

Plutonium

A Wartime Nightmare but a Metallurgist's Dream

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In 1942 the theoretical outline for an atomic bomb was clear: compress enough fissionable material long enough to properly ignite a chain reaction. Construction of an actual weapon, however, required translation of “fissionable material” into real pieces of plutonium or uranium metal. These metals had to be free of impurities that would adversely affect the neutron flux during the chain reaction and yet be fabricable enough that precise shapes could be formed. Whether this would even be possible with plutonium was not then known, however, because plutonium was a new, manmade element and the metal had not been produced.

Accounts of the Manhattan Project have neglected (for security reasons, initially) the important metallurgical work that preceded fabrication of these materials into integral parts of real weapons. For example, the Smyth Report* devotes one short paragraph to the wartime work of the entire Chemistry and Metallurgy Division at Los Alamos—a division that in 1945 numbered 400 scientists and technicians. Our article will attempt to fill part of this gap for plutonium by highlighting key developments of the wartime research and will continue with some of the exciting research that has occurred since the war.

Research from 1943 to 1946

The Los Alamos work on plutonium and enriched uranium, the so-called special nuclear materials, was extensive, covering a variety of research problems ranging from purification of material received from reactors to the prevention of oxidation of the final product. Further, because many chemical processes and physics experiments required very pure materials, such as gold, beryllium oxide, graphite, and many plastics, considerable general materials research was also carried out.

Much of the chemistry and metallurgy of uranium was already known from the production of uranium metal for the uranium-graphite reactor pile at Chicago in 1942. The work remaining on enriched uranium included preparation of high-purity metal, fabrication of components, and recycling of residues. However, the most challenging research and development was carried out on the new element plutonium.

Table I gives the important dates in the early history of plutonium and shows the short time—four years—that elapsed between its discovery and its use in the first atomic device at Trinity. The discovery occurred, as predicted by nuclear theory, when uranium was bombarded with 16-million-

electron-volt deuterons in the cyclotron at Berkeley. Within about a month it was shown that plutonium-239 fissioned when bombarded with slow neutrons, and a decision was made to build large reactors at Hanford for the production of plutonium—this before the uranium-graphite pile at Chicago had demonstrated that a sustained and controlled chain reaction was even possible! That demonstration soon followed, proving that large quantities of plutonium could be produced, although no plutonium was extracted from the Chicago reactor.

At this point only microgram amounts of plutonium had been separated from the targets used in the cyclotrons. Remarkably, the basic chemistry of plutonium was worked out at Berkeley and Chicago on this microgram scale, and it formed the basis for the scale-up—by a factor of a billion—needed for plants that would eventually separate plutonium from spent reactor fuel. At the same time the first micrograms of the metal were produced at Chicago by the

**Henry DeWolf Smyth, Atomic Energy for Military Purposes: The Official Report on the Development of the Atomic Bomb under the Auspices of the United States Government, 1940-1945 (Princeton University Press, Princeton, 1945), pp. 221-222.*

reduction of fluorides, and preliminary metallurgical properties were determined. However, the influence of impurities on such tiny samples distorted many of the results; for example, the melting point of plutonium was first thought to be about 1800 degrees Celsius, considerably above the true melting point of 641 degrees. Ultimately, the properties of plutonium were found to be incredibly sensitive to impurities.

It had been agreed that Los Alamos would not work on batches of plutonium of less than about 1 gram, and the microgram-scale work continued at Chicago. Finally, in early 1944 Los Alamos received plutonium nitrate samples containing half-gram amounts of the element from the "Clinton" reactor and pilot extraction plant at Oak Ridge. Later, larger amounts were received from the production facility at Hanford.

The plutonium nitrate arrived in relatively impure form, and techniques and equipment had to be developed for a number of processes, including purification, preparation of plutonium tetrafluoride and other compounds, reduction to metal, and metal fabrication. Also, because plutonium was in very short supply, it was imperative to develop processes to recycle all residues.

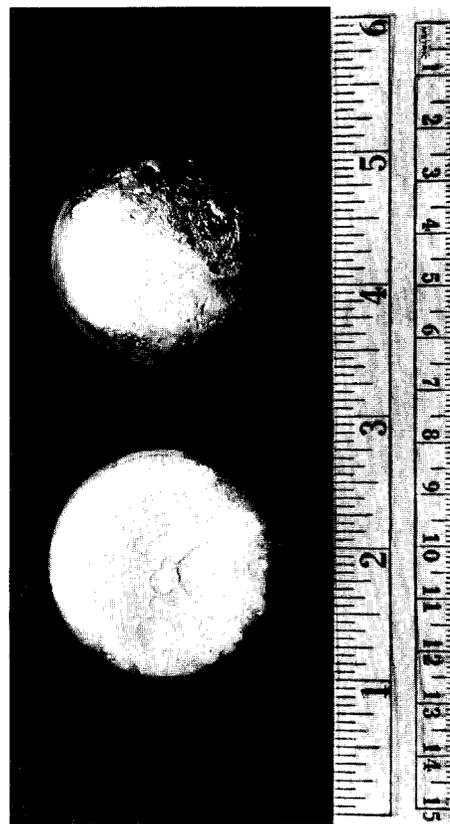
Initially, the purity requirements for the metal were very stringent because some elements, if present, would emit neutrons upon absorbing alpha particles from the radioactive plutonium. These extra neutrons were undesirable in the gun-type plutonium weapon then envisioned: they would initiate a chain reaction before the material had properly assembled into its supercritical configuration, and this "pre-initiation" would decrease the explosive force of the weapon. The purity requirement for certain elements was a few parts per million and for some, less than one part per million. As a result, all the materials used in the preparation of the plutonium metal, everything from the process chemicals to the containers, had to be of very high purity. This necessitated development work on many materials, including an

