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(Quarterly No. 2)

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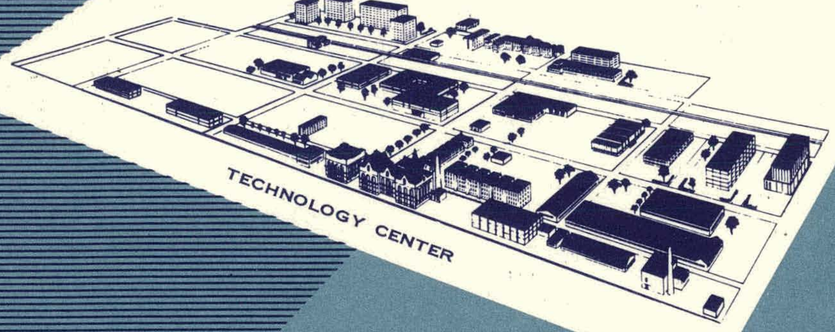

Contract No. AT(11-1)-578
Project Agreement No. 4

THE BORON-CARBON SYSTEM

for

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

Attention: Mr. Martin E. Powers, Director
Development Contracts Division

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ARMOUR RESEARCH FOUNDATION

of

Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

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ARF 2200-6
(Quarterly Report No. 2)

August 1, 1960 - October 31, 1960

for

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

Attention: Mr. Martin E. Powers, Director
Development Contracts Division

November 8, 1960

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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. Additional boron-carbon alloys have been prepared by sintering and arc-melting compacts prepared from boron and high-purity graphite. Metallographic examinations of these alloys are in agreement with alloys previously prepared from lampblack. X-ray investigation of sintered compacts indicates that the solubility range of boron carbide extends almost to pure boron. Boron of various purities has been annealed for times up to four hours, but no structure other than beta-rhombohedral has been detected. Very high purity boron (10 ppm impurity) has been obtained for the study of allotropy and the equilibrium relationships at very dilute carbon contents.

THE BORON-CARBON SYSTEM

I. INTRODUCTION

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

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.

II. EXPERIMENTAL PROGRESS

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. Suppliers of high-purity boron and carbon were contacted. Preliminary alloy studies were made with sintered and arc-melted alloys. Extensive experimentation was necessary to develop satisfactory methods for metallographic examination of alloys. From the preliminary investigation (as discussed in Quarterly Report No. 1) tentative phase relationships were established. These included a single carbide with solubility limits of at least 16-20% carbon and a carbide-graphite eutectic at 30 atomic per cent carbon. Metallography gave no indication of the three-phase relationship between liquid, boron, and boron carbide.

During the second quarter of the contract period experimental investigation of the boron-carbon system has been continued by essentially the same techniques that were established in the first quarter. The investigations during the second quarter covered the following three categories which are described in further detail.

A. New Alloys

Additional alloys have been prepared by identical techniques as were developed previously. However, instead of using carbon in the form of lampblack, high-purity graphite powder was used. Ten-gram compacts were made with carbon contents of 2, 6, 12, 16, 20, 24, 28, 30, 40, 50, and 75 atomic per cent. These were sintered and subsequently arc-melted. It has been necessary to use a binder (Carbowax) in the preparation of alloys containing 24 a/o carbon or greater. As-cast metallographic structures of these alloys were no different than those prepared previously (Figures 1-4 of Quarterly Report No. 1). Similarly, no eutectic or peritectic structure is indicated at low carbon contents.

Dilute alloys were prepared at 0.1 a/o C intervals up to 1.0 a/o C. For the preparation of these alloys a 5% master alloy was used. Metallographic examination of these alloys showed a primary constituent of the carbide phase. Similarly, metallographic examination of several arc-cast specimens of unalloyed boron shows the presence of this carbide phase. Thus, the solid solubility of carbon in boron is indicated as being less than 0.09 w/o carbon (the residual carbon analysis of boron as supplied by Cooper).

