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PLUTONIUM METALLIC FUELS FOR FAST REACTORS

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Abstract

Early interest in metallic plutonium fuels for fast reactors led to much research on plutonium alloy systems including binary solid solutions with the addition of aluminum, gallium, or zirconium and low-melting eutectic alloys with iron and nickel or cobalt. There was also interest in ternaries of these elements with plutonium and cerium. The solid solution and eutectic alloys have most unusual properties, including negative thermal expansion in some solid-solution alloys and the highest viscosity known for liquid metals in the Pu-Fe system. Although metallic fuels have many potential advantages over ceramic fuels, the early attempts were unsuccessful because these fuels suffered from high swelling rates during burn up and high smearing densities. The liquid metal fuels experienced excessive corrosion. Subsequent work on higher-melting U-Pu-Zr metallic fuels was much more promising. In light of the recent rebirth of interest in fast reactors, we review some of the key properties of the early fuels and discuss the challenges presented by the ternary alloys.

Plutonium metallic fuels for fast reactors

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Abstract

Early interest in metallic plutonium fuels for fast reactors led to much research on plutonium alloy systems including binary solid solutions with the addition of aluminum, gallium, or zirconium and low-melting eutectic alloys with iron and nickel or cobalt. There was also interest in ternaries of these elements with plutonium and cerium. The solid solution and eutectic alloys have most unusual properties, including negative thermal expansion in some solid-solution alloys and the highest viscosity known for liquid metals in the Pu-Fe system. Although metallic fuels have many potential advantages over ceramic fuels, the early attempts were unsuccessful because these fuels suffered from high swelling rates during burn up and high smearing densities. The liquid metal fuels experienced excessive corrosion. Subsequent work on higher-melting U-Pu-Zr metallic fuels was much more promising. In light of the recent rebirth of interest in fast reactors, we review some of the key properties of the early fuels and discuss the challenges presented by the ternary alloys.

PACS classification codes: 60 Pu, 70 Pu.

1. Introduction

In 2006, the U.S. Department of Energy announced the Global Nuclear Energy Partnership (GNEP) in response to the President's State of the Union Address call for "safe and clean nuclear energy" as part of a new Advanced Energy Initiative. The GNEP concept involves closed fuel cycles, which not only increases the supply of fissile material through breeding but also reduce the impact of byproducts by transmutation of transuranics and fission products. The new fuel cycles being explored include fast reactors and new fuel designs that include plutonium containing metallic fuels.

Metallic fuels have significant potential advantages for fast reactors and have a rather long history. Kittel et al. reviewed the of the most important steps in fast reactor fuel development.[1] The first prototype fast breeder reactor, Clementine, became operational in 1949 at the Los Alamos Scientific Laboratory. It was based on cast delta-stabilized plutonium and used mercury as coolant. The reactor was shut down after a few years because of failure of the mild steel cladding. Clementine was replaced in the 1960s by the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE-I and LAMPRE-II) fast reactors that used liquid Pu-Fe alloys. The Argonne National Laboratory Experimental Breeder Reactor, EBR-I, began to operate in the same decade using δ-phase

Pu-Al alloys fuel. The early metallic fuels suffered from high swelling rates and a high smearing density, and were replaced by ceramic fuels. In the mid-1980s, the Integral Fast Reactor (IFR) concept at Argonne rekindled work on metallic fuels with higher melting points. Fuels with U-Zr and U-Pu-Zr alloys provided significantly better performance and were able to operate at higher temperatures and higher burnup. In the 1990s, the burnup level of U-Pu-Zr fuels was increased to 19%. A variety of U-Pu-X ternary alloys, where X is Mo, Nb, Ti, or Zr, have been tested as fuels for fast reactors in the United States and Europe with various degrees of success.

Although the technical potential of the IFR concept was promising, the program was discontinued in the mid-1990s because of U.S. policy opposition to closed fuel cycles. Only in the past few years have fast reactors and metallic fuels been re-examined as a way of dealing with the need for abundant, clean energy. In this article we describe some of the important challenges related to metallic plutonium, we provide a historical perspective of some of the alloys used in early fast reactor metallic fuels, and we demonstrate the utility of modern materials modeling in helping us guide the selection and development of new metallic fuels.

2. Plutonium metallurgy and 5*f* electrons

Plutonium fits near the middle of the actinide series, which marks the emergence of the 5*f* electrons in the valence shells of the elements. Plutonium is of interest primarily because of its nuclear structure. The 239 isotope of plutonium fissions when bombarded with neutrons over a large range of neutron energies, releasing enormous amounts of energy in the process. Consequently, plutonium is a key element for nuclear energy and nuclear explosives. Its engineering properties are extraordinarily complex because of its electronic structure. The actinides mark the filling of the 5*f* atomic subshell much like the rare earths mark the filling of the 4*f* subshell (Fig. 1). Yet, the 5*f* electrons of the light actinides behave more like the 5*d* electrons of the transition metals than the 4*f* electrons of the rare earths. At the very beginning of the actinide series, there is little *f*-electron influence and, hence, one finds typical metallic crystal structures, few allotropes, and high melting points. This behavior is best illustrated in the connected phase diagram across the actinides in Fig. 2[2]. As more *f* electrons are present (up to plutonium), they participate in bonding (that is, they are itinerant, much like the *d* electrons in transition metals) and the crystal structures become less symmetric, the number of allotropes increases, and the melting points decrease. At americium and beyond, crystal structures typical of metals return, the number of allotropes decreases, and the melting points rise — all indications of the *f* electrons becoming localized or chemically inert, much like the 4*f* electrons in the rare earths. Since plutonium sits right at the transition point from itinerant to localized 5*f* electrons, it exhibits many unusual properties.[3]

In the room-temperature α-phase, plutonium expands upon heating at almost five times the rate of iron, while contracting upon heating in the fcc δ-phase. It melts at the unusually low temperature of 913 K and contracts upon melting. In the liquid state, plutonium has a very high surface tension and high viscosity. It is a poor electrical and thermal conductor, and it is elastically very compressible. In the fcc δ-phase, which can be retained by alloying, plutonium exhibits the greatest elastic anisotropy of any fcc metal. Upon cooling below room temperature, plutonium's already high electrical resistivity increases as the temperature is lowered to 100 K, before falling upon further

cooling. Its specific heat is 10 times higher than normal at temperatures close to absolute zero. Its magnetic susceptibility, also atypically high, remains constant with perhaps a slight increase as the temperature is lowered, indicating a tendency toward magnetism. But even at the lowest temperatures, plutonium never settles down to a state of long-range order (either magnetic or superconducting) typical of other metals. In addition, plutonium's continuous radioactive decay causes self-irradiation damage that can fundamentally change its properties over time.[4]

