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LASL Advanced Plutonium LMFBR Fuel Program Publications

by

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LASL ADVANCED PLUTONIUM LMFBR FUEL PROGRAM PUBLICATIONS

(An annotated bibliography)

by

Joseph A. Leary

ABSTRACT

Forty articles published by LASL authors are summarized. Subjects include synthesis, fabrication, properties, and irradiation testing of plutonium advanced fuels for fast breeder reactors.

I. FOREWORD

A research and development program on plutonium-containing advanced fuels for fast breeder reactors has been in continuous progress since the early 1960's. This report summarizes the articles published in the program with the intent of providing a useful reference for future work. This bibliography is arranged in chronological order

Some articles on general materials science published by LASL authors have not been included in order to keep the number to a useful minimum and because they do not relate directly to the advanced fuels program.

Many of the details of the work published in these articles are given in progress reports on the advanced fuels program, and in US/UK Libby-Cockcroft Plutonium Fuels Information Exchange Newsletters as well as in the US/Japan Research Newsletters on Ceramic Nuclear Fuels. Contributions to the High Temperature Fuels Committee Meet-

ings also contain additional information. None of these sources has been included in this bibliography, but they are listed here for those interested in seeking details. The earliest progress reports are titled: Quarterly Status Report on Solid Plutonium Fuels, and include

LAMS-2949, Period up to June 30, 1963

(First report)

LAMS-3023, Period July 1-Sept 30, 1963

LAMS-3054, Period Oct 1-Dec 31, 1963

LAMS-3107, Period Jan 1-Mar 31, 1964

(Last report in series).

In 1966 a new series appeared under the title Quarterly Reports - Advanced Plutonium Fuels Program. These are listed below. Quarterly Reports - Advanced Plutonium Fuels Program

LA-3607-MS July 1-Sept 30, 1966

(First report in series)

LA-3650-MS Oct 1-Dec 30, 1966

LA-3686-MS Jan 1-Mar 31, 1967

LA-3745-MS Apr 1-June 30, 1967

LA-3820-MS July 1-Sept 30, 1967
 LA-3880-MS Oct 1-Dec 31, 1967
 LA-3933-MS Jan 1-Mar 31, 1968
 LA-3993-MS Apr 1-June 30, 1968
 LA-4073-MS July 1-Sept 30, 1968
 LA-4114-MS Oct 1-Dec 31, 1968
 LA-4193-MS Jan 1-Mar 31, 1969
 LA-4284-MS Apr 1-June 30, 1969
 (Third annual report)
 LA-4307-MS July 1-Sept 30, 1969
 LA-4376-MS Oct 1-Dec 31, 1969
 LA-4437-MS Jan 1-Mar 31, 1970
 LA-4494-MS Apr 1-June 30, 1970
 LA-4546-MS July 1-Sept 30, 1970
 LA-4595-MS Oct 1-Dec 31, 1970
 LA-4693-MS Jan 1-Mar 31, 1971
 LA-4749-MS Apr 1-June 30, 1971
 (Fifth annual report)
 LA-4841-MS July 1-Sept 30, 1971
 LA-4913-PR Oct 1-Dec 31, 1971
 LA-4993-PR Jan 1-Mar 31, 1972
 LA-5067-PR Apr 1-June 30, 1972
 LA-5106-PR July 1-Sept 30, 1972
 LA-5193-PR Oct 1-Dec 31, 1972
 LA-5284-PR Jan 1-Mar 31, 1973
 LA-5390-PR Apr 1-June 30, 1973
 LA-5477-PR July 1-Sept 30, 1973
 LA-5582-PR Oct 1-Dec 31, 1973
 (Latest report as of June 1974).

II. BIBLIOGRAPHY

1. A. E. Ogard, W. C. Pritchard, R. M. Douglass, and J. A. Leary, "The Powder Metallurgy of Plutonium Fuel Materials," in Power Metallurgy in the Nuclear Age, Plansee Proceedings 1961, F. Benesovsky, Ed. (Metallwerk Plansee Ag., Reutte/Tyrol, 1962) pp. 364-372.

- Reviews methods for synthesizing carbides; results on preparation of PuC, Pu₂C₃, and (U,Pu)C by carbothermic reduction of the oxides; structural analysis by x-ray powder diffraction, preparation of dense pellets by cold compaction and sintering in vacuum and helium.

2. A. E. Ogard, W. C. Pritchard, R. M. Douglass, and J. A. Leary, "The Prep-

aration of Uranium Monocarbide-Plutonium Monocarbide Solid Solutions, Plutonium Sesquicarbide, and Plutonium Monocarbide," J. Inorg. Nucl. Chem. 24, 29-34 (1962).

- Synthesis of single phase and mixed phases of carbides by carbothermic reduction of the oxides, followed by fabrication of dense pellets by conventional powder metallurgical methods.

3. Allen E. Ogard and Joseph A. Leary, "Method for Preparing Uranium Monocarbide-Plutonium Monocarbide Solid Solution," U.S. Pat. No. 3,082,163, March 19, 1963.

- Carbothermic reduction of mixtures of UO₂, PuO₂, and C to produce single phase (U,Pu)C for fast breeder reactor application.

4. A. E. Ogard, C. C. Land, and J. A. Leary, "The Thermal Expansion of PuC and US-PuC Solid Solutions," J. of Nucl. Materials 15, 1(1965).

- Thermal expansion between 25° and 900°C and mechanism for contraction in some PuC compositions on heating to 300°C;

for single phase PuC: $\Delta L/L = (-4.0 \times 10^{-4} + 8.3 \times 10^{-6}t + 3.0 \times 10^{-9}t^2)$,
 (mean coef. $11.0 \times 10^{-6}/^\circ\text{C}$);

for single phase U_{0.87}Pu_{0.13}C: $\Delta L/L = (-3.8 \times 10^{-4} + 8.7 \times 10^{-6}t + 3.0 \times 10^{-9}t^2)$

(mean coef. $11.1 \times 10^{-6}/^\circ\text{C}$).

5. J. A. Leary, R. L. Thomas, A. E. Ogard, and G. C. Wonn, "Thermal Conductivity and Electrical Resistivity of UC, (U,Pu)C and PuC," in Carbides in Nuclear Energy, L. E. Russell Ed. (Macmillan and Co. Ltd., London, 1965) pp. 365-371.

- Thermal conductivities of PuC, UC, and (U,Pu)C over the temperature range 200-400°C; reduction of thermal conductivity by addition of PuC to UC, and corresponding effect on electrical resistivity.