Very high purity boron has been purchased for the investigation of the solubility limit of carbon in boron. Boron obtained from the General Electric Company has the following typical analysis:

Oxygen	<0.01%
Hydrogen	0.02
Nitrogen	<0.003
Carbon	0.05
Tantalum	0.02
Other	0.01
Boron and Carbon	99.93 (difference)

A small quantity of super-pure, zone-refined boron has been purchased from the Eagle-Picher Lead Company ($25 per gram). This material by spectrographic analysis shows no contamination, although the manufacturer estimates it is contaminated to the extent of a total of 10 parts per million.

B. Investigation of Allotropy of Boron

Extensive investigation of the possible allotropy of boron has been undertaken. As yet, no crystal structure other than the beta-rhombohedral structure has been detected. The experimental investigation undertaken in attempts to determine whether any other than the beta-rhombohedral structure is stable is summarized in Table I.

C. Heat Treatment

Initial heat treatments at 2000°C were made in a vacuum of less than one micron pressure. Under these conditions alloys tended to decompose as was evident by surface deterioration and reaction with the tantalum sheet in which they were wrapped. Subsequently, annealing treatments have been successfully executed at 1950°C in an argon atmosphere at a slight positive pressure.

The melting point of boron has been determined by incipient melting techniques. In this procedure the specimen temperature, constantly monitored by an optical pyrometer, is slowly raised. The first sign of the presence of a liquid phase (incipient melting temperature) corresponds to the solidus temperature. For a pure substance this is also the melting temperature. The melting point of boron has been determined both as suspended on a tungsten wire and as supported in a boron nitride boat. The melting temperature as observed by several operators who have compared the melting points of reference substances was found to be 2025° to 2030°C. This is in disagreement with the currently accepted melting point of boron of approximately 2130°C.(1)

III. TECHNICAL DISCUSSION

A. Allotropy

From consideration of data presented in Table I, it is apparent that if any other form of boron than the β-rhombohedral structure is stable, the transformation is exceedingly sluggish. In no instance does the literature report the transformation of β-rhombohedral boron to either the α-rhombohedral or tetragonal form. There is no question that the alpha and tetragonal modifications do exist; however, it is questionable whether these are

TABLE I

SUMMARY OF INVESTIGATION TO ASCERTAIN ALLOTROPY OF BORON

Annealed Condition	Time	Temp., °C	Furnace	Container	Metallography	X-ray
Shieldalloy						
As-received powder	----	----	----	----	----	β-Rhomb.
Loose Powder	168 hr	900	Globar	Quartz tube	----	in process
Loose Powder	48 hr	950	Globar	Quartz tube	----	β-Rhomb.
Loose Powder	72 hr	1100	Globar	Quartz tube	----	β-Rhomb.
Loose Powder	4 hr	1100	Globar	Quartz tube	----	β-Rhomb.
Arc-cast	6 hr	1400	Vacuum Resistance	Ta package	in process	β-Rhomb.
Arc-cast	6 hr	1500	Vacuum Resistance	Ta package	B + (B_4C?)	β-Rhomb.
Arc-cast	6 hr	1600	Vacuum Resistance	Ta package	B + (B_4C?)	β-Rhomb.
Compact Powder	30 min	2000	Vacuum Resistance	Ta package		β-Rhomb.
Arc-melted	----	----	----	----	B + (B_4C?)	β-Rhomb.
"Cooper"						
As-received powder	----	----	----	----	----	β-Rhomb.
Compact Powder	10 min	1600	Vacuum Resistance	Ta package		β-Rhomb.
Arc-melted	----	----	----	----		β-Rhomb.
General Electric						
As-received in solid form	----	----	----	----		β-Rhomb.
Eagle Picher						
As-received in solid form	----	----	----	----	Boron	β-Rhomb.

equilibrium structures. In all instances reported in the literature these structures were formed during the primary reduction of boron.(2,3) In one case, however, α-rhombohedral boron was reported to solidify from a Pt-B eutectic.(4)

Tetragonal boron is very similar to a boron-nickel compound (possibly $B_{25}Ni$).(4) It is likely that in the primary reduction of the iodide or hydride a small nucleus of such a compound is formed and unalloyed boron continues to grow on the nucleus. The fact that α-boron has been found to precipitate from a low-melting eutectic gives reason to believe that this structure is, in fact, an equilibrium structure.

