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Identification and preparation of plutonium monoxide

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Plutonium oxychloride can react with calcium (dissolved in calcium chloride) to form plutonium monoxide.

Plutonium is one of the metals whose phase diagram with oxygen is imperfectly understood. The existence of the lowest oxide of plutonium, plutonium monoxide, is an open question. This problem was discussed in detail by Katz *et al.*[1] As early as 1949, Mooney and Zachariasen reported on the occurrence of PuO as an impurity phase, which was identified by X-ray diffraction analysis.[2] Zachariasen[3] described powder X-ray diffraction patterns that could be attributed to PuO. It was assumed that solid PuO is formed as a film on the surface of plutonium metal.[1] Westrum[4] reported the preparation of solid PuO as a semimetallic substance with almost metallic lustre by the reduction of 5 mg of PuOCl (or PuO_2) with barium vapour at 1250 °C. Akimoto[5] described the preparation of solid PuO by the reaction of microgram amounts of molten plutonium with a stoichiometric amount of oxygen obtained by the thermal decomposition of Ag_2O.

According to published data,[6] PuO was identified by X-ray diffraction analysis; it has an fcc lattice with a parameter of 4.96±0.01 Å, which is consistent with data published by Mooney and Zachariasen.[2] Mulford and Lamar, who studied the evaporation of Pu_2O_3, hypothesised the occurrence of gaseous PuO. However, later on, Mulford *et al.*[7] doubted of the existence of pure PuO. Other attempts to prepare pure PuO were also described; however, the problem remains unclear. On this basis, Katz *et al.*[1] concluded that, although there is evidence for the existence of PuO, it is likely that this compound does not exist as an equilibrium solid phase; therefore, it was not included in the phase diagram.

Indeed, the region of PuO was not marked in the known plutonium–oxygen phase diagrams. Figure 1 demonstrates a credible phase diagram of Pu–O_2.[8] However, the region of PuO is omitted. PuO is marked only in the hypothetical phase diagram (Figure 2) proposed by Chikalla *et al.*[9] This diagram was not supported by experimental data.

However, as early as 1949, we were faced with plutonium monoxide. In 1949, the industrial production of plutonium metal was started at the Mayak plant in Chelyabinsk, Russia. In the early reduction smelting, the yield of plutonium was as low as about 87%. Thus, about 13% of plutonium remained in slag. These slags together with reaction crucible linings were chemically treated for the regeneration of plutonium. In the course of regeneration, an unknown insoluble carbon-like black precipitate was found. It was collected in a small beaker and kept under water. Then, the black powder (about 600 mg) was dried for analysis. On grinding the dry powder with a glass rod, an explosion occurred. This fact, as well as the results of chemical and metallographic analysis of plutonium, suggested that this was an unknown compound of plutonium, admittedly, a lower oxide of plutonium (Pu_2O_3 or PuO) rather than carbon. The properties of these oxides were unknown at that time. However, it was believed that the explosion reaction resulted in the formation of well-known thermodynamically stable plutonium dioxide. The explosion resulted in considerable heat release, which cannot result from the oxidation of trivalent plutonium to the tetravalent state. Moreover, trivalent metal oxides are stable and not pyrophore, whereas the unknown oxide exploded under a very weak external action. Thus, we dealt with a lower plutonium oxide.

We found that the black powder was not formed upon the replacement of the lining material (calcium oxide) by magnesium oxide. Thus, calcium oxide played a key role in this process. On this basis, a hypothetical mechanism of the formation of PuO was formulated.

Although plutonium reduction from the trichloride with calcium occurs relatively rapidly, an insignificant fraction of plutonium chloride reacts with calcium oxide (lining material) to form plutonium oxychloride:

$$PuCl_3 + CaO \rightarrow PuOCl + CaCl_2.$$

This reaction is thermodynamically favourable because the affinity of calcium to chlorine is much greater than that to oxygen.

Moreover, a detectable amount of calcium oxide passes into the slag from the lining because the solubility of calcium oxide in the chloride is as high as 15%. In the laboratory development of a technology for the preparation of plutonium metal, a considerable decrease in the thickness of the lining due to the dissolution of calcium oxide in the slag was observed. Thus, plutonium chloride can also react with this portion of calcium oxide to form plutonium oxychloride.

Calcium metal, which is added in large excess to the charge of reduction smelting, is also soluble in calcium chloride. Therefore, the resulting plutonium oxychloride dissolved in the slag can react with calcium, which is also present in the slag, to form plutonium monoxide:

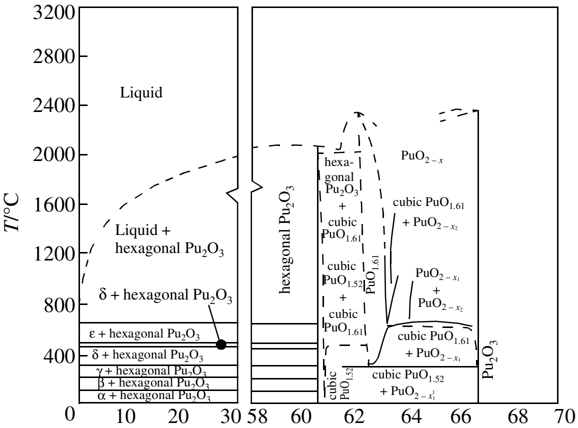

Figure 1 Phase diagram of the plutonium–oxygen system.[8]

