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(Quarterly Report No. 3)

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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Contract No. AT(11-1)-578
Project Agreement No. 4

THE BORON-CARBON SYSTEM

for

U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Mr. H. N. Miller
Contracts Division

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ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

Contract No. AT(11-1)-578
Project Agreement No. 4

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November 1, 1960 - January 31, 1961

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February 6, 1961

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

THE BORON-CARBON SYSTEM

ABSTRACT

A definitive investigation of the boron-carbon equilibrium system is being made by X-ray diffraction, metallographic, and thermal analytical techniques. On the basis of metallographic and X-ray diffraction studies it is concluded that boron carbide has a range of solubility from approximately 10 to 20 atomic per cent carbon at 1500° to 2000°C. The melting point of the carbide-graphite eutectic has been established as 2325°-2350°C. No reversible allotropy of the beta-rhombohedral structure has been observed. The solubility of carbon in boron is very small. The melting point of dilute carbon alloys is found to be essentially the same as that of pure boron (2040°-2050°). No metallographic evidence of a three-phase reaction of dilute alloys is observed.

THE BORON-CARBON SYSTEM

I. INTRODUCTION

Boron has been of interest as a neutron control and burnable poison material for many years. Although boron has been incorporated into reactors in many ways, the most common form has been a dispersion of boron carbide in a structural metal or alloy. To aid the study of reactor components, more detailed basic information on boron-carbon alloys is required.

In accordance with Contract No. AT(11-1)-578, Project Agreement No. 4, entitled "The Boron-Carbon System", a definitive investigation of the phase equilibria in this system is being made. This third quarterly report summarizes the investigation during the period November 1, 1960, to January 31, 1961.

II. EXPERIMENTAL PROGRESS

A. Review of Work During First Two Quarters

During the first quarter of this experimental program, techniques were investigated to determine the boron-carbon equilibrium system with the degree of precision as stipulated in the contract. Extensive experimentation was necessary to develop satisfactory methods for metallographic examination of alloys. Tentative phase relationships were established.

During the second quarter of the contract period experimental investigation continued by essentially the same techniques that were established in the first quarter. Alloys were prepared from higher purity materials. Experiments were initiated to ascertain the nature of the allotropy in pure boron.

On the basis of the research in the first two quarters, the state of our knowledge of the boron-carbon system can be summarized:

1. Metallographic specimens of as-cast compositions indicate a single carbide with a high carbon solubility limit of 20 atomic per cent.
2. There exists a carbide-graphite eutectic at 30 atomic per cent carbon.
3. Annealing treatments of both powder and cast boron fail to confirm any other allotropic form than the beta-rhombohedral structure.
4. X-ray parametric studies of sintered boron-carbon alloys indicate an extensive range of homogeneity of the carbide. In fact, it is possible that boron carbide, per se, does not exist, but that it is a continuous series of solid solutions of carbon in the low-temperature allotropic form of boron.
5. No eutectic or peritectic metallographic structure is observed.
6. The melting point of pure boron was observed to be 2025° - 2030° C.

B. Work During Third Quarter

An apparent ambiguity exists in the data that were accumulated during the first two quarters of the program. On the basis of as-cast microstructures a region of immiscibility between boron and boron carbide is observed, whereas X-ray diffraction studies indicated a very extended solubility with even the possibility that boron carbide is in reality an extended solubility of carbon in a low-temperature allotope of boron. This apparent ambiguity can be rationalized on the assumption that gross segregation results when boron-carbon alloys solidify.

During the third quarter, the ambiguity of the nature of the equilibrium in the boron-carbon system has been eliminated. It is definitely established that boron carbide as an intermediate phase exists and that there is a region of immiscibility between boron and boron carbide.

The pertinent investigations of the boron-carbon system during the third quarter may be summarized under the following categories:

1. Heat Treatment

Arc-cast alloys with carbon contents from 2 to 30 atomic per cent carbon were annealed at 1950° and 1500° C. The observed metallographic structures are summarized in Table I.

