EXTRACTIVE AND PHYSICAL METALLURGY OF PLUTONIUM AND ITS ALLOYS

Edited by **W. D. WILKINSON**

EXTRACTIVE AND PHYSICAL METALLURGY OF PLUTONIUM AND ITS ALLOYS

Including a Special Introduction and Annotated Bibliography by W. D. Wilkinson,
Argonne National Laboratory

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PREFACE

The metallurgy of plutonium has been worked on for approximately 15 years. It has been a facet of metallurgy fraught with unique and challenging problems. Typical are the extreme radioactivity and toxicity requiring glovebox isolation of all operations, the initial requirement of working with very small amounts of material, and the complexity of six allotropic crystal forms between room temperature and 639°C.

The tremendously effective research that has been accomplished in overcoming these problems has received only limited distribution due to the requirement of secrecy (for many years). The publication of of this volume will, at least in a small way, contribute to the long overdue recognition of the excellent scientific achievements of the authors.

The American Institute of Mining, Metallurgical, and Petroleum Engineers takes pride in its part in assisting in the dissemination of this fine work. The symposium on which this volume is based was organized and edited by the following Officers and Committee Members:

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They are congratulated on their leadership in their profession. We hope that publication of this volume and the knowledge of the fascinating problems in plutonium metallurgy will encourage other groups to enter this field of research.

May 2, 1960 W. R. HIBBARD, JR.

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Introduction to Plutonium Metallurgy

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Abstract

This volume contains papers on the extractive and physical metallurgy of plutonium presented at the 1959 Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers. In order to make the book more generally useful, an annotated bibliography of plutonium metallurgy is included, and this chapter contains an introductory outline of plutonium physical metallurgy describing the general properties, allotropes, and transformation behavior of plutonium and including references to the literature on plutonium alloys. The papers on plutonium extractive metallurgy that are reproduced in this book are believed to give an adequate picture of the status of this field.

Because of favorable nuclear properties and relative availability, plutonium is destined to outstrip uranium-235 in importance as a fuel for nuclear reactors. More and more metallurgists and technologists will therefore have to concern themselves with the study of plutonium. There is consequently a need for readily available published information on this subject.

Circumstances are fortunately more opportune than hitherto for the presentation and publication of papers on plutonium metallurgy. Efforts in this direction appear justified, for the first time, by the recent lifting of most remaining security restrictions in this field. For this reason it was practicable to include two sessions on plutonium metallurgy in the program of the 1959 Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME): one on the extractive metallurgy of plutonium and one on the physical metallurgy. This volume contains the papers presented at both sessions, and turns out to be the first published book devoted solely to plutonium metallurgy.

Although chapters on that subject have appeared in at least two other books,* the rapid and continual unveiling of classified information, which has been in progress in recent years, has immediately inundated such compilations with a flood of additional information, and has made any reasonably up-to-date and comprehensive coverage of the subject impossible. Fortunately this deluge is subsiding, and the outflow of information on plutonium metallurgy has essentially reached a normal level, one corresponding to the level of activity in research. It thus becomes possible to prepare a reasonably complete bibliography on the metallurgy of plutonium—a rather comprehensive guide to the literature in this field.

The publishers have suggested that such a bibliography be annotated and included in this volume as well as an introductory outline of what is known about the physical metallurgy of plutonium. These inclusions have been made. They should help to orient readers who are new to plutonium metallurgy and should enable all who are interested to delve more easily into the background literature. It is felt that the papers and the references in this volume on the extractive metallurgy of plutonium cover this field rather well and that no introductory outline of the extractive metallurgy is required.

The papers in this volume on plutonium alloys should likewise bring any reader up to date in this field if he is familiar with what has gone before. When he has studied the literature on this subject listed in the annotated bibliography, he will know almost everything of importance that is now known about plutonium alloys (except for a very narrow region of information that is still restricted).

It should be recognized that this does not purport to be a handbook but merely a compilation of the plutonium-metallurgy papers presented at the 1959 Annual Meeting of the AIME at San Francisco, plus enough background information for ready understanding and evaluation by the average metallurgist.

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* A. S. Coffinberry and M. B. Waldron, "The Physical Metallurgy of Plutonium," Chap. 4 in "Metallurgy and Fuels," H. M. Finniston and J. P. Howe, eds., *Progress in Nuclear Energy*, Ser. V, McGraw-Hill, New York, 1956; and W. D. Wilkinson and W. F. Murphy, *Nuclear Reactor Metallurgy*, Van Nostrand, Princeton, N. J., 1958. Mention should also be made of plutonium-metallurgy papers presented at the 1955 and 1958 United Nations Conferences on the Peaceful Uses of Atomic Energy and the World Metallurgical Congress in Chicago, November, 1957. The latter papers are in process for publication by the American Society for Metals, and will always be of historical importance.