TABLE I
EARLY HISTORY OF PLUTONIUM

| | |
|---|-------------------|
| Plutonium discovered | February 23, 1941 |
| Neutron-induced fission of plutonium-239, proved | March 25, 1941 |
| Decision reached for large, full-scale plutonium production | December 6, 1941 |
| First controlled fission chain reaction achieved, proving method for full-scale production of plutonium | December 2, 1942 |
| Preparation of plutonium metal from microgram quantities produced with cyclotron | November, 1943 |
| Gram quantities of plutonium nitrate from experimental reactor received at Los Alamos | March, 1944 |
| Plutonium nitrate from production reactor received at Los Alamos | mid 1944 |
| Plutonium weapon demonstrated with Trinity test | July 15, 1945 |

extensive effort to obtain pure and nonreactive refractories to contain molten plutonium. The high purity requirements also necessitated the development of new methods for analysis of all materials, including plutonium.

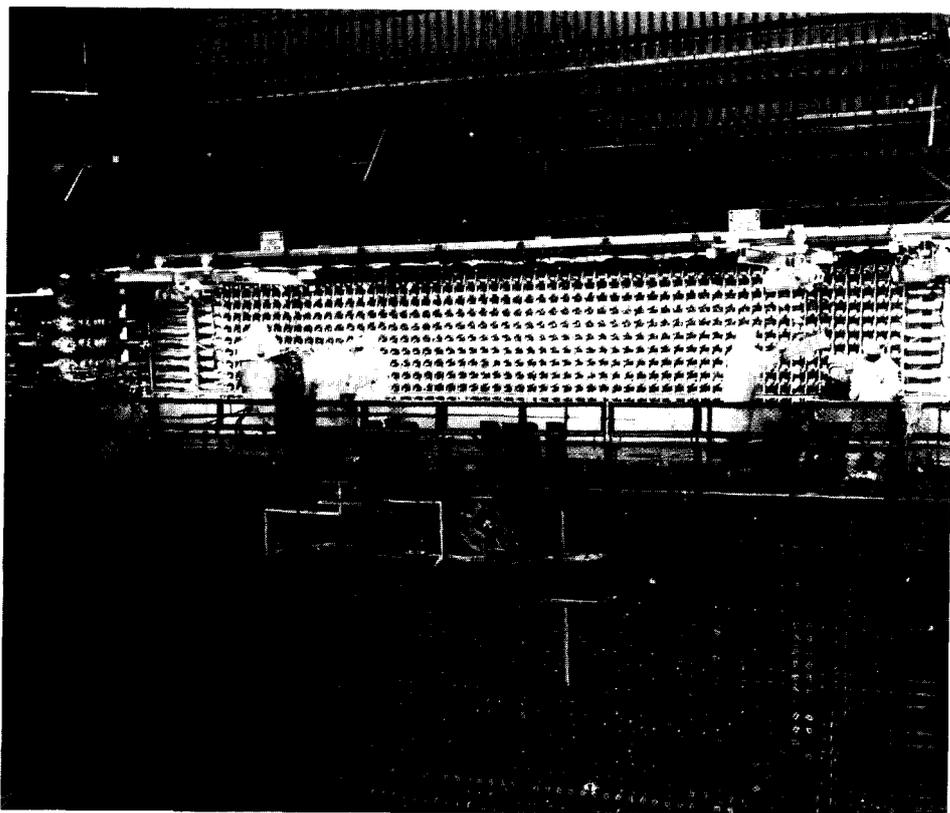
The potential health problem associated with the handling of plutonium had been recognized at Chicago, and work on the subject began with receipt of the first small amounts of plutonium. A Health Group was formed to monitor plutonium work areas, and, within the Chemistry and Metallurgy Division itself, committees were established to design suitable radiation detectors and apparatus for handling plutonium and to formulate safe handling procedures. Because alpha counters then lacked either sensitivity or portability and were in short supply, oiled filter paper was swiped over surfaces to pick up possible stray bits of plutonium and then measured at stationary counters. Similar procedures were used to detect suspected contamination of hands and nostrils. The air-conditioning system in the plutonium laboratory (D Building), which was installed initially to help maintain high purity by filtering out dust, ultimately served the more important function of confining the plutonium. The building was equipped with hoods with minimal ventilation and with the forerunner of the modern glove box—plywood "dry boxes." The successful handling of large quantities of plutonium without serious problems was at that time an outstanding achievement.



Two early discs of plutonium metal after reduction from the tetrafluoride. Plutonium generally arrived at the Laboratory from the Hanford reactors in the form of a relatively impure nitrate solution. Techniques were developed at Los Alamos for purification, preparation of various compounds, reduction to the metal, and metal fabrication.

At first plutonium metal was prepared at Los Alamos either by lithium reduction of plutonium tetrafluoride in a centrifuge, the metal settling out as the closed reaction vessel rotated, or by the electrolysis of fused salts containing plutonium. Soon, however, calcium reduction of the tetrafluoride was perfected. The vessel used to contain this reaction was called a stationary "bomb" because the reaction was highly exothermic and the metal product settled out in the closed, nonrotating vessel simply by gravity. This technique became the preferred method and was used to prepare plutonium for almost all metallurgical studies and for the nuclear devices.

