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TEMPERATURE-INDUCED TRANSFORMATION IN A PU-2.0 AT.% AL ALLOY*

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Transformation of the face-centered-cubic (fcc) δ phase of plutonium stabilized with 2 at.% aluminum to the monoclinic α phase was studied by cooling to liquid nitrogen. The transformation was found to proceed by thermally activated nucleation and displacive/diffusionless growth with a maximum transformation rate at -150°C. The resulting transformation product, designated α', traps aluminum solutes in supersaturated solid solution and results in an expanded monoclinic α lattice, although the aluminum atom is 6% smaller in diameter than the α-Pu atom. This positive deviation from Vegard's law is attributed to a lowering of the valence (and resulting expansion in atomic size) of the α-Pu atoms in the vicinity of the aluminum solutes. The α' transformation product appears plate-like, resembling a lenticular martensite.

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Plutonium is the most complex of the actinide series which constitutes the seventh period in the periodic table. Many of its peculiar properties, such as its low melting point, six allotropic phases, complex crystal structures, and high coefficient of thermal expansion are

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attributed to the participation of 5f electrons in bonding (1). The single atom electron configuration is believed to be $5f^6 7s^2$. Plutonium and its alloys present an excellent opportunity for the study of phase transformations. Figure 1 demonstrates the volume changes and crystallographic phases in unalloyed plutonium. The volume changes are very large. The crystal structures at lower temperatures are complex because the 5f electron wave function lacks symmetry and is not compatible with highly symmetric cubic structures. Only at higher temperatures where the entropy term begins to dominate are the cubic phases stable. However, the close-packed fcc δ phase is 20% less dense than the monoclinic α phase. The highly directional (almost covalent) bonding in the α phase resulting from the 5f electron bonding permits a denser packing than the close packing of highly symmetric atoms. The properties of the monoclinic structure are, as expected, highly directional. These structures are strong and brittle.

It is well known that the δ phase can be stabilized to room temperature by the addition of several percent alloying elements such as Aℓ, Am, Ce, In, Ce, and Ga (2,3). The properties of the δ-stabilized alloys resemble those of aluminum. The δ alloys can be transformed to the α phase by cooling below room temperature, deformation, or hydrostatic pressure (2,3). Very little information exists on the details of the mechanisms and crystallography of the transformation and the properties of the transformation products. In this paper we report on temperature-induced transformation on a δ-stabilized Pu-2 at.% Aℓ alloy. The transformation was monitored by dilatometry and the products examined by optical metallography and x-ray diffraction. Unfortunately, transmission electron microscopy has not yet been accomplished on plutonium because of its reactive nature.

Experimental Techniques

A high-purity Pu-2 at.% Aℓ alloy was cast into a graphite mold at 550°C, slow cooled to room temperature, and homogenized for 200 h at 450°C. Rod specimens were machined to a diameter of 6.36 mm and a length of 12.7 mm and annealed for 1/2 h at 350°C. The specimens were all fcc δ phase with a grain size of 30 μm. Specimens were cooled and heated in a dilatometer (in a glove box enclosure) with a resolution of 5×10^{-4} mm. Tests were conducted at constant cooling and heating rates or isothermally.

All specimens were examined metallographically. Special care is required with plutonium alloys because mounting and polishing operations can easily transform the specimen. We mounted all specimens in a cold-setting polyester resin and electropolished the 1-μm-diamond lapped surfaces for 10 to 15 seconds at 30 to 35 V in a 10% HNO_3- ethylene glycol bath to remove any transformation products produced by mechanical polishing. The specimens were etched in the same bath at 6 to 10 V for 20 to 60s. After metallographic examination the etched surface was removed by a short electropolishing cycle and the surface examined in an x-ray diffractometer using CuK_α radiation.

Results And Discussion

A typical dilatometer trace for cooling at 1.5°C/min is shown in Fig. 2. Transformation starts at -130°C and continues all the way to liquid nitrogen temperature. Upon heating, more transformation occurs initially before the specimen begins to expand elastically. We found

the transformation to be very rate sensitive. Quenching to liquid nitrogen in <20s suppresses the transformation completely. We conducted a few isothermal experiments that indicated the minimum time for transformation to be 35s at -150°C. An insufficient number of tests were run to construct the entire C-curve. One low-temperature cycle such as that shown in Fig. 2 results in ~25% transformation product. Upon heating above room temperature as shown in Fig. 2b, the transformation product transforms at temperatures below the normal $\alpha \rightarrow \beta$ temperature and it transforms directly to the δ phase.

