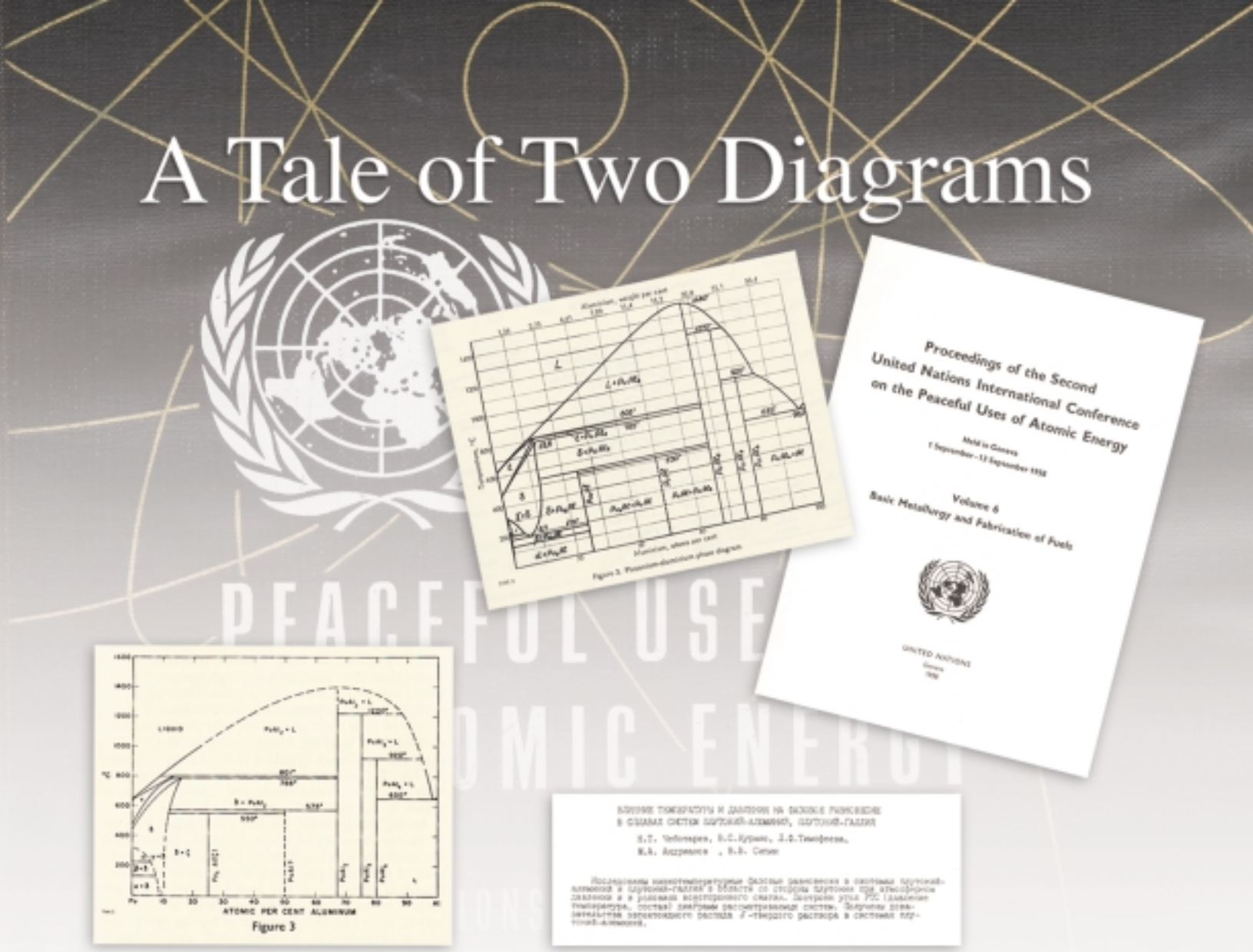
A Tale of Two Diagrams



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It is difficult to believe that in 1999, more than 50 years after the Manhattan Project, the authors as well as other scientists from Russia and the United States still disagreed about the stability of the δ-phase plutonium-gallium (Pu-Ga) alloys used in nuclear weapons. Typically, the face-centered-cubic (fcc) δ-phase of plutonium, which is malleable and easily shaped, is retained down to ambient temperatures by the addition of gallium or aluminum. But do those δ-phase alloys remain stable for decades or do they decompose into the denser, brittle α-phase and something else at ambient temperature? A crucial part of the answer lies in the equilibrium binary phase diagrams for the Pu-Ga and plutonium-aluminum (Pu-Al) systems. Unfortunately, two very different versions of those phase diagrams have existed for several decades—one measured in the laboratories of the United States, the United Kingdom, and France and the other in the laboratories of the former Soviet Union (now Russia).