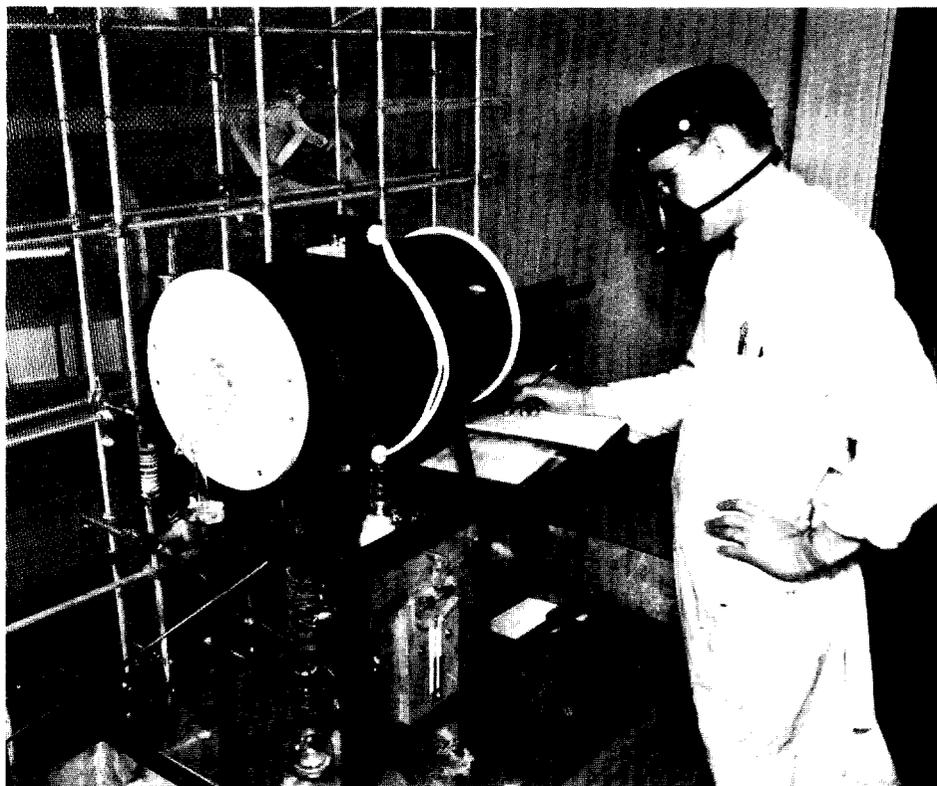
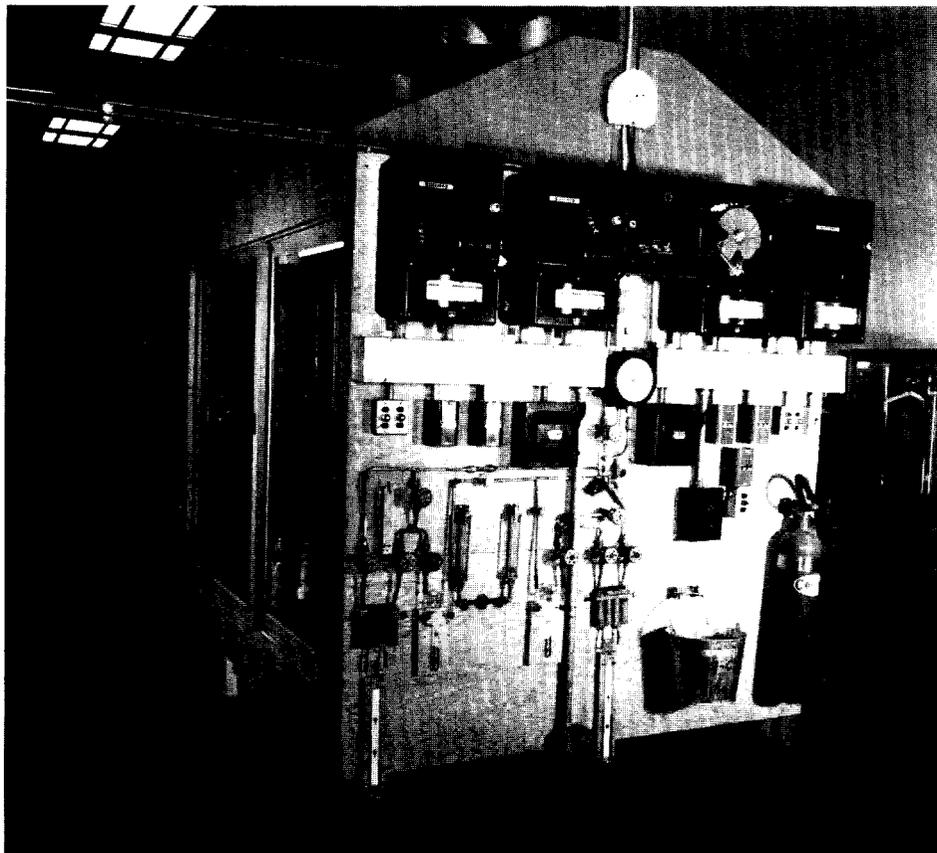
The microgram metallurgy at Chicago had provided values for the density of the metal that clustered about either 16 or 20 grams per cubic centimeter. This bimodal spread, due surely in part to impurities, nevertheless pointed toward interesting metallurgy by hinting that the element had more than one phase. Working with larger amounts, Los Alamos refined these measurements and by the middle of 1944 had discovered that plutonium was a nightmare: no less than five allotropic phases existed between room temperature and the melting point. Unfortunately, the room-temperature alpha (α) phase was brittle, and the metal experienced a large volume change when heated and then cracked upon cooling. These properties made fabrication very difficult, and there was not enough time for detailed fabrication development on the α -phase material. It was thought likely that another phase would be malleable and easily shaped; the problem was how to stabilize such a phase at room temperature. It was then discovered that alloying plutonium with small amounts of aluminum stabilized the delta (δ) phase, which was, in fact, malleable. However, aluminum was one of those elements that emitted neutrons upon absorbing alpha particles and so would exacerbate the pre-initiation problem. Beneath aluminum in the periodic table was gallium, which did not



