NOTES

The Solid Solution Series, Boron–Boron Carbide[1]

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Boron carbide has been produced whose B/C ratio is considerably greater than four; only part of the excess boron can be removed by nitric acid or aqua regia. This observation led to the notion that a degree of solid solution can exist between boron and B_4C. Early difficulties experienced in ascertaining the combining proportions of boron and carbon were probably caused by inconstancy of the B/C ratio.

Three samples of boron carbide were employed in this investigation. Normal Hot-Molded Boron Carbide (B_4C) was designated Sample No. 1. Sample No. 2 ($B_{5.66}C$) consisted of boron carbide fragments obtained as by-product during the manufacture of boron by the "hot wire" method. The boron carbide formed on the surface of the graphite rod prior to deposition of high purity boron. Sample No. 3 (B_7C) was prepared by ball milling a composite of high-boron boron carbide crudes. These crudes were produced in three separate runs in a small closed-shell resistor furnace; the charge in each case consisted of B_4C and B_2O_3 glass. Experimental work encompassed the following chemical and physical properties: B/C ratio, unit cell dimensions, specific gravity, Knoop hardness and lapping characteristics.

The object of this endeavor was threefold: (1) to establish the limit of solid solution of boron in boron carbide; (2) to determine the mechanism of solid solution; (3) to correlate changes in physical properties with change in the B/C ratio.

Historical Review.—The only allusion in the literature to solution of boron in B_4C was made by Clark and Hoard.[2] They suggested that excess boron might be interstitially accommodated in the boron carbide structure.

The following hexagonal unit cell dimensions have been determined on B_4C:

Source	a_0	c_0
Laves[3]	5.62kX. (5.63 Å.)	12.12kX. (12.14 Å.)
Zhdanov and Sevast'-yanov[4]	5.60kX. (5.61 Å.)	12.10kX. (12.12 Å.)
Clark and Hoard[2]	5.60kX. (5.61 Å.)	12.12kX. (12.14 Å.)

Experimental Work

Specimens were X-rayed on a North American Philips Geiger Counter X-Ray Spectrometer over the range $2\theta = 4 - 90°$ with nickel-filtered copper radiation. The appropriate *hk.l* indices were assigned. It was then possible to determine the hexagonal unit cell dimensions a_0 and c_0. As a check on the accuracy of these measurements d/n values were calculated for the various reflecting planes and compared with observed d/n values.

The principal X-ray constants are presented in Table I. Detailed X-ray data appear in Table II.

Table I

X-Ray Constants of B_4C, $B_{5.66}C$ and B_7C

Specimen	1. (B_4C)	2. ($B_{5.66}C$)	3. (B_7C)
c_0, Å.	12.07	12.15	12.19
a_0, Å.	5.61	5.65	5.67
c_0/a_0	2.151	2.150	2.150
Hexagonal unit cell vol. Å.^{3}	328.94	335.86	339.38
Unit cell vol. expansion (over normal B_4C), %	...	2.10	3.17

Samples no. 2 and 3 were subjected to chemical analysis and density measurement after the following treatment. They were reduced to 240 mesh and boiled in concentrated HNO_3 for three hours to dissolve free boron. After acid treatment samples were copiously washed with hot water and dried in an oven. Chemical and specific gravity data are contrasted with ideal data for normal B_4C in Table III.

Decreased bonding strength in high-boron boron carbide was demonstrated by physical tests of Knoop hardness and lapping effectiveness. The following values for Knoop hardness were obtained: B_4C—2810; $B_{5.66}C$—2580. B_7C was too fine grained to permit hardness measurement. As a lapping abrasive the high-boron modification was less effective than B_4C with respect to the following criteria: (1) weight of stock removed and (2) rate of break-down of abrasive grain.

In short, increase in the B/C ratio is reflected by changes in physical properties as follows: (1) dimensions of the unit cell increase; (2) specific gravity, hardness and "strength" decrease.

Mechanism of Solid Solution.—Theoretical densities have been calculated assuming alternate hypothetical solid solution mechanisms. Use was made of the equation

$$\text{S. G.} = \frac{(10.82x + 12.01y)(1.66)}{V}$$

where S. G. is the specific gravity, V is the volume and x and y are the respective numbers of boron and carbon atoms in the unit volume selected. $B_{5.66}C$ was employed in the calculations assuming successively: (1) extra boron atoms are accommodated interstitially, (2) extra boron atoms replace carbon atoms, (3) carbon atoms have been omitted from the structure.

(1) Interstitial Solid Solution

$B_{12}C_3$ plus 5B equals $B_{17}C_3$ in one rhombohedral cell.

$$\text{S. G.} = \frac{[(17)(10.82) + (3)(12.01)]\,[1.66]}{(0.33)(335.86)} = 3.29$$

(2) Substitutional Solid Solution

3 B's replace 3 C's in four rhombohedral cells to give $B_{51}C_9$

$$\text{S. G.} = \frac{[(51)(10.82) + (9)(12.01)]\,[1.66]}{(1.33)(335.86)} = 2.45$$

(3) Omission Solid Solution

$B_{5.66}C$ equals *ca.* $B_{12}C_2$ in one rhombohedral cell.

$$\text{S. G.} = \frac{[(12)(10.82) + (2)(12.01)]\,[1.66]}{(0.33)(335.86)} = 2.28$$

The experimental density of 2.484 is best ex-

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(1) Contribution from the Research and Development Department, Norton Company, Worcester, Massachusetts.