During the first 10 years following World War II, Soviet, American, and British scientists worked in secret to develop a wide range of technologically important phase diagrams for plutonium alloyed with other elements. In 1953, the door for scientific collaboration opened. That year, President Eisenhower spoke to the United Nations, proposing an international effort to promote the peaceful uses of atomic energy. Encouraged by conferences on this topic sponsored by the United Nations, Soviet researchers (Academician A. A. Bochvar, member of the Soviet Academy of Sciences, and S. T. Konobeevsky, a corresponding member) presented their work on plutonium phase diagrams in Moscow (Konobeevsky 1955) and then in Geneva (Bochvar et al. 1958). After the 1955 conference, American and British researchers followed suit at various national and international conferences (Coffinberry et al. 1958).

F. W. Schonfeld of Los Alamos reviewed the early work (1961a, 1961b) and noted that the predictions of δ-phase stability differed significantly in the Soviet and U.S. Pu-Al equilibrium diagrams: "…although it is to be expected that these differences will soon be

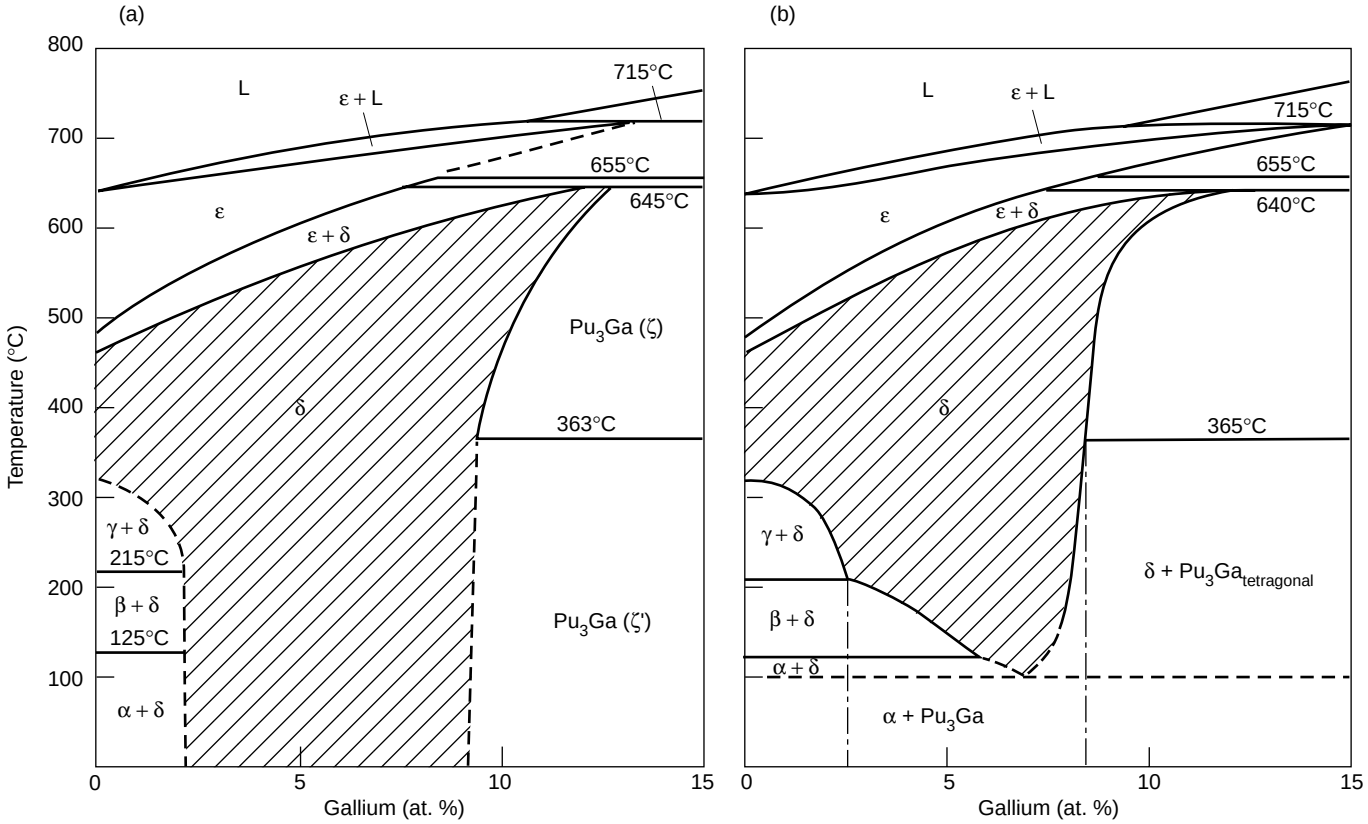

Figure 1. U.S. and Russian Equilibrium Pu-Ga Phase Diagrams

The U.S. equilibrium Pu-Ga phase diagram in (a) was reported by Peterson and Kassner (1988) and is based on the work of Ellinger et al. (1964). The Russian phase diagram in (b) was reported by Chebotarev et al. (1975). The principal difference is that Ellinger et al. found the fcc δ-phase to be retained at room temperature by gallium concentrations greater than approximately 2 at. % and less than approximately 9 at. %, whereas Chebotarev et al. reported a eutectoid decomposition of the δ- to the α-phase plus Pu_3Ga below 100°C. Both diagrams have dashed lines at the lower end of the temperature spectrum because diffusion processes become so slow that it is very difficult to determine what the real "equilibrium" structure is. So, both diagrams represent extrapolations to equilibrium—but with very different conclusions. The dash-dotted lines in (b) represent the metastable phase boundaries.