The first production reactor at Hanford with workmen loading uranium into its honeycomb face. (Photo courtesy of the Department of Energy.)



D Building, the air-conditioned wartime plutonium laboratory, bristling with separate external vents.



The hydrofluorination of plutonium. The upper photograph shows the chemical hoods in D Building used for this process, which converted the oxide to the tetrafluoride. Four furnace controllers are at the top of the panel with one controller open showing the temperature program cut into its rotating disc. Note the bucket of calcium oxide to be used for treatment of hydrogen fluoride burns. The lower photograph shows one of the hydrofluorination furnaces inside the hood.

undergo this type of nuclear reaction. Plutonium-gallium alloys were found to be stable in the δ phase and could be hot-pressed into the required hemispheres. Thus the problem of fabrication was solved. To avoid oxidation of the metal and to contain the radioactivity, the pieces were ultimately coated with nickel.

In July 1944 it was discovered that the plutonium-239 generated in the high-neutron-flux production reactors at Hanford contained too much plutonium-240. Plutonium-240 was undesirable because it had a much higher spontaneous fission rate than plutonium-239 and emitted far too many unwanted neutrons. As a result, pre-initiation in the gun weapon could not be avoided without the difficult task of separating these isotopes. Instead an intense effort was mounted to develop an implosion weapon in which pre-initiation could be avoided because of its higher assembly velocities. This turn of events allowed the purity requirements for the metal to be somewhat relaxed, simplifying many of the process operations. The necessary pieces of plutonium were then fabricated in time to construct the Trinity and Nagasaki devices.

The extreme press of time during the war allowed for the immediate problems of fabrication, stability, and oxidation protection to be solved only empirically. A comprehensive program of basic research on this most fascinating element had to wait until after the war. In Table II we summarize the properties of plutonium metal known in 1945.

Postwar Research and Development

As the war ended, construction began at DP West site on a new, more permanent facility for the plutonium effort. This activity reflected the government's decision to increase production of nuclear warheads and, thus, to scale up all processes associated with the fabrication of plutonium metal parts.

Because the plywood dry boxes of old D Building posed a tire hazard, they were

TABLE II

PROPERTIES OF PLUTONIUM METAL KNOWN IN 1945'

| Phase | Temperature Range of Stability (°W) | Crystal Structure | Density (g/cm ³) | Average Linear Expansion Coefficient (per °C) | Electrical Resistivity (@ cm) | Temperature Coefficient of Resistivity (@cm per °C) |
|---------|-------------------------------------|---------------------|------------------------------|---|-------------------------------|---|
| Alpha | Below 117 | Orthorhombic (?) | 19.8 | 55×10^{-6} | 150 at 25°C | -29.7×10^{-4} |
| Beta | 117 to 200 | Unknown (complex) | 17.8 | 35×10^{-6} | 110 at 200°C | - 0 |
| Gamma | 200 to 300 | Unknown (complex) | Unknown | 36×10^{-6} | 110 at 300°C | - 0 |
| Delta | 300 to 475 | Face-centered cubic | 16.0 | -21×10^{-6} | 102 at 400°C | $+1.5 \times 10^{-4}$ |
| Epsilon | 415 to 637 | Body-centered cubic | 16.4 | 4×10^{-6} | 120 at 500°C | - 0 |
| Liquid | Above 637±5 | | | | | |

