

Phase transformations in Pu–Ga and Pu–Al alloys Effects of pressure and temperature on kinetics of δ -phase decomposition

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Abstract

Pressure effected evolution of equilibrium and metastable binary Pu–Ga (Al)-phase diagrams is discussed. With an increase in pressure δ -solid solution region decreases and disappears, which leads to a change of phase diagram type. In experiments and via thermodynamic calculations boundaries of δ -phase region were established at pressure varying from the atmospheric one to ~ 1 GPa. Temperature of δ -phase eutectoid transformation versus pressure was determined; a fragment pressure–temperature–composition (*PTC*) diagram was constructed, parameters of four-phase equilibrium were found. Influence of static pressure on δ -phase decomposition kinetics is demonstrated, feasibility of decomposing effected by loading with high intensity waves is assessed.

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1. Introduction

The incentive of this work was to get profound apprehension and conception of low temperature transformations in δ -phase plutonium alloys with gallium (or aluminium) with account for their changes at pressure. It was previously demonstrated [1–3] that under atmospheric pressure the thermodynamically equilibrium state in these system is eutectoid (ED) (α -Pu + Pu₃Ga) or (α -Pu + PuAl). However, at low temperatures below ~ 100 °C the diffusion decomposition of the δ -phase to form eutectoid is hard to reach because of the kinetics of the process and elastic stresses effected by high volume changes during transformation. The phase transformation is delayed in time since the origination of newly come phase nuclei and their subsequent growth is made difficult or impossible. The supercooled and retained from high temperatures δ -phase proves to be in the metastable state that features a relative minimum of Gibbs energy, is rather stable and might be retained for a very long period of time.

Pressure rises the ED transformation temperature and accelerates the δ -phase decomposition. Due to this under conditions

of anneal under pressure the equilibrium state is readily achievable. The accomplishment of the equilibrium ED transformations at different pressures allows regularities to be established and prediction of a transformation mode at the atmospheric pressure.

In terms of this, a schematic conception is given pertaining to the pressure effected evolution of the equilibrium and metastable binary Pu–Ga (Al) diagrams, a change is demonstrated in the δ -phase region boundaries constructed experimentally or thermodynamically calculated with the static pressure being increased, the static pressure is shown to influence the kinetics of the δ -phase decomposition and the feasibility of decomposing is assessed upon loading with high intensity waves.

Accordingly, the paper consists of three sections: (1) evolution of phase diagrams (PD) under pressure, (2) experimental determination of δ -region boundaries and thermodynamic calculation, and (3) kinetics of δ -phase decomposition under pressure.

2. Evolution of phase diagrams under pressure

The phase diagram of the binary system at the atmospheric pressure is one of the sections of the pressure–temperature–composition (*PTC*) diagram and is a result of the regular