Because of the hazards involved in working with plutonium, attention is called to references in the bibliography dealing with the safety aspects of such work. This seems appropriate in view of a tragic accident involving a co-author, C. W. Kelley, of one of the chapters included in this volume. The bibliography, aside from the excellent references selected by the authors that are included with their respective reports, will be found in the Appendix.

An outline of the properties and physical metallurgy of plutonium will now be presented. Since this is necessarily a condensed presentation, the values selected for some of the properties differ, in some instances, from other values that have been published. It is impossible to discuss here the reasons for the selections or for the differences. A study of the original references, which will be found in the annotated bibliography, is therefore important.

Physical Metallurgy of Plutonium

Plutonium is characterized by six solid allotropes plus the liquid and vapor phases. The solid allotropes are called α, β, γ, δ, δ', and ϵ. Their respective crystal lattices and parameters are given in a discussion of each allotrope and are summarized by Ellinger, Land, and Cramer on page 157. The characteristics and properties of each allotrope are presented later on in this introduction, although reference to some of the properties will be made earlier in a discussion of atomic structure and nuclear and chemical properties.

Liquid plutonium will be dealt with in this one paragraph as follows. The liquid phase is stable between 639 ± 5 and 3300°C. Its density, ρ, at 655°C is 16.50 ± 0.08 g/cu cm, and its volume expansion per °C is $50 \pm 25 \times 10^{-6}$. Its surface tension, when free of oxide film and adsorbed gases, is probably about 500 dynes/cm. Between 655 and 960°C the density can be obtained from the relation $\rho = [17.56_7 - (1.45_1 \times 10^{-3}T)] \pm 0.021$ g/cu cm, and the surface tension, γ, in dynes per centimeter from the relation $\gamma \cos \theta = 1030 - (0.967)T$. In these relations T is the temperature in °C and θ is the contact angle on liquid plutonium on solid tantalum. When molten, plutonium reacts with and becomes contaminated by many materials, but liquid plutonium can be contained in sintered magnesia or beryllia,* or in tantalum coated with tantalum carbide or, probably, with boride,

* But see page 13.

and can be contained briefly in tantalum or in graphite coated with more nearly inert ceramic materials without extensive reaction In the liquid state plutonium reacts less with tantalum or columbium than with zirconium, chromium, nickel, platinum, palladium, titanium, rhodium, stainless steel or possibly tungsten. Additions of eutectic formers in suitable amounts; namely, 3.2 w/o Fe, 4 w/o Ni, or 9 w/o Os lower the freezing temperature to 430°, 465°, and 495°C, respectively. Although liquid bismuth at its melting point dissolves almost no plutonium, 1 w/o Pu is miscible with the bismuth at 500°C and 20 w/o at 800°C.

Little is known about the vapor phase of plutonium. The pressure equation for pure plutonium is

$$\log_{10} P \text{ (mm Hg)} = 17{,}587 \pm 73/T + 7.895 \pm 0.047$$

where T = °K between 1100 and 1500°C, and the heat of vaporization is 80.46 kcal/mole. On distillation from uranium it appears to obey Henry's law.

Plutonium metal is generally obtained pyrochemically by reduction of a halide but can be obtained by electrolytic reduction in a fused salt bath. Some of the methods of extraction and recovery are discussed in several of the following chapters. When cast, the reduced metal contracts on freezing. Although some blebbing occurs, castings usually have good surfaces and are free of shrinkage cavities and piping. Post-solidification shrinkage enables a casting of pure plutonium to drop out of an inverted mold, but delta-stabilized alloys will not shrink so much and may be difficult to remove.

It is proposed to consider next the general properties of plutonium, mostly nuclear and chemical, then to consider each of the solid allotropes, and, finally, the behavior of plutonium on transforming from one phase to another.

The plutonium atom has many electron energy levels of nearly identical energy and the electron state is rather easily affected by temperature, pressure, its atomic neighbors, and by its magnetic and electric environment. The valence electrons of plutonium are $5f^6 6d^0 7s^2$ for the free atom. Approximate configurations such as $5f^6 6d^1 7s^1$ and $5f^5 6d^3 7s^0$ appear compatible with some of its metallic behavior but do not agree with others based on bond distances. Nonintegral numbers of electrons in these states are probably the rule.