(2) H. K. Clark and J. L. Hoard, This Journal, **65**, 2113 (1943).

(3) F. Laves, *Z. Ges. Wiss. Göttingen, Mathem.-Physik Kl., Neue Folge*, **1**, 57 (1934).

(4) (a) G. S. Zhdanov and N. G. Sevast'yanov, *Compt. Rend. Acad. Sci. URSS*, **32**, 432 (1941); (b) G. S. Zhdanov and N. G. Sevast'yanov, *J. Phys. Chem. URSS*, **42**, 326 (1943).

TABLE II

X-RAY DATA ON B_4C, $B_{5.66}C$ AND B_7C ($d_{hk.l}$ (Å.))

hk.l (hexagonal)	Intensity	1. B_4C Obsd.	1. B_4C Calcd. (from a_0 = 5.61 Å., c_0 = 12.07 Å.)	2. $B_{5.66}C$ Obsd.	2. $B_{5.66}C$ Calcd. (from a_0 = 5.65 Å., c_0 = 12.15 Å.)	3. B_7C Obsd.	3. B_7C Calcd. (from a_0 = 5.67 Å., c_0 = 12.19. Å)
10.1	3	4.49	4.51	4.52	4.54	4.53	4.55
00.3	4	4.02	4.03	4.04	4.05	4.06	4.06
01.2	7	3.78	3.79	3.81	3.81	3.81	3.82
11.0	3	2.81	2.81	2.82	2.82	2.83	2.83
10.4	8	2.57	2.57	2.59	2.58	2.58	2.59
02.1	10	2.38	2.38	2.40	2.40	2.41	2.41
11.3	1	2.30	2.30	2.32	2.32	2.32	2.32
00.6	1	2.02	2.01	2.04	2.02	...	...
21.1	1	1.82	1.82	1.83	1.83	...	...
20.5	3	1.714	1.713	1.725	1.724	1.730	1.730
11.6	1	1.637	1.635	1.645	1.645	1.651	1.652
10.7	1	1.628	1.625	1.634	1.635	...	...
30.3	2	1.505	1.503	1.516	1.513	1.519	1.518
12.5	3	1.463	1.462	1.474	1.474	1.477	1.477
01.8	3	1.446	1.442	1.455	1.451	1.455	1.455
02.7	3	1.407	1.407	1.416	1.416	...	...
22.0	3	1.403	1.403	1.412	1.412	1.419	1.418
00.9	2	1.345	1.342	1.350	1.350	1.354	1.354
13.1	2	1.342	1.340	1.347	1.348	...	...
22.3	2	1.326	1.325	1.333	1.334	1.339	1.339
20.8	1	1.286	1.283	1.293	1.290	1.296	1.295
30.6	2	1.261	1.263	1.270	1.270	1.273	1.274
04.2	1	1.191	1.191	...	...	1.204	1.204

TABLE III

CHEMICAL AND SPECIFIC GRAVITY DATA ON B_4C, $B_{5.66}C$ AND B_7C

	1. B_4C	2. $B_{5.66}C$	3. B_7C
C, %	21.71	16.18	13.27
B, %	78.29	82.48	83.69
SiO_2, %	...	...	0.42
B_2O_3 (uncombined), %	...	...	0.42
N_2, %	...	...	0.14
Total, %	100.00	98.66	97.94
B/C	4.00	5.66	7.00
Sp. gr. (29/4°)	2.51	2.484	2.47

plained by the substitutional solid solution mechanism.

Assuming substitution of boron atoms for carbon, the theoretical density of B_7C was calculated.

9 B's replace 9 C's in eight rhombohedral cells to give $B_{105}C_{15}$.

$$\text{S. G.} = \frac{[(105)(10.82) + (15)(12.01)][1.66]}{(2.66)(339.38)} = 2.42$$

The experimental density was 2.47.

Clark and Hoard have shown that the B_4C structure is an approximate NaCl type referred to rhombohedral axes, with a compact group of 12 boron atoms substituting for Na^+ and a linear group of 3 carbon atoms for Cl^-. The central carbon atom has as immediate neighbors only the two end carbon atoms. Each end carbon atom has, on the other hand, four immediate neighbors, *i.e.*, three boron atoms and one carbon atom. The central position would seem more favorable for trivalent boron than either end position. Whatever the mechanics of the substitution, it would appear that the bonding strength between boron groups and carbon groups is diminished. This would be the normal accompaniment of increase in size of the unit cell and decreased specific gravity. Decreased Knoop hardness and inferior lapping characteristics attest to diminution of bonding strength within the high-boron boron carbide structure.

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The Solubility and Absorption Spectrum of Iodine in Sulfuric Acid Solutions

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The colors exhibited by iodine in different solvents have been the subject of extensive interest for more than fifty years. Substances in which iodine dissolves may be put in two general classes; "violet" or "inert" solvents in which iodine has the color of its vapor and "brown" solvents in which the color ranges from brown to dark red. The "brown" solvents have attracted the attention of many investigators since spectroscopic data have been obtained indicating the formation of 1:1 molecular complexes in some of these media. Detailed work on iodine in benzene, substituted benzenes, naph-