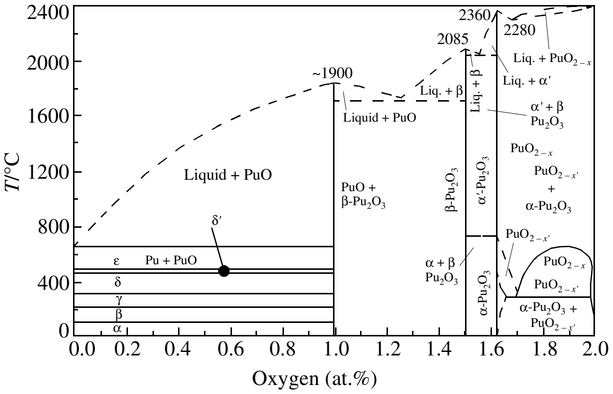

Figure 2 Hypothetical phase diagram of the plutonium–oxygen system.[9]

$$2PuOCl + Ca \rightarrow 2PuO + CaCl_2$$

Note that this reaction can occur only by the interaction of plutonium oxychloride with calcium dissolved in calcium chloride for the following reasons: first, the calcium content of slag is low, and calcium is homogeneously distributed. Second, the thermodynamic (or chemical) activity of calcium in solution is lower. Plutonium will be reduced to the metal with the use of free calcium metal.

We reproduced the described process in the laboratory. Plutonium oxychloride was prepared by heating a well-stirred $PuCl_3 + CaO$ mixture; calcium chloride was also added to the mixture in order to simulate the conditions of reduction smelting. The mixture was prepared with a small excess of plutonium chloride to provide the complete reaction of CaO and thus to facilitate the isolation of pure plutonium oxychloride. To prevent the charge material from contamination with other oxides, the mixture was heated in a nickel crucible. The reaction products were treated with water. The resulting $CaCl_2$ and the small excess of $PuCl_3$ added to the charge material passed into solution, whereas PuOCl formed a precipitate because it is water-insoluble. The resulting plutonium oxychloride was identified by chemical analysis. Next, calcium chloride with dissolved calcium metal was prepared. For this purpose, the dry chloride was mixed with calcium chips and heated in an inert atmosphere until the melting of calcium chloride, and the resulting mixture was held for a time at this temperature. The calcium solution in the chloride was thoroughly mixed with powdered PuOCl, and the mixture was heated in an inert atmosphere. In this case, a metal crucible was also used. Calcium as a solution in calcium chloride was added to the charge material in an excess to provide the complete reduction of PuOCl to PuO in order to obtain the expected compound without PuOCl impurities. The resulting product was treated with an ammonium nitrate solution. As a result, a uniform black powder was obtained, which was identical in appearance to the powder obtained at the Chelyabinsk plant upon the treatment of reduction smelting slag in 1949.

A similar experiment was also successfully performed as described below. A mixture of calcium chloride with calcium metal chips was loaded to the bottom of a crucible. Next, plutonium oxychloride was loaded, and it was covered with calcium chloride. The mixture was heated to 1200 °C. The cooled product was also treated with an ammonium nitrate solution.

The dry powder exhibited weak lustre; it was readily soluble in hydrochloric acid. The PuO powder was stored in air for a long time with no detectable changes; in particular, its oxidation was not detected. Therefore, published data on the instability of free PuO are incorrect.

Thus, the theoretical or hypothetical identification of the unknown product found in plutonium chloride reduction smelting slag as PuO allowed us to perform studies in an appropriate direction and to support the hypothesis proposed.

In summary, pure plutonium monoxide was prepared for the first time. Its existence is beyond question. The described technology makes it possible to readily produce it in gramme amounts. Metallographers should supplement the phase diagram of $Pu–O_2$ with plutonium monoxide and refine its area close to PuO.

References

1 *The Chemistry of the Actinide Elements*, 2nd edn., eds. J. J. Katz, G. T. Seaborg and L. R. Morss, Chapman and Hall, New York, London, 1986, vols. 1 and 2.

2 R. C. L. Mooney and W. H. Zachariasen, in *The Transuranium Elements, Nat. Nucl. En. Ser., Div. IV*, McGraw-Hill Book Co., Inc., New York, 1949, vol. 14B.

3 W. H. Zachariasen, *Acta Crystallogr.*, 1949, **2**, 388.

4 E. F. Westrum, Jr., in *The Transuranium Elements, Nat. Nucl. En. Ser., Div. IV*, McGraw-Hill Book Co., Inc., New York, 1949, vol. 14B.

5 Y. Akimoto, *(1960) Chemistry Division Semiannual Report*, November 1959, UCRL-9093, p. 73.

6 C. E. Holley, R. N. R. Mulford, E. J. Huber, E. L. Head, F. H. Ellinger and C. W. Bjorklund, *Thermodynamics and Phase Relationships for Plutonium Oxides*, Unversity of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, 1958.

7 R. N. R. Mulford, F. H. Ellinger and K. A. Johnson, *J. Nuclear Mater.*, 1965, **17**, 324.

8 F. H. Ellinger and N. N. O'Boyle, *Constitution of Plutonium Alloys*, LA-3870, 1968.

9 T. D. Chikalla, E. E. McNeilly and R. E. Skavdahl, *J. Nuclear Mater.*, 1964, **12**, no. 2.

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