In compounds such as $PuNi_{1-5}$ plutonium resembles cerium in that it has free f electrons, and in compounds such as Pu_2Ni_{17} plutonium resembles thorium in that it possesses free d electrons. The temperature coefficients of magnetic susceptibility are negative in the case of beta, gamma, and epsilon plutonium, positive in the case of delta prime, and nearly nil in the case of alpha plutonium. It is theorized that negative coefficients represent an increase of f electrons, and positive coefficients represent a decrease. The absence of change is believed associated with free d electrons.

A negative thermal coefficient of expansion, which characterizes delta and delta-prime plutonium, is attributed in one theory to a continuous change from $5f$ to $6d$ states on heating and to corresponding attractions between layers of hybridized directional bonds. The coexistence of delta, delta prime, and epsilon has been confirmed for some temperature regions, just as two types of atoms can coexist in manganese or tungsten. If different atomic structures coexist in proportions that vary sufficiently with temperature, it appears likely that a negative coefficient might result.

Thermodynamic considerations by Varley indicate that if $(\partial S/\partial V)_T$ is negative, where S is entropy and V is atomic volume, a negative thermal coefficient is possible. For this to occur there is some evidence that the electronic specific heat must be high and the Gruneisen constant must be negative. Attempts have been made to test this by measuring the absolute thermoelectric power, ϵ, which, for a given temperature, is thought to be equal to a constant times R_ϵ, the rate of change with energy of the number of states per unit energy in overlapping $5f$-$6d$ bands. The R_ϵ is thought to be proportional to the electronic contribution to $(\partial S/\partial V)_T$. Since the value of ϵ calculated for delta plutonium from Pu-Pt thermocouple emf's is positive, the rate of change R_ϵ must be positive. This line of reasoning would invalidate Varley's thermodynamic explanation.

It is possible, however, that some fallacy exists somewhere in this reasoning. For example, $\epsilon = (1/e)(d\bar{\mu}/dT)$, where $\bar{\mu}$ is merely the electrochemical potential of the free electron, and arises when a temperature gradient is applied to a homogeneous electronic conductor. It is conceivable that electronic shifts (such as $f \rightarrow d$ and possibly $s \rightarrow d$) can be made without significantly affecting the electrochemical potential (hence, without affecting the absolute thermoelectric power). Such shifts might well affect the atomic radius, however, and the spin alignments in such a way that $(\partial S/\partial V)_T$ is negative. This is the principal requirement of Varley's explanation.

Since the addition of alloying elements changes the concentration and energy per atom of electrons, it might be expected to affect the sign of the expansion coefficient of delta plutonium, and this is what actually happens. Three weight per cent (w/o) of aluminum, for example, results in a positive temperature coefficient at all delta temperatures, and smaller additions have this effect at the lower delta temperatures.

The nuclear properties of plutonium and plutonium alloys are of interest to metallurgists from a safety standpoint as well as from a technological standpoint. These will now be considered.

Plutonium-239 is produced by the reactions

$$\text{U-238} \xrightarrow{n,\gamma} \text{U-239} \xrightarrow[23.5\text{ min}]{\beta^-} \text{Np-239} \xrightarrow[2.33\text{ days}]{\beta^-} \text{Pu-239}$$

The raw material, U-238, is 140 times as abundant as U-235, and the product, Pu-239, produces 16% more neutrons per fission and has a relatively high cross section to fast neutrons. These are favorable properties for fuels used in fast breeder reactors.

Depending upon details of production, various other isotopes; namely, Pu-238, Pu-240, and Pu-241, will be present in various amounts. Of the isotopes, Pu-238. Pu-239, and Pu-240 are principally alpha emitters, and Pu-241 is an emitter of beta and gamma activity. The half-lives of the four isotopes are 90, 24,300, 16,600, and 14 years, respectively.

We are primarily concerned with Pu-239, the principal isotope. Once it is absorbed into a human system, through the lungs or the bloodstream, the alpha radiation is extremely damaging to surrounding tissues. The alpha particles will not penetrate through the walls of a rubber glove, yet a mass of plutonium equal to that of a copper cent would constitute lethal doses for about three million people. A body burden of plutonium exceeding 0.6 of a microgram is beyond permissible limits. For this reason plutonium and plutonium compounds are never handled with bare hands and are normally confined so that they cannot contaminate the atmosphere.

