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Thermophysical Properties of Coexistent Phases of Plutonium

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Abstract. Plutonium is the element with the greatest number of allotropic phases. Thermally induced transformations between these phases are typically characterized by thermal hysteresis and incomplete phase reversion. With Ga substitutal in the lattice, low symmetry phases are replaced by a higher symmetry phase. However, the low temperature Martensitic phase transformation ($\delta \rightarrow \alpha'$) in Ga stabilized δ-phase Pu is characterized by a region of thermal hysteresis which can reach 200°C in extent. These regions of thermal hysteresis offer a unique opportunity to study thermodynamics in inhomogeneous systems of coexistent phases. The results of thermophysical properties measured for samples of inhomogeneous unalloyed and Ga alloyed Pu will be discussed and compared with similar measurements of their single phase constituents.

1. INTRODUCTION

The element plutonium has an unmatched six solid allotropic crystalline phases at ambient pressures ranging in symmetry and density from the monoclinic α-phase with a density of $19.86 g/cm^3$ to face-centered cubic δ-phase with a density of $15.8 g/cm^3$, respectively. The metallic radii for the various phases of Pu and thus the density is recognized as a function of the combined electronic configuration of 5*f* and valence electrons, atomic coordination number of the crystal structure, and thermal expansion of the phase. As might be expected with such an unusual range of atomic bonding environments in metallic Pu, the monoclinic α-phase has eight unique Pu site in its crystal structure and face-centered cubic δ-phase has one unique Pu site, the elastic moduli and thermal expansion exhibits a broad variety of behaviors from extreme elastic anisotropy to negative thermal expansion.

When alloyed at levels between 1.5 and 10 atomic percent with gallium, plutonium is stabilized into the face-centered cubic δ-phase over a broad temperature range. At low temperatures, this single phase field is terminated by a two phase-field boundary marking the temperature at which the Pu-Ga alloy is no longer stabilized and a Martensitic phase transformation occurs ($\delta \rightarrow \alpha'$). The α'-phase has a monoclinic structure and atomic position similar to α-phase Pu but with a slightly larger volume ($\simeq$2%). This region of the Pu-Ga binary phase diagram offers a rich region in which to study the thermodynamics of coexistent phases in a quasi-equilibrium state due to slow kinetics and significant internal stresses resulting from a density mismatch on scales ranging from atomic to micrometer scale.

2. EXPERIMENTAL

The materials utilized in this investigation were cast unalloyed and Ga alloyed Pu polycrystalline metals. Electro-refined Pu with a typical starting purity of 99.95% was cast at 1000°C utilizing induction heating into graphite molds heated to 680°C and furnace cooled to ambient temperatures.

Alloying Pu with Ga at the level of 1.8 at.% was employed to stabilize the δ-phase, but alloying was kept at sufficiently low concentrations to ensure a two-phase microstructure (i.e., monoclinic α-phase and face-center cubic δ-phase) at ambient temperature. Post-cast annealing at temperature of up to 450°C was necessary to ensure homogenization of the Pu-Ga alloys. Samples were fabricated by slow-speed diamond blade saw or via lathe machining to rectangular parallelepiped or cylindrical geometry, respectively. Sample dimensions were typically of size 5mm x 5mm x 5mm or smaller and the mass of these samples varied from 1g to 15g. For this study, all the homogeneous single phase and two phase or coexistent phase materials are polycrystalline aggregates with crystallites of microscopic size (i.e., ~10μm-30μm in diameter).

Density of the samples utilized in this study was determined by immersion density. In order to measure density accurately with this technique is challenging because the samples are self-heating - a by-product of radioactive decay and self-irradiation. Thus, immersion fluid thermal expansion must be well known and instantaneous temperature must be continuously monitored. The immersion liquid used is the 3M Corporation brand Fluorinert FC-43. The process utilized to determine the immersion fluid thermal expansion has been described elsewhere [1]. The density of the FC-43 is determined before each series of measurements using a NIST lead silica glass standard calibrated to 20°C. As a control charting activity, a sample of Invar is utilized to ensure consistent performance of the bath over time and temperature. Instantaneous temperature of the immersion bath is monitored and corrections are made for the immersion fluid thermal expansion.