The property of plutonium with greatest engineering consequences is its instability. As shown in Fig. 3, plutonium is notoriously unstable – with temperature, pressure (stress), chemical additions, and time. The stable phase at room temperature is the brittle, monoclinic α-phase. Transformation to the α-phase with the large volume changes experienced in unalloyed plutonium can be avoided by alloying pure plutonium with a few atomic percent gallium or aluminum. Dimensional changes with temperature of two lean Pu-Ga alloys are compared to unalloyed plutonium in Fig. 4 [5]. The Pu-Ga alloys also expand slightly during solidification, but then experience very little volume change during cooling to room temperature. The δ-phase retained to room temperature is face-centered cubic (fcc) and is as ductile as commercially pure aluminum. The exhaustive phase diagram studies of Ellinger et al. [6] showed that the addition of most trivalent elements (such as Ga, Al, Ce, Am, Sc, In) to plutonium favors retention or stabilization of the δ-phase. The mechanisms for retention or stabilization are not well understood. Although the fcc δ-phase is preferred for engineering applications, it is the least understood from a physics point of view.

3. Relevant properties of early plutonium reactor fuels

We review the early fast reactor fuels that used either δ-phase alloys or liquid eutectics. The δ-phase alloys have attractive engineering properties but suffer from a low melting point. Some of the key characteristics of such alloys have been recently reviewed by Hecker et al.[3] The fact that additions of aluminum or gallium retain the fcc δ-phase of plutonium was established during the Manhattan Project. The experimental studies reported by Gschneidner et al.[7 ,8] and Ellinger et al. [6] have served as the principal guides for practitioners. In addition to the elements that easily retain the δ-phase to room temperature (Al, Ga, Ce, Am, Sc, In and Tl), there is a second class of elements (Si, Zn, Zr, and Hf) that retain the δ-phase in metastable state under conditions of rapid cooling. There are also some indications that the δ-phase in Pu-Th alloys can be retained by very rapid quenching [7]. Gschneidner et al. [7] also found a number of the trivalent lanthanides (Dy, Er, Tm, Lu, and possible Tb) to favor δ-phase retention, but none show δ-phase stability in their phase diagrams with plutonium. Ellinger et al. [6] showed that neptunium extended the monoclinic α-phase region. No other element was found to have any equilibrium solubility in the α-phase and uranium favors the retention of other low-symmetry, complex structures.

These alloys also exhibit some unusual properties. As illustrated in Fig. 3a, the fcc δ-phase for unalloyed plutonium is the least dense in spite of having the only close-packed crystal structure. It exhibits an unusual negative thermal expansion coefficient. It is also the most elastically anisotropic fcc element in the periodic table [9]. In δ-phase Pu-Ga alloys, the fcc phase also displays a comparatively low density. Its thermal

expansion coefficient varies from slightly negative to slightly positive (an Invar-like effect) depending on alloying concentration and temperature. Its electrical resistivity is unusually large and does not decrease in a conventional manner below room temperature. Thermal conductivities of pure α-phase plutonium and δ-phase alloys do not exhibit the anomalous low-temperature behavior found in resistivity measurements. Andrew [10] reported thermal conductivities for high-purity, well-homogenized δ-phase Pu–3.35 at.% Ga alloys to vary smoothly from 0.022 cal $s^{-1}cm^{-1}K^{-1}$ at 300K to 0.0098 cal $s^{-1}cm^{-1}K^{-1}$ at 80 K. Lewis *et al.* [11] reported thermal conductivities calculated from thermal diffusivity measurements on high-purity Pu–3.35 at.% Ga alloys at high temperatures. Their calculated room-temperature value of 0.0205 cal $s^{-1}cm^{-1}K^{-1}$ at 300 K increased to 0.04 cal $s^{-1}cm^{-1}K^{-1}$ at 673 K. The δ-phase Pu-Ga alloys also exhibit a very large low-temperature specific heat and an unusually large paramagnetic susceptibility, although no local moments have been found [12].

Prediction of phase stability and phase diagrams from first-principles is still beyond our reach today. A more quantitative, phenomenological approach to predicting phase diagrams was developed by Kaufman and others [13,14,15]. The success of CALPHAD (calculation of phase diagrams), their computational thermodynamics approach to predicting phase diagrams of multi-component alloy systems, was reviewed Chang *et al.* in Turchi, Gonis, and Shull.[16] Applications of computational thermodynamic modeling to plutonium and its alloys is being developed, but is limited by the lack of good thermodynamic data on plutonium, its alloys, and its compounds. Adler[17] used available thermodynamic data to construct the Pu-Ga equilibrium phase diagram. He concluded that the Russian version, which exhibits an eutectoid decomposition of the δ-phase above room temperature is most likely correct. Stan recently applied his own software to determine a set of thermodynamic parameters that are consistent with the Russian eutectoid point. He found that a sub-regular model is required to describe the properties of the δ-phase. [18] The existence of the eutectoid was further confirmed by molecular dynamics calculations (Baskes et al, [19]). However, the accuracy of the calculated temperature and composition of the eutectoid point is limited by inadequate thermodynamic data on Pu_3Ga. As shown by Stan et al [20], the properties of Pu-Ga alloys change with radiation damage and the very concept of "phase stability" must be re-examined.