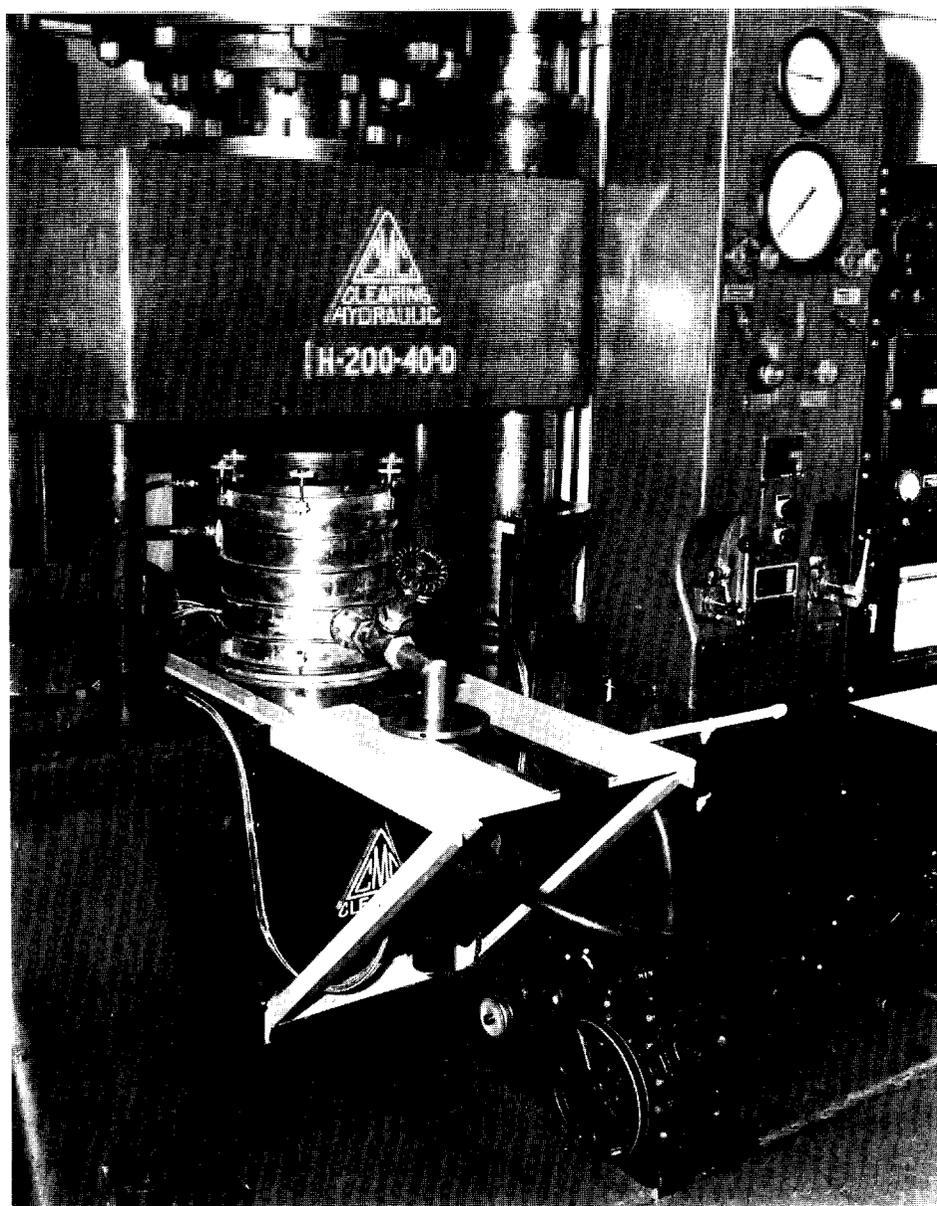
'From Cyril Stanley Smith, Journal of Nuclear Materials 100,3-10 (1981).

replaced with stainless-steel glove boxes. To better contain the plutonium, the glove boxes were equipped with elaborate ventilation-filtration systems devised to keep the atmosphere within each glove box at a lower pressure than the surrounding air so that any leak in the system would not release plutonium to the room. In addition, the breathing air in the laboratories was filtered and changed several times each hour.

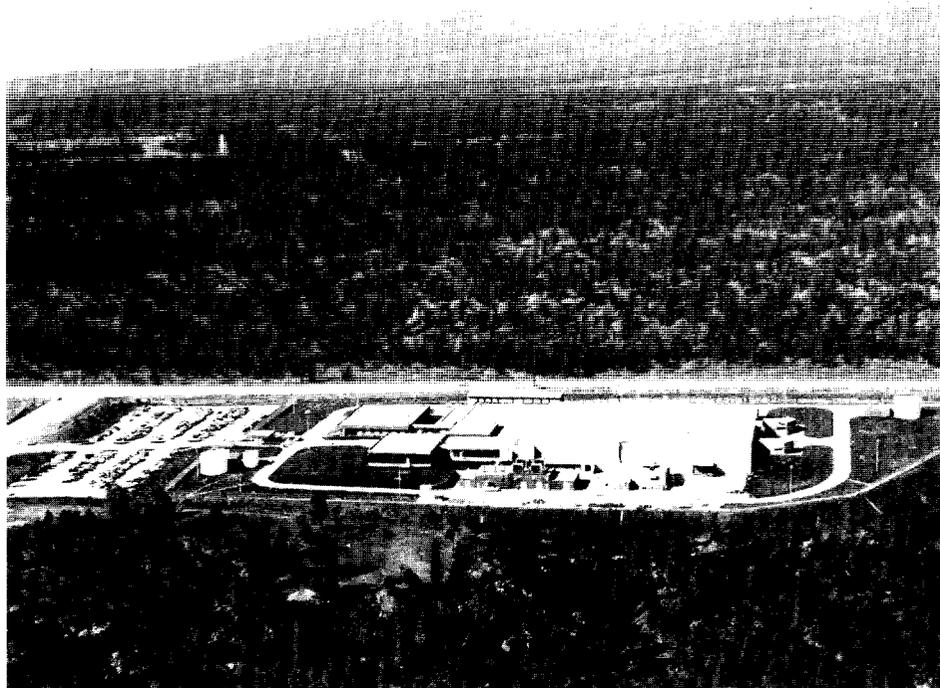
Since all of the processes for purification, preparation, and fabrication of the metal and for recycling of the residues of plutonium and enriched uranium were developed at Los Alamos during the war, there was no other place for the production of nuclear warheads. It was decided that Los Alamos should not continue in production but should concentrate on research and development. The transfer of all the special processes to be used in the new production plants was a major postwar undertaking. Plutonium processes were transferred to Hanford, Savannah River, and Rocky Flats. The enriched uranium processes were transferred to Oak Ridge.

