from the decomposition of FSO_2OOF, O_3F_2, or O_2F_2 and not from FSO_2OOSO_2F, FSO_2OF, or OF_2.

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Plutonium Borides[1]

BY HARRY A. EICK[2]

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Although the chemistry of many refractory plutonium compounds has been investigated extensively in the past 10 years, little effort has been directed toward study of the plutonium borides. The first report of these borides appeared in 1960 in a communication[3] which lists four compounds, PuB, PuB_2, PuB_4, and PuB_6, together with the crystal structure, lattice parameters, and interatomic distances of each species. The melting points of nominal compositions corresponding to the above have been reported,[4] but no additional information is available.

Since McDonald and Stuart[3] report the presence of extra unidentified lines in their X-ray powder diffraction photographs, and since the existence of PuB_{12} was suspected, the system was re-examined. Another point of interest was the NaCl-type monoboride which they report. No other metal has been shown unequivocally to form a monoboride with this type of structure; thus if it indeed exists, it would be most interesting.

Experimental

Two procedures were followed. In the first method, which differed from that reported by McDonald and Stuart only in the use of a vacuum instead of an argon atmosphere, plutonium (99.99% pure) was heated with elemental boron (98.7% pure; 0.5% Mg and Si, 0.05% Al, Cu, Mn, Fe, Ni, and Ca) in various atom ratios in either a BN or a ZrB_2 container in an evacuated tantalum resistance-heated tube furnace. The product was removed from the cell, crushed, ground in an Alundum mortar, and reheated in the furnace to achieve homogeneity. Temperatures ranging from 800 to 2060° were used. The BN crucible was found to react with plutonium at 1200° to form PuB_2 and thus was not a satisfactory container.

The second method consisted of arc melting in a purified argon atmosphere samples of plutonium and boron in the atom percentages, plutonium to boron, 67:33, 50:50, 33:67, 20:80, 14:86, 12:88, 10:90, 5:95, and 0.8:99.2

The products of both preparations were examined by X-ray powder diffraction using a 114.59-mm. diameter Debye–Scherrer powder camera and copper Kα radiation (λ_{α_1} 1.54050 Å.). In addition, the arc-cast specimens were examined micrographically. The 1:1 specimen was annealed for 8 hr. at 1600° and 8 hr. at 1700° to check for monoboride formation.

As a check for homogeneity ranges, the lattice parameters of a large number of preparations were determined using the extrapolation procedure described by Vogel and Kempter.[5]

Results and Discussion

Table I lists the phases present in the arc-cast samples, as determined by X-ray powder diffraction analysis and confirmed by micrography. The 1:6 and 1:12 compositions may have been somewhat deficient in boron because of its volatility and the difficulty involved in collecting into the arc-cast button that material which had distilled onto the cold hearth. These particular compositions were sensitive to thermal shock and (usually) fractured violently during cooling after the arc had been extinguished. The boride X-ray diffraction patterns of all specimens were sharp; large single crystals were present in the 14:86 preparation. In those preparations containing metallic plutonium, the metal pattern was diffuse and weak, but clearly present. Lines present in the photographs of all but the 95:5 composition were explainable on the basis of the phases listed in Table I.

TABLE I
PHASES OBSERVED IN ARC-CAST SPECIMENS
OF PLUTONIUM AND BORON

Compn., Pu:B atom ratio	Measured density, g./cc.	Phases present by X-ray	Phases present by micrography
67:33	. . .	α-Pu, PuB_2	α-Pu, PuB_2
50:50	. . .	α-Pu, PuB_2	α-Pu, PuB_2
33.3:66.7	12.06	PuB_2, PuB_4 (trace)	PuB_2, PuB_4 (trace)
20:80	9.21	PuB_4, PuB_6 (trace)	PuB_4, PuB_6
14:86	7.21	PuB_4, PuB_6	PuB_4, PuB_6
12:88	6.79	PuB_6, PuB_{12}	3 phases, see text
10:90	6.25	PuB_6, PuB_{12}	3 phases, see text
5:95	5.63	PuB_6, PuB_{12}	3 phases, see text
0.8:99.2	2.73	PuB_{12}, PuB_{100}	PuB_{100}, PuB_{12} (trace)

The micrographic examination of the 12:88, 10:90, and 5:95 specimens indicated the presence of three constituents, while the X-ray patterns showed only two phases, PuB_6 and PuB_{12}. All the observed microstructures are compatible with the following construction for the temperature–composition phase diagram: PuB_4 melts congruently, while PuB_2, PuB_6, PuB_{12}, and "PuB_{100}" melt peritectically. A eutectic exists between PuB_{12} and "PuB_{100}." The eutectic composition is greater than 95 atomic % boron. Thus the above three alloys, listed in Table I as showing three phases under the microscope, consisted of primary PuB_6 and secondary PuB_{12} surrounding the PuB_6. The third constituent was the last liquid to solidify and consisted of a eutectic mixture of PuB_{12} and "PuB_{100}." The eutectic mixture either was too fine to resolve

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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[3] B. S. McDonald and W. I. Stuart, *Acta Cryst.*, **13**, 447 (1960).