A detailed x-ray diffraction examination indicated that the transformation product is primitive monoclinic, similar to the α phase, but with different lattice parameters. The normal α phase has no equilibrium solubility for aluminum. Under conditions of low-temperature transformation, the aluminum solutes are trapped in the α phase in supersaturated solid solution. Density and x-ray measurements on a number of alloys indicated that the aluminum atoms were present substitutionally. Most interestingly, however, the smaller aluminum atoms (1.43A atomic radius compared to 1.52A for α-Pu) expand the α lattice by approximately 2%. We have designated this expanded α phase as α'. The α' phase also exhibits a greater coefficient of thermal expansion, lower elastic moduli, and a lower Debye temperature. Trapping the trivalent aluminum solute encourages the surrounding α-Pu atoms to assume a lower valence and larger (and probably more symmetric) size (4). This effect overrides the Vegard's law contraction expected. Similar valence changes and subsequent positive deviations from Vegard's law have been reported for a number of solutes in δ-phase plutonium alloys (5,6).

The morphology of the α' phase formed during cooling is shown in Fig. 3. The plate-like appearance resembles a lenticular martensite. There exists a definite geometric relationship between the α' and the parent δ phase. We have not worked with sufficiently large grains to identify the specific crystallographic relationships. The α' platelets typically are short with respect to the grain diameter, are nucleated homogeneously throughout the structure, do not cross grain boundaries, and are highly segmented. The short, segmented nature of the α' phase is most likely a result of the large volume change caused by the transformation. The sequence of transformation appears to be δ → α'. We found no evidence of other phases. Lomer (7) and Spriet (8) have previously suggested a possible lattice correspondence requiring a homogeneous shear plus a slight atomic shuffle. The mechanism of transformation appears to be isothermal martensite-like. Nucleation is definitely thermally activated and growth is displacive/diffusionless. According to currently accepted definitions (9), the transformation is not truly martensitic because the large volume change precludes the requisite invariant plane strain.

The reversion of α' to δ during heating (Fig. 2b) is simply considered to be the same mechanism in reverse. It occurs at lower temperatures than the normal α → β transformation and proceeds α' → δ because all the atoms are still in their undisturbed positions from the δ → α' transformation. In fact we believe that some reversion occurs during heating from liquid nitrogen to room temperature, which partially accounts for the segmented appearance of the α' platelets. We have established that the

aluminum will diffuse out of the α' lattice at room and slightly elevated temperatures, returning the α' lattice to the normal α lattice.

Conclusions

The δ phase stabilized with 2 at.% aluminum transforms to a monoclinic α' phase at low temperatures by a thermally activated nucleation and displacive/diffusionless mechanism. The α' phase is an expanded monoclinic lattice suggesting a valence change in the α-Pu atoms as a result of trapping smaller, trivalent aluminum atoms. The transformation sequence appears to be directly $\delta \rightarrow \alpha'$. The α' product is platelike, resembling a lenticular martensite.

