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Evidence that Alpha-Phase Plutonium Is a 9R Martensite

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ABSTRACT

We suggest that there may be different precursors of the alpha phase of plutonium in the martensitic δ → α transformation, depending upon whether the metastable δ-phase alloy is compressed or cooled below ambient. The precursors may be either the orthorhombic (γ) phase, which is observed, or an hcp structure which can transform rapidly to alpha.

We postulate that the martensitically formed alpha phase of plutonium (δ → α or β → α) has the characteristics of a modified 9R martensite. The development of such a structure can explain the anomalous low-temperature physical property behavior of both α-Pu and its δ-phase stabilized alloys.

I. INTRODUCTION

Similarities have been observed in the low-temperature physical property behavior of α-phase plutonium and δ-phase stabilized alloys of plutonium. The properties include electrical resistivity,[1,2] longitudinal acoustical attenuation,[3,4] heat capacity,[5] and Young's modulus.[6,7]

Elliott, Olsen, and Louie[8] first suggested that the δ-phase stabilized alloys transform martensitically to α-Pu on cooling below room temperature, based on electrical resistivity measurements on Ce, Al, and Zn solid-solution alloys. The δ → α transformation in plutonium-base alloys also has been found to occur under compression[9] or deformation.[10] Goldberg and Shyne[11] concluded that the δ → α transformation takes place martensitically in some δ-stabilized alloys under nonequilibrium conditions, and that the transformation was strongly influenced by applied stresses. This author recently postulated that the low-temperature behavior of α-Pu depends on whether the β → α phase transformation is martensitic or diffusion controlled.[12]

The similarity in the properties of α-Pu and δ-phase stabilized alloys at low temperatures appears to be a peculiarity of the α-Pu structure formed under martensitic conditions. In this connection, Warlimont and Delaey[13] noted that effects of ordering are responsible for orthorhombic and monoclinic distortions of martensitic structures.

One purpose of this report is to show that α-Pu may act like a 9R martensite when formed martensitically. This possibility is suggested because the δ-phase alloy (fcc) and its martensitically formed product phases (γ (orthorhombic) and α (monoclinic)) have been observed associated together[9,10] like nonferrous 3R and 9R martensitic structures[13*,14] (also designated as 1R and 3R by some authors).

Another purpose of this report is to show that the low-temperature behavior of plutonium and its alloys is not anomalous, but that the metal and alloy are acting in a manner typical of nonferrous martensites. Martensitic transformations can lead to long-period antiphase as well as long-period stacking shift structures, but these structures are not restricted to the martensitic mode of formation.[13**] Evidence for the possibility of an antiphase or stacking modulated structure in both α-phase Pu and δ-phase stabilized plutonium alloys at low temperatures has been previously presented.[5] Long-period stacking order (LPSO) is observed in 9R-type martensites.[15] If the α-Pu structure were capable of assuming the long range order of such a martensite, it would explain the antiphase-like behavior of α-Pu and partially transformed δ-phase alloys.

II. LITERATURE SURVEY

The δ → α martensitic transformation temperature depends upon the element stabilizing the δ phase and on its concentration.[8,16] Published results suggest that an intermediate phase, γ, appears when the δ-phase alloy is compressed[9] or deformed.[10]

A. Transformations of δ-phase stabilized plutonium alloys

Elliott, Olsen, and Louie[8] found that the δ → α transformation temperature depended on the alloying element and its amount. They suggested that the β phase (b c monoclinic) was an intermediate product in the δ → α transformation on cooling and the α → δ transformation on heating. The suggestion

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[*] Reference 13, p. 28.

[**] Reference 13, pp. 109-111.

was based on steps in their low-temperature resistivity curves for Ce-stabilized alloys. Orme, Faiers and Ward[16] found that increased Ga content depressed the δ → α transformation to lower temperatures, in agreement with Elliott et al.[8] They concluded that the δ → α transformation occurred by a massive or a martensitic transformation.

The investigation of Hambling, Spicer, and White[9] indicated that the γ phase (orthorhombic) was the only precursor of the α phase under uniaxial compression. They suggested that with Pu-0.85 at.% Al alloy, the process was metastable δ → γ → α (concurrent transformation); but that with Pu-2.2 at.% Ce alloy, it was metastable δ → γ and γ → α (consecutive transformations). They considered that the Pu-0.85 at.% Ga alloy transformed from δ to α phase at 296 K and at 328 K through intermediate β and γ phases.