6. Joseph A. Leary and Robert L. Nance, "Method of Preparing Plutonium Mononitride,"

- U.S. Pat. No. 3,279,898, Oct 18, 1966.
- Describes method of preparing non-pyrophoric plutonium nitride from plutonium metal by conversion to the hydride and reaction with nitrogen.
7. J. A. Leary, "Recent Developments in High-Temperature Plutonium Compounds," Trans. Amer. Nucl. Soc. 9, 37(1966).
- A review of developments in advanced uranium-plutonium materials, including properties as thermal conductivity, thermal expansion, phase relationships and structure analysis, thermodynamic properties.
8. J. A. Leary, R. L. Nance, W. C. Pritchard, J. G. Reavis, M. W. Shupe and A. E. Ogard, "Preparation and Properties of Plutonium Mononitride and Uranium Mononitride Solid Solutions," American Ceramic Society, Portland, Oregon, Oct. 26-28, 1966.
- Methods for preparing subject nitrides as fine powders and as dense pellets; reaction of PuN with PuO_2 ; lattice dimensions of solid solutions of PuN in UN; differential thermal analysis of nitrides to melting; decomposition pressures of actinide nitrides; Gibbs free energy of formation of PuN at 700°K was (-60 ± 1) kcal/mole by emf measurements. (See Appendix A)
9. G. M. Campbell and J. A. Leary, "Thermodynamic Properties of Plutonium Mononitride from Electromotive Force Measurements," J. Phys. Chem. 70, 2703-2705 (1966).
- The standard free energy of formation of PuN was measured in a pair of emf cells.
10. J. A. Leary, W. C. Pritchard, R. L. Nance, and M. W. Shupe, "Refractory Plutonium Fuel Materials," in Plutonium 1965, A. E. Kay and M. L. Waldron, Eds. (Chapman and Hall, London 1965) pp. 639-653.
- Synthesis of PuC , $\text{PuC}_{2/3}$, and $(\text{U,Pu})\text{C}$ powders and fuel pellet fabrication reaction of PuN with PuO_2 to form Pu_2O_3 and N; solid solubility of PuO in PuN.
11. J. L. Green, G. P. Arnold, J. A. Leary, and N. G. Nereson, "A Low Temperature Magnetic Transition in Plutonium Monocarbide," J. Nucl. Materials 23, 231-232 (1967).
- Low temperature neutron diffraction indicated an antiferromagnetic transition at 100°K.
12. J. G. Reavis, M. W. Shupe, C. W. Bjorklund, and J. A. Leary, "Phase Relations in the High-Carbon Portion of the U-Pu-C System," Trans. Amer. Nucl. Soc. 10, 111 (1967).
- High-temperature differential thermal analysis study of $(\text{U,Pu})\text{C}_{2/3}$ and $(\text{U,Pu})\text{C}_2$ compositions; x-ray powder diffraction, metallographic, and electron microprobe analyses; U_2C_3 and Pu_2C_3 form solid solutions over wide range of composition; UC_2 and PuC_2 form wide range of solid solutions; transition temperatures for $\text{M}_2\text{C}_3 + \text{C} = 2\text{MC}_2$; melting of Pu_2C_3 at 1980°C, melting of MC_2 at 2425°C for U, $\text{Pu}_{0.8}\text{C}_{0.2}$.
13. J. L. Green, G. P. Arnold, J. A. Leary, and N. G. Nereson, "Crystallography and Magnetic Ordering in Plutonium Carbides by Neutron Diffraction," Bull. Amer. Ceram. Soc. 46, 893(1967).
- Low temperature neutron diffraction study of PuC and $\text{PuC}_{2/3}$.
14. C. W. Bjorklund, R. M. Douglass, and J. A. Leary, "Self-Irradiation Damage in Plutonium Ceramics," Bull. Amer. Ceram. Soc. 46, 901(1967).
- The lattice dimensions of various compounds including PuO_2 , PuN, and several Pu carbides were determined after storage in the -200° to +400°C range. Dose rates were varied by increasing the ^{238}Pu isotopic abundance.

15. G. M. Campbell, L. J. Mullins, and J. A. Leary, "Thermodynamic Properties of Plutonium Compounds by EMF Techniques," Thermodynamics of Nuclear Materials, 1967, (International Atomic Energy Agency, Vienna 1968) pp. 75-88 (no editors).

- Measurements on properties of PuCl_3 , PuN , PuRu_2 , PuC , and Pu_2C_3 over temperature range 950°-1100°K;

for the reaction: $2\text{Pu}(\ell) + 3\text{C}(\text{s}) =$
 $+ \text{Pu}_2\text{C}_3(\text{s}) - \Delta G_T^\circ = 52.5 - 0.0147T$
 kcal/mole;

for the reaction: $\text{Pu}(\ell) + (1-x)\text{C}(\text{s}) =$
 $+ \text{PuC}_{(1-x)}(\text{s}) - \Delta G_T^\circ$
 $= 17.2 - 0.0023T$ kcal/mole.

16. J. A. Leary and A. E. Ogard, "Plutonium Carbides," chapter for unpublished Reactor Materials Handbook No. 3. (See Appendix B)

- Review article with properties, etc.

17. J. A. Leary and K. W. R. Johnson, "Thermal Conductivity of Uranium-Plutonium Carbide Fuels," in Int. Symp. on Plutonium Fuels Technology, K. E. Horton, R. E. Macherey, and R. J. Allio, Eds. (A.I.M.E., New York, N.Y. 1968) pp. 309-321.

- Thermal conductivities and thermal diffusivities of UC, PuC, and (U,Pu)C; effects of sample porosity, stoichiometry, temperature, impurities, and solid solution formation.

18. J. G. Reavis, J. Buchen, and J. A. Leary, "Differential Thermal Analysis Apparatus for Observation of Refractory Plutonium Compounds." (See Appendix C)

- Describes apparatus for measuring melting points and temperatures of crystallographic transitions for plutonium compounds in 1000°-2440°C range.

19. K. W. R. Johnson and J. A. Leary, "The Thermal Conductivity of Uranium-Plutonium Carbides," Trans. Amer. Nucl. Soc. 12, pp. 591-592 (1969).

- Thermal conductivity and porosity effects over temperature range 100°-1000°C

$$K_p = (a + bT) \left(\frac{1-P}{1+\beta P} \right)$$

where T = temperature in °C

$$a = 0.0394; b = 2.53 \times 10^{-5}$$

$$\beta = 4.01$$

P = pore fraction

K_p = conductivity in cal/sec cm °C

20. J. A. Leary, M. W. Shupe, R. Honnell, and A. E. Ogard, "Synthesis and Fabrication of Carbide Fuels," Trans. Amer. Nucl. Soc. 12, pp. 577-578 (1969).

- Synthesis and fabrication of single phase (U,Pu)C fuel for properties and irradiation testing; review of U.S. processes.

21. J. A. Leary, "Present Status of the Uranium-Plutonium-Carbon Phase Diagram," Ceramic Nuclear Fuels, Owen L. Kruger and A. I. Kaznoff, Eds. Proceedings of the International Symposium on Ceramic Nuclear Fuels, (Amer. Ceramic Soc., Special Publication No. 2, 1969) pp. 38-50.

- Phase diagrams and structure analysis for the U-Pu, the U-C, and the Pu-C systems; phase relationships in the U-Pu-C system over wide range of composition and temperature; no ternary compounds.

22. R. A. Kent and J. A. Leary, "Mass Spectrometric Studies of Plutonium Compounds at High Temperatures. IV. The Vaporization of PuN," J. of High Temp. Sci. 1, 176-183 (1969).

- The mononitride vaporizes congruently to the elements;

$$\log P_{\text{Pu}} (\text{atm}) \approx (6.445 \pm 0.055)$$

$$- (21,958 \pm 98)/T$$

_K

$$\Delta H_{\text{F298}}^\circ = -71.2 \pm 2.5 \text{ kcal/mole}$$

$$\Delta S^\circ = -19.9 \pm 2.0 \text{ e.u.}$$

23. J. A. Leary and R. A. Kent, "Ceramic Plutonium Fuel Materials Research at Los Alamos Scientific Laboratory," talk pre-

sented at Japan Atomic Energy Research Inst., Tokai-Mura, Japan, Sept 1969.

- Description of LASL Advanced Fuels Program; summary of important results to date; mean linear thermal expansion of Pu_2C_3 over the temperature range $20^\circ\text{--}1600^\circ\text{C}$ was $15.6 \times 10^{-6}/^\circ\text{C}$; mean linear thermal expansion of PuC over the range $1750^\circ\text{--}2000^\circ\text{C}$ was $21 \times 10^{-6}/^\circ\text{C}$; neutron diffraction studies on ^{243}PuC and $^{240}\text{Pu}_2\text{C}_3$ at $20\text{--}100^\circ\text{K}$; structural analysis of Pu_2C_3 and U_2C_3 ; differential thermal analysis on $(\text{U,Pu})\text{O}_2$, $(\text{U,Pu})\text{C}$, and $(\text{U,Pu})\text{C}_2$; thermochemical properties of PuCl_3 , PuN , Pu_2C_3 , PuC , $(\text{U,Pu})\text{C}$, and $(\text{U,Pu})\text{O}_2$. (See Appendix D)
24. M. Tokar, A. W. Nutt, and J. A. Leary, "Mechanical Properties of Carbide and Nitride Reactor Fuels," *Trans. Amer. Nucl. Soc.* **12**, 592-293 (1969).
- Creep measurements on $\text{U}_{0.8}\text{Pu}_{0.2}$ from $1200^\circ\text{--}1600^\circ\text{C}$ and $2000\text{--}6000$ psi; elastic moduli at room temperature by ultrasonic pulse echo and mode conversion technique.
25. A. E. Ogard, J. G. Reavis, and J. A. Leary, "Characterizing the High-Temperature Thermophysical and Thermochemical Properties of Irradiated Fuels - Present Status and Future Needs," *Proceedings of the 16th Conf. on Remote Systems Tech.* (1969).
- Describes equipment for use in hot cell to determine high temperature heat content and high temperature differential analysis; indicates some future requirements and problem areas such as micro scale measurements of properties.
26. G. M. Campbell, "Thermodynamic Properties of Plutonium Nitrides by Galvanostatic Potential Determination," *J. Phys. Chem.* **73**, 350-355 (1969).
- Describes equipment and technique for determining thermodynamic properties of materials; for the

reaction

The free energy of formation of PuN is given by

$$-\Delta G_T^\circ = 73.8 - 0.0225T \quad \text{kcal/mole} \\ \text{K}$$

and

$$-\Delta H_{298}^\circ = 72.5 \text{ kcal/mole}.$$

27. G. M. Campbell, R. A. Kent, and J. A. Leary, "Thermodynamic Properties of the Plutonium-Carbon System," in Plutonium 1970 and Other Actinides, William N. Miner, Ed. (A.I.M.E. New York, N.Y., 1970) pp. 781-790.