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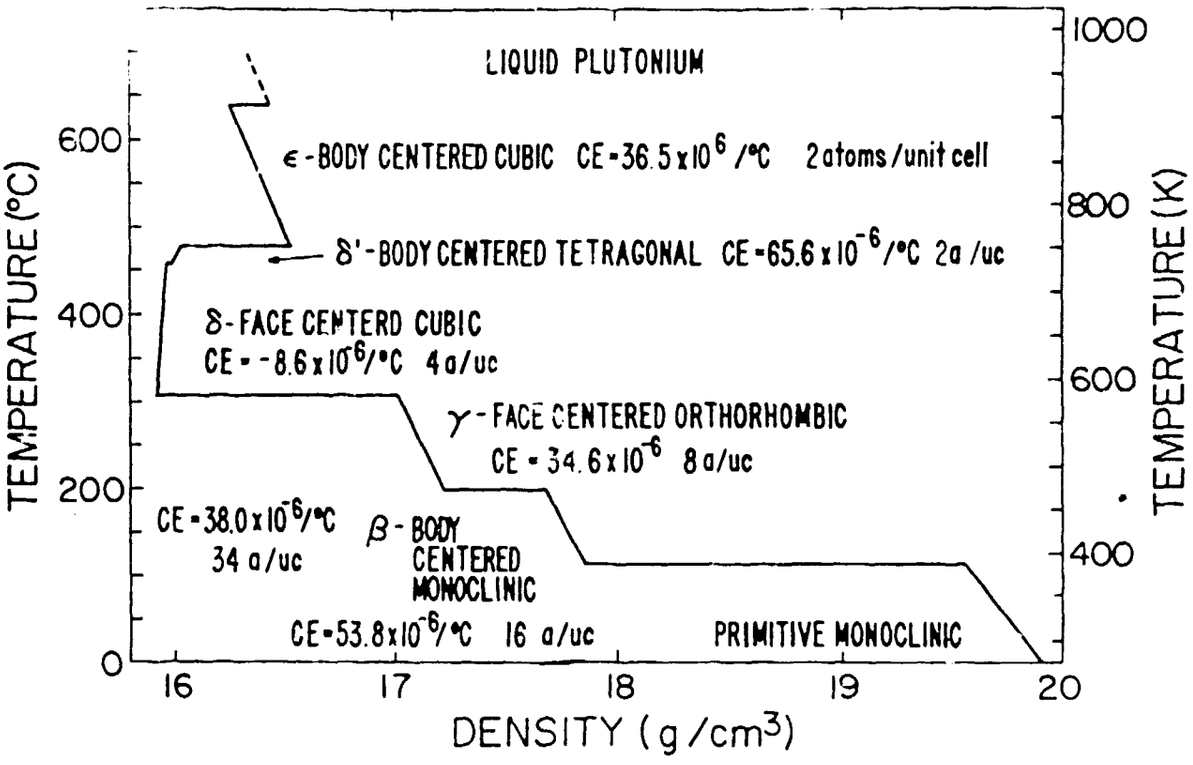

Figure 1. Some properties of plutonium.

