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Connections between the Pu–Ga phase diagram in the Pu-rich region and the low temperature phase transformations

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Abstract

Significant progress has been made in recent years regarding the equilibrium phase diagram of the Pu–Ga system. For decades, researchers outside of the former Soviet Union considered the δ phase in Pu–Ga alloys to be in the state of thermodynamic equilibrium down to low temperatures. Recently, decades of experimental work in Russia have been published that indicate the existence of a eutectoid decomposition of the metastable δ phase to α phase and Pu_3Ga. Phase diagram calculations by a number of researchers have predicted this eutectoid transformation as well. In this work, we review the experimental and calculated phase diagrams and also comment on the expected consequences of the IIIrd law of thermodynamics with respect to the form of the delta phase field. Assembled data from the literature on the martensite start (M_S) and reversion (R_S) temperatures for the $\delta \rightarrow \alpha'$ transformation as a function of Ga content are used to consider the possible trend of the T_0 line describing the equivalence of the free energies of the α and δ phases in the phase diagram. It is suggested that in order to reconcile the need for the existence of a driving force for both the compositionally variant eutectoid reaction, as well as a compositionally invariant martensitic transformation in a Pu—2 at.% Ga alloy, the actual T_0 line may lie higher than that indicated by the present thermodynamical modeling.

Keywords: Actinide alloys and compounds; Phase diagrams; Phase transitions; Solid-state reactions; Thermodynamic properties

1. Introduction

Several papers [1–11] have addressed the Pu–Ga phase diagram, both experimentally and (increasingly) theoretically. Of special interest is the Pu-rich portion, say up to ∼10 at.% Ga. A few details here are still not accurate enough, yet the phase diagram in this range of composition is an important basis for the understanding and interpretation of phase transformations, pre-transformation effects, conditioning of samples, the behavior of martensitic transformations, and the results of various property measurements. The observed behaviors of samples heat treated both above and below the ambient temperature, and particularly if cooled to temperatures well below the ambient, can be often related to the details of the phase diagram.

2. The phase diagram

The most up-to-date information on the Pu–Ga-rich portion of the phase diagram is presented in the well-known publication “A Tale of Two Diagrams” (Fig. 1) [3]. Fig. 1a is based on Ellinger’s early work [1] and on subsequent assessment by Peterson and Kassner [8]. These authors refer to Ref. [2], but do not comment on the form of the δ phase field in this diagram, nor the occurrence of the eutectoid reaction. However, the extensions of the phase boundaries of this phase to very low temperatures have been questioned recently and are clearly highly improbable as proposed if one considers the restrictions imposed on solid solubility and phase boundaries by the Nernst Principle and the IIIrd law of thermodynamics (see for example, Abriata and Laughlin [9]). Essentially, because the entropy of mixing is dictated to be zero at 0 K, all random solid solubility is excluded and is reduced to pure elements, or perfectly ordered compounds. There are two possible solutions that conform to the IIIrd law. One can assume that the delta-phase field will progressively narrow and converge to a single point at 0 K corresponding

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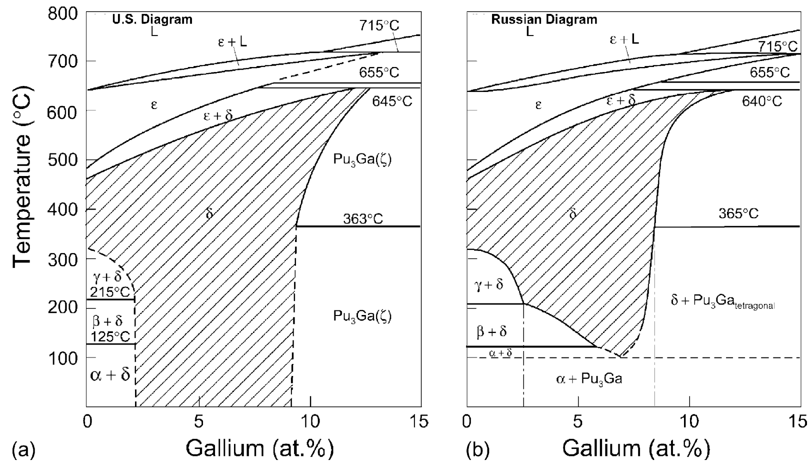

Fig. 1. Phase diagrams as discussed in "A Tale of Two Diagrams" by Hecker and Timofeeva [3]. The phase diagram shown in (a) is considered a "working" phase diagram because the δ phase can be retained to room temperature in a metastable state for extended periods of time. The diagram in (b) exhibits a eutectoid transformation in which the metastable δ phase will decompose to α-Pu and Pu_3Ga.