We provide a brief review of the properties of liquid plutonium because of its early application as a reactor fuel in the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) program. Early measurements of the properties of liquid plutonium, including compatibility with container materials, were reported by Comstock (Comstock 1952). Liquid plutonium is highly corrosive and easily oxidized. There is general agreement today that the melting point of pure plutonium is 913 ± 2K. The low melting point, with respect to its position in the periodic table, has many consequences on the practical properties of plutonium. In addition to restricting the temperature range of applications, it also affects all thermally activated processes, which scale with the melting point.[21]

Liquid plutonium has many peculiarities, including a density greater than the last three solid allotropes. Its heat of fusion of ~2800 J mol^{-1} is unusually small. The stability of liquid plutonium has been attributed to the nature of 5*f*-electron bonding in plutonium by Hill and Kmetko[22] and Brewer.[23] Its melting point decreases with increasing

pressure up to 3 GPa[24,25] consistent with the volume contraction on melting. Other materials such as gallium, bismuth, antimony, germanium, silicon, tellurium, and water show similar behavior. Merz *et al.* [26] and Boivineau [27] also reported an increase in sound speed in liquid plutonium with increasing temperature, with a slope of 0.08 to 0.1 m $s^{-1}K^{-1}$. Using a rapid heating technique, Boivineau showed that the sound speed increases to 2000 K before undergoing a rapid change in slope to a negative value from 2000 K to 3600 K. Similar results have been reported for cerium[28], in which 4*f* electrons also play a role in bonding under pressure. Lawson *et a*l. [29] and Lawson [30] modified Lindemann's rule for melting to include the temperature dependence of the elastic properties. Lawson *et al.* explain the anomalously low melting point of plutonium and the trend across the light actinides by temperature-induced elastic softening.

The viscosity of liquid plutonium was measured by Wittenberg and coworkers at the Mound Laboratory [31,32,33,34,35]. Jones et al. [36] reported the viscosity of liquid plutonium to follow the relation:

$$\log \eta = 672/T + 0.037 \text{ (in centipoise)},$$

which yields a viscosity of 6cP at the melting point. This is one of highest viscosities measured for metals; similar to the melting point viscosity of 6.53cP for uranium (Wittenberg [37]) and 5.8cP for iron (Ofte et al [34]). Ofte *et al.* pointed out that the viscosity of plutonium and its fluid flow properties place it in a class of metals whose melting points are substantially higher than that of plutonium. However, if one accounts for its high mass and low Debye temperature, then plutonium falls only somewhat above the correlation established by Iida *et al.*[38] for most liquid metals.

Plutonium when alloyed with iron, nickel or cobalt forms a low-melting eutectic. For iron, the composition is Pu_6Fe with a melting point of 410° C. This low-melting composition formed the basis for the liquid fuel for the LAMPRE program. Ternary alloys of Pu-Ce-Co and Pu-Ce-Ni were also considered at Los Alamos, but never used as fuel. Blank[39] reviewed the measurements of viscosity on liquid Pu–Fe alloys by Ofte, Wittenberg and coworkers[40,41,42]. The viscosities of Pu–Fe alloys were uniformly high. That of a Pu–9.5 at.% Fe eutectic alloy (near the compound Pu_6Fe) was a remarkable 25.2 cP at 684 K (and decreased to 6.14 cP at 1081 K). Blank [39] provides great detail in his summary of the Pu–Fe system. Wittenberg *et al.* [40] found the activation energy for viscous flow for the eutectic alloy to be 21.9 kJ mol^{-1}. Ofte *et al.* [35] reported viscosities for Pu–Ce and Pu–Ce–Co alloys in excess of that for plutonium. The viscosity of Pu–28.4 at.% Ce–23.7 at.% Co was reported as 23cP at its melting point, nearly matching the viscosity of the Pu–Fe eutectic alloy. The Debye temperatures for these alloys are not available, so it is not possible to check if the viscosities fit the correlation established by Iida *et al.* [38]

The accepted value for the surface tension of unalloyed liquid plutonium is that reported by Spriet[43], namely 0.55 N/m. Wittenberg [37] also reported 0.55 N m^{-1} for plutonium and 1.5 N m^{-1} for uranium. The value for plutonium fits the correlation of surface tension with melting point and molar volume proposed by Iida *et al.* [38] for most elements in the periodic table. That of uranium appears to be anomalously high.

We reviewed the properties of δ-phase alloys and plutonium liquids to provide background information on the early plutonium fuel experience for fast reactors. Both

were demonstrated to be inadequate fuels for fast reactors; the δ-phase alloys suffered from excessive swelling and the liquids were too corrosive. Subsequent developments at Argonne National Laboratory and experience in other countries pointed the way toward metallic fuels with higher melting points, particularly the U-Pu-Zr system.

4. Modern metallic fast reactor fuels

There is a variety of nuclear fuel materials, each of them with advantages and disadvantages, the most common fuel types being oxide, nitride, carbide, and metals. Comparative studies of reactor performance and thermo-mechanical properties of various fuel types have been performed for specific reactor concepts such as Liquid Metal Reactor[44], the Fast Fuel Test Facility[45], and the Self Consistent Nuclear Energy System.[46] In other studies, the properties of the U-Pu-Zr fuels have been evaluated in comparison with the U-Zr fuels.[47] It was shown that although there are numerous similarities between the two systems, such as similar power reactivity decrements, the few difference can be critical. For example, the effective radial expansion due to increase in power-to-flow ratio is larger for the plutonium based fuels, leading significant differences in the reactor design, especially the ducts, load pads and core restraints.

Together with efficiency and cost, safety plays an important role in determining the best choice for a reactor fuel. Studies of the behavior of oxide, carbide, and metal fuels during accident scenarios showed that the given the low melting temperature of metal fuels, and as a consequence the low operating temperature can contribute to the reduction in the severity of the accidents. On the other hand, the metal-fueled core requires long times for fuel vaporization, leading to large reactivity addition rates due to fuel slumping.[48] It was also demonstrated that metal fuel cores are more sensitive to small perturbations that oxide fuel cores.[49]

Here is a brief summary of the requirements for a reactor core that contains plutonium-based fuel. The reactor must operate at highest possible temperature and the highest possible burnup to minimize fuel doubling times and must be as compact as possible to minimize fuel inventory costs. The fuel material must have high density of fissile Pu239 atoms, a high thermal conductivity, and few moderating atoms. The material should be resistant to swelling and allow for the fast fission products gas release. Anisotropic irradiation growth and swelling is often a limiting factor for plutonium metal fuels. A swelling limit of no more than 30% is generally accepted. Another common issue is the interaction between the fuel and the cladding. Pu based alloy fuels are known to form solid-state or molten eutectic reactions with stainless steel cladding. The correlation between the fuel type and the coolant material revealed that sodium is the most favorable coolant types for metal fuels[50], due to its high specific heat and high thermal conductivity that allows for a fast and efficient transfer of heat to the coolant.