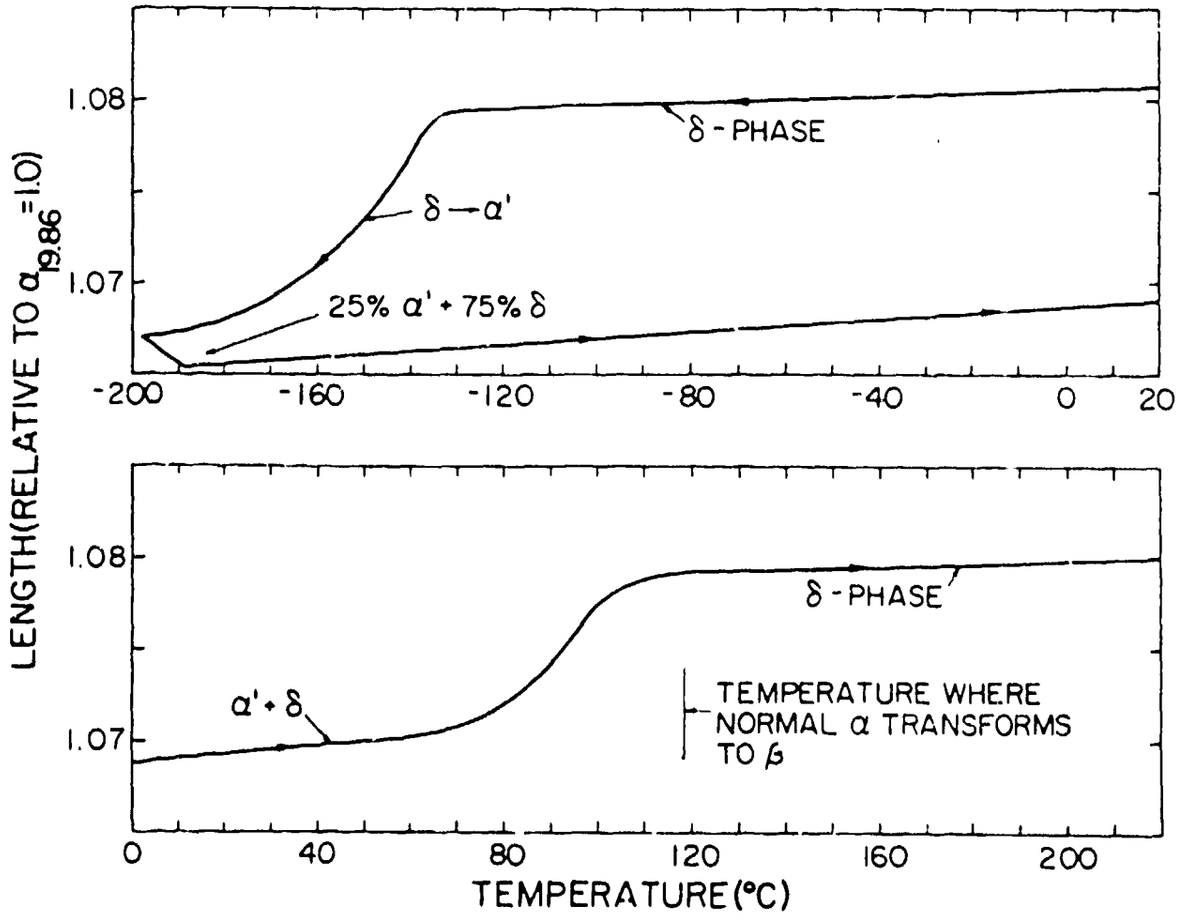

Figure 2. Dilatometric behavior of Pu-2.0 at% Al during transformation by subzero cooling, and then heating

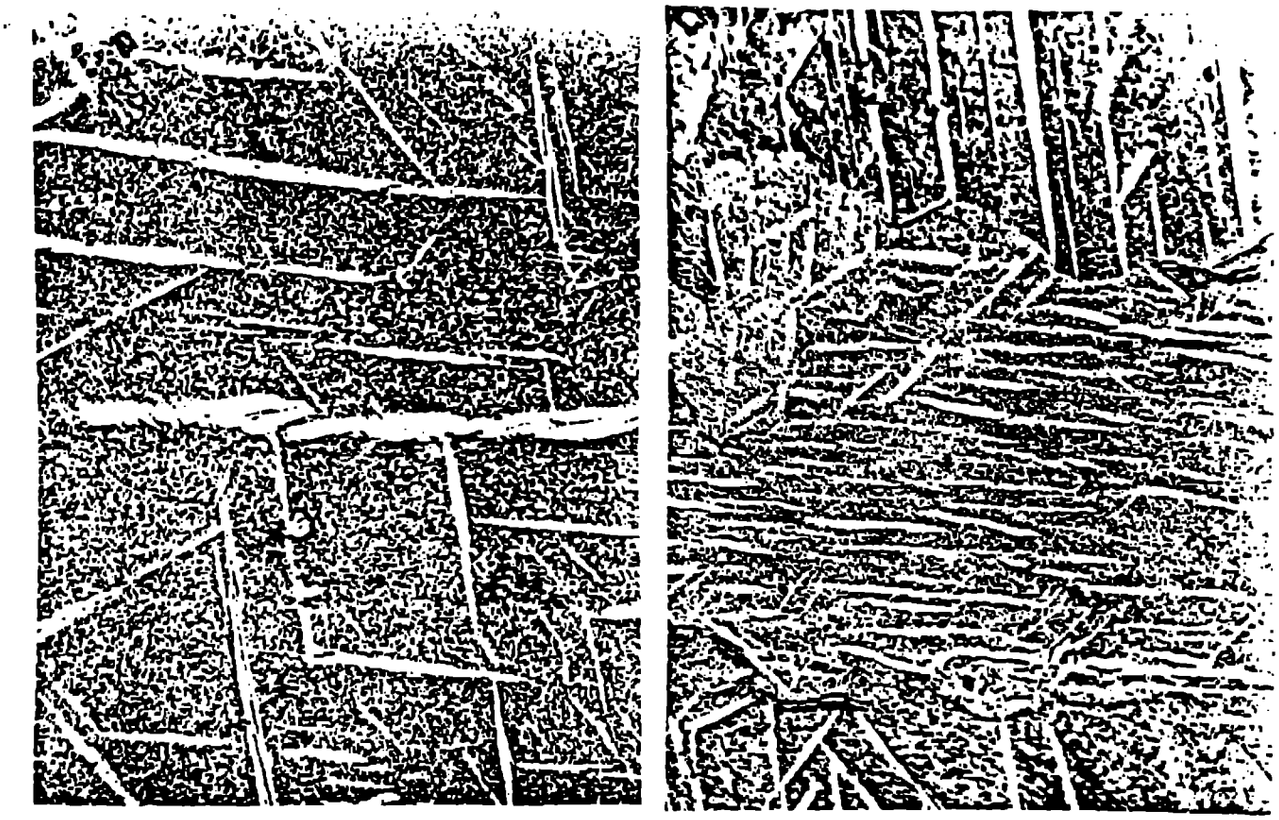

Figure 3. Microstructures of α' formed by subzero cooling.