Microstructure Changes Caused by Annealing of U-Pu-Zr Alloys

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ABSTRACT

Thermally induced microstructural changes in five uranium-plutonium-zirconium alloys (38U-22Pu-40Zr, 49U-19Pu-32Zr, 33U-27Pu-40Zr, 19U-41Pu-40Zr, and 20U-12Pu-68Zr, compositions in at%) were examined by comparing as-cast alloys with alloys that had been annealed at 500 °C for 168 hours using scanning electron microscopy. All of the as-cast and annealed alloys had high-Zr inclusions not predicted from currently available phase diagrams. Microstructures in all alloys except U-12Pu-68Zr demonstrate increasing development of irregularly shaped polygons with high-actinide, low-Zr boundaries as a result of annealing.

MAIN BODY

The Fuel Cycle Research and Development (FCRD) project is examining ways to reduce the long-term radiotoxicity of nuclear waste by incorporating minor actinides into U-Pu-Zr alloys for transmutation to radionuclides with shorter half-lives. It is important to understand how phases and microstructures in fuels change as a result of conditions during service. Although these changes involve effects of both radiation and heating, it is useful to understand thermal and irradiation effects separately.

Thermally induced changes in five un-irradiated U-Pu-Zr alloys (Table 1) were investigated by comparing microstructures in as-cast and annealed samples. As-cast samples were prepared by arc-melting U, Pu, and Zr feedstocks in appropriate proportions, then homogenizing the material by allowing it to cool, inverting it, and re-melting it at least twice. The alloys were melted a final time and drop-cast into quartz molds to produce cylinders ~4 mm in diameter. Annealed samples were prepared by holding sections of the as-cast cylinders at 500 °C (~775 K) for seven days (168 hours) and allowing them to cool in the furnace for about one day.

Individual samples of the as-cast and annealed cylinders were prepared for analysis by scanning electron microscope (SEM) by cutting crosswise sections, embedding the sections in acrylic or epoxy, grinding and polishing by hand in an air-atmosphere glovebox with a water lubricant, and applying a thin layer of sputtered Pd to reduce sample charging. Sample surfaces were left somewhat rough to reduce personnel exposure during grinding and polishing.

Samples were examined using a JEOL JSM 7100F scanning electron microscope operating at a nominal voltage of 20 kV. X-ray maps showing qualitative distributions of individual elements were obtained using the Zr L α , U M α , and Pu M β X-rays.

Table 1. Alloy compositions

Nominal composition (at%)	Nominal composition (wt%)	Actual composition (wt%)
38U-22Pu-40Zr	50U-30Pu-20Zr	49.6U-28.5Pu-19.8Zr
49U-19Pu-32Zr	61U-24Pu-15Zr	23.1U-59.3Pu-14.4Zr
33U-27Pu-40Zr	43.5U-36.5Pu-20Zr	41.8U-34.9Pu-20.3Zr
19U-41Pu-40Zr	25U-55Pu-20Zr	23.4U-33.9Pu-63.4Zr
20U-12Pu-68Zr	35U-20Pu-45Zr	33.9U-19.1Pu-43.3Zr

Figure 1 shows SEM images of the as-cast and annealed samples. Microstructures in each sample are qualitatively homogeneous on a scale of hundreds of micrometers to millimeters except near the outer edges of the samples, where the alloys were in contact with the molds.

High-Zr inclusions are common in all of the alloys. With the possible exception of U-12Pu-68Zr (at%), none of the alloys has a high enough concentration of Zr to form α -Zr according to published U-Pu-Zr phase diagrams [1]. High-Si inclusions and pores were also observed, but are less common than the high-Zr inclusions. No systematic differences in these features were observed in comparisons of as-cast and annealed samples.

As-cast microstructures in U-22Pu-40Zr, U-19Pu-30Zr, and U-27Pu-40Zr consist of a light-contrast matrix surrounding dark high-Zr inclusions (Figures 1a, 1b, and 1c). Subtle variations in contrast (particularly evident in Figure 1a) correspond to variations in concentrations of U and Zr. Linear features are visible in some images (e.g., at arrows in Figures 1d and 1g), and may be obscured in other areas by surface scratches. Small light and dark areas (possibly individual crystallites a few tens of nm across) are also visible in some images.

Annealed samples of these alloys show linear features bounding irregular polygons a few tens or hundreds of micrometers across (Figures 1b, 1c, 1e, 1f, 1h, and 1i). Details differ between samples: boundaries in U-22Pu-40Zr appear either as raised areas or as broad, flat areas with unusually light contrast (e.g., at arrows in Figure 1b), boundaries in U-19Pu-32Zr have parallel zones of material with darker and lighter contrast, and boundaries in U-27Pu-40Zr appear as areas of uniformly lighter contrast. X-ray maps (Figure 2) show that the boundaries in all three samples are depleted in Zr relative to the materials in the interiors of the polygons. Boundaries in annealed U-22Pu-40Zr have distinct high-U and high-Pu regions.

The material in the interiors of the polygons in annealed U-22Pu-40Zr and U-19Pu-32Zr includes irregularly shaped light-contrast areas that appear similar to the polygonal boundaries (e.g., Figures 1c and 1f). The interiors of the polygons in annealed U-27Pu-40Zr contain elongated regions of light-contrast material, which commonly intersect one another at approximately right angles.