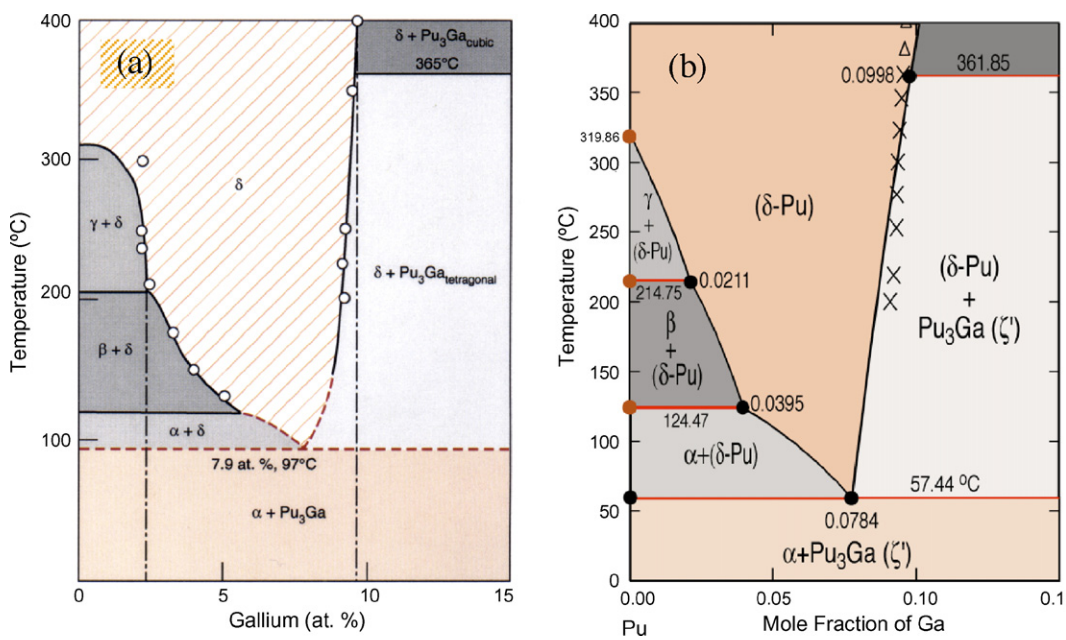

Fig. 2. (a) Proposed equilibrium phase diagram including experimental data points [3,10]. (b) Calculated phase diagram [7] also including experimental data points.

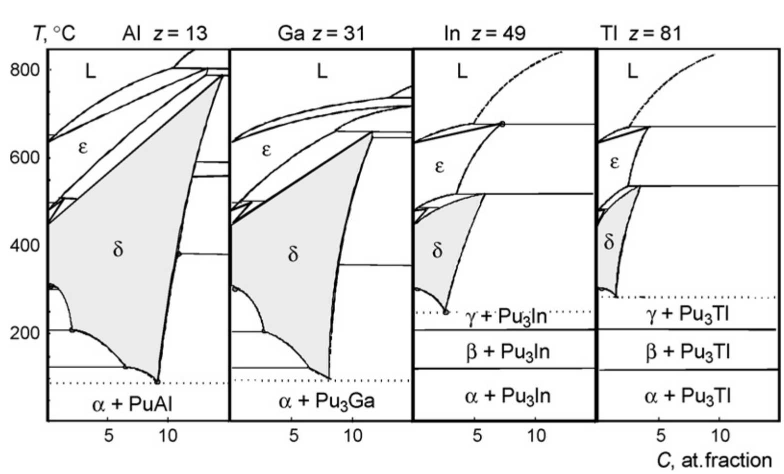

Fig. 3. Proposed phase diagrams of Pu alloys with Al, Ga, In, and Tl [11] illustrating the influence of alloying element on the δ phase stability.