In most metal fuels, a major problem is ensuring a high melting point. Composition must be such that low eutectics are avoided. Unfortunately, there is a lack of information regarding phase stability in U and Pu based multi-component alloys for fast reactors. For example, the binary phase stability diagrams in the U-Pu-Zr system are uncertain (see Fig. 5, a, b, and c). This is generated by the complexity of the binary systems. A recent report from the Bhabha Atomic Research Center[51] provides the best compilation of thermodynamic data for U-Pu-Zr alloys. The report includes optimized free energy functions for all the phases and proposes sections of the ternary phase

diagram. Ellinger *et al.*[52] published a preliminary evaluation of the of Pu-U phase diagram, in the Pu rich domain. A more complex assessment was performed by Peterson and Foltyn[53] The Pu-Zr diagram was subject of extensive experimental studies by Marples[54]. He concluded that the phase transformations in these systems are extremely slow, making the determination of equilibrium properties very difficult. This is reflected in the discrepancies between various assessments of the phase diagram, such as Leibowitz *et al.*[55] and Maeda *et al.*[56] The phase diagram of U-Zr was assessed several times, starting with Leibowitz[57] and more recently by Sheldon and Peterson [58] and by Ogawa and Iwai.[59] Although subject of numerous revisions, this is the best understood diagram of the three binaries. The least understood is the Pu-U-Zr ternary. Since limited experimental data is available [55,60,61] the models of the ternary interactions must rely on geometrical extrapolations of the binary free energies.[51]

Assessments of the properties of multi-component systems such as light alloys are undergoing in several countries. However, the current models involve *fitting* of known data followed by extrapolations or interpolations into new temperature or pressure regimes. The CALPHAD method [62], as an example, allows for the construction of a ternary phase diagram if the properties of the components, *and* intermediate compounds, *and* solution phases are all known.[63] In this method, the excess free energy of solutions is represented using Redlich-Kister polynomials [64] that are optimized by fitting thermodynamic properties to experimental data or first principles calculations.

A recently published method for binary systems[65] allows for the calculation of the equilibrium phase diagrams using limited information about the components. Material's properties are captured using a semi-empirical Lennard-Jones/Embedded Atom Method inter-atomic potential. By the means of molecular dynamics calculations, the potential is used to calculate the free energies and the chemical potentials in the solid and liquid phases, resulting in the equilibrium phase diagrams. A similar approach, using this time the Modified Embedded Atom Method to derive the many-body inter-atomic potential was applied to the low temperature, low Ga content region of the Pu-Ga system.[66]

To predict phase stability in the U-Pu-Zr system, multi-scale models and simulations are necessary. The multi-scale method used at Los Alamos National Laboratory incorporates theory-based atomistic and continuum models into finite element simulations to predict phase stability and transport phenomena. By relating micro and nano-scale models to the macroscopic equilibrium and non-equilibrium simulations, the predictive character of the method is improved. The models are validated using experimental results of thermal conductivity and oxygen diffusivity. The multi-scale approach was applied to calculations of point defect concentration, helium bubbles formation, oxygen diffusivity, and simulations of heat and mass transport in UO_{2+x}.[67] The application to the U-Pu-Zr system is currently in progress at LANL.

Any such calculation must be accompanied by the evaluation of the uncertainty associated with the phase boundaries. Bayesian statistics analysis of uncertainty was recently applied to the PuO_2-UO_2 system,[68] providing calculated confidence intervals (error bars) for the phase boundaries. Using a similar approach we are currently evaluating the uncertainty of multi-component actinide alloys of relevance for nuclear fuels applications.

5. Summary

We reviewed some fundamental aspects of plutonium metallurgy and how they impact the properties of δ-phase alloys and liquid eutectic alloys that were part of the early fast reactor program. We paid special attention the properties of liquid plutonium and the Pu-Fe alloys used in an early reactor concept because very little has been reported about these in the past few decades.

We also reviewed the thermo-mechanical properties of metallic fuels, in comparison with other fuel types, and summarized the requirements for high quality metallic fuels. The review of the status of the assessment of phase stability in the U-Pu-Zr system revealed that only the U-Zr binary is well understood. Since the composition of metallic fuels involves uranium-rich alloys, the delicate nature of the 5f electron behavior in plutonium metal and plutonium-rich alloys may not have a strong impact on phase stability. However, it is timely and possible to develop a multi-scale, multi-physics approach to understanding properties of complex U and Pu based fuel materials, leading to improved tools for predicting phenomena such as phase stability, heat transfer, species diffusion, and fission products retention.

References

Figure Captions:

Fig. 1. The actinides and their outermost configurations of electrons for isolated atoms.

Fig. 2. The experimentally determined, connected binary phase diagram of adjacent actinide elements (from Smith and Kmetko

Fig. 3. Plutonium instability with a) temperature, b) pressure, c) chemical addition (U.S. version of Pu – Ga phase diagram), and d) time.

Fig. 4. Length changes for unalloyed plutonium compared to Pu-3 at.% Ga and Pu-4.5 at.% Ga alloys.

Fig. 5. Binary phase diagrams of the U-Pu-Zr system.