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resolved through the performance of further experimental work in both countries, it is difficult at this stage to speculate in any particular case regarding the probable outcome of such further work." What Schonfeld thought would be resolved "soon" took almost another 40 years. The tale of two diagrams is fascinating from both a scientific and a social perspective.

Why Is It Important to Know if δ-Plutonium Decomposes?

During aging, thermally activated kinetic processes are at work, constantly trying to drive the solid toward equilibrium (its lowest-energy configuration). Hence, any nonequilibrium structures are subject to change during aging. One of the greatest concerns about plutonium and its alloys is phase stability because the large volume changes that accompany phase changes can compromise structural integrity. During the Manhattan Project (and later in the corresponding project in the Soviet Union), gallium was purposely added to plutonium to retain the fcc δ-phase down to ambient temperatures, making it possible to shape plutonium into requisite shapes. The monoclinic α-phase of pure plutonium was brittle and totally unwieldy from a metallurgist's viewpoint. Because of its relevance to nuclear weapons, the Pu-Ga diagram was not reported by either country until both sides realized that the omission itself signaled its appeal to their nuclear weapons programs.

By 1964, U.S. researchers published the Pu-Ga phase diagram in the open literature (Ellinger et al. 1964), showing that gallium, just like aluminum, retains the fcc δ-phase to room temperature. French researchers published very similar results (Hocheid et al. 1967). In 1975, S. Hecker heard Professor N. T. Chebotarev of the Bochvar Institute present the Soviet version of the Pu-Ga diagram at the Plutonium 1975 Conference in Baden-Baden, Germany. Soviet researchers had reached conclusions that were strikingly different from those of researchers in the West. As illustrated in Figure 1, the U.S. equilibrium diagram shows that alloys with gallium

concentrations between 2 and 9 atomic percent (at. %) are in the δ-phase at ambient temperatures, whereas the Russian equilibrium diagram shows that those alloys decompose at ambient temperatures into a eutectoid, or mixture of phases, consisting of α-plutonium and Pu_3Ga. Both diagrams show dotted lines at these temperatures, indicating that diffusion processes are very slow and that the phases shown represent an extrapolation to equilibrium.

It is important to know whether a thermodynamic driving force is pushing the fcc δ-phase to decompose into a eutectoid mixture because such a transformation would produce volume changes, dimensional distortions, and potentially undesirable property changes. If slow kinetics is the only obstacle to the transformation, we must fully understand all the factors that could speed up the kinetics. Atomic diffusion, the rate-limiting step, could speed up over decades if, for example, lattice damage from self-irradiation were to accumulate as plutonium ages.

At the Baden-Baden conference, Hecker mentioned that U.S. researchers had found no such decomposition and asked Professor Chebotarev if Soviet researchers had enhanced the kinetics. The reply was that they had annealed at high pressure to speed up the eutectoid transformation. In the published proceedings, Chebotarev et al. (1975) wrote that the decomposition was achieved by the "long-term annealing [of] alloys at high pressure." Hecker's attempts to get clarification from Professor Chebotarev after the presentation were unsuccessful.

Back in Los Alamos, Hecker and his colleagues attempted to duplicate the Soviet results in the late 1970s and early 1980s. They found that new phases and different microstructural features can be readily found if Pu-Ga alloys are annealed under pressure. However, they were unable to duplicate the Soviet phase diagram. The Soviet work was considered a temperature-composition diagram valid only at high pressures. It was not accepted as valid at atmospheric pressure because pressure was viewed as an additional thermodynamic parameter.

Lack of Scientific Contacts Prolongs the Mystery

Until 1998, the tales of the two diagrams remained very separate—not because either country considered them secret but because the Cold War prohibited scientific peer review and discussions of this work. The United States (as well as the United Kingdom and France) believed that the fcc δ-phase was stable at room temperature and above. It was well known in both the Soviet Union and the West that, for low concentrations of aluminum or gallium and below room temperature, the fcc δ-phase can transform martensitically to an α-like phase known as α′. This phase has the monoclinic structure of the α-phase but contains dissolved gallium (the equilibrium α-phase has absolutely no solubility for gallium). Martensitic transformations are sudden, displacive, and diffusionless. Therefore, they trap the gallium within the monoclinic lattice. In contrast, the eutectoid decomposition to the α-phase plus Pu_3Ga is a diffusional transformation.

Until 1990, Soviet scientists continued to study the approach to equilibrium at temperatures just above room temperature for additions of gallium and other Group IIIB elements in the periodic table. The results of their studies confirmed the eutectoid decomposition. At an international conference on the actinides held in Tashkent, Timofeeva presented a brief summary, which was then published in a Russian journal not well known in the West (Chebotarev et al. 1990).