[4] R. E. Skavdahl, Document HW-78388, Hanford Atomic Products Operation, Richland, Wash., p. 5.1-22.

[5] R. E. Vogel and C. P. Kempter, *Acta Cryst.* **14**, 1130 (1961).

with the microscope or divorced during solidification. The small amount of the "PuB_{100}" phase present and the weakness of the numerous lines in its powder pattern precluded seeing this phase in the X-ray diffraction examination of the above three compositions.

The average values obtained from a number of lattice parameter determinations, the numbers given in parentheses, are the following: hexagonal PuB_2, $a_0 = 3.1857 \pm 0.0002$ Å., $c_0 = 3.9485 \pm 0.0004$ Å. (3); tetragonal PuB_4, $a_0 = 7.1018 \pm 0.0003$ Å., $c_0 = 4.0028 \pm 0.0001$ Å. (3); cubic PuB_6, $a_0 = 4.1134 \pm 0.0003$ Å. (7); face-centered cubic PuB_{12}, $a_0 = 7.4843 \pm 0.0003$ Å. (2); and simple cubic "PuB_{100}," $a_0 = 23.43 \pm 0.04$ Å. (1). The errors reported for all but the hectoboride were computed from the standard deviations of the individual samples. The error for the hectoboride was estimated.

As already mentioned, preparations were made by heating plutonium with boron as well as by arc-melting. At $Pu:B < 1:20$ the plutonium reacted with the boron immediately adjacent to it and then flowed through the loose boron powder, forming PuB_2. That the reaction was exothermic was observed by dropping a piece of plutonium metal into a BN cell packed with boron and observing the interior of the cell with a pyrometer as the temperature was increased. At about 800° the cell interior suddenly glowed brightly red as the plutonium melted and reacted with the boron, forming a mixture of PuB_2 and boron. Since plutonium melts at 640°, a probable explanation of the 800° reaction temperature is that at 800° the oxide film encasing the molten metal ruptured and contact between boron and the liquid plutonium was achieved. Crushing and further heating of the PuB_2 clinker with the unreacted boron produced higher borides. Plutonium diboride could be formed at temperatures up to 1750° in contrast to the report of McDonald and Stuart that it formed only at 800°.

In general, mixtures of the boride phases were formed when stoichiometric preparations were heated for 1 hr. at temperatures below 1600°, whereas the same specimens heated to slightly higher temperatures generally became monophasic. However, excessive heating (4–5 hr.) at temperatures of 1950° and above resulted in loss of either boron or plutonium, or both, depending upon the initial composition.

Specimens of PuB_4, PuB_6, and PuB_{12} were heated to 2150° without melting; thus the melting points of these compounds are above 2150°.

The reflections observed in the powder patterns of the various plutonium boride phases are listed in tables deposited with the American Documentation Institute.[6] For PuB_2, PuB_6, and PuB_{12} all possible reflections are listed. For PuB_4 only the first 51 possible reflections are given. Space-group extinctions are not included, but reflections with intensities fortuitously zero or close to zero are. The calculated intensities and *d* spacings were obtained with an IBM 7094 computer using a code developed by A. C. Larson of this laboratory. An absorption factor $\mu_r = 5.0$ was assumed. The film from which the data on the hectoboride were obtained showed PuB_{12} lines in addition to the hectoboride lines.

As Table I indicates, the NaCl-type PuB phase was not observed in the present work despite compositions and heat treatments which should reasonably have produced it. No sign of a PuB phase was seen either by X-ray or by micrography. Although face-centered cubic monoborides have been reported for titanium, zirconium, and hafnium as well as for plutonium, the existence of such a phase is always suspect because borides usually form only when the boron can bond to itself in chains or networks. In the face-centered cubic NaCl-type structure the bonding is metal-to-boron.

If one assumes that the radius of plutonium is 1.64 Å. or the same as that of the metallic δ modification in which it has the coordination number 12, as does the reported boride, and that the radius of boron is 0.87 Å., the minimum single bond radius of boron in borides, the lattice parameter expected for PuB would be about 5.02 Å., which is considerably larger than the reported 4.92 Å. value.

Since the radius of boron is larger than that of carbon, the monoboride should exhibit a lattice parameter greater than that of the NaCl-type plutonium monocarbide. However, the lattice parameter of PuC, extrapolated to the stoichiometric composition, is 4.978 Å.,[7] considerably larger than the 4.92 Å. reported for the boride. The latter value is similar to the lattice parameter reported for PuN ($a_0 = 4.906$ Å.).[8] Because the reported lattice parameter is much smaller than would be expected and is similar to that of PuN, it seems likely that the plutonium boride specimen prepared by McDonald and Stuart was stabilized by nitrogen. This explanation is not unreasonable, since they heated their samples in an argon atmosphere and nitrogen is a common contaminant in argon.