From these data it is concluded that boron and boron carbide are immiscible and that boron carbide has a range of homogeneity from approximately 10 to 20 atomic per cent carbon.

As has been previously pointed out, it was speculated that perhaps at low temperatures boron and boron carbide were miscible, and that the immiscibility observed in as-cast metallographic specimens originated from gross segregation during casting. On the basis of the observed metallographic structures of annealed specimens such an hypothesis is untenable. If there was gross segregation during casting, subsequent annealing would promote diffusion to the equilibrium structure. This was not observed. The annealed structures were in all respects identical to the as-cast structures. No evidence of agglomeration or diffusion was observed.

In conjunction with the investigation of the allotropy of boron, a cast sample containing 2 atomic per cent carbon was annealed for 35 days at 1200° C. Metallographically as well as by X-ray diffraction, the micro-constituents were found to be boron plus boron carbide.

2. Solubility Limits of Boron Carbide by X-Ray Diffraction

Compacts of boron and graphite containing 0.50, 1.0, 1.5, 2, 3, 5, 7, 10, 12, 14, 16, 18, 20, 24, 28, and 30 atomic per cent carbon have been prepared for the determination of the extent of solubility of carbon in boron carbide. These were sintered at 1600° and 2000° C in an argon atmosphere for thirty minutes. Examination of compacts after sintering showed that they had reacted. This was confirmed by X-ray diffraction.

Previous experience had led us to believe that powder compacts would not react at 1200° C. A sample containing 7 atomic per cent carbon was sintered at 1200° C. A cursory examination showed that there had been no reaction. This was subsequently confirmed by X-ray diffraction which showed the constituents to be boron and graphite as in the loose powder that was

TABLE I
SUMMARY OF METALLOGRAPHIC DATA

Nominal Composition, atom pct.	Microconstituents Observed	
	1950° C - 4 hr	1950° C - 4 hr, 1500° C - 2 hr
2	B + carbide	B + carbide
4	B + carbide	B + carbide
6	B + carbide	B + carbide
8	B + carbide	B + carbide
10	B + carbide	carbide
12	carbide	carbide
14	carbide	carbide
16	carbide	carbide
18	carbide	carbide
20	carbide + G-eutectic*	carbide + G-eutectic
22	carbide + G-eutectic	carbide + G-eutectic
24	carbide + G-eutectic	carbide + G-eutectic
26	carbide + G-eutectic	carbide + G-eutectic
28	carbide + G-eutectic	carbide + G-eutectic
30	G-eutectic	G-eutectic

* Graphite eutectic, carbide + graphite.

charged. It is planned to react the boron-carbon compacts at 1600° and subsequently anneal at 1200° C.

The sintered boron-carbon compacts were examined by X-ray diffraction techniques, both by the diffractometer and film methods. As has been previously shown in Figure 1, Quarterly Report No. 2, there is a parametric variation with carbon content. The 1600° C and 2000° C data showed such a variation but were not sufficiently accurate to permit phase boundaries to be established.

It was considered that the technique of using a single reflection to show the parametric variation was not sufficiently sensitive. The Cohen method for the least-squares solution of X-ray parametric data was programmed on the Foundation's Univac 1105 computer. By such a computation, the "best" values of the crystal parameters are calculated from the entire indexed pattern. The parameters of the boron-carbon alloys sintered at 1600° C were determined by this method. The trend of the "c" and "a" values of the boron carbide (as indexed by an hexagonal lattice) did not support the solubility limits as established by measurement of individual lines. The c/a ratio in the composition range 9 to 14 atomic per cent carbon increased from 2.14 to 2.17.