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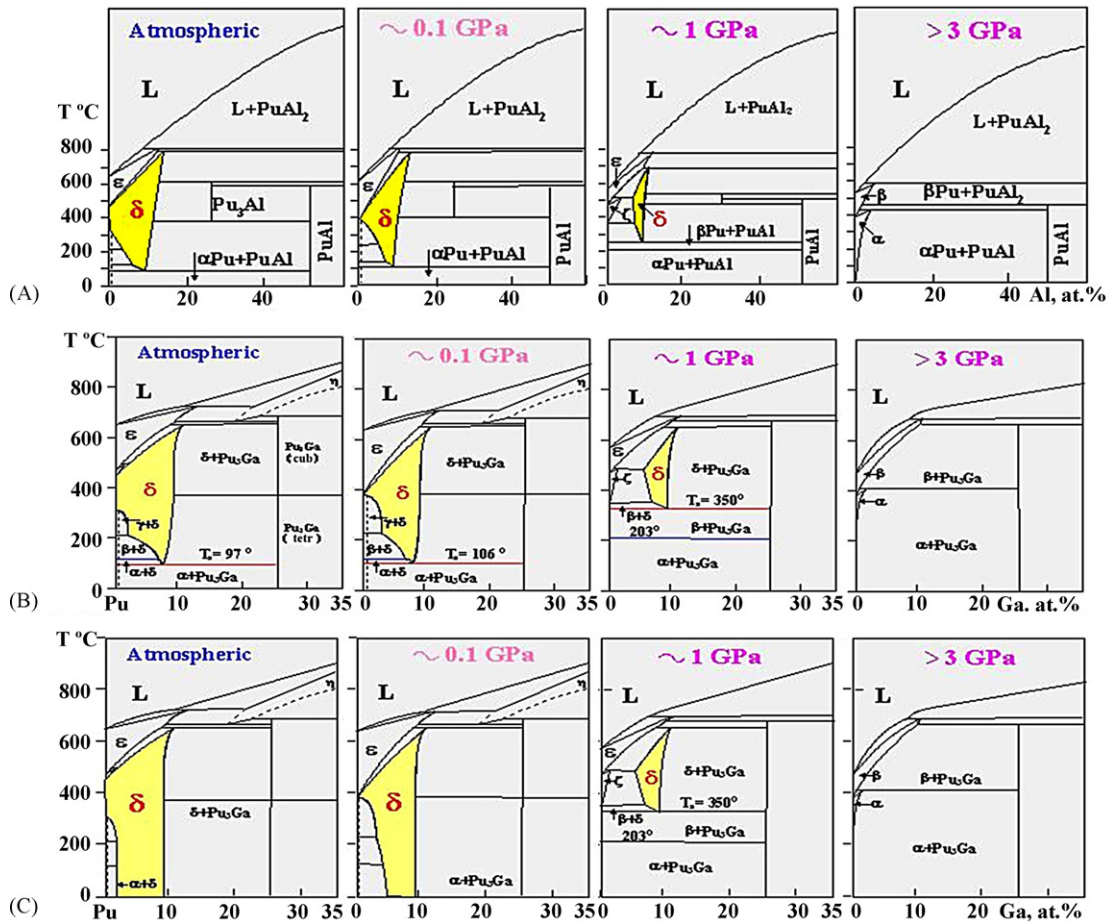


Fig. 1. Evolution of binary diagrams with pressure: (A) Pu–Al, at P_{atm} —eutectoid; (B) Pu–Ga, at P_{atm} —eutectoid; (C) Pu–Ga, at P_{atm} — δ -solid solution.

variation of the phase regions in space. Consideration is given to a series of schematic isobaric sections of the Pu–Ga and Pu–Al systems in the range of pressures up to $P \geq 3$ GPa that were constructed on the basis of the PT diagram of plutonium, experimentally found TC diagrams of the binary systems at atmospheric pressure with account for the PC diagrams of the δ -phase alloys [1–5] (Fig. 1).

The PT diagram of plutonium determines the constitution of isobaric sections (PD at $P = \text{const}$) in the space PTC diagram of binary systems. With a pressure rise as phases are disappearing from Pu the kind of the binary phase diagram alters; the eutectoid type diagram that is intricate at the atmospheric pressure transforms to an adequately simple one at high pressures. With a decrease and disappearance of the δ -phase region as the pressure rises it might become a peritectoid type diagram, see Fig. 1.

The triple points available on the PT diagram of plutonium define qualitative changes in the PD construction at different pressures. Thus, in the triple point at $P \sim 0.1$ GPa where the δ -phase disappears from plutonium on the isobaric sections of the Pu–Ga and Pu–Al diagrams four lines of solubility emanate from a single temperature point on the axis of Pu (Fig. 1). On the PT diagram of plutonium there are six triple points such as those ones; on the isobaric sections passing through each of them, four lines might emanate, if alloying elements

are soluble in plutonium phases that participate in the ternary equilibrium.

The evolution of the phase diagram in Fig. 1A–C inevitably leads to the fact that between the pressures of 0.1 and 1 GPa a section has to be where the temperatures of the δ -phase eutectoid decomposition and of the $\alpha \rightarrow \beta$ transformation coincide, i.e., at the same temperature four phases— α , β , δ and Pu₃Ga (or PuAl) are in equilibrium which corresponds to the four-phase equilibrium on the PTC diagram of the binary system.