Without being aware of that summary, Paul Adler of Lawrence Livermore National Laboratory published (1991) a thermodynamic analysis in which he concluded that the Russian diagram most likely was correct. Adler suggested that, if a δ-phase alloy were transformed martensitically to the α′-phase and then annealed, it would decompose to the eutectoid seen in the Russian diagram. But such experiments were not performed mainly because programmatic interest in plutonium research had waned before the advent of the Stockpile Stewardship Program. The official western Pu-Ga phase diagram as published in the American Society for Metals International compilation of phase diagrams (Peterson and Kassner 1988) is an update of the diagram of Ellinger et al. (1964).

In 1998, the authors of this article met for the first time through the continuing scientific exchange between U.S. and Russian researchers that has developed since the end of the Cold War and the dissolution of the Soviet Union. Academician Boris Litvinov from the All-Russian Research Institute of Theoretical Physics (VNIITF), who had worked with Hecker during the past six years on cooperative nuclear-security programs, introduced the authors at the Bochvar Institute in Moscow. Timofeeva presented her work on plutonium phase diagrams at the International Conference on Ageing of Materials held in Oxford in July 1999 (both authors were invited to that conference). She had conducted that work under the leadership of Academician A. A. Bochvar almost 30 years before the Oxford conference.

At that meeting and during subsequent discussions, one of the greatest pieces of the puzzle was resolved. As it turned out, the Russian work had not involved annealing under pressure. Instead, the samples were subjected to pressure and plastic deformation and were subsequently annealed for very long times at atmospheric pressure. The role of pressure and plastic deformation was to "precondition" plutonium alloys and thus enhance the kinetics of the δ-phase decomposition. This approach is similar to that suggested by Adler in 1991, but the Russian work had already been carried out 20 years before.

The proper determination of equilibrium diagrams at low temperatures has long been a point of disagreement in the metallurgical community because slow diffusion rates at low temperatures make it very difficult to achieve equilibrium.

Timofeeva's preconditioning treatments introduced slight amounts of the α-phase and initial densities far above and below the equilibrium density, enabling her to study the approach to equilibrium from both sides of the equilibrium density. She had to convince Soviet scientists that this unconventional approach was valid. Fortunately, Academician Bochvar supported her. Nevertheless, confusion about the exact nature of the treatments continued in the Soviet scientific community and apparently resulted in the statements made in 1975 that long-term annealing was performed under pressure. We will describe Timofeeva's experiments to clear up the confusion surrounding the Russian phase diagram.

The Russian Approach to Equilibrium at Low Temperatures

In initial studies, Timofeeva prepared Pu-Ga and Pu-Al alloys ranging in composition from 0 to 25 at. %. Samples with less than 10 at. % gallium or aluminum were prepared in a conventional manner. It is well known that such alloys must be homogenized at high temperature for long times to minimize microsegregation of gallium or aluminum and to ensure that the fcc δ-phase is retained to room temperature. As expected, when those δ-phase samples were annealed from room temperature to 300°C for long periods, they showed no decomposition reactions. These initial results were identical to those produced in the West. If the equilibrium state below 100°C was not the fcc δ-phase, then diffusion under normal conditions was too slow to bring it about.

To speed up diffusion and encourage the eutectoid decomposition transformation shown in Figure 1(b), Timofeeva applied two preconditioning treatments (I and II), which partially transformed the δ-phase to the α-phase. Long-term annealing experiments followed. We show the results for Pu-Al alloys because those alloys had been studied in depth before the Pu-Ga system was investigat-