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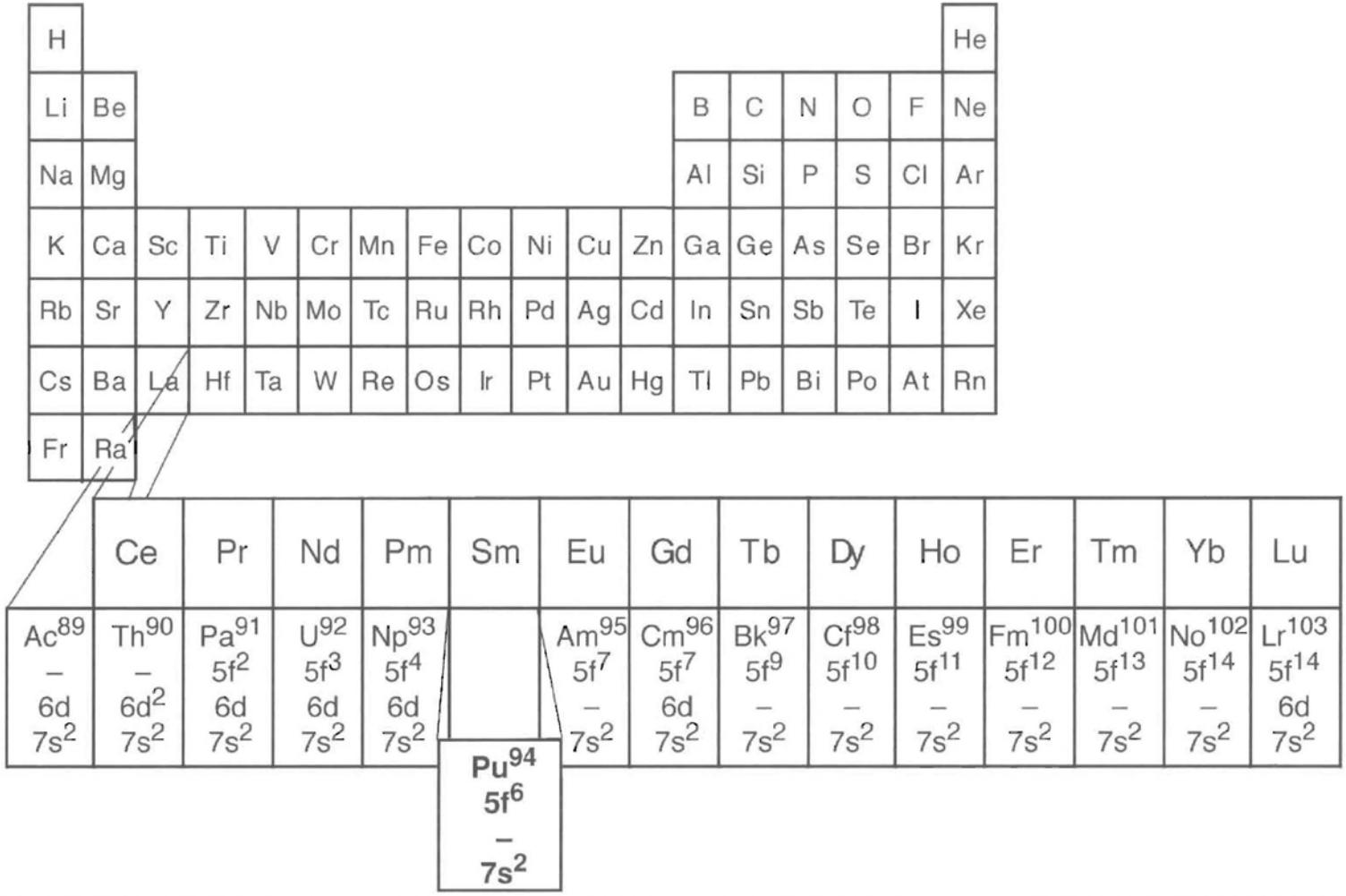

Fig. 1. The actinides and their outermost configurations of electrons for isolated atoms.

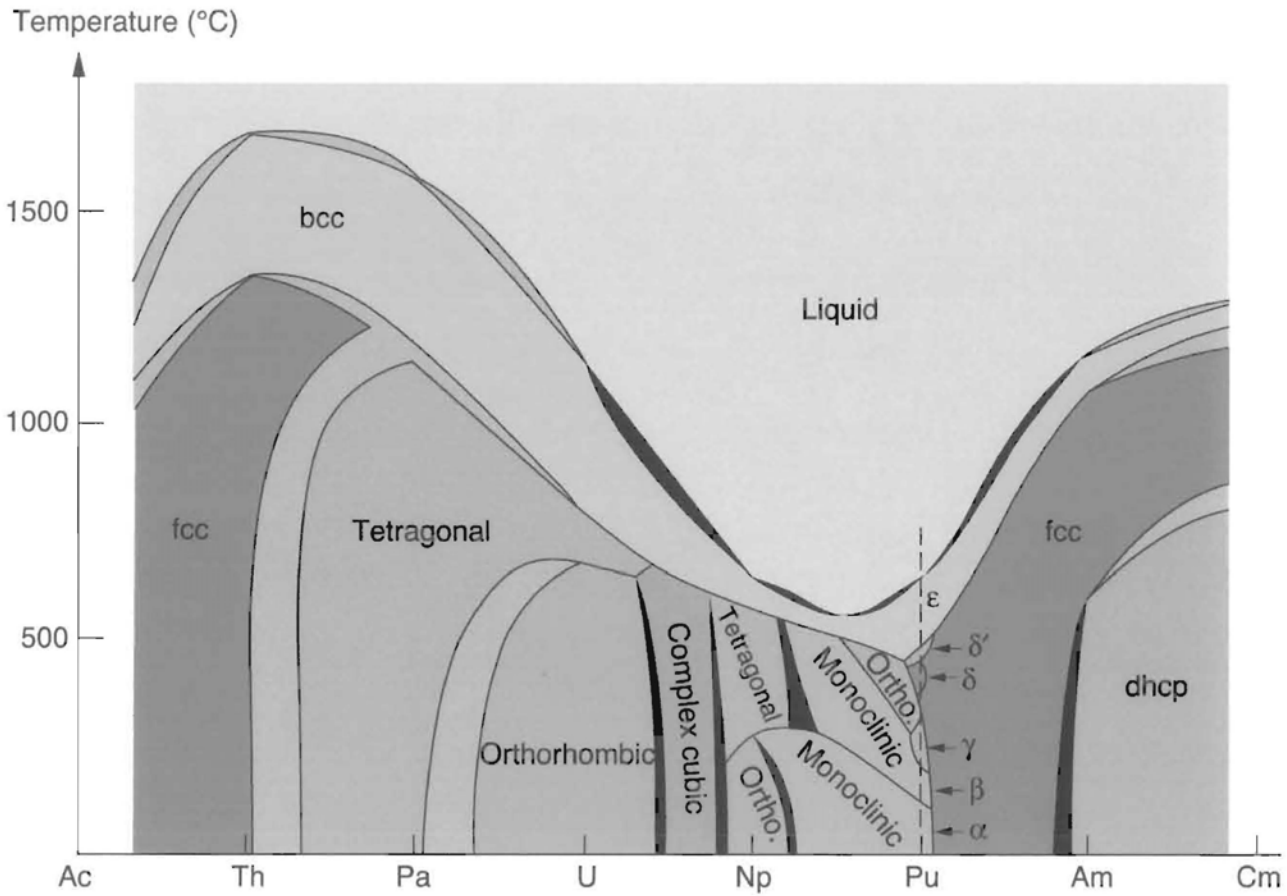

Fig. 2. The experimentally determined, connected binary phase diagram of adjacent actinide elements (from Smith and Kmetko [2]).

