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ON GALLIUM IN THE ALPHA AND DELTA PLUTONIUM LATTICE

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INTRODUCTION

The stability of delta-phase plutonium-gallium alloys is a subject of great interest to plutonium metallurgists. A survey of progress on the subject could begin with reference to the paper by Goldberg and Shyne¹ and the use of the references given in that paper.

The present effort introduces some general ideas that are offered in an attempt to further an understanding of the nature of the delta-phase plutonium-gallium alloys and their stability. Special attention is given to a hypothesis relating to the role of gallium atom positions in the plutonium lattice.

GALLIUM SITES

One can consider where the gallium atoms might be located in delta-phase alloys. The gallium atom is too large to be an interstitial atom in delta plutonium, so it should substitute for plutonium atoms in the delta unit crystal cell. The limit of this substitution is found to be about 12.5 atomic percent,² or the replacement of one-eighth of the plutonium atoms in the structure. (This limit might be considered a gallium-saturated delta phase at 655°C.) Thus, when more than 1 gallium atom per 2 delta unit cells is present, the Pu_3Ga compound* with 1 gallium atom per unit cell can form. The structural change from the delta cell to the Pu_3Ga cell is interesting to contemplate. One imagined change is shown in Figure 1.

In the gallium-saturated delta cell just imagined, the gallium atoms have been located where they are surrounded with plutonium atoms, and the cell symmetry is preserved. Why is this choice made instead of random or clustered locations? The answer is suggested by considering the volume change of the delta structure as gallium is added.

*Cubic AuCu_3 type (363-677°C), or tetragonal Sr Pb_3 type (below 363°C).³

- Plutonium sites.
- x Gallium sites in saturated delta phase.
- Additional gallium sites to form Pu_3Ga .

Fig. 1 - Hypothetical change from delta to Pu_3Ga structure on the addition of gallium atoms. Eight delta cells shown and two Pu_3Ga cells shown. Lattice dimensions change slightly on formation of Pu_3Ga .

Data by Ellinger, et al,² reveal that the addition of gallium to delta plutonium results in a greater decrease in volume than obtained for the calculated additive value of gallium.* In effect, this is a negative deviation from Vegard's Law. The negative deviation is an indication that the attraction between gallium and plutonium atoms in the delta-phase structure is greater than the attraction of the similar atoms. Therefore, one would expect a tendency for the gallium atoms to be surrounded by plutonium atoms. This would be a short-range order for these delta-phase alloys. The negative deviation also is taken as evidence of an exothermic reaction as gallium is added to the delta structure; a theoretical point of minor practical importance.

For a model, the gallium atoms are imagined to occupy various lattice sites of the face-centered-cubic structure and to tend to have nearest neighbors of plutonium atoms.

EFFECT OF PRESSURE

If sufficient isostatic pressure is applied to the plutonium-gallium delta-phase alloys at ambient temperatures, at least some of the structure transforms to alpha. This skip transformation has a reversible tendency when the pressure is released, especially for the alloys with more than 1 atomic percent of gallium.

The direct transformation from delta to alpha phase seems surprising because the face-centered-cubic delta lattice appears so unrelated to the monoclinic alpha lattice. However, as shown by Lomer,⁴ there is a correspondence of the structures. Spriet⁵ diagrammed this shear-shuffle correspondence, and one can see that a number of atom shuffles of less than atomic-diameter distance would also suffice geometrically for the transformation. Whatever the actual mechanism, the skip transformation seems reasonable to imagine.

*See Appendix.

When the delta phase is transformed by pressure to alpha phase at ambient temperature, 4 delta unit cells could transform to 1 alpha cell. Now the gallium atoms are sited in an alpha cell because diffusion processes are kinetically slow at such temperatures.

While atoms in a face-centered-cubic delta cell have similar geometric environments, those in the monoclinic alpha cells have 8 different types of environments. If a gallium atom is substituted for a plutonium atom in an alpha lattice under equilibrium conditions, it is suggested that one of the 8 types of sites might be a preferred position.

In the transformation of delta cells to alpha cells, one can readily imagine that a gallium atom sited somewhere in 4 delta cells will not be found necessarily on its preferred site in the alpha cell. In a Pu-1 wt % Ga alloy, there is a chance of about 1 in 8 that a gallium atom would occupy a delta cell site that could ultimately be a gallium-preferred alpha cell site. Short-range diffusion promoted by heating could result in the movement of the gallium to preferred sites in alpha cells, if the hypothesis is valid. Pressure would be needed to retain the alpha phase in an attempt to use heat to move the gallium to preferred sites.

Of the 8 different sites in alpha cells, there may be a range of preference for gallium sites. Also, the alpha cell is made up of sixteen atoms with pairs of atoms having similar environments. This would allow 2 most-preferred sites for gallium atoms per alpha cell. The composition would be 12.5 atomic percent which, coincidentally, is the saturation limit for delta phase. No significance of this observation is suggested.

SUMMARY

An interesting circumstance dealing with gallium atom positions in delta-and-alpha-phase plutonium-gallium alloys is hypothesized. The hypothesis can be considered as studies of the delta to alpha transformation and its reversion are carried out.

