientation, suggesting that kinetics of microstructural coarsening may be influenced by crystallographic relationships at phase boundaries. Both of these phenomena may require special consideration when modeling microstructural evolution during annealing and irradiation.

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Figures

Figure 1: SEM and FIB images. a) Low-magnification back-scattered electron (BSE) SEM image showing light-contrast matrix surrounding darker inclusions. b) Higher-magnification BSE SEM image. Black arrows show high-Zr inclusions, large white arrows show high-RE inclusions, and small white arrows show elongated features. c and d) High-contrast secondary electron (SE) FIB images. Arrows show elongated features.

Figure 2: TEM images of the matrix. Circles in parts a, b, c, e, and f, and circle labeled “EDX” in part d indicate approximate locations measured by EDX spectra in Table 2. Circle labeled “DP” in part d shows the location of the diffraction patterns in Figure 4. “RE” indicates high-RE inclusions.

Figure 3: Locations of TEM-EDX spectra in Table 3. RE and Zr indicate high-RE and high-Zr inclusions. Short white lines near edges of images indicate boundaries of elongated features. a) Higher-magnification view of the central portion of Figure 2d. b) Small high-RE inclusion overlapping a bend in an elongated feature. c, d) Inclusions with high-Zr and high-RE materials.

Figure 4: Experimental (left column) and simulated (right column) electron diffraction patterns from the area labeled “DP” in Figure 2d. Rings (e.g., at arrows in part a) are from nanocrystalline actinide oxides. Arrows in part g (which is otherwise identical to part e) show anomalously bright reflections matched by the simulated pattern in part h.

Table 1: Chemical analyses of bulk sample

Element	Wt%		At%	At%
	Nominal	Actual		No REs
U	52	51.6	40.43	44.5
Pu	20	16.5 ^a	12.88	14.2
Am	3	3.74	2.89	3.2
Np	2	2.54	2.00	2.2
Zr	15	15.9	32.59	35.9
Ce	2.00	1.64	2.18	
La	0.48	0.313	0.42	
Pr	1.28	0.717	0.95	
Nd	4.24	4.37	5.66	
RE Total	8	7.04	9.21	
Analytical total	100.00	97.32	100.00	100.0

^aPu-239 and Pu-240

Table 2. Matrix composition (at%) from large-area TEM-EDX spectra

Spectrum	Image (Figure 2)	At% (normalized to 100% and rounded to closest 1%)					
		O	Zr	U	Np	Pu	Am
1A matrix 1	a	0	35	44	5	14	2
1A4-19	b	0	41	38	5	13	2
1A4-20	b	0	43	35	5	15	3
1A matrix 2	c	1	30	49	5	14	1
1C matrix 1	d	8	34	40	4	13	2
1C matrix 2	e	0	36	44	5	14	2
1C matrix 3	f	0	39	40	5	14	3

Table 3. Compositions from individual dark and light areas. Spectra from dark materials are in bold type and those from light materials are in italics. Horizontal lines separate data from different areas.

Spectrum	Image (Fig. 3)	At% (normalized to 100%)					Am
		O	Zr	U	Np	Pu	
1A2-6	-- ^a	2	9	70	6	13	1
<i>1A2-8</i>	-- ^a	<i>1</i>	<i>61</i>	<i>23</i>	<i>2</i>	<i>11</i>	<i>2</i>
<i>1A2-9</i>	-- ^a	<i>2</i>	<i>56</i>	<i>25</i>	<i>2</i>	<i>13</i>	<i>2</i>
1A2-10	-- ^b	3	12	66	6	14	0
1A2-11	-- ^b	4	15	62	5	13	1
1A2-12	-- ^a	0	12	69	5	13	1
<i>1A2-13</i>	-- ^b	<i>4</i>	<i>50</i>	<i>33</i>	<i>1</i>	<i>11</i>	<i>2</i>
<i>1C3-5</i>	<i>a</i>	<i>36</i>	<i>39</i>	<i>17</i>	<i>1</i>	<i>6</i>	<i>1</i>
<i>1C3-6</i>	<i>a</i>	<i>34</i>	<i>38</i>	<i>19</i>	<i>1</i>	<i>7</i>	<i>1</i>
1C3-7	a	23	5	58	4	9	1
1C3-8	a	27	6	53	4	9	0
<i>1C3-9</i>	<i>a</i>	<i>35</i>	<i>38</i>	<i>17</i>	<i>2</i>	<i>8</i>	<i>1</i>
1C3-10	a	21	7	57	4	10	0
<i>1C3-11</i>	<i>a</i>	<i>23</i>	<i>47</i>	<i>18</i>	<i>1</i>	<i>9</i>	<i>1</i>
1C3-12	a	19	15	47	4	12	1
1C3-DP	-- ^c	20	6	58	5	11	1
<i>1A3-16</i>	<i>b</i>	<i>0</i>	<i>59</i>	<i>25</i>	<i>2</i>	<i>12</i>	<i>2</i>
1A3-17	b	0	26	56	5	13	1
1A3-18	b	0	14	68	5	13	1
<i>1A3-19</i>	<i>b</i>	<i>0</i>	<i>63</i>	<i>22</i>	<i>2</i>	<i>12</i>	<i>2</i>
<i>1C7-34</i>	<i>c</i>	<i>0</i>	<i>59</i>	<i>25</i>	<i>2</i>	<i>12</i>	<i>2</i>
<i>1C7-35</i>	<i>c</i>	<i>0</i>	<i>52</i>	<i>30</i>	<i>2</i>	<i>13</i>	<i>1</i>
1C7-36	c	2	25	55	4	12	1
<i>1C5-17</i>	<i>d</i>	<i>0</i>	<i>60</i>	<i>24</i>	<i>2</i>	<i>13</i>	<i>2</i>
1C5-18	d	0	33	52	4	11	0

^aFrom continuation of elongated feature beyond right edge of Figure 3b

^bClose to (but not part of) continuation of elongated feature beyond right edge of Figure 3b

^cFrom dark material in area labeled "DP," Figure 2d