- Thermochemical data by mass spectrometer-Knudsen cell and by emf methods over the range $900\text{--}2200^\circ\text{K}$ and composition range Pu to $\text{PuC}_2 + \text{C}$; standard heats and entropies of formation for $\text{PuC}_{0.9}$, Pu_2C_3 , and PuC_2 .

28. J. G. Reavis, K. A. Johnson, and J. A. Leary, "Melting Behavior of (U,Pu) Monocarbides," in Plutonium 1970 and Other Actinides, William N. Miner, Ed. (A.I.M.E. New York, N. Y., 1970) pp. 791-798.

- Solidus and liquidus temperatures for $(\text{U,Pu})\text{C}$ solid solutions from 0-50 mol% PuC by DTA and metallography. Solidus and liquidus of UC-20 PuC were 2275 and 2485°C , respectively.

29. R. A. Kent, "Mass Spectrometric Studies of Plutonium Compounds at High Temperatures V. The Plutonium-Carbon System," in Recent Developments in Mass Spectroscopy Koreichi Ogata and Teruo Hayakawa, Eds. (University of Tokyo Press, 1970) pp. 1124-1131.

- There are three regions of the Pu-C system which give rise to invariant but not congruent vaporization ($\text{PuC} + \text{Pu}_2\text{C}_3$, $\text{Pu}_2\text{C}_3 + \text{C}$, and $\text{PuC}_2 + \text{C}$); the sesquicarbide has a range of homogeneity at 1550°C ; transition of Pu_2C_3 to PuC_2 occurs at 1660°C ; standard heat and

entropy of formation for PuC and Pu_2C_3 .

30. J. L. Green, G. P. Arnold, J. A. Leary, and N. G. Nereson, "Crystallography and Magnetic Ordering Studies of Plutonium Carbides Using Neutron Diffraction," *J. of Nucl. Mater.* 34, 281-289 (1970).
- Low temperature neutron diffraction measurements on PuC and Pu_2C_3 ; magnetic transition in PuC at 100°K; no magnetic ordering found in Pu_2C_3 ; magnetic unit cell of PuC and parameters for Pu_2C_3 .
31. J. A. Leary, A. E. Ogard, M. W. Shupe, and J. O. Barner, "Synthesis, Fabrication, and Behavior of Single Phase U-Pu Carbides for Fast Breeder Reactors," in Proc. Intern. Mtg. on Fast Reactor Fuel and Fuel Elements, M. Dalle Donne, K. Kummerer, K. Schroeter, Eds. (Gesellschaft fuer Kernforschung, Karlsruhe, Germany, 1970) pp. 436-453.
- Processing of powders and pellets of various densities and enrichments, thermal redistribution of Pu in mixed two-phase carbides, fabrication of Na-bonded pins, irradiation program design, electron microprobe studies on un-irradiated fuel.
32. J. G. Reavis and J. A. Leary, "Differential Thermal Analysis Observations of (U,Pu) Dicarbides," in Plutonium 1970 and Other Actinides, William N. Miner, Ed. (A.I.M.E. New York, N.Y., 1970) pp. 809-817.
- Results on UC_2 - PuC_2 pseudobinary over full range of composition, with x-ray diffraction and metallographic supplemental studies, structures and transition temperatures in the range 1000°C to 2500°C.
33. J. L. Green and J. A. Leary, "Thermal Expansion and Phase Equilibria of the Carbon-Saturated Plutonium Carbides," *J. Appl. Physics* 41, 5121-5124 (1970).
- Description of high temperature diffractometer; mean linear thermal expansions of Pu_2C_3 and PuC_2 (fcc).
34. J. G. Reavis, G. R. Brewer, D. B. Court, and J. W. Schulte, "A Differential Thermal Analysis Apparatus for Observation of Irradiated Pu-Containing Reactor Fuels," *Proceedings of the 19th Conf. on Remote Systems Technology* pp. 112-117 (1971).
- Description of hot-cell apparatus and results on irradiated $(\text{U,Pu})\text{O}_2$; later used for irradiated $(\text{U,Pu})\text{C}$.
35. M. Tokar and J. A. Leary, "Compressive Creep and Hot Hardness of Uranium-Plutonium Carbide," 73rd Annual Mtg. of the Amer. Ceram. Soc., Apr 1971 (see later reference of same title).
36. J. A. Leary, "Nuclear Fuels Work in the U.S.," talk at Karlsruhe Nuclear Research Center, Karlsruhe, Germany (May 1971).
37. J. O. Barner, "Behavior of Sodium-Bonded (U,Pu)C Fuel Elements After Moderate Burnup," Fast Reactor Fuel Element Technology, Ruth Farmakes, Ed. (Interstate Printers, Danville, Ill., 1971), pp. 819-848.
- Results of irradiation of (U,Pu)C fuel in annealed type 316 stainless steel clad at 30 kW/ft to burnups of 3.7 and 5.0 atom % without failure.
38. J. C. Clifford, "Thermal Neutron Irradiation of Sodium-Bonded Solid Solution (U,Pu)C Fuel," Los Alamos Scientific Laboratory report LA-4951 (February 1973).
- Irradiation of small samples with fuel surface temperature of 730°C, maximum power density of 760 W/g, and maximum burnup of 13 atom %, possible evidence for plutonium metal reaction with noble metal fission products such as ruthenium, palladium, rhodium and with silicon.
39. Michael Tokar, "Compressive Creep and Hot Hardness of U-Pu Carbides," *J. Amer. Ceram. Soc.* 56, 173-177 (1973).
- Compressive creep of $\text{U}_{0.79}\text{Pu}_{0.21}\text{C}_{1.02}$ was studied at 1300°-1500°C and 2000-6000 psi
 $\dot{\epsilon} = 7.96 \times 10^{-4} \sigma^{2.44}$

$\exp (-126.4 \text{ kcal/ml/RT})$

where $\dot{\epsilon}$ = creep rate, per hour

σ = stress, psi

T = temperature, °K

The hardnesses of monocarbides with various Pu/U ratios were measured over the range 25-1200°C. Mechanisms are discussed.

40. M. Toxar and J. L. Green, "Hot

Hardness Testing of Uranium-Plutonium Ceramics," The Science of Hardness Testing and Its Research Applications, J. H. Westbrook and H. Conrad, Eds., Amer. Soc. Metals, Metals Park, Ohio (1973) pp. 241-248.

- Results from References 24, 35 and 39 plus new data on PuN.

APPENDIX A

PREPARATION AND PROPERTIES OF PLUTONIUM MONONITRIDE AND URANIUM MONONITRIDE-PLUTONIUM MONONITRIDE SOLID SOLUTIONS^a

by

J. A. Leary, R. L. Nance, W. C. Pritchard, J. G. Reavis, M. W. Shupe, and
A. E. Ogard

(University of California, Los Alamos Scientific Laboratory, Los Alamos,
New Mexico, U.S.A.)

Mononitrides of uranium and plutonium have potential advantages as nuclear fuels. Metal atom density, melting point, thermal conductivity, and compatibility with economic fuel clad appear to be favorable in comparison to other fuels.

Uranium mononitride powders have been synthesized by reaction of uranium hydride with nitrogen to form uranium sesquinitride, followed by thermal decomposition of the sesquinitride to form single phase, stoichiometric uranium mononitride. Plutonium mononitride is the only compound known in the plutonium-nitrogen system. Powders of monophasic plutonium nitride were prepared directly by reaction of plutonium hydride with nitrogen at 800°. Solid solutions of plutonium mononitride in uranium mononitrides were prepared by sintering mixtures of the individual mononitride powders.

Dense pellets of single phase uranium mononitride, plutonium mononitride, and solid solution mononitrides have been produced by cold compaction and sintering in the 1600°-1900° temperature range. The effects of fabrication variables such as particle size range of the powders, pressing pressure, and sintering conditions on pellet density and integrity are reported.