Alpha particles in a lump of plutonium cannot escape, as such, unless they are at the surface. Although their maximum energy is 5.15 mev, their range is very low, being 3.68 cm in air or 45 μ in tissues of the body. Most of them accumulate in the plutonium lattice as helium particles, accumulating at the rate of 0.05 cu cm of helium per cubic centimeter of plutonium per year. The resulting stress and strain, due to the helium pressure, will therefore be greater in old castings than in new ones, and the respective creep strengths should differ. It would probably take one or two centuries, however, for the helium pressure in alpha plutonium to reach the breaking stress.

Self-heating is another consequence of alpha emission. The temperature of an uninsulated specimen increases with its size and compactness. The surface temperature of uninsulated compact specimens weighing fifty to one-hundred grams, for example, will be about 5°C warmer than the ambient temperature, for the self-heating coefficient is 1.923×10^{-3} w/g (0.459 cal/g of plutonium per second). This property has been utilized in adiabatic dilatometry and in measurements of thermal conductivity and of specific heat. It also accentuates a tendency to corrode. Large specimens stored in insulated containers will feel warm when touched with a gloved hand.

Standard plutonium, that which is most commonly available for fuel element use, is 99.8 w/o pure and is ordinarily a mixture of plutonium isotopes some of which emit low-energy gamma radiation. This radiation may necessitate restrictions on the number of hours per week plutonium may be handled with gloves. The total activity of x-rays and gamma rays in a 1-kg sphere of massive Pu-239 is approximately 900 mr/hr at contact, whereas that from a 1-kg sphere of Pu-241 is 20 to 30 r/hr. These are soft gamma rays that, for the most part, are easily absorbed by glovebox materials such as stainless steel. The beta emission is insignificant from a safety standpoint.

Of more concern is the neutron emission from plutonium and plutonium alloys, compounds, and mixtures with light elements. Some of the neutrons may be produced by α,n reactions and some by fission.

Recycled plutonium is that which has been recovered from plutonium fuel for re-use. Its total irradiation intensity may be 8 to 9 roentgens/kg/hr, two-thirds of which will be from fast neutrons. Workers, even when wearing gloves, should operate with the recycled plutonium at least one meter distant.

Various low atomic weight ("light") elements undergo α,n reactions in which the impact of alpha particles from the plutonium causes fast neutrons to be emitted from the light nuclei. Some nuclear engineers would limit fast neutron exposures to no more than 80 mr/40 hr week.

The neutron emission rate can be calculated from the relation

$$n = E(A^1 + BN)$$

where n = the neutron emission rate, E = the light-element concentration in ppm, $A^1 = A[(\alpha - 239) + (\alpha - 240)]/\alpha - 239$, $\alpha_i = \alpha$ disintegration rate per gram of mixture for species i, A = a constant for Pu-239 (see Table I), B = a constant for Pu-238 (see Table I), and N = the atoms of Pu-238 per atom of Pu.

TABLE I

Effect of Light-Element Impurities in Plutonium[a]

			Light-element impurities in 1 kg sphere of plutonium,[b] ppm (Based on 1000 mr/40 hr week at contact)			
Light element *L*	Pu-239 *A* (*n*/g min ppm of *L*)	Pu-238 *B* (*n*/g min ppm of *L*)	49	49 + 13.5% 40	49 + 1000 ppm 48	49 + 13.5% 40 + 1000 ppm 48
Li	2.92	1.09×10^{-3}	11	7.3	8	5.8
Be	43.2	1.91×10^{-4}	0.47	0.31	0.32	0.24
B	12.6	6.38×10^{-3}	1.59	1.06	1.1	0.79
C	7.3×10^{-2}	38.4	2,575	1,716	1,680	1,265
N	6.6×10^{-4}	5.46	750,000	33,500	6,100	5,800
O	2.9×10^{-2}	15.5	6,500	4,330	4,200	3,175
F	3.49	2.01×10^{3}	5.8	3.83	3.7	2.76
Na	0.266	1.53×10^{2}	9.8	66	62	47
Mg	0.139	1.095×10^{2}	1,350	900	760	590
Al	0.179	1.355×10^{2}	145	97	83	64
Si	0.359	5.29×10^{2}	280	166	100	84
Cl	4.78×10^{-2}	89.6	1,100	733	580	328
A	0.106	1.515×10^{2}	212	142	88	73
K	1.06×10^{-2}	20.0	3,200	2,133	1,110	945
Ca	9.3×10^{-3}	18.25	5,650	3,765	1,900	1,630
Sc	1.06×10^{-3}	3.10	28,250	18,850	7,200	6,400
Fe	6.6×10^{-4}	2.74	250,000	165,000	55,000	50,000

[a] E. D. Arnold, *Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/1838.