A Mettler Toledo Model AT201 semi-microbalance and a motorized lab jack was employed as the automated density station. The temperature of the immersion fluid was monitored with a Platinum resistor which follows an industry standard curve from 73 K to 873 K with good sensitivity (0.3 ohm/K) at T_o=290K. Utilizing a four probe resistance measurement, sensitivity on the level of +/-0.002 K is easily achieved. This temperature data is used in the density corrections that occur from drifting in FC-43 temperature. Precision dry and wet weights and temperature data are collected in sets of two hundred data points to improve accuracy of the reported density data sets for the Invar and lead silica glass standards and the samples. Using care in all material handling steps, the accuracy of the reported density $\rho_o=\rho(T_o)$ is typically better than ± 0.001 g/cm^3 for samples over 10 g and typically better than ± 0.01 g/cm^3 for samples less than 1 g.

Linear thermal expansion ($\Delta L/L_o$) measurements of samples of initial length L_o were conducted in a Netzsch 402 dilatometer under high purity He gas atmosphere to minimize surface oxidation and to ensure good thermal control and minimize thermal gradients. This dilatometer utilizes a high resolution linear variable differential transducer capable of +/-1.25nm resolution with a typical repeatability of 0.3%. As seen in figure 1, thermal expansion measurements were made on Ga alloyed and unalloyed Pu samples over an extensive temperature range ($-160°\text{C} < T < 450°\text{C}$) depending on the thermal history being sought. Heating and cooling rates of 1K/min were utilized. For the low temperature dilatometer runs, a hold time of 1hr. was employed at the lowest temperatures to allow the alloys to carry the δ → α' Martensitic transformation to completion. For homogenization runs, the samples were held at 450°C for approximately 50 hrs. to ensure a uniform Ga concentration (see figure 2(b)). All runs were corrected for the thermal expansion of the silica sample holder.

Resonant ultrasound spectroscopy (RUS) was utilized to measure the elastic moduli by using the resonant modes of a sample.[2] Measurements using 20–30 resonance peaks were made to determine the two independent quasi-isotropic effective elastic moduli. This method sweeps the frequency driving a broadband transducer in weak contact with the specimen, and detects the macroscopic-vibration resonance frequencies. Knowing a sample's dimensions, weight and rough elastic moduli allows one to predict resonant modes. Iterating the experimentally measured modes vs. the predicted modes, while allowing moduli to float, results in a very accurate measurement of the elastic moduli. This technique works best with regular shapes such as cylinders, cubes and spheres where codes are easily available to predict resonant modes.