It is characteristic that as the pressure increases and the ED decomposition temperature rises, beginning with a certain pressure the PD kind will be identical for different versions of the diagrams at the atmospheric pressure: metastable or equilibrium initial states, as is shown in Fig. 1B and C for Pu–Ga alloys.

The resultant conceptions of the PD evolution under pressure were used for the experimental construction of PD for different pressures.

3. Experimental determination of δ -region boundaries and thermodynamic calculation

Proceeding from the results of isothermal anneals under conditions of static pressures in the range from the atmospheric one to 0.6–0.8 GPa the boundaries of the δ -region were constructed for Pu–Ga and Pu–Al systems (Fig. 2). Using the method of

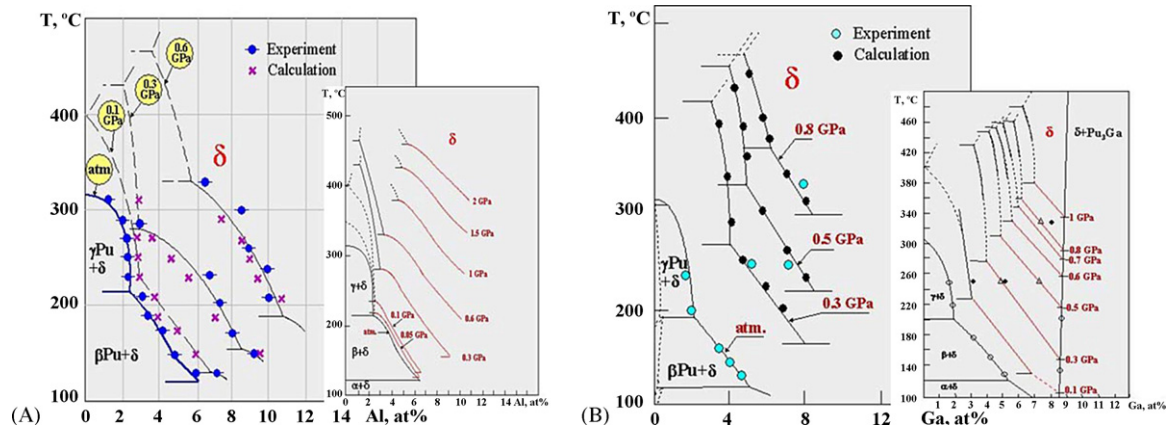


Fig. 2. δ -Phase boundary displacement, experiment and calculation: (A) Pu–Al system; (B) Pu–Ga system. Insertions: calculated lines of solubility for $P = 1\text{--}2$ GPa.

thermodynamic calculation that demonstrated a good agreement with the experiment the displacement of the δ -region boundaries was assessed up to the pressures $P \cong 2\text{--}3$ GPa by L. Kaufman method. The δ -region boundary on the plutonium side is displaced to the side of higher concentrations of Al or Ga while on the side of intermetallics the displacement is insignificant to the side of Pu. The δ -phase region is diminishing up to the disappearance. Via intersecting the boundaries in $N_{\text{mol}}^{\text{Al(Ga)}} - 1/TK$ coordinates the temperatures of the eutectoid decomposition (T_{ED}) of the δ -phase were determined at different pressures and T_{ED} versus pressure plots were constructed for both the systems of the alloys (Fig. 3). In the figure, the dependences of the temperatures of the $\alpha \rightarrow \beta$ transformation of unalloyed plutonium and the $\alpha + \delta \rightarrow \beta + \delta$, $\alpha + \text{Pu}_3\text{Ga (PuAl)} \rightarrow \beta + \text{Pu}_3\text{Ga (PuAl)}$ transformation of Pu–Ga and Pu–Al alloys versus pressure are plotted. In essence, they are PT diagrams of binary systems in a

low temperature range on the plutonium side and represent projections on the PT plane of the surfaces of three-phase equilibria that characterize the volume PTC diagrams.