[b] Here, 49 designates Pu-239, 40 designates Pu-240, and 48 designates Pu-238. Plutonium-241 does not participate in α,n reactions.

Table I gives the constants *A* and *B* and the concentrations of light metal alloying elements (for a 1 kg sphere of various mixtures of plutonium isotopes) that will give fast neutron dosages of 1000 mr/40 hr week at contact by virtue of the α,n reaction. Because of the range of energies of fast neutrons and some ignorance concerning their relative biological effectiveness it is difficult to convert this to mrem per 40 hr week, but it should be possible to handle a 1-kg sphere of alloy safely at a distance of three feet without shielding.

For spheres up to one kilogram, spontaneous fission may not pose any handling problem in the case of Pu-239, but it may be a factor in the case of isotopic mixtures. Table II indicates some of the fast neutron activity that might be expected. The "equilibrium mixture" listed in Table II is that which might be obtained from a given reactor under certain operating conditions.

TABLE II

Spontaneous Fission Dose Rates at the Surface and at One Meter from a Kilogram Sphere of Plutonium[a]

Pu isotopes	Spontaneous fission neutron flux at surface (n/cm^2 sec)	Spontaneous fission dose rate At surface (mr/hr)	 At one meter (mr/hr)
Pu-239	0.667	0.114	3.12×10^{-5}
Pu-239 + 20% Pu-240	5600	920	0.252
Pu-239 + 20% Pu-240 + 10% Pu-242	1.06×10^4	1810	0.496
Pu-239 + 1000 ppm Pu-238	75	13	3.56×10^{-2}
Pu-239 + 20% Pu-240 + 10% Pu-241 + 1000 ppm Pu-238	1.061×10^4	1810	0.496
Equilibrium Pu (36% Pu-239 + 14.7% Pu-240 + 8.8% Pu-241 + 40.3% Pu-242	2.44×10^4	4160	1.04

[a] A. E. Arnold, *Second United Nations Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/1838.

The intensity of the α,n reaction depends largely upon the intimacy of mixing: those light elements that form compounds with plutonium are capable of achieving the most intimate mixture. Elements such as lithium would undergo an important α,n reaction if they were intimately mixed with plutonium. The immiscibility of lithium with plutonium and its disinclination to form an intermetallic compound makes Pu-Li alloy relatively unimportant as a source of neutrons. Compounds such as PuF_3 and PuF_4 are more important neutron emitters, since the fluorine undergoes an α,n reaction and it is combined with the plutonium. The emission of neutrons per second per kilogram of PuF_4 will be about one-eighteenth that of $PuBe_{13}$.

The intermetallic compound $PuBe_{13}$ is a convenient neutron source to use. Being a compound rather than a mixture it is homogeneous and its neutron emission rate; namely, 6.7×10^4 n/sec g, does not need to be calibrated. Higher neutron yields are, however, obtainable when the concentration of Pu-239 exceeds the stoichiometric requirement.

If very stringent concentration limitations on light-metal impurities cannot be met, alpha-produced neutrons can very easily become the major source. Spontaneous fission will, however, be the most important contributor to the over-all dose from plutonium when it is relatively pure.

Pure Pu-239 has a spontaneous fission rate of 1.008×10^{-2} SF's (spontaneous fissions)/g sec. This is equivalent to 0.667 n/cm^2 sec at the surface of a kilogram sphere. With neglect of neutron capture this flux corresponds to 0.11 mr/hr fast neutron dose rate.

If this plutonium contains 20% Pu-240 + 10% Pu-242, the spontaneous fission rate is increased to 1.62×10^2 SF's/g sec. This rate corresponds to 1.06×10^4 n/cm^2 sec or to a dose rate of 1.81 r/hr at the surface of the sphere.

The neutrons from spontaneous fissions have an energy of 2 mev/neutron, and there are about 3 neutrons per fission.

The quantity and disposition of plutonium in storage must be controlled from the criticality standpoint. The minimum critical mass of plutonium metal is somewhat more than 300 g in an unreflected sphere of solution but somewhat less than 300 g when in a reflected solution. As the concentration of Pu-239 in organic extractant increases from 0.01 to 10 kg/liter, the atomic ratio of hydrogen to plutonium decreases from 2000 to approximately one, and the critical thickness of an infinite liquid slab decreases from about 10 in. to either about 1 or 3 in., depending upon whether the solution is water-reflected or is contained between $^1/_{16}$ in. thick stainless steel.