The work at DP West thus settled into a program of basic research and development, and major advances were made in the fledgling plutonium technologies of vacuum casting, metal working, machining, electrorefining, and aqueous processing of scrap. Several plutonium reactor fuels, both metallic and ceramic, and the plutonium-238 heat sources for thermoelectric generators for space and other missions had their beginnings at DP West.

In 1978 the plutonium activities at DP West were moved to the newly completed Los Alamos Plutonium Facility, the most modern and complete plutonium research



Presses used during the war to hot press plutonium metal into the shapes required for the Trinity and Nagasaki devices.



The current Los Alamos plutonium research and development facility. Note, in contrast to the wartime laboratory, the absence of external ventilation on the large research building to the right (upper photograph). The facility uses the most modern equipment, including a computerized plutonium accountability system (lower photograph).

and development center in the country. It incorporates state-of-the-art designs and equipment for the safe containment of plutonium and the protection of workers during all credible accidents or natural disasters, including earthquakes and tornado-force winds.

After the war the continued improvement in process chemistry and applied metallurgy of plutonium came about through a better understanding of its basic properties. Aqueous processes were developed for separating plutonium from virtually every element in the periodic table. The wartime "bomb" reduction process was augmented with other pyrochemical processes such as direct reduction of the oxide and electrorefining. These processes not only yielded a purer product but also minimized the amount of plutonium-bearing residues and the associated radiation exposure of personnel.

Plutonium casting was first carried out with ceramic crucibles and molds because they were known to be compatible with molten plutonium. The discovery that slightly oxidized tantalum was quite unreactive with molten plutonium led to the development of reusable foundry hardware. Also, the development of several ceramic coating processes, based on either calcium fluoride or the stable oxides of zirconium or yttrium, permitted the use of easily machined graphite molds. It was discovered that microcracks resulting from the multiple phase changes that occur as the metal cools and freezes could almost be eliminated by casting the pure metal into chilled aluminum molds, a process that virtually by-passes most of the intermediate phase transformations.

The development of new plutonium alloys for both reactor and weapons use proceeded hand in hand with the determination of the equilibrium phase diagrams of plutonium with most other elements, and the associated complex crystal structures of phases and compounds. Early on we realized that we were dealing with alloys that were metastable in many environments. Thus, it became

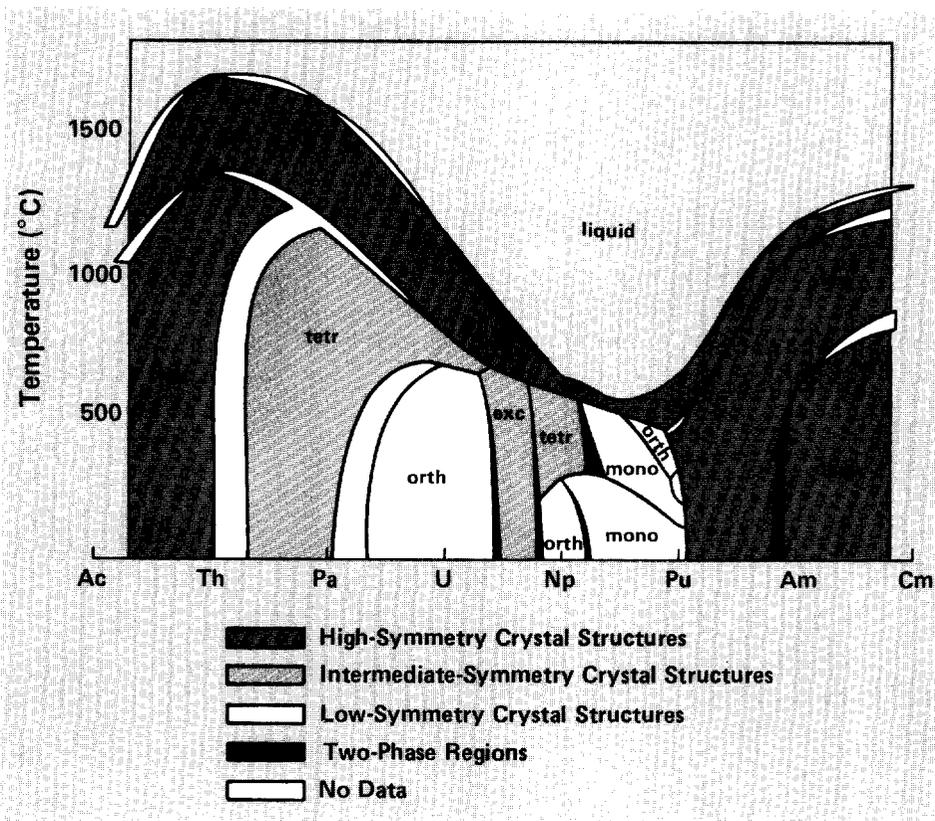


Fig. 2. A connected phase diagram of binary alloys of the actinides (prepared by E. A. Kmetko and J.L. Smith) shows the preponderance of low-symmetry crystal structures, the large number of phase changes, and the depression @melting points in the vicinity of plutonium. The crystal structures are body-centered cubic (bcc), face-centered cubic (fcc), tetragonal (tetr), orthorhombic (orth), exotic cubic (exe), monoclinic (mono), and double hexagonal close-packed (dhcp).

main classified.