As-cast microstructures in U-41Pu-40Zr consist of irregular hexagons a few tens of micrometers across (Figure 1j). Boundaries of the hexagons are light-contrast material, bracketed by darker-contrast stripes. The interiors of the hexagons are filled with elongated areas of light-contrast material, some of which terminate at the light-contrast material at the hexagonal boundaries. X-ray maps indicate that the light-contrast areas are enriched in U, slightly depleted in Pu, and strongly depleted in Zr relative to adjacent materials (Figure 2).

Microstructures in the annealed sample also consist of irregular polygons (Figures 1k and 1l); however, the boundaries of the polygons appear thicker and the light-contrast areas inside the polygons are smaller. X-ray maps show that the material in the boundaries is significantly higher in U and lower in Zr than the material inside the polygons, and that the concentration of Pu is similar in both materials (Figure 2).

Microstructures in the as-cast U-12Pu-68Zr alloy consist of lines of elongated high-Zr precipitates bounding irregularly shaped polygons of lighter-contrast material (Figure 1m). EDX maps show that there are no significant variations in concentrations of U or Pu in the lighter-contrast material.

Microstructures in annealed U-12Pu-68Zr also show lines of high-Zr precipitates (Figures 1n and 1o); however, it is subjectively less clear that the lines form polygonal boundaries. Based on the available SEM images, it appears that the high-Zr precipitates may be smaller in the annealed sample than in the as-cast one. However, further quantitative measurements are needed to confirm this assessment.

U-Pu-Zr phase diagrams suggest that the alloys considered here crystallized as ternary solid solutions between the body-centered-cubic (bcc) phases γ -U, ϵ -Pu, and β -Zr, then transformed to lower-temperature phases during cooling [1]. An isothermal section at 500 °C (Figure 3) indicates that the equilibrium phases for the U-19Pu-32Zr, U-22Pu-40Zr, and U-27Pu-40Zr alloys are ternary solid solutions related to ζ -(U,Pu) and δ -UZr₂. Although the temperatures of the reactions forming ζ -(U,Pu) and δ -UZr₂ vary with composition, ζ -(U,Pu) forms at a higher temperature than δ -UZr₂ in each alloy. More recent neutron-diffraction data confirms that the phases present in an alloy with 61.5 at% U, 16 at% Pu, and 22.5 at% Zr alloy are ζ -(U,Pu) and δ -UZr₂ at temperatures between 500 and 595 °C, and that the ζ -(U,Pu) forms at a higher temperature than the δ -UZr₂ [2].

The SEM data presented here are consistent with identification of the lower-Zr matrix phase in annealed U-19Pu-32Zr, U-22Pu-40Zr, and U-27Pu-40Zr alloys as ζ -(U,Pu) and the higher-Zr matrix phase as δ -UZr₂.

The isothermal section is incomplete for high-Pu compositions but suggests that equilibrium phases for the U-41Pu-40Zr alloy at 500 °C may include η -(U,Pu) and δ -UZr₂ (Figure 3). Depictions of the reaction surface at which the bcc solid solution transforms to lower-temperature phases [1, 3] suggest that δ -(Pu,Zr) may have been one of the first phases to form from the bcc solid solution. This implies that the low-Zr phase in the samples of U-41Pu-40Zr is η -(U,Pu) and the higher-Zr phase is δ -(Pu,Zr) or δ -UZr₂. If the high-Zr phase is δ -UZr₂, the sample composition and relatively homogeneous distribution of Pu shown by the X-ray maps indicate that this phase may have a significantly higher concentration of Pu than is indicated by the isothermal section.

Figure 3 indicates that the equilibrium phase for the U-12Pu-68Zr alloy is δ -UZr₂. The apparent partial disappearance of the high-Zr inclusions during annealing suggests that they are not stable at 500 °C.

Although the phase identifications presented here are tentative, the microstructures in all alloys except U-12Pu-68Zr demonstrate increasing development of irregularly shaped polygons bounded by high-U, low-Zr phases. Similar segregation in higher-temperature samples has been attributed to formation of ζ -(U,Pu) at prior grain boundaries in the original bcc solid solution [4]. If this explanation for the polygonal boundaries in the samples considered here is correct, it demonstrates the importance of the early cooling histories of U-Pu-Zr alloys for predicting later development of microstructures in these alloys.

FIGURE CAPTIONS

Figure 1. Back-scattered electron (BSE) SEM images of U-Pu-Zr alloys. Images in each row have the same composition, which is indicated in at%. Images in the left column are from as-cast material; those in the middle and right columns are from annealed samples. Arrows show examples of polygonal boundaries. Images a, b, j, l, and n are from reference [5].

Figure 2. X-ray maps showing distributions of U, Pu, and Zr in as-cast and annealed samples of U-22Pu-40Zr and U-41Pu-40Zr, including areas of Figures 1b, 1j, and 1k. Contrast and brightness were adjusted separately for individual maps. Arrows in as-cast BSE image of U-22Pu-40Zr show surface contamination.

Figure 3. 500 °C isothermal section proposed by O'Boyle and Dwight [1] (re-drawn after [6]). δ , ζ , and η are ternary solid solutions corresponding to δ -UZr₂, ζ -(U,Pu), and η -(U,Pu), respectively.

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