The dimension of plutonium mononitride crystal lattice is independent of the equilibration temperature, up to the melting point, and is independent of the nitrogen partial pressure up to a pressure of one atmosphere. Plutonium mononitride is isostructural with F. C. C. uranium mononitride, and the two compounds form a continuous series of solid solutions over the entire range of composition. The lattice dimension increases uniformly from 4.8892 for pure uranium mononitride to 4.9048 Å for pure plutonium mononitride. Regardless of sintering temperature, the lattice parameters display slightly negative deviations from Vegard's law for compositions containing less than 50 percent plutonium mononitride, and slightly positive deviations for greater than 50 percent plutonium mononitride.

^aWork performed under the auspices of the United States Atomic Energy Commission

Thermal decomposition of mononitrides occurs in the temperature range ~ 2500°C. The thermal stability of the mononitrides as a function of temperature and nitrogen pressure are discussed and compared with that of oxide and carbide fuels. Other properties of interest to nuclear fuel applications such as thermal expansion, thermal conductivity, and thermodynamic properties, are compared with those of other potential fast breeder reactor fuels.

APPENDIX B

PLUTONIUM CARBIDES

J. A. Leary and A. E. Ogard

Los Alamos Scientific Laboratory

Preparation:

Methods which have been used in the preparation of the plutonium carbides are direct arc melting of plutonium and graphite,^(1,2,3,4,5,6) carbon reduction of PuO_2 at $1100 - 1450^\circ\text{C}$,^(1,7,8,9,10,11,12) sintering of mixtures of carbon powder and plutonium metal or plutonium hydride powder at temperatures up to 1400°C ,^(7,13,14) and reaction of hydrocarbons with plutonium at $600-800^\circ\text{C}$.⁽¹⁵⁾ Each method of preparation has advantages. Arc melting produces a dense carbide that is essentially free of oxygen and nitrogen impurities. However, the composition is difficult to control and the product is inhomogeneous unless extensive heat treatment is performed. This is especially true of the monocarbide. Carbon reduction of PuO_2 is a consistent and economical procedure. It is difficult, though, to prepare single phase PuC_{1-x} and impossible to eliminate completely all of the oxygen. Single phase PuC_{1-x} of controlled carbon content can readily be prepared by sintering a mixture of graphite powder and plutonium hydride powder. An inert gas atmosphere glove box is necessary for this procedure since the plutonium hydride is pyrophoric. Even with the use of an inert gas atmosphere most carbides that are made from powders contain up to 1000 ppm of oxygen.

Phase Relationships:

The phase diagram of the plutonium-carbon system was first proposed by Mulford et al.⁽¹⁾ Figure 1 is basically the proposed diagram modified by more recent results.⁽²⁹⁾ Four carbide compounds have been identified: the zeta-phase at Pu_3C_2 , a carbon deficient PuC_{1-x} , Pu_2C_3 , and the high temperature phase, PuC_2 .

The transformation temperatures of the six plutonium allotropes do

not appear to be affected by the dissolution of carbon.^(1, 16) The melting point of plutonium is lowered by up to 8°.^(1, 6) Above this eutectic the solubility of carbon in liquid plutonium can be expressed by the equation $\log_{10} \text{ atom fraction carbon} = 0.50 - 2.3 \times 10^3/T (700-950^\circ\text{K})$.⁽¹⁷⁾

The structure of Pu_3C_2 has not been determined but appears to be related to that of PuC_{1-x} . X-ray powder diffraction patterns of the Pu_3C_2 phase have been described by several authors.^(1, 6, 18) Pu_3C_2 decomposes by a peritectoid reaction to $\epsilon - \text{Pu} + \text{PuC}_{1-x}$ in the range of 558-585°C.^(1, 6, 18)

Plutonium monocarbide has the fcc NaCl-type structure.⁽¹⁹⁾ It is a non-stoichiometric compound that is deficient in carbon, and has a composition range of homogeneity as shown in Table I. The room temperature lattice parameter increases from a value of 4.953 to 4.973 Å as the carbon content is increased from the hypo- to the hyperstoichiometric composition.^(1, 6, 7, 20, 21) The lattice parameter increases slowly with time owing to self-irradiation damage of the lattice.^(21, 24, 25) The high solubilities of oxygen and nitrogen in PuC_{1-x} also cause wide variations in lattice dimension.^(22, 23) An antiferromagnetic transition occurs at ~100°K in PuC_{1-x} .⁽²⁷⁾ The monocarbide melts peritectically at $1658 \pm 5^\circ\text{C}$ to form liquid + Pu_2C_3 .^(1, 26)

The structure of Pu_2C_3 is body centered cubic.⁽²⁸⁾ A small variation in lattice parameter has been found suggesting a small range of composition: 8.126 - 8.132,⁽¹⁾ 8.129,⁽⁷⁾ 8.131 - 8.134,⁽¹⁰⁾ and 8.121 - 8.126.⁽²⁰⁾ Volume fraction analysis of heat treated $\text{PuC} + \text{Pu}_2\text{C}_3$ samples show a lower phase boundary of Pu_2C_3 at ~59 at/o carbon at temperatures above 855°C.⁽¹⁸⁾ The transition of $\text{Pu}_2\text{C}_3 + \text{C}$ to PuC_2 occurs at approximately 1650°C, and does not appear to be affected by the carbon concentration.⁽²⁹⁾ Peritectic melting of Pu_2C_3 to liquid + PuC_2 occurs at $2020 \pm 40^\circ\text{C}$.^(1, 29, 30)

Tetragonal PuC_2 exists at temperatures above 1650°C.^(1, 13, 29, 30, 31) On cooling, the transformation of PuC_2 to Pu_2C_3 is so rapid that difficulty is encountered in quenching in the PuC_2 phase. The peritectic melting point of PuC_2 to

Table I
The Carbon Content of PuC_{1-x}

<u>Temperature</u>	<u>Reference</u>	<u>Pu_3C_2 - PuC Boundary a/o Carbon</u>	<u>PuC - Pu_2C_3 Boundary a/o Carbon</u>
< 300°C	2	45.4-45.5	...
400	20	45.4-46.8	...
555	18	43-44	48
575	2	41.1-43.2	...
570-595	6	43.5	48
600	21	40	49
610	18	42-43	48
634	21	38	49
1000	20	45.4	...

liquid + carbon is $2240 \pm 10^\circ$.^(1,29) Tetragonal PuC_2 is isostructural with tetragonal $\alpha\text{-UC}_2$; no evidence for the existence of a PuC_2 analog of cubic $\beta\text{-UC}_2$ has been reported.*

Physical Properties:

The physical properties which have been experimentally determined for the plutonium carbides are listed in Table II. It is important to note that the physical properties listed in Table II have not been determined as a function of the carbon concentration except the measurements of hardness.

A comparison of the free energies of formation expressed in Table II with the free energies of formation of the uranium carbides⁽⁴⁵⁾ indicates that plutonium carbides generally are less stable than the corresponding uranium carbides, but far more stable than originally reported.⁽⁴⁶⁾

It is difficult at this time to calculate the thermodynamic values at 298°K with any certainty. The heat content of PuC_{1-x} has been measured in a drop calorimeter.⁽⁴⁴⁾ These results were combined with reported equilibrium data and tabulated functions for plutonium and carbon to give the standard thermodynamic quantities at 298.15°K shown in Table III. Since the heat capacity of Pu_2C_3 has not been determined, only the heat of reaction is shown for the sesquicarbide. The results calculated for PuC_{1-x} from vaporization data^(39,40) do not agree internally, nor do they agree with those derived from the electromotive force measurements.⁽⁴¹⁾ The absolute entropy of PuC_{1-x} from electromotive force results is in fairly good agreement with that of UC (14.2 e.u.). Similarly the heat of formation of Pu_2C_3 obtained by electromotive force measurements is approximately the same as that of U_2C_3 . It is somewhat surprising that the heat capacity of PuC_{1-x} is less than that of UC , in view of the fact that U and UO_2 have lower heat capacities than Pu and PuO_2 .^(47,48,49,50) Obviously the thermochemical data on plutonium

* Recently the Harwell workers reported evidence for the existence of cubic PuC_2 above 1800°C .