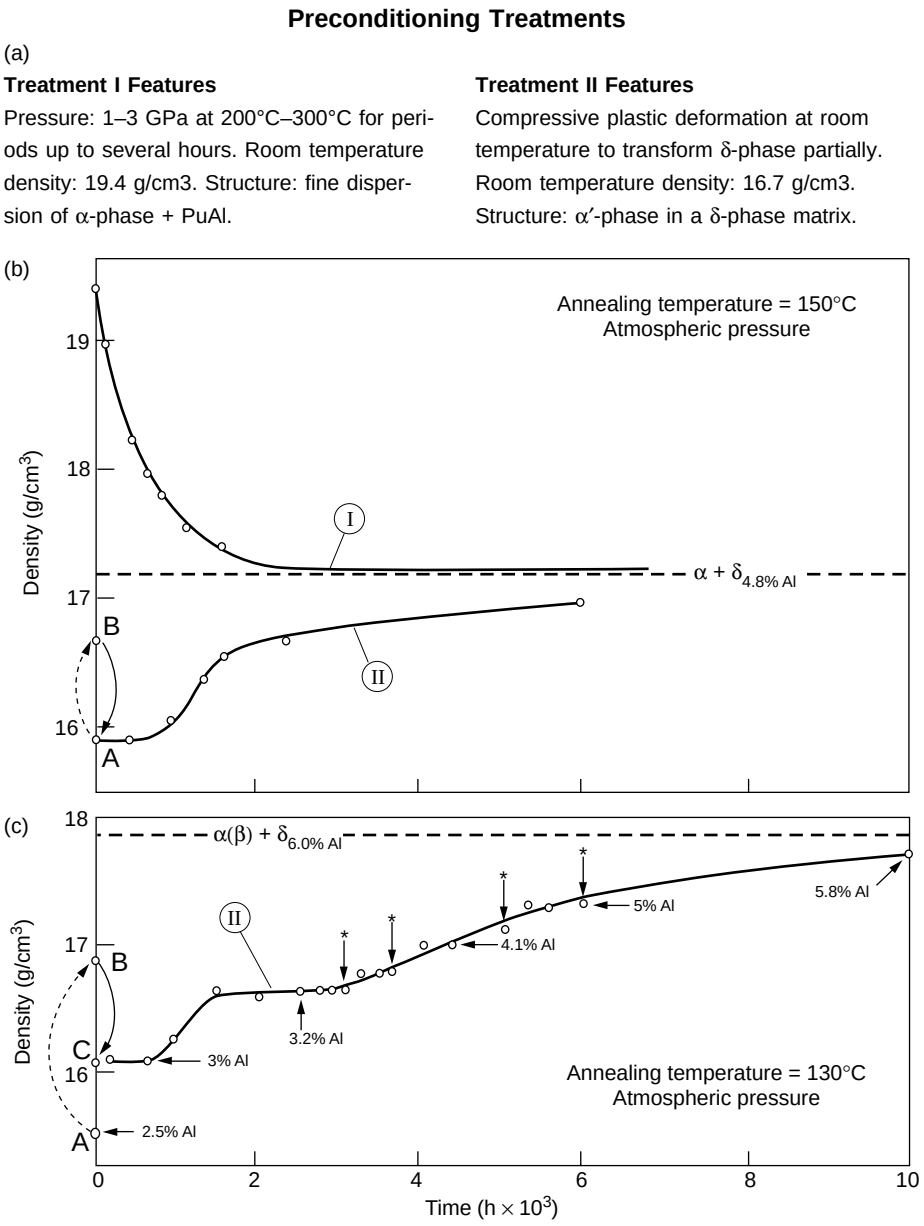

Figure 2. Long-Term Annealing Experiments with Pretreated Samples
Samples of well-homogenized fcc δ-phase Pu-Al alloys (2.5 at. % aluminum) with a starting density of ~15.8 g/cm^3 were preconditioned with treatment I or II as outlined in (a). Group I and II samples, labeled according to the type of preconditioning treatment they received, were annealed for thousands of hours at atmospheric pressure. Density changes with time for annealing at 150°C and at 130°C are shown in (b) and (c), respectively. The starting density for the all-δ-phase samples in (c) was somewhat low, most likely because of the presence of microcracks. The designation α(β) indicates that, at the annealing temperature, the β-phase is present, which then transforms to the α-phase during cooling to room temperature (all measurements are made at room temperature). The subscript of various percent aluminum in the δ-phase designation refers to the atomic percent of aluminum dissolved in the δ-phase. For group II samples, we show the starting density (point A), the initial density following treatment II (point B), and the change in density (see arrows) upon heating to the annealing temperature.

ed. For considerations discussed here, aluminum and gallium are virtually interchangeable. Figure 2(a) outlines treatments I and II, and Figures 2(b) and 2(c) show the results of long-term annealing experiments conducted at atmospheric pressure for a Pu-Al alloy (2.5 at. % aluminum) with a starting density of about 15.8 grams per cubic centimeter (g/cm^3).

We refer to the samples preconditioned with treatment I and treatment II as group I and II samples, respectively. Figure 2(b) shows the changes in density and phase as a function of time for group I and II samples annealed at 150°C. Immediately after treatment, group I samples have an initial density of about 19 g/cm^3. Their density drops rapidly with time and approaches a value of 17.1 g/cm^3. Group II samples have an initial density of 16.7 g/cm^3 (point B), but their density drops back to the starting density (point A) upon heating to 150°C. That density remains constant for the first 500 hours of annealing and then gradually increases. After 6000 hours, the densities of group I and II samples approach the same value. The open circles indicate the times at which the samples were returned to room temperature for detailed examination, including density measurements, metallographic examination, x-ray diffraction lattice-parameter measurements, and microhardness measurements. Those examinations revealed unequivocally the phases present at each stage of the annealing.

Figure 2(c) shows the results for annealing group II samples at 130°C. Upon heating to that temperature, the initial density of group II samples (point B) drops to point C rather than to the starting density (point A), as was the case for annealing group II samples at 150°C—see Figure 2(b). Again, there is an incubation period before the group II sample density starts to increase, in this case toward 17.8 g/cm^3 (although not shown in the figure, group I samples approached this density from the high-density side). During various periods of annealing group II samples, the density changes ceased. It appeared that transformation from the δ- to the β-phase at 130°C had stalled because of very slow diffusion. Therefore, at the points marked by arrows, samples had been returned to room temperature and plastically deformed before the annealing treatments were continued. No additional δ to α′ transformation was induced during deformation, but the rate of transformation did increase, as shown, following the deformation treatments. Figure 2(c) also shows that the concentration of aluminum in the δ-phase increased with annealing times. Those concentrations were inferred from the x-ray diffraction measurements of the δ-phase lattice parameter taken at those times.