Upon exposure to air, the 2:1 and 1:1 arc-cast specimens crumbled and oxidized slowly, a result expected for a mixture containing elemental plutonium, as all the other boride phases are very corrosion resistant.

Thus, the existence of the NaCl-type pure monoboride phase seems dubious.

To check for homogeneity ranges, X-ray data from two-phase mixtures were examined carefully. No variations in the lattice parameters of PuB_2, PuB_4, and PuB_6 were found when these phases were in equilibrium with phases more or less rich in boron. The variation in the lattice parameter reported for PuB_6 by McDonald and Stuart could not be reproduced. To check further for variation in lattice parameter, a PuB_6–PuB_{12} mixture was heated at temperatures higher than 2000° in a

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(6) These tables have been deposited as Document No. 8407 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(7) F. H. Ellinger, private communication.

(8) W. M. Olson and R. N. R. Mulford, *J. Phys. Chem.*, **68**, 1048 (1964).

ZrB_2 cell until enough boron had been lost by volatilization to produce a PuB_4–PuB_6 mixture. No variation of the PuB_6 lattice parameter was observed during this process. This experiment, together with other experiments in which PuB_2 was converted into PuB_4 by evaporation of plutonium, imply that the tetraboride evaporates congruently.

It is possible to draw a parallel between the boride phases of the lanthanides and those of the actinides. The existence, or nonexistence, of lanthanide borides is correlated closely with the radii of the metal atoms involved. Thus dysprosium and holmium, which have radii close to that calculated for plutonium from the unit cell dimensions of PuB_4 and PuB_2, form MB_2, MB_4, MB_6, and MB_{12} phases. These four borides were found for plutonium in the present work. In addition, a hectoboride reported for some lanthanides[9] exists also in the plutonium system.

Uranium and erbium have similar effective radii (calculated from unit cell volumes) and both form MB_2, MB_4, and MB_{12} phases.[10] The MB_6 structure cannot be prepared with a cation radius comparable to that of erbium.[11]

The effective radius of thorium is large, comparable to that of lanthanum or cerium, both of which form only MB_4 and MB_6 phases. Thus only ThB_4 and ThB_6 are found.[12]

Borides with boron contents of MB_{12} or less appear to be fairly well understood. The situation as regards higher borides is not as well defined. Lundin[13] reports an yttrium boride of composition near YB_{70}, the X-ray pattern of which he has indexed tentatively with tetragonal symmetry with $a_0 = 11.75 \pm 0.04$ Å., $c_0 = 12.62 \pm 0.04$ Å. Seybolt[14] reports that a micrographic examination of 1 to 2 atomic % yttrium–boron compositions heated in a BN crucible showed a boride estimated to be YB_{50}. Post[15] reports the preparation of cubic borides of holmium, terbium, and ytterbium of composition near MB_{70}, all with the same lattice parameter of 11.75 Å. as determined from powder patterns. Post states further, however, that examination of single crystals showed the true lattice parameter to be 23.50 Å. Smith and Gilles[9] report, for gadolinium and ytterbium, cubic MB_{100} phases with lattice parameters of 16.50 ± 0.02 Å.

The 99% B–1% Pu arc-melted specimen was found micrographically to contain two phases, one of which was PuB_{12}. When the PuB_{12} lines were subtracted from the X-ray powder pattern, the remaining lines could be indexed completely only on the basis of a simple cubic unit cell with $a_0 = 23.5$ Å. Either the 11.7 or 16.5 Å. (1.414 × 11.7) cubic cells accounted for part, but not all, of the lines. On this basis the plutonium "hectoboride" is assumed to be similar to that reported by Post and by Smith and Gilles. The plutonium analog of the tetragonal boride reported by Lundin was not found. Two extra, very weak lines appeared in the powder pattern of the 95:5 specimen. These lines, which did not correspond to the MB_{100} phase, were found in no other preparation and were too few and weak to attempt to fit to any structure.

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Correspondence

Assignment of 64.2-Mc. B^{11} Nuclear Magnetic Resonance Spectrum of Pentaborane-11

Sir:

The B^{11} n.m.r. spectrum of B_5H_{11} (containing ~10% B_5H_9) at 12.8 Mc. was assigned as follows: A high-field doublet[1] representing the apex boron alone *with a single terminal hydrogen* and a superpositioned lower field doublet[2] and triplet[2] representing the base BH groups and BH_2 groups, respectively; a small unobscured member of a doublet could be unambiguously assigned to the ~10% B_5H_9 contaminant. Shortly after publication[2] J. R. Spielman and A. B. Burg furnished a sample of B_5H_{11} in which B_5H_9 was presumed to be absent. The B^{11} n.m.r. spectrum at 12.8 Mc. supported their conclusion and thus constituted the first B^{11} n.m.r. spectrum of pure (95+%) B_5H_{11}. Since the original assignment appeared to be unambiguous the spectrum of the pure material was not published. In the past few years B^{11} n.m.r. spectrometry has become more popular and at least two reviews[3,4]

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[3] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York N. Y., 1963, p. 135.

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