APPENDIX

In a classic treatment of the study of binary solid solutions, one can plot the volume of 1 gram mole of a solution against the atomic percent composition. Such a plot for Pu-Ga and Pu-Al delta phase alloys is shown in Figure 1, (Appendix), which is based on Ellinger, et al,^{1, 6} x-ray data. The volume, V , of 1 gram mole of the Pu-1 wt % Ga alloy, which is 14.8 cm³, consists of the volume occupied by the Pu atoms plus the volume occupied by the Ga atoms. The apparent volume which would be occupied by 1 gram mole of Pu in this alloy solution, is the partial molar volume of Pu and is termed $\bar{V}_{Pu}$. Similarly, we have $\bar{V}_{Ga}$.

Mathematically,

$$\bar{V}_{Pu} = \left\{ \frac{\partial V}{\partial n_{Pu}} \right\}_{T,P,Ga} \quad \text{and} \quad \bar{V}_{Ga} = \left\{ \frac{\partial V}{\partial n_{Ga}} \right\}_{T,P,Pu}$$

$\bar{V}_{Pu}$ is the rate of increase in the volume of the solution when an infinitesimal amount (dn_{Pu} moles), of Pu is added. When small amounts dn_{Pu} and dn_{Ga} of Pu and Ga are both added, the change in the volume of the solution, ΔV , is

$$\Delta V = \bar{V}_{Pu} dn_{Pu} + \bar{V}_{Ga} dn_{Ga}$$

Since the values of $\bar{V}_{Pu}$ and $\bar{V}_{Ga}$ depend only on the composition of the solution, and if the constituents are added simultaneously, in the same proportion as they are present in the alloy, then

$$V = \bar{V}_{Pu} N_{Pu} + \bar{V}_{Ga} N_{Ga}$$

where N_{Pu} and N_{Ga} are the mole fractions of Pu and Ga in the solution.

The values for $\bar{V}_{Pu}$ and $\bar{V}_{Ga}$ can be obtained graphically by drawing tangents to the curves for each composition and finding the intersections at $N_{Pu} = 1$, and

$N_{\text{Ga}} = 1$. In Figure 1, (Appendix), because of the linearity, we can simply extrapolate the curves. The values found are $\bar{V}_{\text{Pu}} = 15.05 \text{ cm}^3$, and $\bar{V}_{\text{Ga}} = 6.66 \text{ cm}^3$. We would like to compare this $\bar{V}_{\text{Ga}}$ with the molar volume of *pure* gallium in the face-centered-cubic structure but pure gallium does not exist in the face-centered-cubic structure. Thus, we turn to a similar review of the situation for the delta-phase Pu-Al alloys.

Referring to Figure 1, we can obtain a $\bar{V}_{\text{Al}}$ of 8.12 cm^3 , compared to V_{Al} of 10 cm^3 . Aluminum atoms are thus indicated to have a *smaller* apparent molar volume in the alloy than would be the case for an ideal solid solution where $\bar{V}_{\text{Al}}$ would equal V_{Al} . Because of the related nature of aluminum and gallium (valence + 3, amphoteric, corrosion films, periodic table association), we argue that it seems reasonable that gallium might also have smaller $\bar{V}$'s in the delta-phase Pu-Ga alloys. Therefore, if we alloy plutonium with gallium, we assume that the volume of the delta-phase alloy is less than the sum of the individual volumes of the metals before alloying, assuming a hypothetical face-centered-cubic volume for the gallium. Assuming this contraction of the molar volume of the mixture, we suggest that the attractive force between plutonium and gallium atoms in solution may be greater than the attractive force in either pure metal. This is the usual case for binary metal solid solutions. (A better expression of this situation is that the total energy of the solution is lower when the atoms are distributed on lattice sites in such a way as to increase the number of dissimilar atoms that form nearest neighbors).

This conclusion, if valid, would mean that in homogenized delta-phase Pu-Ga alloy, we would expect gallium atoms to be surrounded with plutonium atoms rather than adjacent to other gallium atoms. Obviously, this would not be a

Fig. 1 (Appendix) - Molar volumes of Pu-Be and Pu-Al delta phases. From computer plot of X-ray data. Data are extrapolated beyond about 10 atomic percent.

random distribution (which would have to allow some adjacent gallium atoms). Thus, we tentatively conclude that a short-range, even distribution seems reasonable if only in the sense that the gallium atoms might avoid being closest neighbors.

For our best model, we can imagine gallium atoms occupying various lattice sites of the face-centered-cubic structure and having nearest neighbors of plutonium atoms.

REFERENCES

1. Alfred Goldberg and John C. Shyne, Thermodynamic Analysis of Stress and Pressure Effects on the Delta to Alpha Transformation in Plutonium Alloys, Journal of Nuclear Materials, Vol. 60, (1976) p. 137-144.
2. F. H. Ellinger, C. C. Land, and V. O. Struebing, The Plutonium-Gallium System, Journal of Nuclear Materials, Vol. 12, No. 2, (1964) p. 226-236.
3. O. J. Wick, ed., Plutonium Handbook, Gordon and Breach, New York, (1967), Vol. 1, p. 206.
4. W. M. Lomer, Solid State Communications, Vol. 1, No. 96, (1963).
5. B. Spriet, Study of Allotropic Transformation of Plutonium, Plutonium 1965, A. E. Kay and M. B. Waldron, eds., Chapman and Hall, London, (1967), p.88.
6. F. H. Ellinger, C. C. Land, and W. M. Lomer,
The Solubility Limits of Aluminum in Delta Plutonium and Some Revisions of the Plutonium-Aluminum Phase Diagram, Journal of Nuclear Materials, Vol. 5, No. 2, (1962), p. 165-172.