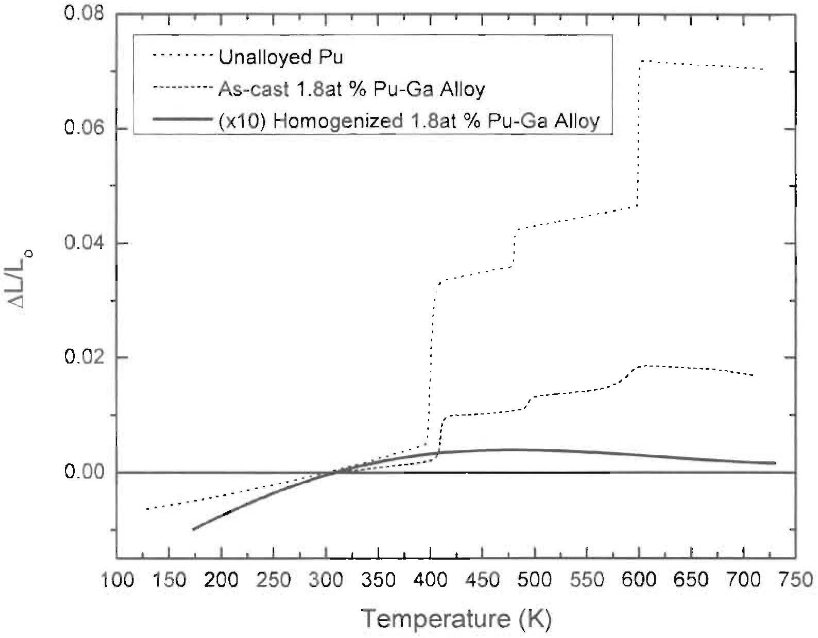

Figure 1. Thermal expansion traces for unalloyed and as-cast and homogenized 1.8 at.% Pu-Ga alloys. The trace for the homogenized 1.8 at.% Pu-Ga has been scaled to 10X for clarity.

3. RESULTS AND DISCUSSIONS

Solid state thermodynamics are typically defined in terms a few thermodynamic quantities: thermal expansion, elastic moduli, density or specific volume, and specific heat. These intrinsic quantities are sufficient to specify the equation of state for a solid and so are typically those measured quantities which are utilized to validate electronic structure calculations. Thermodynamics also drive phase transformations.

Polycrystalline materials are solids comprised of irregularly shaped anisotropic grains whose principle crystallographic axes are mostly randomly oriented in space. From a properties perspective, these materials may be considered polycrystalline aggregates which act with statistically isotropic properties. Single phase polycrystalline properties can be determined from single phase single crystal properties by averaging techniques which means the integration of directional dependencies. Because all the single phase samples used in this study were polycrystalline, such averaging techniques will not be discussed here; however, well known techniques developed by Voigt, Reuss, and Hill are typically employed.

A convenient estimate of volumetric expansion for polycrystalline and isotropic materials is found by combining ambient temperature immersion density with linear thermal expansion to obtain the volumetric thermal expansion or density as a function of temperature is $3\Delta L/L_o \approx \Delta v/v_o = -\Delta\rho/\rho_o$, where L_o, v_o, and ρ_o is the initial sample length, volume, and density, respectively. The error in making this approximation grows with ΔL as $(\Delta L/L_o)^3$ with the same sign as the linear thermal expansion. For most materials, this error remains extremely small. Even with unalloyed polycrystalline Pu undergoing the transformations from the dense α phase (ρ_o=19.86g/cc) to the less dense δ phase (ρ_o=15.8g/cc), a volumetric change of nearly 20%, the error in the approximation remains less then 0.03% which is much smaller than any of the measurements.

The elastic behavior of the polycrystalline material is determined by properties averaged over the grains and the bonding between grains, but spatial scale is also important. For elastic properties of polycrystalline materials determined by resonance methods such as RUS, an inhomogeneous material looks homogeneous to a propagating wave when the wavelength of the acoustic wave is much greater than the length scale of the features of inhomogeneity. In order to determine that length scale, Ulrich, et. al. [3] made the following conservative estimate: for a one-dimensional elastic medium with free boundaries, the resonance wavelength of a standing wave is $\lambda=2l/n$, where l is the length of the sample and n is an integer number of nodes in the standing wave. In utilizing RUS, the first ten resonance frequencies are sufficient to accurately determine two elastic constants. Based on this practice and the resonance wavelength of a standing wave, a sample may be considered homogeneous if the maximum size of an inhomogeneity ε is much much smaller than resonance wavelength of a standing wave in the smallest dimension of the sample or $\varepsilon \ll l_{min}/5$, where $l_{\min}$ is the smallest dimension of the sample. Because the smallest samples utilized in the study were of approximate dimensions 3mm x 3mm x 3mm, then $l_{min}/5 = 600\mu m$. The maximum size of an inhomogeneous feature for the materials utilized in this study are grains of size 30μm.