Similar experiments were run at several annealing temperatures and for alloys of varying aluminum concentrations. The combined results were used to deduce the Pu-Al equilibrium phase diagram shown in Figure 3(a). Similar experiments involving treatments I and II and extended annealing times were performed on Pu-Ga alloys and led to the Pu-Ga phase diagram shown in Figure 3(b).

Several differences were observed between the gallium and aluminum alloys. First, the intermetallic compound formed in the aluminum alloys is PuAl, whereas that in the gallium alloys is Pu_3Ga. Second, in the aluminum system, the δ-phase transforms to the α′-phase during the plastic deformation of treatment II, whereas in the gallium system, some γ′-phase forms in addition to the α′-phase. Third, the gallium alloys pretreated according to treatment II required even longer times to come to equilibrium—up to 16,000 hours at 130°C.

Is Decomposition the Equilibrium State?

The eutectoid decomposition shown in Figure 3 was never seen directly, but convincing evidence for that endpoint is inherent in Figures 2 and 3. These figures show that annealing at temperatures from 130°C to 200°C causes plutonium alloys with a few atomic percent aluminum or gallium to transform to a pure α-phase plus a δ-phase enriched in aluminum or gallium (for temperatures above the α to β transformation, the alloys transform to a pure β-phase plus a δ-phase enriched in aluminum or gallium). Figure 2 shows the gradual progress of the transformation in Pu-Al samples preconditioned with treatment II. Detailed examination showed that the structure of group II samples consists of the α′-phase interspersed in a δ-phase matrix. At the initial point of the 150°C anneal, most of the α′-phase in group II samples has transformed directly back to the δ-phase alloy, as indicated by the drop in density to point A in Figure 2(b). At the initial point of the 130°C anneal, more of the α′-phase remains in group II samples—the density drops only to point C in Figure 2(b). During the first few hundred hours, nothing else happens, but then the density begins to increase.

At the temperature of the anneals, the density increase is associated with the formation of pure β-plutonium and the rejection of gallium into the remaining δ-phase. (Pure β-plutonium reverts to pure α-plutonium as the temperature is cooled below the β to α transformation.) These conclusions were confirmed by room-temperature examinations conducted periodically during the annealing treatments. In spite of the very different starting structures for samples in groups I and II, both structures converged to pure β-plutonium plus δ-plutonium enriched in aluminum or gallium following an annealing period of several thousand hours. We note that, in the case of the Pu-Al alloy, small amounts of aluminum may be soluble in β- and γ-plutonium as shown in Figure 3(a). Because the samples in groups I and II converged to the same density on a common structure from above and below the limiting density, Timofeeva