In order to establish whether it is possible to convert the β-rhombohedral form of boron to α-rhombohedral (or possibly the tetragonal form), a series of high-purity boron samples will be annealed for very long times (at least one month) in the temperature range of 1000° to 1200°C.

B. The Solid Solubility of Boron Carbide

Work by Glaser, Moskowitz and Post(5) in 1953, in which sintered boron-carbon mixtures were examined by X-ray diffraction, showed a wide homogeneity range of boron carbide extending from at least 4 to 28 a/o carbon. Such a solubility range is incompatible with diagrams as constructed by Russian investigators(6) and by National Carbon Co.(7) The diagram presented by the latter shows two carbides without solid solubility. National Carbon Co.(8) has revised this diagram to show a single carbide with an extensive range of solid solubility from 10 to 26 atomic per cent carbon at the B_4C-graphite eutectic temperature (2390°C). At temperatures below 1800°C it is proposed that the solid solubility is decreased to essentially the stoichiometric ratio B_4C. (The boron used in this investigation was only 98.9%).

Sintered boron-carbon mixtures prepared for the present investigation have been examined by X-ray diffraction. In complete agreement with the work of Glaser et al., the data indicate that there is a continuous solid solubility from approximately 2 a/o C through approximately 28 a/o C. In Figure 1 typical data of the Bragg angle as a function of carbon content as