The parameters of the four-phase equilibrium (δ , α , β , Pu_3Ga or PuAl) at point “H” on PT binary Pu–Ga, Pu–Al diagrams were determined. Point “H” is a projection on the PT plane of the HH line of the intersection of two surfaces of three-phase equilibria on the PTC diagrams (Fig. 3). This is an important (key) point that is related to the transformation kinetics since below the pressure at the “H” point the eutectoid decomposition of the δ -phase proceeds via the $\delta \rightarrow \alpha\text{-Pu} + \text{Pu}_3\text{Ga}$ (PuAl) reaction while above the “H” point it proceeds via the $\delta \rightarrow \beta\text{-Pu} + \text{Pu}_3\text{Ga}$ (PuAl) reaction. In the latter instance upon the formation of β -Pu volume changes are less than upon the formation of α -Pu, accordingly, the role of elastic stresses diminishes and the ED transformation of the δ -phase proceeds at a higher rate.

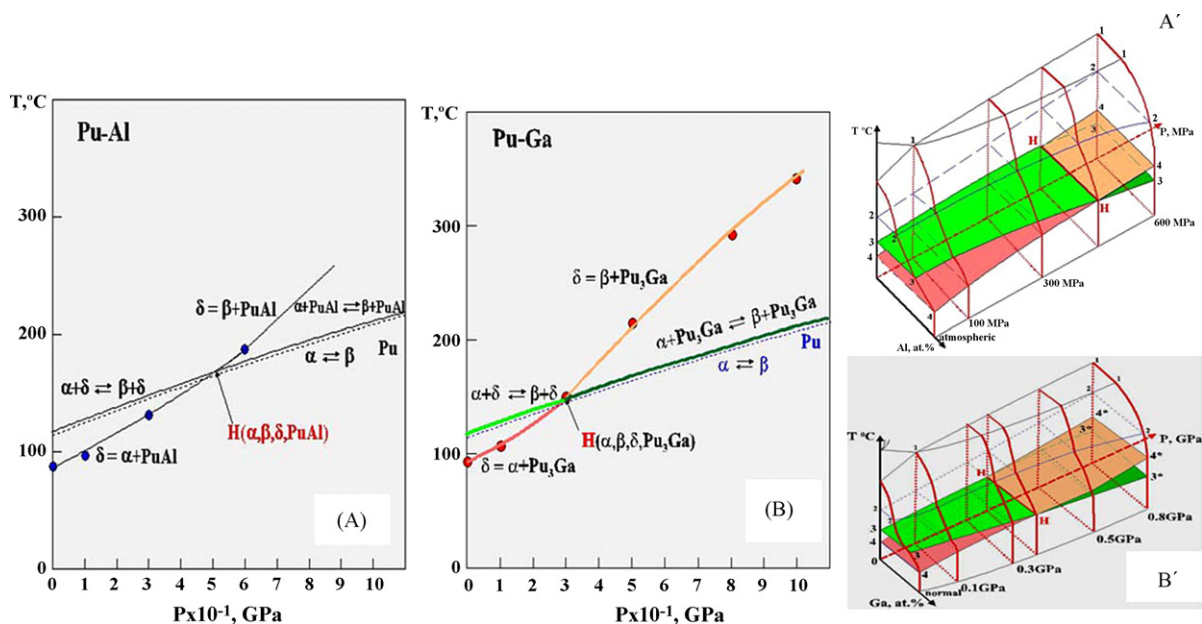


Fig. 3. Effect of static pressure P on T_{ED} and $T^{\alpha \rightarrow \beta}$ Pu; PTC diagram: (A and A') Pu–Al system; (B and B') Pu–Ga system. Equilibrium planes correspond the reactions—33HH: $\alpha + \delta \rightarrow \beta + \delta$; HH3*3*: $\alpha + \text{Pu}_3\text{Ga} \rightarrow \beta + \text{Pu}_3\text{Ga}$; 44HH: $\delta \rightarrow \alpha + \text{Pu}_3\text{Ga}$; HH4*4*: $\delta \rightarrow \beta + \text{Pu}_3\text{Ga}$.