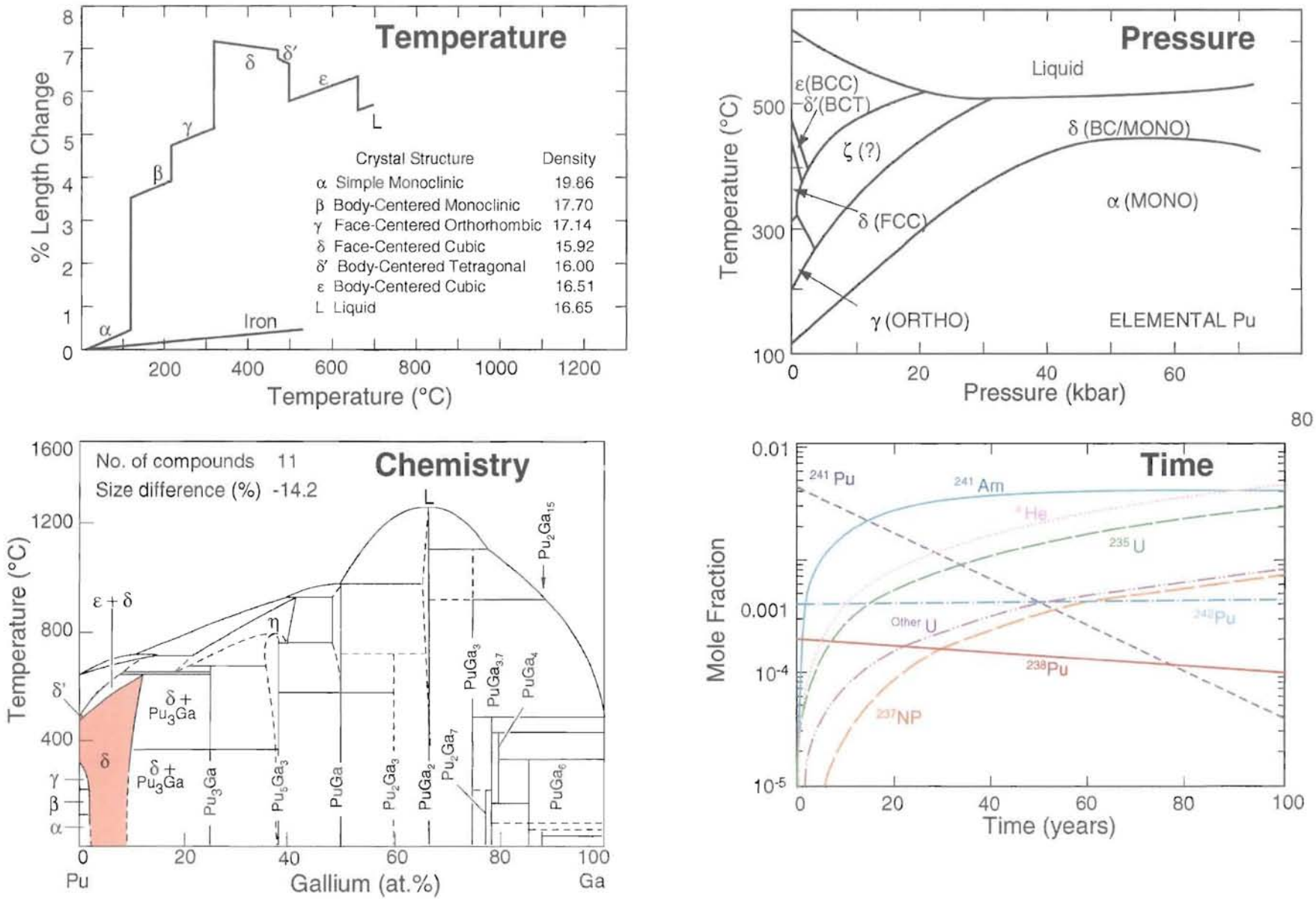

Fig. 3. Plutonium instability with a) temperature, b) pressure, c) chemical addition (U.S. version of Pu – Ga phase diagram), and d) time.

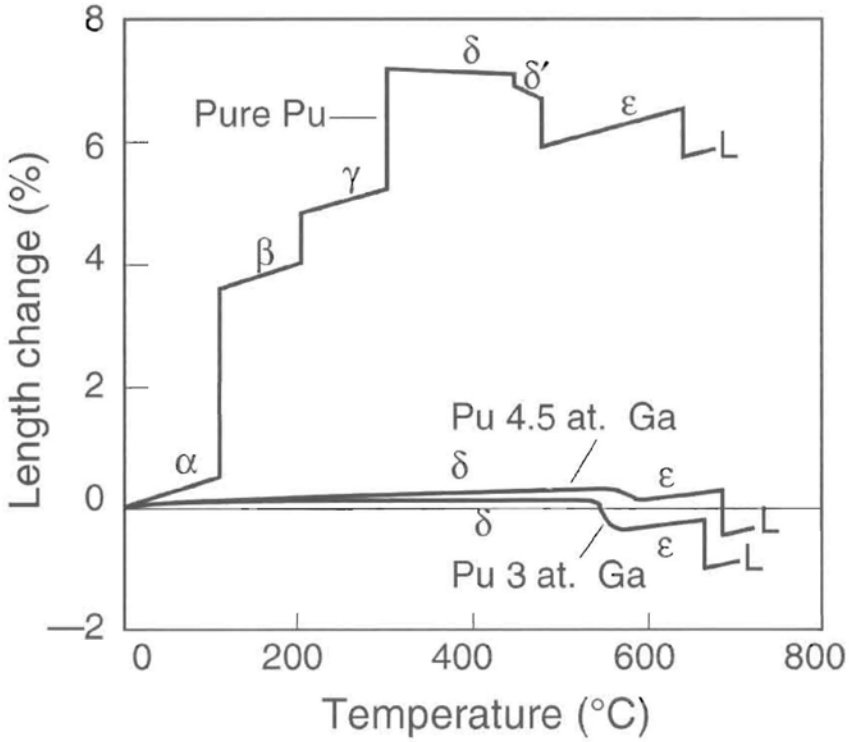

Fig. 4. Length changes for unalloyed plutonium compared to Pu-3 at.% Ga and Pu-4.5 at.% Ga alloys.