Goldberg, Rose, and Shyne[10] studied the effect of stress and plastic deformation on the martensitic δ → α phase transformation in Pu-1 at.% Ga alloy. They noted that two product phases, α (monoclinic) and γ (orthorhombic), occurred together with the original δ phase in specimens deformed by compression at 296 K. The α + γ products exhibited both a layered and granular structure. The fine structure of bands seen in an electron micrograph (longitudinal cross section) appeared to consist of parallel alternating layers or plates of the two product phases. This behavior suggests that δ-phase stabilized plutonium alloys transform like ordinary nonferrous martensites. Goldberg et al.[10] found that only the α phase formed on cooling Pu-1 at.% Ga alloy below its M_s transformation temperature at 281 K. They proposed that the transformation on cooling was initiated athermally, but once started, it occurred isothermally.

Stress-induced martensitic transformations may result in a different structure[*] from that produced by a quench-induced transformation of the same alloy.[13] This suggests that there may be different precursors of the α phase in the δ → α transformation, depending on whether the specimen is compressed or cooled below room temperature.

B. Similarities between α-phase Pu and δ-stabilized Pu alloys

Rosen, Erez, and Shtrikman[4] found that the low-temperature longitudinal acoustical attenuation of two δ-phase stabilized alloys (6 at.% Ce and 5 at.% Al) was very similar to the longitudinal attenuation behavior previously observed[3] with α-phase plutonium between ~ 10 and 300 K. The sharp peak in the longitudinal wave attenuation[3] of α-phase plutonium at 66 K is also displayed by cerium and aluminum alloys.[4]

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[*] Reference 13, pp. 113-114.

There is additional physical property evidence for some sort of structural transition in α-Pu in the temperature range 50-70 K. Lallement[17] found a minimum in dilatation at ~50 K, which suggests a partial phase transition to a structure of lower density, possibly hcp, below this temperature. A change in the lattice parameters of α-Pu below 70 K was noted by Lee, Marples, Mendelssohn, and Sutcliffe.[18] This change also suggests the appearance of a structure of lower density. Sandenaw[19] reported a C_p maximum at ~60 K in the C_p vs T curve with a specimen of electrorefined α-Pu. He also observed a lower, reproducible heat capacity between 60 K and 320 K. The lower curve can now be interpreted as caused by heat evolution when a quenched martensite is heated, or when a long-period superlattice (antiphase-like structure) is formed.

III. DISCUSSION

A. Significance of the martensitic 9R structure

The method of describing a structure based on symmetry and number of layers in the unit cell is due to Ramsdell.[20] A rhombohedral structure involving successive stacking of ordered close-packed layers is designated by R. The number 9 indicates the number of close-packed layers in the repeat sequence. Thus, an ordered orthorhombic structure is indicated by the repeat sequence ABCBCACAB. By this terminology, a 3R structure has an fcc structure with a repeated sequence of 3 close-packed layers, i.e., ABC. These structures are identified differently by Warlimont and Delaey[13*] and Sato, Toth, and Honjo.[21] By their usage, the fcc structure is designated as 1R and the 9-layered orthorhombic (martensitic) structure is designated as 3R. Ramsdell's terminology will be used in this discussion, because it is better able to describe, for example, a recently reported modified (nonideal) 9R martensitic structure (monoclinic) having a long-period stacking order.[14,15,22]

An ideal (normal) close-packed 9R structure can be produced from structure by introducing a stacking fault every three layers.[13*,14] An orthorhombic unit cell is formed when the lattice constants are close to those of the ideal close-packed 9R structure, but a monoclinic unit cell can result when the lattice constants deviate from the ideal 9R structure.[14] The 9R-type LPSO martensitic structures can be stress induced. The systematic

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[*] Reference 13, p. 28.

[**] Reference 13, pp. 109-111.

introduction of a stacking fault in a layer of atoms permits the periodic modulating of a regular close-packed structure by low-energy boundaries. The 9R structure is believed to result from the minimization of stress and strain energy produced by the martensitic transformation. The displacement vectors of the stacking faults produce antiphase boundaries, along with the stacking faults in this type of martensite. The normal (ideal) 9R structure (orthorhombic) is not closest packed, and the more close-packed layer structure, which is monoclinic, is expected to form at lower temperatures. This appears to be the case with α-Pu, because the monoclinic structure has the highest density of any of the plutonium phases.

B. Low-temperature ordering in δ-phase stabilized alloys

The product phases, γ (orthorhombic) and α (monoclinic), were observed by Goldberg et al.[10] in the martensitic δ → α transformation. The simultaneous formation of parallel alternating layers or plates of these phases, observed through an electron micrograph, suggests a periodically ordered distribution of stacking shifts into an antiphase-like structure of a 9R martensite. The parallel alternating layers of γ and α phases also suggest that there are alternate paths for the martensitic transformation. There is, however, the additional possibility that layering is due to the compressive deformation of δ phase.