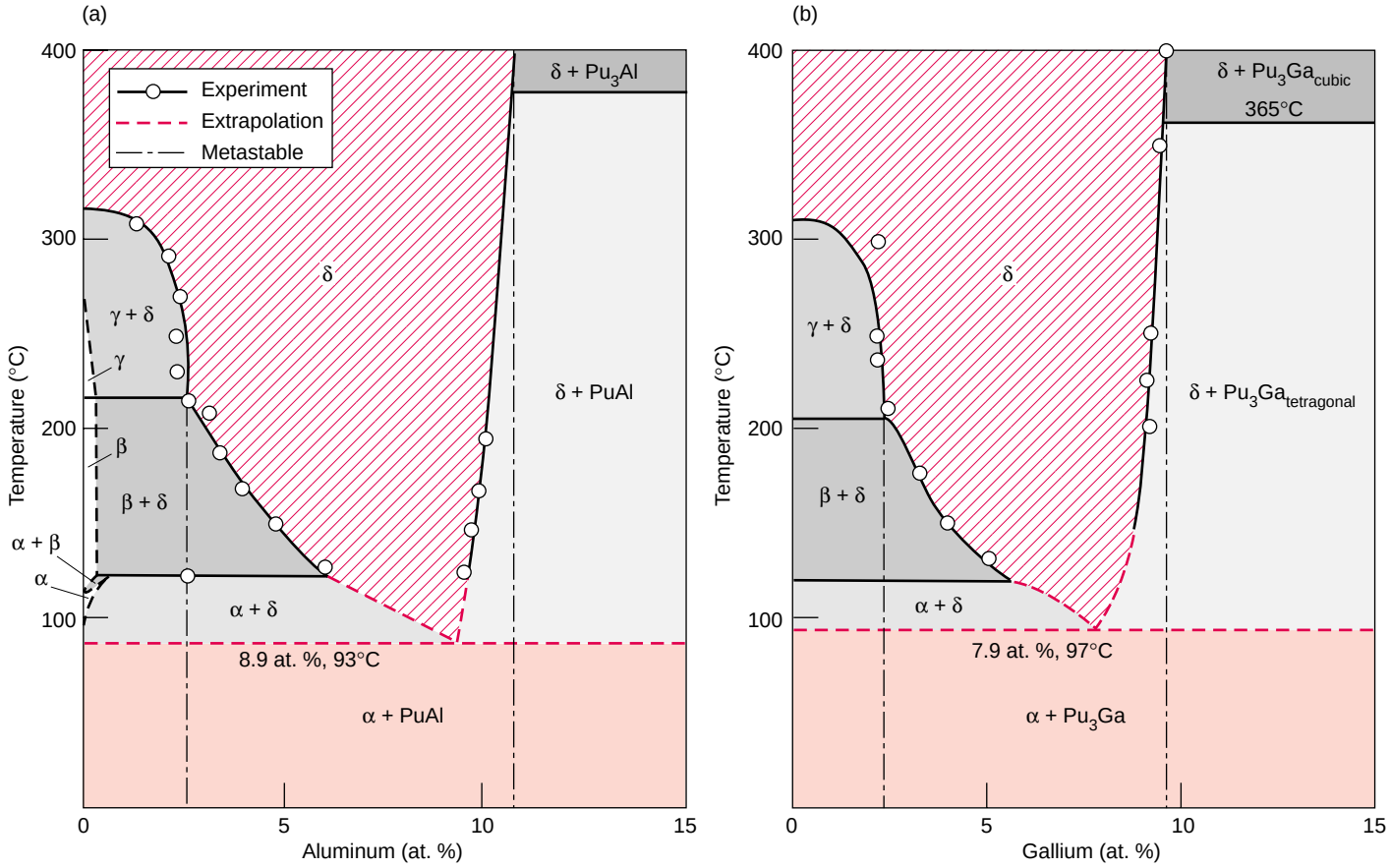

Figure 3. Pu-Al and Pu-Ga Equilibrium Phase Diagrams

This figure shows the plutonium-rich part of the Pu-Al equilibrium phase diagram (a) and the Pu-Ga diagram (b) as reported by Chebotarev et al. (1990) and Timofeeva (2000). Each solid circle represents an experiment of the type depicted in Figure 2. The dashed lines represent the extrapolation of the experimental points to temperatures below which diffusion was too slow to allow the transformation to proceed in a reasonable time. The dash-dotted lines are the metastable phase boundaries determined without preconditioning treatments.

was confident that equilibrium had been achieved. She found that inducing the presence of the α-phase (by preconditioning) was essential to promoting the transformations observed. The residual α- or β-phase structures served as nucleation sites for the transformation occurring at elevated temperatures and long times.

Below 130°C, no long-term phase decomposition from the δ- to the α-phase plus enriched δ-phase was observed for group I and II samples. Diffusion was simply too slow. Hence, the phase boundaries in Figure 3 had to be extrapolated (dashed lines) to a eutectoid point. Chebotarev et al. (1990) and Timofeeva (2000) showed that the logarithm of the aluminum (or gallium) concentration of the phase boundary is a linear logarithmic function of $1/T$. Because the relationship between concentration and temperature was linear on a log-log plot, L. Timofeeva was able to extrapolate the annealing data in the range 130°C–200°C to the eutectoid points for aluminum (8.9 at. %, 93°C) and gallium (7.9 at. %, 97°C).

The western phase diagrams lead one to expect very different results for the same pretreatments and annealing conditions. The Pu-Al and Pu-Ga samples should have transformed back entirely to δ-plutonium or to δ- with very small amounts of α-plutonium. In no case would one expect significant amounts of β-plutonium forming at the annealing temperatures, nor would one expect to find δ-plutonium with the enriched concentrations of aluminum or gallium as in Figures 2 and 3. Because of the different expectations, no attempts at pretreatments followed by elevated-temperature annealing were pursued in the West. Moreover, because the incubation periods are on the order of 500 hours even with the pretreatment, it is unlikely that the experiments would have been continued for the extended times necessary to detect the evidence for phase decomposition. Most of the focus in the West was on the martensitic transformation of the δ- to the α′-phase at temperatures below room temperature.