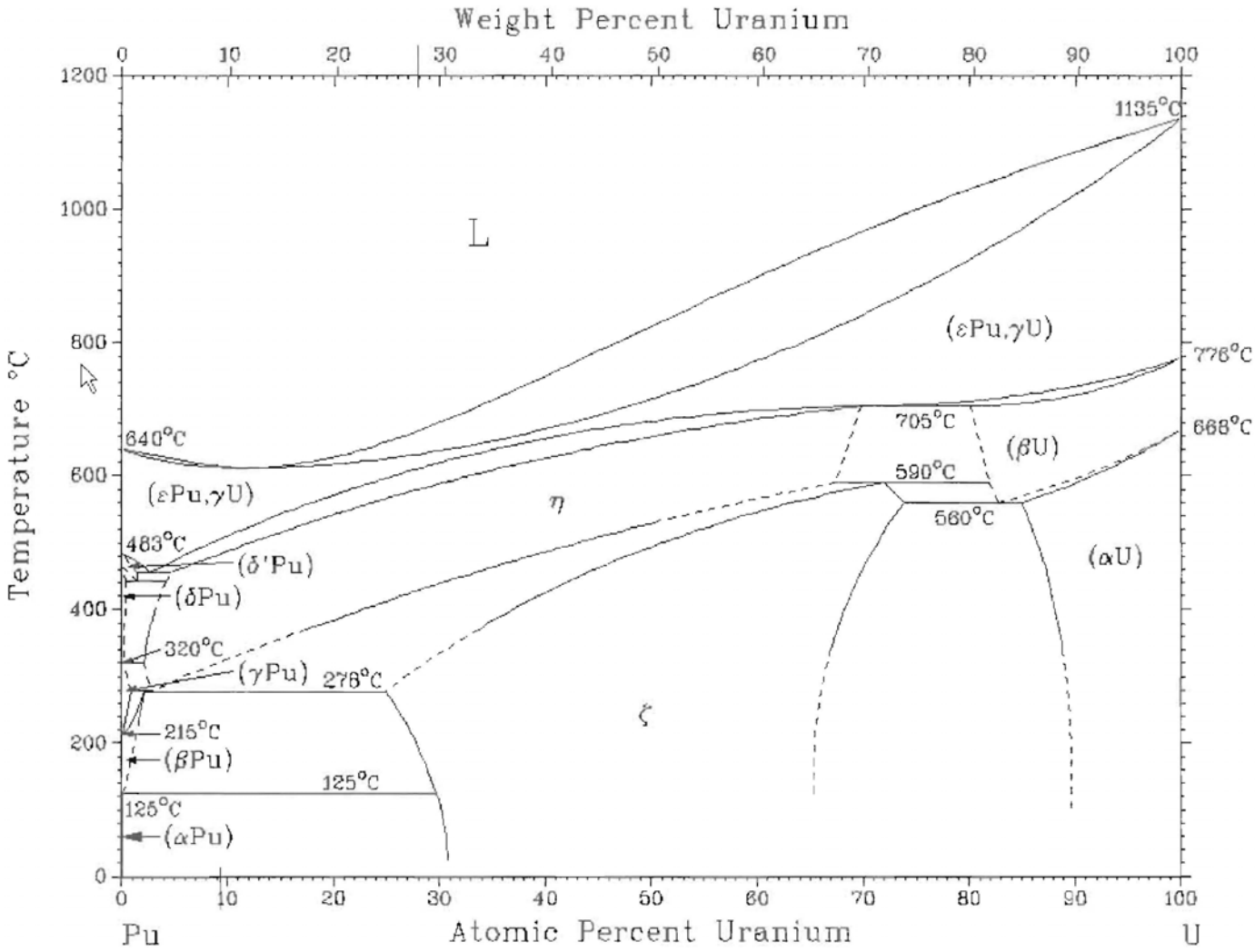

Fig. 5 a) Pu-U phase diagram (from Massalski [])