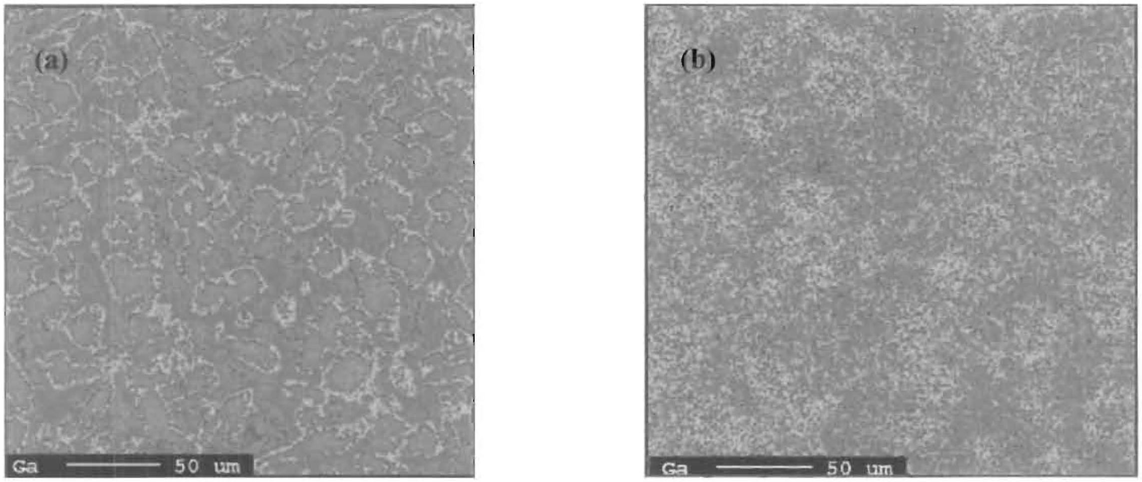

Figure 2. Elemental Ga maps of (a) as-cast and (b) homogenized 1.8at.% Pu-Ga alloys. The darker regions in figure 1 (a) identify areas of higher Ga concentration (up to 2.3at.%) and therefore δ-phase Pu; whereas, the lighter regions identify areas of lower Ga concentration (down to 0.5at.%) and therefore α-phase Pu with soluble Ga. Grains formed are typically ≤30μm in diameter.

Because the thermal expansion is dependent on the initial density of the material and the elastic moduli is dependent on the thermal expansion, there are a system of equations which must be solved concurrently to obtain the correct model for the polycrystalline aggregate. Does the aggregate act as an isotropic medium or anisotropic similar to laminate or fiber composite? For polycrystalline aggregates, the effective density is determined by

$$\rho^{*} = \sum_{i} V_i \rho_i \tag{1}$$

where V_i is the volume fraction of the phase i and ρ_i is the density of the phase i. The effective elastic moduli for a polycrystalline aggregate of two phases are difficult to determine exactly in the general case. [4] As such, lower bound, the Reuss limit, and upper bound, the Voigt limit, for the bulk modulus K and on the shear modulus G are given by,

$$K_R = K_1 + \frac{V_2}{1/(K_2 - K_1) + 3V_1/(3K_1 + 4G_1)} \tag{2}$$

$$K_V = K_2 + \frac{V_1}{1/(K_1 - K_2) + 3V_2/(3K_2 + 4G_1)} \tag{3}$$

$$G_R = G_1 + \frac{V_2}{1/(G_2 - G_1) + 6V_1(K_1 + 2G_1)/5G_1(3K_1 + 4G_1)} \tag{4}$$

$$G_V = G_2 + \frac{V_1}{1/(G_1 - G_2) + 6V_2(K_2 + 2G_2)/5G_2(3K_2 + 4G_2)} \tag{5}$$

where $K_1<K_2$ and $G_1<G_2$. Utilizing these averaging techniques, the effective bulk and shear moduli also are then determined by taking the arithmetic average of K_V and K_R and G_V and G_R, respectively. The values are known individually as the Voigt and Reuss averages, and the combined averages are known as the Voigt-Reuss-Hill values. The Young's modulus and the Poisson's ratio for phase i or for the other averages is given by $E_i=9K_iG_i/(3K_i+G_i)$ and $v_i=0.5(3K_i-2G_i)/(3K_i+G_i)$, respectively.