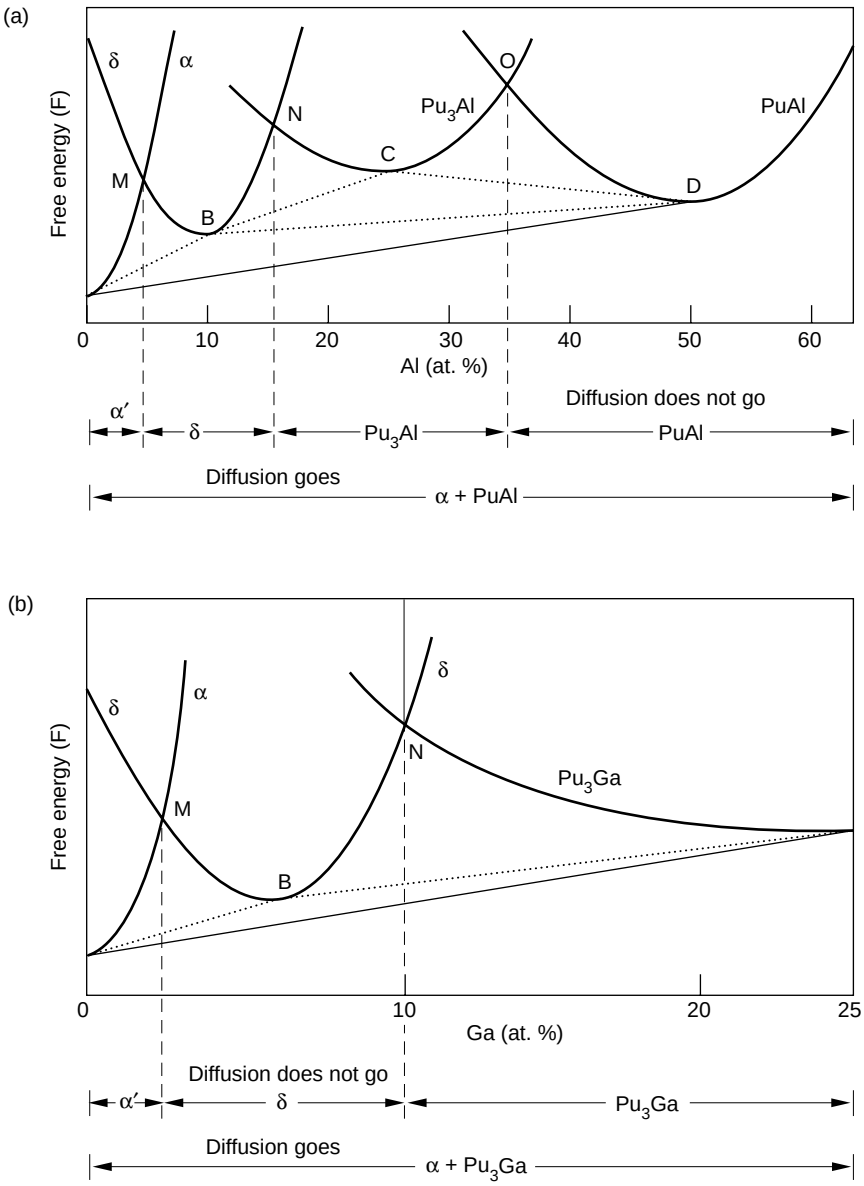

Figure 4. Free-Energy Diagrams for Pu-Al and Pu-Ga Alloys

These schematic free-energy diagrams for Pu-Al (a) and Pu-Ga (b) alloys were developed by Russian scientists (Chebotarev et al. 1990, Timofeeva 2000). Under equilibrium conditions, the straight tie line between the free-energy curves for the α-phase and the intermetallic compound (PuAl or Pu_3Ga) represents the lowest energy as long as diffusion is sufficiently rapid to allow the decomposition to occur. If diffusion is not rapid enough, then other tie lines can be drawn as shown, and the δ-phase would persist over some range of aluminum or gallium concentrations.

Decomposition of the δ-Phase: Practical Consequences

The Russian equilibrium phase diagram shows convincingly that all δ-phase alloys stabilized by additions of aluminum or gallium are metastable at ambient temperature. The situation is best depicted by the free-energy diagrams shown in Figure 4.

Both Russian and western experiences have shown that diffusion is too slow to allow the decomposition transformation to occur. So, although the "equilibrium" diagram shows decomposition occurring below 100°C, that phenomenon has never been observed. We have not observed any decomposition in δ-phase alloys that are 20 to 30 years old. Therefore, for practical purposes, the U.S. diagram shown in Figure 1(b) is adequate—it represents the metastable condition. In fact, the same metastable boundaries are shown in the Russian diagrams in Figure 3. Timofeeva estimated that even a preconditioned Pu-Al alloy at room temperature would take on the order of 11,000 years to decompose based on room-temperature data on self-diffusion in δ-phase plutonium. The Pu-Ga alloys are expected to take even longer to decompose. The situation in plutonium alloys is similar to that in steel. Note that, in steel, equilibrium favors carbon to be present as graphite; however, because diffusion at ambient temperature is also limited in steels, carbon is either tied up in the intermetallic compound Fe_3C or stuck in the iron lattice. Our highway bridges do not decompose into iron plus graphite.

So, why be concerned? One must always respect the power of a thermodynamic driving force because the system (in this case, the plutonium alloy) will always tend to lower its energy. If only kinetics protects the system from changing to a lower-energy configuration, then it is important to understand fully the factors controlling the kinetics. Regarding plutonium, we must develop a better understanding of how the relentless process of self-irradiation (that displaces every plutonium atom once every 10 years) affects diffusion and consequently phase stability. In addition, the effects of impurities (either adsorbed on the surface or transmuted from self-irradiation during aging) on phase stability must be better understood. These problems will be not only an important area of research, but also a scientifically fascinating one. ■

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Left to right: Academician Boris Litvinov, Lidia Timofeeva, Evgeny Kozlov, and Sig Hecker at the Bochvar Institute in Moscow, in 1998. Academician Litvinov and Evgeny Kozlov are with the All-Russian Research Institute of Theoretical Physics.

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