Table II
Reported Physical Properties of Plutonium Carbides

Property	Pu ₃ C ₂	PuC _{1-x}	PuC ₁₋₃	PuC ₂
Average Coefficient of Thermal Expansion ($\alpha \times 10^{-6}/^{\circ}\text{C}$)	~ 11 [2]	10.8 ± 0.2 [2, 32, 33, 14] (25 - 900 ^o C)	15.5 ± 0.7 [32, 33] (20 - 900 ^o C)	...
Thermal Conductivity (cal/cm-sec- ^o C)	...	$0.0155 + 38.5 \times 10^{-6} T$ [35] (200 - 400 ^o C)	...	...
Resistivity (μ ohm cm)	...	230 - 270 [7, 35, 36] (25 - 900 ^o C)	500 [37] (25 ^o C)	...
Thermal Electric Power (microvolt/ ^o K)	...	0 - 17.5 [36] (60 - 1200 ^o K)	0 - 23 - 20 [37] (0 - 100 - 200 ^o K)	...
Hardness (DPHN)	100 ± 50 [1, 18]	500 - 900 [18]	~ 1100 [18]	...
Lattice Parameter, A	...	4.953 - 4.973 [1, 6, 7, 20, 21]	8.121 - 8.134 [1, 7, 10, 20]	a = 3.63 [31] c = 6.09 [31]
Theoretical Density (g/cm ³)	...	12.5 ± 0.1	12.7 ± 0.1	10.9
Magnetic Susceptibility	...	Maximum at $\sim 20^{\circ}\text{K}$ [38]	...	...
Vapor Pressure of Pu over a Mixture of the Carbide and the next higher Carbide (log p, mm)	...	- 19,160/T + 5.30 [39] (1366 - 1835 ^o K) - 18,091/T + 4.686 [40] (1761 - 1907 ^o K) - 51,100/T + 22.3 [42] (1773 - 1838 ^o K)	- 20,330/T + 4.39 [39] (1541 - 1989 ^o K)	-17,920/T + 2.779 [43] (2000 - 2400 ^o K) -18,732/T + 3.618 [40] (2017 - 2472 ^o K)
Free Energy of Formation, ΔG_f (kcal/mole)	...	- 17.2 + 0.0023 T [41] (971 - 1060 ^o K) - 11.053 - 0.00064 T [39] (1366 - 1835 ^o K) - 5.610 - 0.00361 T [40] (1761 - 1907 ^o K)	- 26.2 + 0.0072 T [41] (974 - 1091 ^o K) - 13.310 - 0.00239 T [39] (1511 - 1989 ^o K) - 18.0 [40] (2023 ^o K)	... -3,300 - 0.0052 T [1] (2000 - 2400 ^o K) -4,350 - 0.00577 T [2] (2017 - 2472 ^o K)
$H_f \rightarrow H_{2g}$ (kcal/mole)	...	$-5035 + 13.08 T + 5.718 \times 10^{-4} T^2 + 3.232 \times 10^5 T^{-1}$ [14] (425 - 1300 ^o K)	...	...
Heat Capacity, C_p (cal/mole- ^o K)	...	$13.08 + 11.44 \times 10^{-4} T - 3.232 \times 10^5 T^{-2}$ [14] (425 - 1300 ^o K)	...	...

Table III
Standard Thermodynamic Properties of Plutonium Carbides
at 298.15°K

<u>Compound</u>	<u>$-\Delta H_{298}^{\circ}$ kcal/mole</u>	<u>ΔS_{298}° e. u.</u>	<u>$\sqrt{S_{298}^{\circ}}$ e. u.</u>	<u>Reference</u>
PuC_{1-x}	10.04	3.49	18.2	39
"	4.6	6.46	21.2	40
"	16.2	0.55	15.3	41
Pu₂C₃	21.2			39
"	11.4			40
"	48.1			41

carbides must be considered as provisional.

Plutonium monocarbide containing ~10% Pu_2C_3 impurity has been found to react with the nickel in stainless steel when heated in contact at 1050°C for 120 hours.⁽¹⁴⁾ It is unlikely that PuC_{1-x} that contains significant amounts of free plutonium metal will be compatible with Ni, Co, or Fe base alloys, as low melting binary eutectics are formed. Less reaction has been found between Pu_2C_3 and the refractory metals. The amount of reaction zone decreased in the order niobium > molybdenum > tantalum > tungsten.

Irradiation:

Plutonium carbides by themselves are not normally considered as potential power reactor fuels, and very little irradiation experience has been obtained. A few irradiations of arc-cast PuC_{1-x} powder and vibratory compacted PuC_x have been reported.⁽⁵¹⁾ Burn-ups of $\sim 3 \times 10^{19}$ fissions/cc of the arc-cast specimens and up to 12.9×10^{20} of the vibratory compacted PuC_{1-x} have been obtained. Most specimens cracked during irradiations and one specimen of vibratory compacted PuC_x of 6.22 w/o carbon reacted disastrously with the 304 stainless steel cladding after 12.9×10^{20} fissions/cc. The fission gas release, where measurable, was low, ~0.24%.

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APPENDIX C

Differential Thermal Analysis Apparatus for Observation of Refractory Plutonium Compounds *

by

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ABSTRACT

An apparatus has been constructed and used for measurement of melting points and temperatures of crystallographic transitions of refractory compounds of Pu and other intense alpha emitters potentially useful as reactor fuels. The thermal analysis apparatus responds to light energy radiated by the sample and furnace and temperatures are measured by optical pyrometry. The specialized nature of the equipment made necessary an intensive calibration study over the temperature range 1000-2440°C.

* Work performed under the auspices of the Atomic Energy Commission

I. Introduction

Measurement of the properties of refractory materials potentially useful as reactor fuels presents difficulties not only of containment to avoid unwanted chemical reactions at high temperatures, but also containment of the intense alpha activity for protection of laboratory personnel. The differential thermal analysis apparatus described by Rupert⁽¹⁾ is an excellent apparatus for determination of transition temperatures in the range 1000-3000°C, but a number of modifications were necessary in application of the apparatus to studies of intense alpha-emitting refractories such as (U, Pu)C, (U, Pu)N, and UO₂-PuO₂. Additionally, measurements in this high temperature region have been standardized by development of a series of reference materials for temperature calibration. It was necessary to develop this series for periodic verification of the accuracy of measurements, since the accuracy could not be rechecked by substitution of a standard lamp in the position of the furnace.

II. Apparatus

A schematic view of the apparatus is shown in Fig. 1. Power to heat the furnace is supplied by a 25 kW, 0.45 MHz generator the output of which is coupled to the furnace by an induction coil and current concentrator similar to that previously described.⁽²⁾ The output level of the generator is controlled by an electronic unit which can be adjusted either manually or by use of a motorized drive. Controlled heating and cooling rates in the range 10-1000 deg/min can be attained; heating rates of greater than 2500 deg/min can be accomplished by manual power adjustment, but the furnace shown in Fig. 1 will not cool more rapidly than about 1000 deg/min.

The furnace assembly is enclosed by a glove box that retains all radioactive particles. The furnace consists of a susceptor, an inner crucible, a lid penetrated by a 1 mm diameter hole, and several radiation reflectors. The use of the reflectors and inner crucible reduces the magnitude of the thermal gradients

Figure 1. Schematic Drawing of the DTA Apparatus

which may exist in the susceptor. The furnace susceptor is 25 mm high and 19 mm dia. The materials of construction usually are Ta, W or graphite, the choice being made to minimize reaction with the sample to be heated. For observations of melting of noble metals, ThO_2 crucibles with ThO_2 lids were used as liners for Ta inner crucibles. Thin flakes of ThO_2 are placed on top of the highly reflecting metal samples to avoid direct reflection of the sight hole in the field viewed by the optical pyrometer.

The optical system which transmits radiant energy from the furnace to the optical pyrometer* is simple. Approximately one third of the diverging beam emerging through the window in the top of the current concentrator is intercepted by a mirror and reflected to the pyrometer used for actual temperature measurement. The remaining two thirds of the beam passes through a convex lens and an iris diaphragm and is reflected by a mirror to produce a magnified image of the top of the furnace in a vertical plane outside the glove box. One photoconducting diode** is positioned in this plane so that its active area is covered by the image of the hole in the crucible lid. A second diode is covered by the image of a small area of the surface of a radiation shield as seen through the second hole in the susceptor lid.

Signals from the diodes are amplified by a system very similar to that previously described.⁽¹⁾ Electrical outputs proportional to (1) temperature (T) of the sample, (2) difference between sample temperature and radiation shield temperature (ΔT), and (3) derivative of sample temperature with respect to time (dT/dt) are produced. T and ΔT signals are recorded simultaneously by a two-pen strip chart recorder while a storage oscilloscope is used to record T as a function of dT/dt . For very fast thermal cycles, the oscilloscope is found more useful in the recording of T and ΔT as a function of time. The recorder trace indicating temperature is calibrated by observing temperatures with the pyrometer

*Micro Optical Pyrometer, The Pyrometer Instrument Co., Inc., Bergenfield, N. J.
**Diode 1N-2175, Texas Instruments, Inc., Dallas, Texas.

during actual thermal cycling of samples.