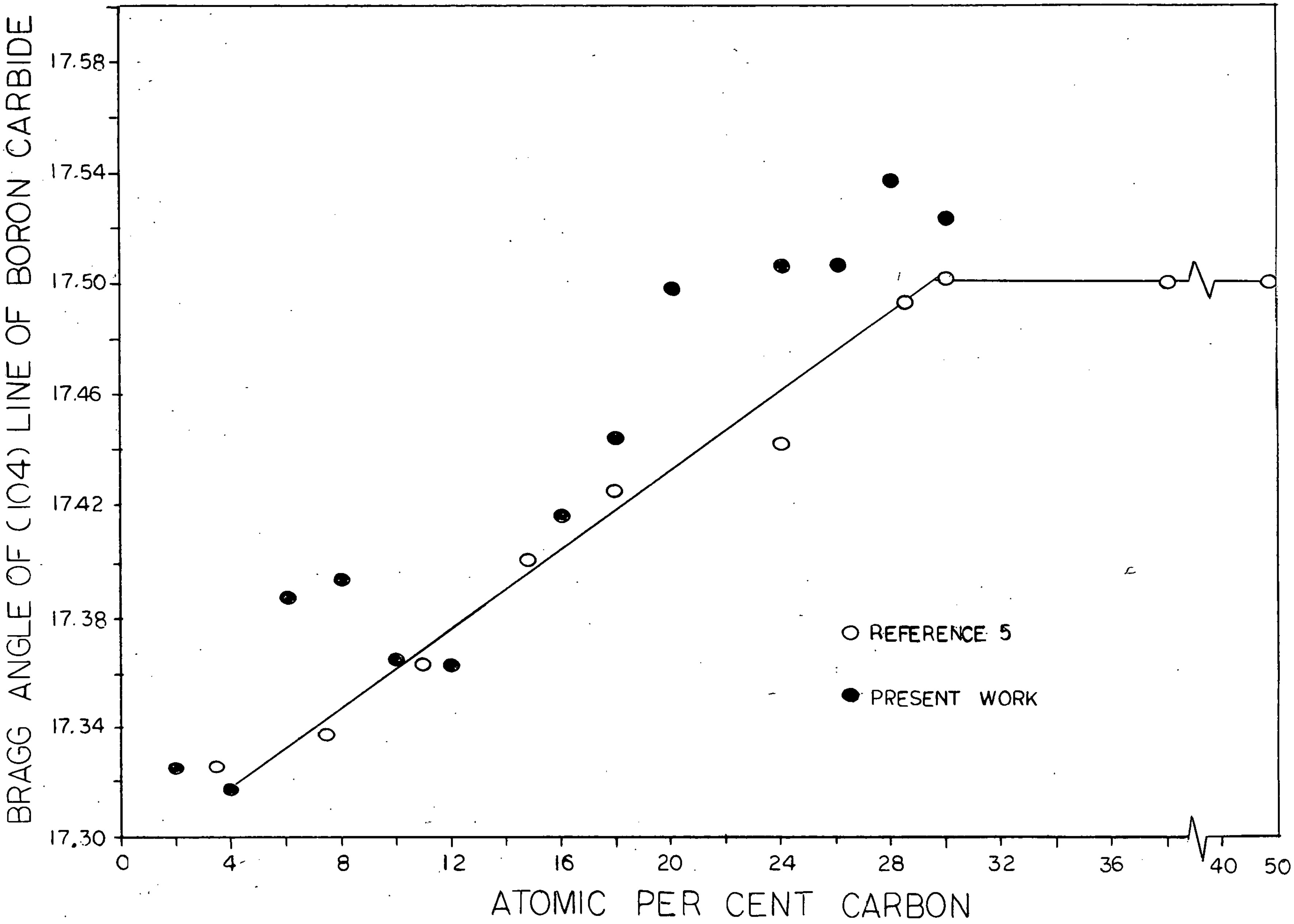

FIGURE 1 - VARIATION OF X-RAY DATA WITH CARBON CONTENT

measured from powder patterns have been superimposed upon similar data taken from Reference 5. The data of Glaser et al. are for compacts sintered at 2000°C, that of the present investigation for compacts sintered at 1600°C. It is apparent from a comparison of these two sets of data that there is no reduction in the solubility limits in this 400° interval. This is in disagreement with the revised diagram presented by National Carbon.(8)

There is the possibility that boron carbide, per se, does not exist but that in reality there is a continuous series of solid solutions of carbon in boron up to 28 a/o. Such a diagram would apparently be in contradiction to the metallographic observations of two-phase structures in the range from pure boron to approximately 20 a/o C. However, if the liquid and solid in equilibrium at a given temperature were of extremely different composition, the non-equilibrium as-cast structures could lead one to the faulty conclusion of a miscibility gap between boron and its carbide.

To establish the nature of the solid solubility of carbon in boron and boron carbide, more definitive X-ray parametric data in the low-carbon region must be obtained. If there is continuous solid solubility, it should be possible to produce a single-phase solid solution by annealing the as-cast two-phase structure.

IV. FUTURE WORK

During the next quarter, work will proceed along the following lines:

(a) Annealing of as-cast, beta-rhombohedral boron for very long times in attempts to produce alpha-rhombohedral or tetragonal boron.

(b) Annealing of as-cast boron-carbon alloys to establish whether there is continuous solubility. If it is established that there is a miscibility gap, the nature of the three-phase reaction must be established. If there is continuous solid solubility, the incipient melting temperatures must be determined.

(c) Investigation of the solid solubility limits of carbon in boron in the vicinity of pure boron, and as a function of temperature, by X-ray diffraction methods.

V. PERSONNEL AND LOGBOOKS

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

Rodney P. Elliott - Project Leader
R. J. Van Thyne - Project Supervisor
Ronald Wibel - Project Technician

Pertinent experimental data are recorded in ARF Logbook C 1191.

Respectfully submitted:

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