In the past decade we have also turned our attention toward a more fundamental understanding of plutonium on the atomic level. This effort has opened a most fascinating chapter in solid-state physics—the electronic properties of the actinides, the seventh period in the periodic table. Interest in the actinides had stemmed primarily from their special nuclear properties. Yet, it is the properties of the electrons (not the nuclei) that govern all chemical and structural behavior. The actinides are characterized, as shown in Fig. 1, by the progressive filling of $5f$ electron orbitals. It is the participation of these $5f$ electrons in atomic bonding that leads to the peculiar and complex behavior of actinide metals and alloys.

Although details of the $5f$ bonding in the actinides are still being contested, it is gener-

ally agreed that the $5f$ electrons in the early actinides (through plutonium) are not fully localized and thus participate in bonding. The $5f$ bonding increases to a maximum at plutonium and vanishes as the electrons become localized near americium. The effects of $5f$ bonding on the behavior of the lighter actinides are dramatic, and most dramatic for plutonium. We will highlight here only three of the most important effects. These are demonstrated in Fig. 2, a connected binary alloy phase diagram of the elements in the actinide series. First, as one moves from actinium to plutonium, a change from highly symmetric cubic to low-symmetry crystal structures occurs. Second, the number of allotropic phases increases. Finally, the melting points decrease dramatically.

How can these effects be explained? To

begin, the wave functions of electrons (like those of p electrons and unlike those of s and d electrons) have odd symmetry. This property is not compatible with symmetric cubic crystal structures but rather favors the low-symmetry crystal structures and, thus, the stability of monoclinic and orthorhombic phases. Only with increased temperature and lattice vibrations is the f character sufficiently overcome in plutonium to permit cubic crystal structures. Beyond plutonium the localization (nonbonding) of the f electrons leads to a return of more typical metallic behavior. Also, because the f electrons are just on the verge of becoming localized and magnetic, small changes in temperature, pressure, or alloying have dramatic effects on phase stability and properties. Hence, allotropy is promoted. Finally, the f electrons bond quite easily in the liquid phase because its less rigid structure increases rotational freedom. This ease of bonding promotes the stability of the liquid (or, equivalently, limits the stability range of the solid) and lowers the melting points.

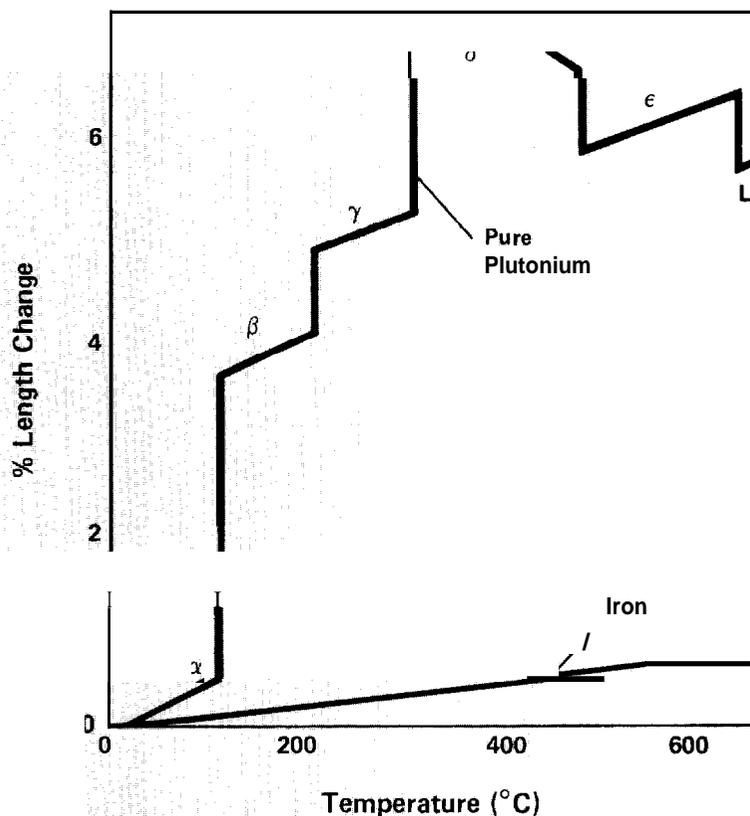
We see that the f electrons are the cause of many of plutonium's peculiarities and complexities, which have important practical consequences. Its low melting point and limited solid stability are particularly important because, as a liquid, plutonium is extremely reactive and corrosive and hence difficult to contain. Liquid plutonium also has the greatest known surface tension and viscosity among metals because of bonding. A less obvious consequence arises from the fact that most rate processes in solids depend upon homologous temperature, that is, temperature relative to the absolute melting point. Hence, diffusion and other thermally activated processes are quite rapid at room and slightly elevated temperatures.

The most significant consequence of plutonium's large number of phases is thermal instability of the solid. This property is best illustrated by a plot of length change during heating. Figure 3 compares the behavior of

plutonium with that of iron. Most phase transitions in plutonium are accompanied by large length and thus volume changes. Such volume changes are difficult to accommodate in solids at relatively low temperatures without loss of physical integrity. In addition, plutonium's α , β , γ , and ϵ phases have very large thermal expansion coefficients. For example, the thermal expansion coefficient of the α phase is about five times greater than that of iron. Therefore special compatibility problems arise wherever plutonium is in contact with other metals. Figure 3 illustrates two exceptionally peculiar properties of plutonium: the negative thermal expansion coefficients of the δ and δ' phases and the contraction upon melting, which results from increased f -electron bonding in the liquid phase.