A martensitic transformation should occur with an undistorted and unrotated habit plane separating the two phases in order to maintain continuity between parent and product phases. This has been noted by Goldberg and Shyne.[11] Thus, δ-phase Pu (fcc) should not be able to transform directly to α-Pu, as appears to be indicated by cooling experiments.[10] Another possible precursor of the α-Pu is the hcp structure. The simplest martensitic transformation is that from a high-temperature fcc phase to a low-temperature hcp phase. The two structures are interrelated. The monoclinic α-Pu structure is very close to hcp. The α-Pu might form rather easily from an hcp precursor. The sequence could be metastable δ → hcp → α (concurrent transformations) upon cooling δ-stabilized alloy below room temperature.

The γ phase (orthorhombic) might be expected as an intermediate phase in the δ → α transformation,[9] because it would be easy to form from an fcc structure (δ) by the introduction of stacking faults.[13*,15] The stress build-up due to the volume change of this transformation should produce the required

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[*] Reference 13, p. 28.

stacking faults for the formation of the modified (nonideal) 9R structure of closest packing; i.e., monoclinic (α phase) should be the final product. It is the plutonium structure normally stable at room temperature and below.

Similarities in the low-temperature physical property behavior of δ-phase stabilized alloys and α-Pu result from the similar martensitic mode of formation of the α phase in each case. The result may be a 9R-type martensite with an LPSO structure. The long-period stacking order is undoubtedly responsible for the low-temperature antiphase-like properties of α-Pu. The case for an antiphase structure in α-Pu and δ-phase alloys has been previously presented in considerable detail.[5]

C. Possibility of α-Pu stacking variants

There appear to be at least two stacking variants of the α-Pu crystal structure, although both may show the same structure by x-ray diffraction. The first appears to show LPSO properties, as noted above. The second variant appears to be due to a diffusion-controlled β → α phase transformation. In this case, there may be no requirement for an LPSO structure because the stress and strain energy of the β → α transformation is relieved, e.g., by cycling in the diffusion-controlled temperature range of the transition[23] (between room temperature and ~395 K). Ordered stacking faults may be altered to give the α-phase structure of highest density.

Repeated temperature cycling of an α-Pu specimen in the diffusion-controlled region of the β → α phase transformation (as determined by White)[23] should produce pure α-Pu because all higher temperature transitions, e.g., β → α, δ → α, etc., will be completed. This appears to be proven by a heat capacity study[24] of high-purity ^{242}Pu. After five heat capacity runs between 298 K and 373 K, no evidence was found for low-temperature phase transitions in α-Pu or for heat evolution from the formation of an antiphase structure.

The structural transition of α-Pu in the range 50-70 K, which was inferred from the evidence presented above in Section 2.2, is probably martensitic. The lower limit of the long-period stacking order may be in this temperature range. It was noted[19] above that heat evolution apparently started when a specimen of electrorefined plutonium was warmed above 60 K.

The particular variant of α-Pu observed may depend greatly on purity, as well as on previous specimen history. Joel, Jodet, and Mandet[25] studied the effect of impurities on the residual resistivity and density of α-Pu specimens. They found that elements such as Al, Ga, Ce, and In, which stabilize the δ phase of plutonium, seemed to have an effect on both residual resistivity and density which was greater than expected with the actual impurity content. This suggests that elements stabilizing the β or δ phases may prevent the formation of a pure α-Pu which is free of any form of stacking order.

IV SUMMARY

Orthorhombic and monoclinic are close-packed structures which can appear associated together in 9R-type martensites. Since these are the crystal structures observed after a martensitic δ → α transformation in δ-phase stabilized alloys, it is claimed that the behavior of these alloys is not anomalous, but is normal for martensites.

It is suggested that the similarity in the low-temperature physical property behavior of α-Pu and δ-phase stabilized alloys is due to the martensitic mode of formation of α-Pu (from either the β phase or the δ phase).

It is postulated that there are at least two stacking variants of the α-Pu crystal structure. If formed martensitically, α-Pu appears to show the characteristic behavior (LPSO) of a modified 9R martensite. When formed under diffusion-controlled conditions, high-purity α-Pu has been observed to be almost completely free of the physical properties associated with a long-period stacking order.

It is also suggested that there may be different precursors of the α phase in the δ → α transition depending upon whether the metastable alloy is compressed or cooled.

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