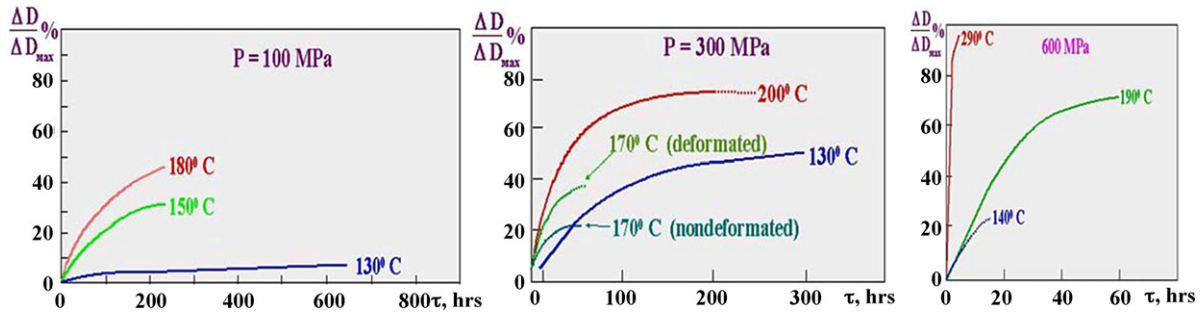


Fig. 4. Effect of temperature and pressure on kinetics of δ -phase decomposition, Pu–Al alloys.

4. Kinetics of δ -phase decomposition

The availability of equilibrium or metastable states is related to the specific features inherent in the phase transformations. A higher solubility of alloying elements on the δ -phase boundary on the plutonium side and the displacement of the boundaries with an increase of the pressure lead to a change in the kinetics of phase transformations of solid solutions. The pressure noticeably reduces the size of the newly formed phase centre at which the limiting role of the lattice restructuring is replaced by the limiting effect of a diffusion growth.

It has been established experimentally [2,3] that with temperature and pressure increases both in Pu–Ga and Pu–Al alloys the rate of the diffusion decomposition of the δ -phase becomes higher and the process mode alters. The incubation period of the decomposition reaction of the δ -solid solution $\delta_0 + \alpha'(\beta') \rightarrow \delta_x + \alpha(\beta)_{eq}$ is shortened from hundreds of hours at 150 °C, atmospheric pressure to several minutes at $P=0.6$ GPa (Fig. 4). The activation energy of the process determined for Pu–Al alloys in two ways, i.e., by Avrami equation and the method of isothermal cross-section, drops from 30 kcal/mol at 0.1 GPa to 8 kcal/mol at $P=0.6$ GPa.

At relatively low pressures the alloys of both the systems are subject to eutectoid decomposition. The eutectoid morphology in the systems differs, viz., in Pu–Ga alloys of the hypoeutectoid composition it is a typical platelet eutectoid at a pressure

a little higher than 1 GPa, in Pu–Al alloys it is a skeleton-like spheroidized one due to a long-term anneal at a pressure of 25–30 GPa (Fig. 5).

With account for the accelerated decomposition and a decrease in the process activation energy with a rise of pressure it is of interest to discuss an issue of a feasible diffusion ED transformation of the δ -phase under conditions of shock-wave loading. At a first glance, it seems that this is not feasible since the δ -solid solution exists in a space limited by temperature, pressure and composition, and the heating rate under conditions of adiabatic loading is enormous. However, upon shock-wave loading proceed that create some preconditions for the ED transformation of the δ -phase. They entail the following: (1) several times accelerated diffusion rate which is evidenced, e.g., by a growth of filamentary crystals in the centre of a sphere in samples loaded by a shock wave [5]; (2) formation of huge quantities of sites for nucleation of new phases due to formation of a finer structure [7,8]; (3) decrease in activation energy of ED transformation with pressure; (4) elastic stress reduction which facilitates decomposition conditions due to less volume changes as a result of $\alpha \rightarrow \beta$ transformation with a growth of pressure according to the equation $\Delta V/V=9.2 - 0.17P$ [6]; (5) extension of a region of $\alpha'(\beta')$ solid solutions that form as a result of non-diffusional transformation of the δ -phase at relatively low pressures and the opened up potential for a diffusion decomposition of already $\alpha'(\beta')$ -phase Pu.