Recently an intense back-reflection line of the sintered boron-carbon alloys has been used as an indicator of the parametric variation of the boron carbide with carbon content. This line at a Bragg angle of approximately 75° is out of the range of the diffractometer, and so film techniques are required. High-angle lines, if resolved, are best for the determination of lattice parameters for two reasons: (a) the absolute value of angular variation with parameter is large, and (b) the error of measurement is small since absorption errors are minimized. As shown in Figure 1, the parametric variation of this high-angle line shows the solubility limits of carbon in boron carbide to be 9 and 20 atomic per cent. This is in agreement with the observed metallographic data in Table I.

3. Allotropy of Boron

Table I of Quarterly Report No. 2 gave an extensive list of heat treatments that had been attempted to establish whether boron exists in

FIG. 1. - ANGULAR VARIATION WITH CARBON CONTENT
OF STRONG BACK REFLECTION BORON CARBIDE LINE

equilibrium in any other than the beta-rhombohedral structure. Listed as in process was the heat treatment of loose powder at 900°C for 168 hours. This was likewise established to be beta-rhombohedral.

Pieces of high-purity General Electric and Eagle-Picher boron have been annealed for at least thirty days at 1000°, 1100°, and 1200°C in quartz containers. After heat treatment a thin enamel-like coating was observed on the specimens. This was etched off with hydrofluoric acid solution for the specimen annealed at 1000°C. X-ray diffraction data showed the beta-rhombohedral boron structure for both General Electric and Eagle-Picher boron annealed at 1000° and 1200°C. (A few extra lines attributed to the contaminating coating were observed in the 1200°C specimen.) The data for specimens annealed at 1100° are not yet available.

It must be concluded on the basis of the extensive annealing treatments that beta-rhombohedral boron is stable at 1000°C. The long-time annealing treatments will be repeated in protective wrappings of tantalum foil.

4. Melting Temperatures

By incipient melting techniques the melting points of the following alloys have been determined:

Pure Boron	2045° - 2050° C
B-1a/o C	2030° - 2040° C
B-4a/o C	less than 2080° C
B-30a/o C	2325° - 2350° C

The value recorded for pure boron in the above listing represents previously reported values but adjusted slightly upward according to revised calibration curves.

The melting point of the carbide-graphite eutectic is in relatively good agreement with the value of 2390[±] 20° C as determined by Dolloff.

The melting points of pure boron and dilute boron-carbon alloys are about 100° lower than those reported by Dolloff. That the melting point of boron is essentially the same as dilute boron-carbon alloys is consistent

with phase diagrams noted in other systems in which the liquidus rises sharply from the pure constituent. The observed small solubility of carbon in boron and the lack of metallographic evidence of a three-phase reaction are also consistent with such a diagram.

III. FUTURE WORK

The status of the investigation of the boron-carbon system is a matter of refining the accuracy of the established solubility limits and melting temperatures. Specific areas of investigation include:

1. The incipient melting surface. A large number of alloys will be melted in order to establish the variation of the solidus temperature with carbon content.
2. The solubility limits of boron carbide
 - a) Alloys are in preparation for the delineation of the solubility limits of boron carbide by metallography. Alloys at 0.5% intervals have been prepared between 7.0 and 21.0 atomic per cent carbon.
 - b) Additional X-ray diffraction parametric measurements will be made on alloys annealed at 1200°C to establish solubility limits of carbon in boron carbide. Compacts will be sintered at 2300° to establish the high carbon solubility limit of boron carbide near the carbide-graphite eutectic.
3. Confirmatory anneals will be made at 1000°, 1100°, and 1200°C with high purity boron to establish the validity of the conclusion that boron does not exhibit a reversible allotropic change.
4. Alloys containing 0.025, 0.050, 0.075 and 0.10 atomic per cent carbon will be prepared to establish the solid solubility limit of carbon in boron.

IV. PERSONNEL AND LOGBOOKS

During this period of investigation the following have been associated with the experimental program:

Rodney P. Elliott	-	Project Leader
Ronald Wibel	-	Project Technician

Pertinent experimental data are recorded in ARF Logbook C1191.

Respectfully submitted,

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