III. Calibration

Whenever an absorbing glass is placed between an optical pyrometer (disappearing filament type) and an incandescent object the relationship between the true and observed temperatures (expressed in degrees Kelvin) is closely approximated by

$$\frac{1}{T_o} = \frac{1}{T} + A \quad (1)$$

where T_o is the observed temperature, T is the true temperature, and A is a constant for a given absorber.⁽³⁾ By use of a calibrated optical pyrometer and a tungsten strip lamp over the range 1000-1800°C, the value of A was found to be $19 \times 10^{-6} \text{ deg}^{-1}$ for a mock-up of windows and a mirror to be used in the assembled apparatus. The precision of the measurements used in calculation of the value of A in equation (1) indicated uncertainties in the temperature correction for absorbance by the optical system of $\pm 2^\circ$ at 1000°C increasing to $\pm 9^\circ$ at 3000°C.

Additional uncertainties in the value of A could arise from use of a slightly different geometry of actual construction of the apparatus or from change of absorbance of the components (including the window of the glove box enclosure) with passage of time. These considerations made it necessary to check periodically the accuracy of measurement of temperatures in the assembled apparatus. Since placement of a calibrated tungsten strip lamp in the position of the furnace is impossible, the alternative procedure of observations of transitions of reference materials was adopted for final calibration of the apparatus. The choice of this method produces a correction curve which accounts for optical absorption, pyrometer scale errors and systematic errors involved in recording and interpreting DTA curves. The materials chosen for reference are listed in Table I.

**Table I. Reference Materials Used in Calibration
of the DTA Apparatus**

<u>Material</u>	<u>Container</u>	<u>Transition</u>	<u>Transition Temp., °C</u>	
			<u>Lit.^(a)</u>	<u>Observed^(b)</u>
Cu	C	melting	1083	1081
Pt-C	C	eutectic	1734	1735
Pt	ThO ₂	melting	1770	1770
Rh	ThO ₂	melting	1960	1960
Al ₂ O ₃	W	melting	2050	2047
MoC ₆₋₇	C	eutectic	2205	2205
Ir	ThO ₂	melting	2440	2440

(a) Literature values selected after study of ref. 4-9.

(b) See text for discussion of accuracy.

IV. Performance

The apparatus has operated satisfactorily over a period of more than 2 years of observation of thermal effects in carbides, nitrides, and oxides of uranium and plutonium. Repeated observations of duplicate samples have shown that a single isolated measurement of a transition temperature has an uncertainty limit of about $\pm 10^{\circ}$ if proper care is taken to exclude systematic errors such as those arising from reaction between sample and container, decomposition of the sample or fogging of the current concentrator window by vaporization of the sample or furnace parts. Fogging of the window can be a serious problem during measurements in vacuo but was almost eliminated by filling the apparatus with an inert gas. The reference materials listed in Table I were observed under Ar.

Two or more samples of each reference material were observed. Transition temperatures observed during heating (melting) were found to be more easily reproducible than those observed during cooling because of severe undercooling shown by almost all samples. Reversibility of the transition was shown in each case by slight reduction of furnace power to produce freezing before melting was completed.

Observed and literature values of transition temperatures of each reference material were used to calculate a value of A (Equation 1) for that observation. These values of A were averaged to produce a new value of $20.5 \times 10^{-6} \text{ deg}^{-1}$ to replace the value of $19 \times 10^{-6} \text{ deg}^{-1}$ derived by use of the mock-up and the W strip lamp. The new value of A was used to generate a smoothed correction curve for the range 1000–3000 $^{\circ}$ C. Absorbance corrections from this smoothed curve were added to the uncorrected transition temperatures determined for the reference materials. These values are listed as "Observed" transition temperatures in Table I. The number of determinations of the transition temperature of any given reference material was not sufficiently great

to allow meaningful determination of standard deviations at each temperature. The standard deviation of individual observed transition temperatures from their respective literature values over all the series was $\pm 6^{\circ}$ after application of the smoothed correction curve. The averaged values of transition temperatures listed in Table I show a standard deviation of $\pm 1.5^{\circ}$ from their respective literature values.

It appears that reference materials are needed to achieve a high degree of accuracy in measurements of transition temperatures. The values listed in Table I are about 12° higher at 2440° and 3° higher at 1080° than those based on the A-value determined by use of the window mock-up and the W strip lamp. Although this difference has about the same value as the uncertainty of a single determination, use of the new correction curve gives a significant improvement in the accuracy of transition temperatures based on multiple observations.

The validity of the correction curve has been rechecked periodically over a period of several months of use by observation of reference materials selected from those listed in Table I. No significant change has been detected even though many macro samples of intense alpha emitters have been observed during this period. Greater changes may be expected, however, in systems in which windows are subjected to high levels of more penetrating radiations or to extremes of temperature.

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APPENDIX D

**CERAMIC PLUTONIUM FUEL MATERIALS RESEARCH
AT LOS ALAMOS SCIENTIFIC LABORATORY**

by

J. A. Leary and R. A. Kent

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CERAMIC PLUTONIUM FUEL MATERIALS RESEARCH AT LOS ALAMOS SCIENTIFIC LABORATORY

by

J. A. Leary and R. A. Kent

INTRODUCTION

Plutonium high temperature research at Los Alamos Scientific Laboratory is sponsored primarily by the Division of Reactor Development of the USAEC. Other associated programs involve studies on the compatibility of plutonium fuels with potential cladding materials, and the irradiation performance of such fuels. All of these programs are directed toward the utilization of plutonium in fast breeder nuclear reactors.

The high temperature materials research program may be divided into three broad categories: (1) synthesis and fabrication, (2) physical properties, and (3) chemical properties. Procedures have been developed for synthesizing and fabricating plutonium monocarbide, plutonium sesquicarbide, plutonium dicarbide, plutonium dioxide, plutonium sesquioxide, and plutonium mononitride. In addition, solid solutions of most of these compounds with the corresponding uranium compounds have been produced. In all cases the objective is to prepare well characterized pure single phase materials. In the second category, the thermal conductivity, thermal diffusivity, electrical resistivity, compressive creep, hot hardness, and thermal expansion of fuel materials are being determined. The third category includes characterization by chemical analysis, crystallographic structure analysis, and measurement of thermochemical properties. This paper is concerned only with this third category, and each phase of research in this category will be discussed briefly.

STRUCTURE ANALYSIS

X-ray diffraction: The structures of plutonium materials at room temperature are determined by conventional X-ray powder diffraction techniques. In addition, an X-ray powder diffractometer furnace has been designed and fabricated for use in the investigation of the high temperature crystallographic properties of plutonium and uranium-plutonium carbides. The furnace design is based on a precisely located, resistance heated graphite strip which also serves as the sample support. The unit can be used for the collection of quantitative diffraction data at temperatures up to approximately 2600°C. The primary uses of the apparatus are phase identification, basic structure studies, and the determination of lattice parameters as a function of temperature. The capability of obtaining diffraction data at the temperature of interest allows the direct observation of phase transitions with positive identification of phases present, thus avoiding the uncertainties involved in indirect methods such as quenching studies. X-ray diffraction studies of PuC₂ have shown the following:

1. When samples of PuC_{2+x} are quenched from high temperature, only tetragonal PuC₂ is obtained. However, the only stable dicarbide is the cubic modification. No region of stability has been found for the tetragonal modification. It appears that the tetragonal dicarbide is a metastable species.
2. Pu₂C₃ has a relatively large coefficient of thermal expansion; the mean linear coefficient of expansion between 20°C and 1600°C is 15.6×10^{-6} per °C.
3. The thermal expansion of cubic PuC₂ is large. The average expansion coefficient over the temperature range 1750°C to 2000°C is 21×10^{-6} per °C.
4. The mechanism and kinetics of the transition of plutonium

sesquicarbide to dicarbide appear to be rather complex.

An additional high temperature furnace is being designed for studies on oxide systems.

Neutron diffraction: A neutron diffraction study of plutonium monocarbide at low temperature using plutonium-240 has been completed. Neutron diffraction patterns for this target were taken at various temperatures between room temperature and 20°K. At approximately 100°K an antiferromagnetic transition was indicated by the appearance of four small but well defined magnetic reflections.⁽¹⁾ Similar experiments with $^{240}\text{Pu}_2\text{C}_3$ targets did not reveal any magnetic transitions.