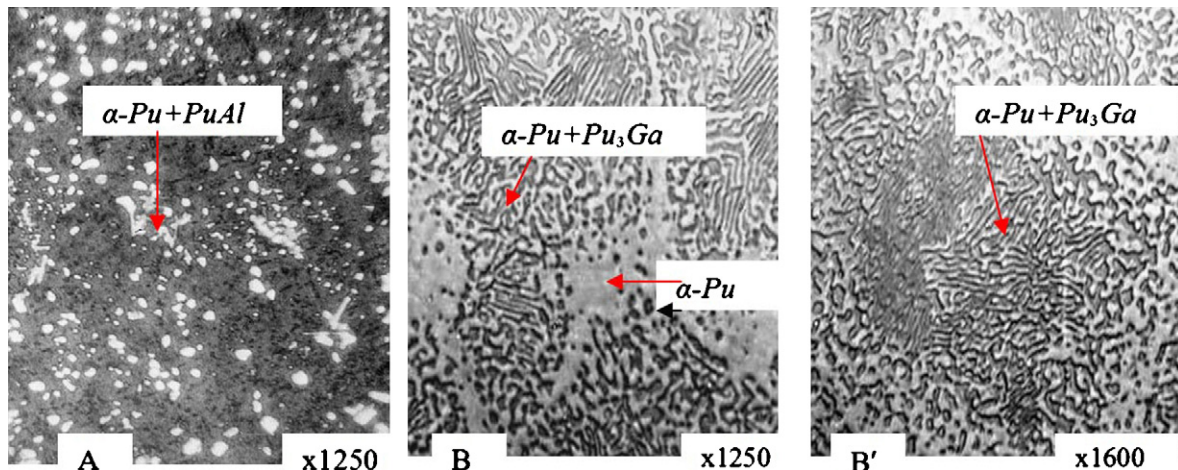


Fig. 5. Microstructure of hypoeutectoid alloys: (A) Pu–Al, the anneal under $P=2.5$ GPa, eutectoid α -Pu + PuAl; (B and B') Pu–Ga, the anneal under $P \geq 1$ GPa, eutectoid α -Pu + Pu₃Ga.

The identification of such regions evidencing the ED decomposition in samples subjected to shock-wave loading is of high scientific interest as it extends our conception of how pressure influences the kinetics of diffusion phase transformations.

5. Conclusions

Experimentally and by methods of thermodynamic calculation and analysis it is established that with a pressure rise the boundaries of δ -solid solution region on PD of binary Pu–Al and Pu–Ga systems are displaced in the regular way, the temperature of ED transformation becomes higher, the δ -phase region is reduced and disappears at specific pressures. The eutectoid type diagram transforms into diagram of peritectoid type.

As pressure increases the diffusion decomposition of δ -phase accelerates, the process activation energy and the extent of volume changes as well as elastic stresses that attend the transformation decrease. Pressure dependences of ED temperature have been established experimentally and fragments of Pu–Al and Pu–Ga *PTC* diagrams on the side of Pu have been constructed. The parameters of the four-phase equilibrium were determined at a point on the *PT* diagram of binary alloys and on the *PTC* diagram along the line of the intersection of two surfaces of

three-phase equilibrium. Above this line the ED transformation conditions are facilitated. The role of equilibrium states is shown to grow with pressure and temperature. As pressure lowers down to the atmospheric one the transformation kinetics slows down, the role of metastable equilibria is reinforced and to reach the thermodynamically equilibrium state becomes difficult.

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