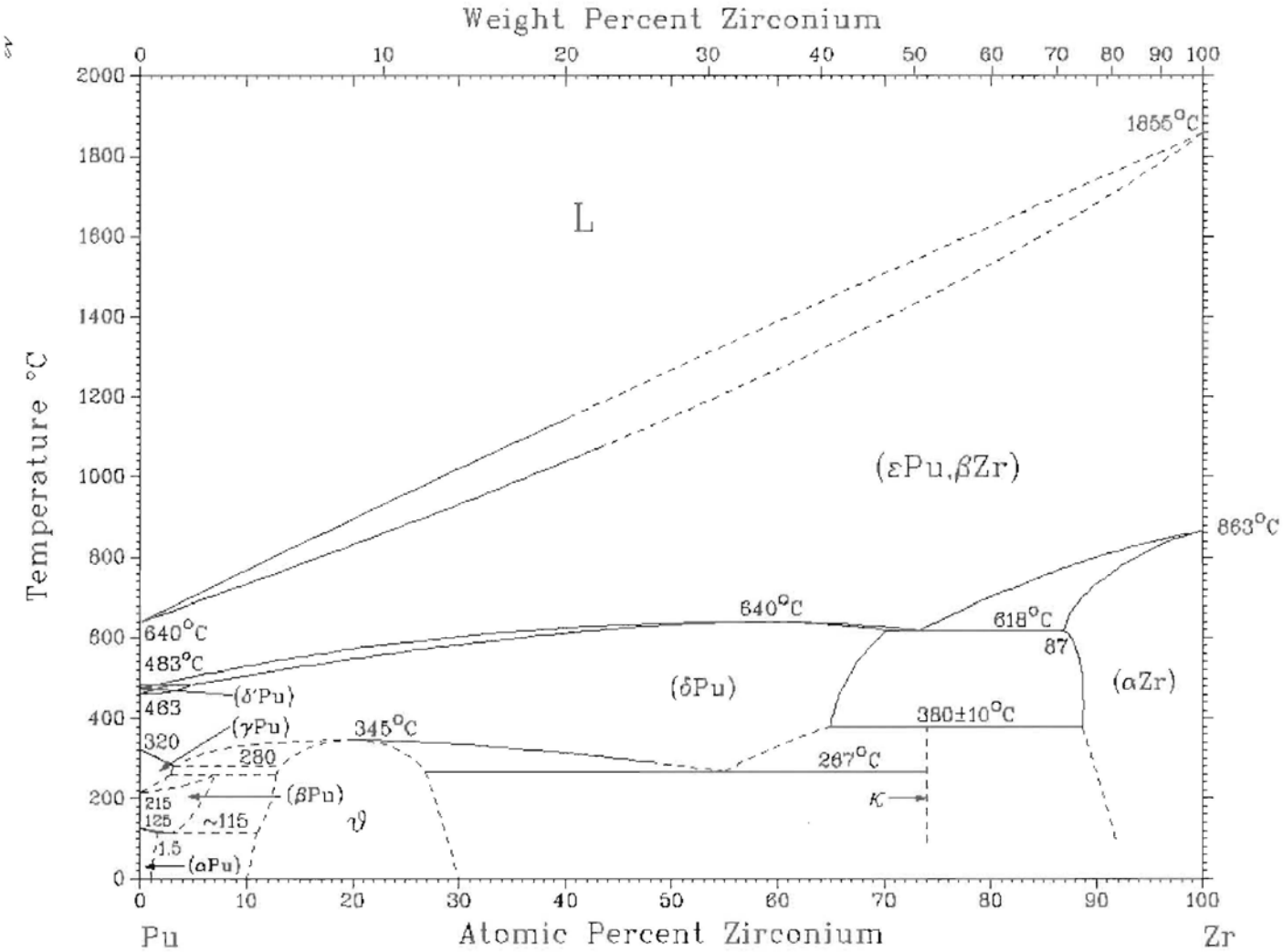

Fig. 5 b) Pu-Zr phase diagram (from Massalski [])

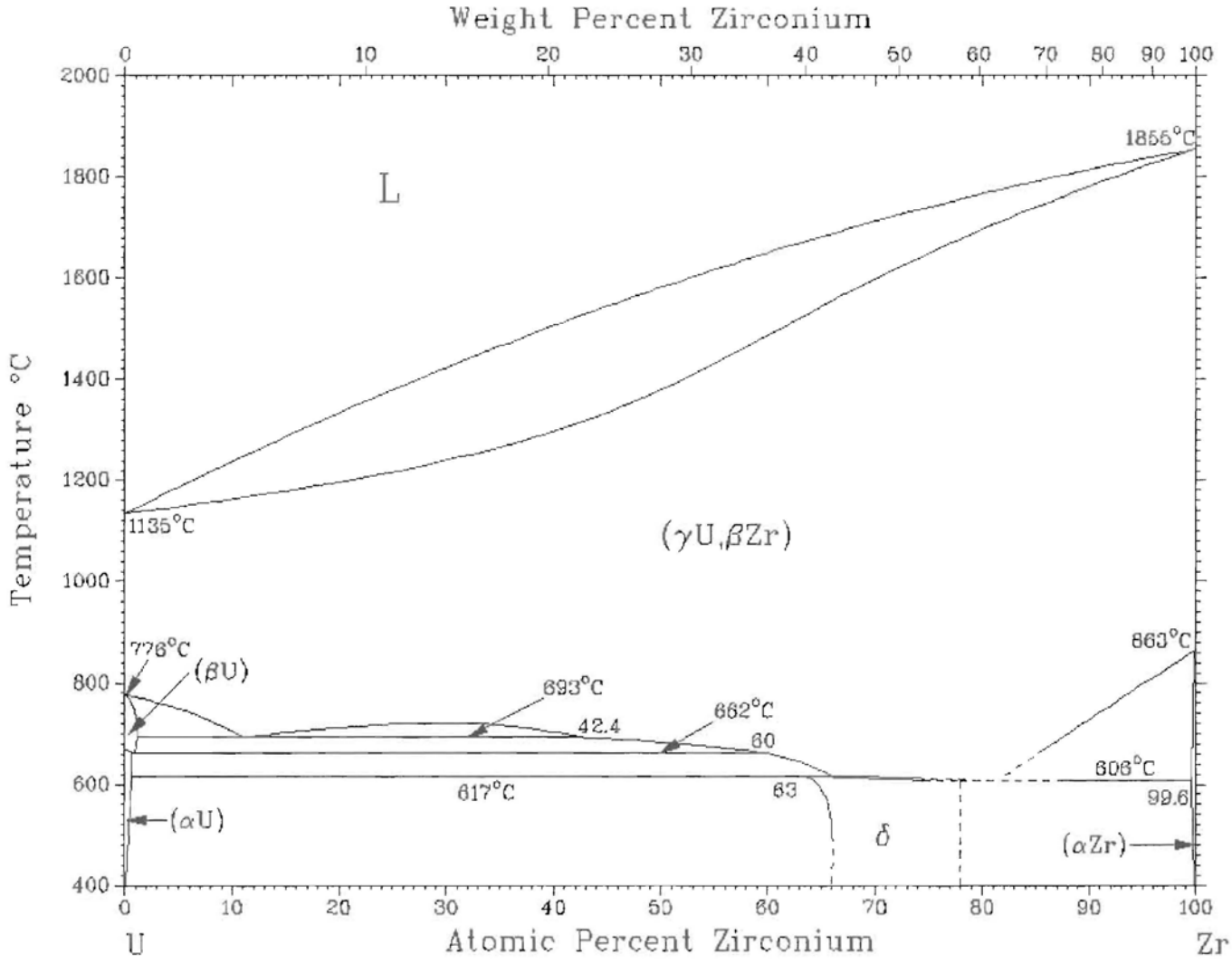

Fig. 5 c) U-Zr phase diagram (from Massalski [])