The carbon atoms in the Pu_2C_3 structure occur as dicarbide groups. This bond length was found to be 1.39 Å in Pu_2C_3 and 1.42 Å in U_2C_3 .

High temperature neutron diffraction equipment capable of measurements up to 2000°C is now in the design stage.

Differential thermal analysis (DTA): The DTA apparatus for plutonium materials shown in Figure 1 has been described in detail.⁽²⁾ This apparatus provides thermal information in various optional forms such as the temperature of sample as a function of time, the difference in temperature of unknown sample and standard sample as a function of time, the time derivative of temperature as a function of temperature or time, etc. Transitions in samples weighing a few grams can be determined with this instrument, even when the enthalpy change is small. In addition to measuring the temperature of transition, the heat of transition can be determined by the use of suitable standards.

Normally the results of thermal analysis are supplemental by metallography, electron microprobe examination, and X-ray and neutron diffraction studies. In addition, high temperature dilatometry is used to provide direct support of the transition temperatures observed by thermal analysis.

The DTA apparatus has been used to determine the melting point (2780° solidus, 2820°C liquidus) of $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{1.97}$ in sealed W containers, as

well as a heat of fusion of 19.4 kcal/mole. The melting point of PuO_2 was found to be 2445°C , while that of UO_2 was 2850°C . Similarly the melting points of nitrides have been measured in open crucibles under various atmospheric conditions. Plutonium mononitride melts at 2305°C at a nitrogen pressure of 8 mm of Hg, and at 2540°C under 380 mm of Hg. At an argon pressure of 400 mm Hg (no nitrogen) the melting point of $\text{U}_{0.80}\text{Pu}_{0.20}\text{N}$ is 2500°C .

The carbides have been studied in considerable detail. Solidus and liquidus temperatures of various monocarbide compositions are plotted in Figure 2. Solidus and liquidus values of the particularly important composition $\text{U}_{0.80}\text{Pu}_{0.20}\text{C}$ are $2285 \pm 20^\circ$ and $2485 \pm 20^\circ$, respectively.

DTA has also been used to outline the major phase fields in $(\text{U}, \text{Pu})\text{C}_2$ containing excess C. Thermal arrest temperatures are plotted on Figure 3. Samples have been quenched from all fields for X-ray powder diffraction analysis. Even though samples quenched from the $\text{MC}_2 + \text{C}$ region contain tetragonal MC_2 , high temperature X-ray diffraction experiments have shown that the stable high temperature form of MC_2 is cubic. In the presence of excess carbon, tetragonal UC_2 is the stable form from 1515° to 1765° . Although bcc U_2C_3 is the stable lattice below 1515°C , samples of tetragonal UC_2 can be held at 1450°C for days without transition to U_2C_3 . However, when $(\text{U}, \text{Pu})\text{C}_2$ compositions are held below the transition temperature, the $(\text{U}, \text{Pu})_2\text{C}_3$ structure forms rapidly. Over the range 0 to 20 percent PuC_2 in $(\text{U}, \text{Pu})\text{C}_2$, tetragonal dicarbide appears to be stable. However, the limits of this region are not yet well defined.

THERMOCHEMICAL PROPERTIES

Vapor pressure methods: Although the use of the Knudsen technique to measure vapor pressures and heats of sublimation and/or vaporization is well established, vaporization processes at high temperatures are often complex and a detailed knowledge of the identity and relative concentrations of the vapor species in

equilibrium with the condensed plutonium phases is required if the vaporization process is to be characterized.

In order to determine both the vapor species present over condensed plutonium materials at high temperatures and the partial pressures of these vapor species, the high temperature mass spectrometer assembly shown in Figure 4 has been constructed. The unit consists of two basic components, an oven assembly incorporating an electron bombardment-heated Knudsen cell, and a quadrupole mass spectrometer. These component parts are contained in a differentially pumped Type 304 stainless steel vacuum envelope. Vacuum of the order of 10^{-8} torr is achieved with the Knudsen cell at 1600° by means of two ion pumps, one rated at 400 l/sec , connected to the quadrupole region, the other, rated at 100 l/sec , connected to the oven region.

The molecular beam which effuses from the Knudsen cell passes through a collimating slit in a movable shutter plate and into the quadrupole region. The movable shutter plate allows one to close the slit to the molecular beam so as to distinguish sample vapors from background species.

The high voltage power supply is capable of heating the Knudsen cell to 2100° by electron bombardment from a tungsten wire filament and in tests the Knudsen cell has been held at $1600 \pm 5^{\circ}$ for as long as 24 hours.

The temperature of the Knudsen cell is measured by sighting with a micro optical pyrometer through calibrated windows into a black body hole in the base of the cell.

This apparatus has been used to determine the gaseous species and their vapor pressures above a number of plutonium-containing condensed species.

Plutonium metal was effused from tungsten and thoria Knudsen cells over the range $1426\text{--}1658^{\circ}\text{K}$. The results are shown in Figure 5. Liquid plutonium vaporizes to monomeric plutonium gas with a boiling point of 3466°K . The standard heat and entropy of vaporization are $83.0 \pm 0.5\text{ kcal/mole}$ and

29.1 ± 0.5 eu, respectively.⁽³⁾

Plutonium trifluoride was heated in tantalum Knudsen cells over the range 1243 - 1475°K and the principal vapor species was found to be plutonium trifluoride gas.⁽⁴⁾ The results are shown in Figure 6.

Studies of the equilibria among gaseous species over the mixture liquid plutonium plus solid plutonium trifluoride have established the dissociation energy of plutonium monofluoride gas to be $D_{298}^{\circ} = 5.53 \pm 0.30$ eV.

Plutonium mononitride was effused from tungsten Knudsen cells over the range 1658-1976°K. The results, which are shown in Fig. 7, indicate that the mononitride vaporizes congruently.⁽⁵⁾ Using estimated thermodynamic functions for plutonium mononitride, the heat and entropy of formation were calculated to be -71.2 ± 2.5 kcal/mole and -19.9 ± 2.0 eu, respectively.

Electromotive force techniques: The majority of experiments on electromotive force methods have employed molten LiCl-KCl eutectic as the electrolyte. Two principal methods have been used: (1) the conventional steady-state measurement, and (2) the galvanostatic or chronopotentiometric method. Procedures and results have been described in detail.^(6,7,8) The free energies of formation of plutonium trichloride, plutonium mononitride, plutonium sesquicarbide, plutonium monocarbide, and uranium-plutonium monocarbide have been determined. In general the results are in agreement with those obtained by vapor pressure methods at this Laboratory.

Most of the recent work has employed the galvanostatic method, as this technique appears to give more reliable results. The procedure involves electro-deposition of plutonium metal from the fused salt electrolyte onto the micro-electrode by a current of constant magnitude, followed by anodic stripping of the metal at constant current. By recording the potential during the procedure and having a theoretical knowledge of the effect of diffusion on the Pu^{+3} concentration at the electrode surface, the equilibrium potential can be determined. Experiments

which made use of a Pu/Pu^{+3} as well as those which made use of a U/U^{+3} as reference electrodes indicate the technique is probably accurate to ± 1 mV in melts of high purity. The purity of the electrolyte is indicated by the residual current observed in the chronopotentiometric trace.

This galvanostatic technique has been used to determine the emf of the Pu/Pu^{+3} couple vs that of a plutonium mononitride electrode in LiCl-KCl , PuCl_3 melt, over the temperature range 714° to 1031°K .

Since nitrogen is known to react with plutonium over the range of temperatures of these experiments the cell reaction is properly written as

However the solubility of nitrogen in plutonium is not great enough to cause a significant difference in the emf at these temperatures. For this reason the results are treated as if the cell reaction were

and the schematic representation of the cell is

The results from three cells (after correcting for the thermal emf of Ta vs W and for the difference between the measured pressure of N_2 and 1 atm) are represented by the equation

$$E = 7.90071 - 2.31690 \times 10^{-2} T + 2.517855 \times 10^{-5} T^2 \\ - 9.1644 \times 10^{-9} T^3 (\pm 0.003 \text{ V})$$

with E in volts and T in $^\circ\text{K}$.

The results of previous experiments by an indirect method gave 0.8745 (± 0.005) V for the emf at 700°K .⁽⁶⁾ The recent experiments indicate that the emf at 700°K is 0.8765 (± 0.003) V which is in good agreement.