The crystal structures and the corresponding densities are also listed in Fig. 3. Note that the three structures that are stable at temperatures closest to room temperature are of low symmetry. The cubic structures that are typical of most metals appear only at high temperatures where the $5f$ -electron bonding is overwhelmed. The low-symmetry structures (especially the α phase) exhibit very directional bonding. The α -phase monoclinic structure is essentially covalently bonded. Its unit cell contains 16 atoms with 8 different bond lengths ranging from 2.57 to 3.71 angstroms. Consequently, most of its physical properties are also very directional. In addition, the α phase is a poor conductor and is highly compressible.

The low symmetry and nearly covalent nature of bonding in the α phase greatly affect its mechanical properties, which more nearly resemble those of covalently bonded minerals than those of metals. The α phase is strong and brittle because the low symmetry controls the nature and motion of defects. The face-centered cubic δ phase, on the other hand, behaves much like a normal metal. In fact, the δ phase possesses the strength and malleability of aluminum. One must remember, however, that at δ -phase temperatures



| | Crystal Structure | Density (g/cm ³) |
|------------|----------------------------|------------------------------|
| α | Simple Monoclinic | 19.86 |
| β | Body-Centered Monoclinic | 17.70 |
| γ | Face-Centered Orthorhombic | 17.14 |
| δ | Face-Centered Cubic | 15.92 |
| δ' | Body-Centered Tetragonal | 16.00 |
| ϵ | Body-Centered Cubic | 16.51 |
| L | Liquid | 16.65 |

Fig. 3, A plot of percentage length change as a function of temperature illustrates the dramatic changes that occur with each of plutonium's phase changes. The more sedate behavior of iron is shown for comparison.

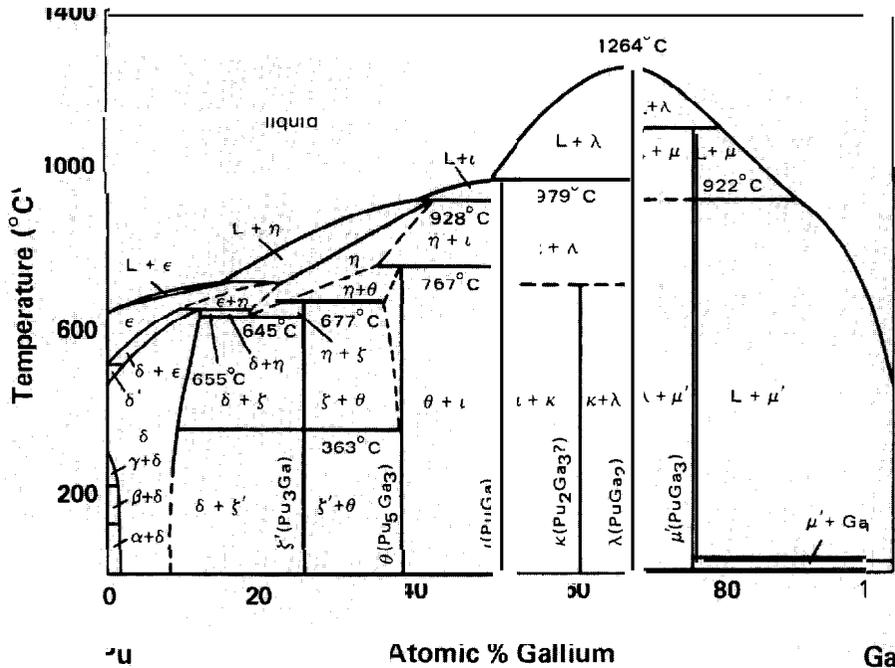


Fig. 4. The plutonium-gallium phase diagram serves as an example of the complexities that occur when plutonium is alloyed. The region of concern during the war was the lower left corner where the malleable δ phase extends down to room temperature at gallium concentrations below 10 per cent.

the $5f$ bonding is essentially gone.

The δ phase can be stabilized to room temperature by alloying. As we pointed out earlier, this fact was already recognized during the war and led to the use of gallium to stabilize this phase. It is now recognized that most trivalent solutes, such as gallium, aluminum, cerium, americium, iridium, and scandium, stabilize the δ phase. Figure 4

shows the plutonium-gallium equilibrium phase diagram as determined at Los Alamos in the postwar era. Note the expanded field of the δ phase on the left and the enormous complexities that result from alloying plutonium. The δ phase in plutonium alloys behaves much like a normal metal and has several advantages over the α phase, including excellent ductility (fabricability), a much

larger range of thermal stability, and a lower thermal expansion coefficient (nearly zero for most alloys).

So far we have not mentioned the effects of pressure. As one might expect, hydrostatic pressure tends to collapse the low-density crystal phases. Hence, in pure plutonium the δ phase disappears at pressures of less than 1 kilobar. Here is where the seventh allotrope of plutonium, the ζ phase, appears before giving way to α or β phases at high pressures. Only moderate pressures are required to collapse the alloyed δ phase to higher density phases. When dealing with alloys at high pressures, we are faced with the problem of what happens to the solute atoms, since they are generally insoluble in the α and β phases. This topic and the question of the response of alloys under nonequilibrium cooling conditions typify the fascinating world of nonequilibrium phase transformations in plutonium, which is beyond the scope of this article.

Plutonium is without question the most complex and interesting of all metals. More so than in any other metal, a fundamental understanding of its metallurgical behavior must be rooted in an understanding of electronic structure. We have highlighted the peculiarity and complexity of plutonium resulting from the $5f$ electrons. The complexity, hidden until after the war, makes the accomplishments of the metallurgists and chemists during the Manhattan Project even more remarkable. ■

Further Reading

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