The thermal expansion coefficient $\alpha=1/L_o\, dL/dT$ for a two phase composite will be given for two cases here, that of an isotropic composite which is

$$\alpha^* = \alpha_1 + \frac{(\alpha_1 - \alpha_2)(1/K^* - 1/K_1)}{(1/K_2 - 1/K_1)} \tag{6}$$

and that of a fiber composite comprised of aligned short fibers which is

$$\alpha_L^* = \alpha_1 + \frac{(\alpha_1 - \alpha_2)}{(1/K_2 - 1/K_1)}\left[\frac{3(1-2v_L)}{E_L^*} - \frac{1}{K_1}\right] \tag{7}$$

where the longitudinal Young's modulus and the Poisson's ratio are given by $E_L^*= V_1E_1+V_2E_2$ and $v_L^*= V_1v_1+V_2v_2$, respectively. [4]

Equations (1) through (7) were solved concurrently to obtain the calculated values against which measured values could be compared. Those calculated and measured value for density, bulk and shear moduli, and thermal expansion are presented in table 1. Measured values for the as-cast 1.8% Pu-Ga alloy were chosen for comparison at near transformation temperatures since the existence of Ga in the lattice influenced thermal expansion at increasing values as seen in the rounding of $\Delta L/L_o$ in figure 1.

Table 1. Measured and calculated thermophysical properties of single and two-phase unalloyed and Ga alloyed Pu.

Phase Mix	Measured Density (g/cm^3)	Calculated Density (g/cm^3)	Measured Bulk Modulus (GPa)	Measured Shear Modulus (GPa)	Calculated Bulk Modulus (GPa)	Calculated Shear Modulus (GPa)	Measured Thermal Expansion Coefficient (x10^{-6}1/K)	Calculated Thermal Expansion Coefficient (x10^{-6}1/K)
α	19.6	-	48 to 82 [2]	40 to 60 [2]	-	-	40 to 60	-
β	17.7	-	34 [6]	17.5 [6]	-	-	36	-
γ	17.3	-	25 [5]	15 [5]	-	-	34	-
δ_{HT}[a]	15.9	-	-	-	-	-	-11	-
δ_{LT}[a]	15.8	-	23 to 37	12 to 20	-	-	8 to -1	-
$0.90\delta_{LT} +0.10\alpha'$	16.2	16.3	-	-	39.4	22.7	16	15.6
$0.81\delta_{LT} +0.19\alpha$	16.4	16.5	33	17	34.7	19.8	20	19.7
$0.81\delta_{LT} +0.19\beta$	16.0	16.1	-	-	27.3	15.4	10 to 40	11.9
$0.81\delta_{LT} +0.19\gamma$	15.9	16.0	-	-	24.4	13.5	12 to 80	12.4

[a] The acronyms δ_{HT} and δ_{LT} stand for the high temperature stabilized δ-phase Pu and the low temperature Ga stabilized δ-phase Pu.

The thermal expansion of the δ_{LT} and α and δ_{LT} and α' samples were fitted best by a aligned short fiber composite described by equation (7) rather than a isotropic composite described by equation (6). This is likely due to the influence of the anisotropic thermal expansion exhibited by α-phase Pu and is best represented by the needle like α' platelets which form during the Martensitic phase transformation $\delta\rightarrow\alpha$' in Pu-Ga alloys.[7]

4. CONCLUSIONS

The thermophysical properties of density, thermal expansion, and elastic moduli for unalloyed and Ga alloyed Pu materials have been measured as a function of temperature. The coexistent phases of the as-cast alloy Pu-Ga alloy exhibits a crossover behavior between the unalloyed and homogenized alloy the measured thermophysical properties. Although the materials studied exhibit phase segregation, the heterogeneity was on a sufficiently small scale not to be influential on the elastic moduli; however, the anisotropy of the monoclinic phase was a likely cause for a larger thermal expansion than would be expected for an isotropic composite.

Acknowledgments

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