Above the melting point of plutonium the potential is given by the equation

$$E = 1.0672 - 3.258 \times 10^{-4} T (\pm 0.003 \text{ V})$$

This results in

$$-\Delta G_T^{\circ} = 73.8 - 0.0225 T \text{ kcal/mole}$$

for the Gibbs free energy of formation of plutonium mononitride in the temperature range 915° to 1031° K.

At present the electromotive force technique is being applied to determining the thermochemical properties of uranium-plutonium carbides.

Calorimetry: Three calorimeters are being used to evaluate high temperature heat contents and heat capacities of plutonium materials. The high temperature (1300°-2900° K) drop calorimeter has been used to measure these properties with UO_2 , $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{2.00}$, and $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{1.98}$. Details of procedure and results have been reported.⁽⁹⁾ A schematic drawing of the apparatus is shown in Figure 8. The calorimeter block is a copper cylinder weighing approximately 28 kg. The central cavity of the block contains a removable insert upon which the electrical calibration resistance heater is wound. A massive off-center copper shutter is incorporated as part of the receiver block. This shutter is interconnected to another antiradiation shutter located at the bottom of the furnace. All surfaces of the calorimeter block are gold plated as is the inside of the container vessel surrounding the block. The exterior of the calorimeter block is wound with one half of a differential copper resistance thermometer. A 1-cm portion is exposed to the falling capsule so that a very accurate zero time is recorded. The other half of the differential resistance thermometer is made of manganin wire wound on a small core and attached to the constant-temperature water jacket. The difference in output between these two thermometers is recorded on a Minneapolis-Honeywell recorder with full range 0 to 20.2 mV in ten steps. The Wheatstone bridge circuit is adjusted so that 1-mV output is

approximately equal to 1°C temperature difference between the two thermometers.

The calibration constant of the calorimeter block is determined periodically by supplying a known amount of electrical energy to a manganin heater wound on the calorimeter insert. An Electronic Measurements Co., Inc. 0- to 3-A dc power supply is used to supply the electrical energy to the heater. The output is put through a dummy heater until stabilization of the power supply is obtained. It is then switched to the calorimeter heater by a Baird-Atomic Precision Timer Model-930 for a preset length of time. The current and voltage are measured using a Calibration Standard Corp. dc Voltmeter across a 0.01 ohm Biddle-Gray Standard Resistor, and a Hewlett-Packard Digital Voltmeter. A value of 2586 cal/mV ($\pm 0.5\%$) has been obtained for the calibration constant over a period of one year.

The furnace consists of a tungsten mesh heating element surrounded by tungsten radiation shields. A temperature up to approximately 2700°C can be reached with 25 V and 1100 A.

The sample temperature is measured using a Pyro Micro-Optical Pyrometer. This pyrometer was calibrated against a tungsten-ribbon filament lamp, which in turn was calibrated against a National Bureau of Standards calibrated tungsten-ribbon filament lamp. The uncertainty in temperature measurements using this pyrometer is $\pm 0.5\%$ at all temperatures.

The tungsten capsule shown in Figure 9 is used to contain the materials. Two methods are used to make the capsules; spark discharge machining of G. E.-15 crack-free tungsten and also normal slip-casting techniques. The capsules are loaded with sintered pellets and then welded shut with $1/3$ atmosphere of argon or helium internal pressure.

At the present time measurements have been made only on unirradiated material. The heat contents to 2400°K of unirradiated UO_2 , $\text{U}_{0.82}\text{Pu}_{0.198}\text{O}_{2.00}$, and $\text{U}_{0.82}\text{Pu}_{0.198}\text{O}_{1.98}$ are shown in Figure 10. The heat content of PuO_2 is now

being determined but as yet there are not enough results to publish. It is planned that the heat content of PuO_2 will be determined up to the melting point. The heat of fusion will also be measured.

In addition, an adiabatic calorimeter has been constructed for direct measurement of heat capacity at temperatures up to 1200°C , and an intermediate range ($300^\circ\text{--}1500^\circ\text{K}$) drop calorimeter is now in use.

ADDITIONAL PLUTONIUM HIGH TEMPERATURE CHEMISTRY RESEARCH

Several additional plutonium research programs are being conducted for applications other than fast breeder reactor fuels.

Plutonium electrorefining: Conventional plutonium metal and its alloys are electrorefined routinely on the multikilogram scale. Metal produced by this process has a purity of 99.99 percent, and is distributed by the U.S. National Bureau of Standards as a plutonium chemical standard. For special applications plutonium-238 and plutonium-242 also are electrorefined. The process, which is well described in the literature,⁽¹⁰⁾ involves the chemistry of molten plutonium metal and molten salt electrolytes. In support of this application, the pseudobinary temperature - composition diagrams of plutonium trichloride with each of the alkali chlorides and each of the alkaline earth chlorides (except for francium, beryllium, and radium chlorides) have been determined and reviewed.^(11, 12)

Phase relationships between plutonium trichloride, plutonium oxychloride, and plutonium metal also have been reported.^(13, 14) In the area of high temperature metallurgical chemistry, the equilibrium solubilities of all of the refractory metals in liquid plutonium have been determined,^(15, 16, 17, 18) and the thermochemistry of plutonium process reactions at high temperature have been reviewed.⁽¹⁹⁾

Radioisotopic heat sources: Conventional plutonium-238 has a specific power of 0.456 watts per gram of total plutonium isotopes, which is approximately 200 times that of plutonium-239. Coupled with its long half life, this makes plutonium-238 an ideal heat source material. The development of a heat source for use in an implantable artificial heart in humans is being conducted at the Laboratory. Interesting high temperature chemistry research has evolved from plutonium associated with the synthesis and characterization of extremely pure special compounds such as $^{238}\text{PuO}_2^{1c}$ and $^{238}\text{PuN}^{15}$ for this application.^(20,21) The high temperature chemistry of a solid solution of $^{238}\text{PuO}_2^{1c}$ and ThO_2^{1c} also is being investigated. This material appears to offer favorable high temperature properties that can be utilized in space electric power heat source applications.

CONCLUDING REMARKS

Ten years ago essentially all plutonium chemistry research at the Los Alamos Scientific Laboratory was conducted at temperatures below 100°C in aqueous and organic solvent systems. Today essentially all plutonium chemistry research is in the high temperature field. This remarkable change was caused by the need to utilize plutonium in its numerous forms. Successful utilization requires a detailed knowledge of high temperature properties, and research at the Laboratory is currently directed toward expanding our knowledge in this area.

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Figure 1. Differential Thermal Analysis Apparatus

Figure 2. Melting Behavior of U, Pu Monocarbides (C/M = 0.95 to 1.00)

Figure 3. Thermal Arrests Observed for (U, Pu) Carbides Containing Excess C

Figure 4. Mass Spectrometer - Knudsen Cell Assembly.

$$\log_{10} P_{\text{Pu}}(\text{atm}) = (4.924 \pm 0.120) - \frac{17420 \pm 184}{T, ^\circ\text{K}}$$

$$(1426 - 1658^\circ\text{K})$$

$$\Delta H_{\text{V}298}^{\circ} = 83.0 \pm 0.5 \text{ kcal/mole}$$

$$\Delta S_{\text{V}298}^{\circ} = 29.1 \pm 0.5 \text{ eu}$$

Figure 5. Results for the Vaporization of Liquid Plutonium

$$\log_{10} P_{\text{PuF}_3} = (9.288 \pm 0.087) - \frac{20734 \pm 118}{T, ^\circ\text{K}}$$

$$(1243 - 1475 ^\circ\text{K})$$

$$\Delta H_{298}^{\circ} \text{ sub} = 101 \pm 3 \text{ kcal/mole}$$

$$\Delta S_{298}^{\circ} \text{ sub} = 51.6 \pm 2.5 \text{ eu}$$

Figure 6. Results for the Sublimation of Plutonium Trifluoride

$$\log_{10} P_{\text{Pu}} (\text{atm}) = (6.445 \pm 0.055) - \frac{21958 \pm 98}{T, ^\circ\text{K}}$$

$$(1658 - 1976 ^\circ\text{K})$$

$$\text{PuN} (\text{s}) \quad \Delta H_{\text{f}298}^{\circ} = -71.2 \pm 2.5 \text{ kcal/mole}$$

$$\Delta S_{\text{f}298}^{\circ} = -19.9 \pm 2.0 \text{ eu}$$

Figure 7. Results for the Vaporization of Plutonium Mononitride

Figure 8. High Temperature Drop Calorimeter

Figure 9. Tungsten Capsule for High Temperature Calorimetry

Figure 10. Heat Contents of Various Oxides