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Attention: Mr. H. N. Miller, Director
Contracts Division

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THE BORON-CARBON SYSTEM

ABSTRACT

The boron-carbon equilibrium diagram has been determined by X-ray, metallographic, and thermal analysis of sintered and arc-cast alloys. A single carbide having a range of solubility from approximately 9 to 20a/o carbon and melting congruently exists in the system. The terminal solubility of carbon in boron is 0.1-0.2a/o. The freezing reaction between boron and the carbide is a degenerate peritectic-eutectic reaction at the composition and melting temperature of elemental boron; there is a eutectic reaction at 29a/o carbon and 2375°C. No allotropy of boron was observed.

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THE BORON-CARBON SYSTEM

I. INTRODUCTION

To aid the study of reactor components, more detailed basic information was required concerning the equilibrium in the boron-carbon system. 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 was undertaken. This Final Technical Report summarizes this investigation for the period May 1, 1960, through April 30, 1961.

II. HISTORICAL BACKGROUND

Boron and boron carbide have been of interest for a number of years because of their high hardness and resistance to chemical attack. More recently boron has been considered as a possible base for light, high-melting alloys, and boron carbide as a refractory material.

Boron materials are also of great importance in the nuclear field because of the high neutron capture cross section. 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 method has been a dispersion of boron carbide in a structural metal or alloy. The equilibrium of boron and carbon has been investigated by many individuals, but unfortunately the agreement has been poor. The present investigation was undertaken as a definitive study of the equilibrium in the boron-carbon system.

A. Boron

There is incomplete agreement concerning the melting point of boron. The first determination was made by Weintraub⁽¹⁾ in 1913 in which the melting

point was reported to be 2400°C. Cueilleron⁽²⁾ determined the melting point to be 2000°-2075°C, the latter figure considered the more reliable. Cooper⁽³⁾ has estimated the melting point to be between 2100° and 2200°C. A later determination⁽⁴⁾ places the melting point at 2300°C.

Probably no other element has been reported to crystallize in so many unit cells. When elemental boron is produced at temperatures above 1500°C, the crystal structure is invariably rhombohedral (designated β -rhombohedral, $c_o = 23.811\text{\AA}$, $a_o = 10.944\text{\AA}$ when referred to an hexagonal lattice). Elemental boron produced at temperatures below 1000°C is again rhombohedral, but in the form designated α -rhombohedral, $c_o = 12.567\text{\AA}$, $a_o = 4.908\text{\AA}$ when referred to an hexagonal lattice. The products of decomposition in the temperature range between 1000° and 1500°C are of varied crystal structures. A tetragonal form of boron is consistently produced in this temperature range. When boron is heated at temperatures above 1500°C, the crystal structure invariably assumes that of β -rhombohedral boron. No one as yet has converted β -rhombohedral boron to another form by annealing.

Hoard and Newkirk⁽⁵⁾ have recently reviewed the literature thoroughly. It is their conclusion that boron may be thermodynamically stable in one of three possible crystal forms: β -rhombohedral from the melting point to at least 1500°C and possibly lower, and α -rhombohedral at temperatures below 1000°C; a "possible" stable range for tetragonal boron ($c_o = 5.068\text{\AA}$, $a_o = 8.740\text{\AA}$) is between 1100° and 1300°C. The many reported "allotropic" forms of boron can be explained by the reduction processes. Metal borides in equilibrium with boron usually are very high in boron; e.g., MB_{25} is possible. The common method of producing elemental boron is by decomposition on a metal substrate. It is hypothesized⁽⁵⁾ that the many crystal forms of boron arise from a continued growth of boron atoms in the basic configuration of the high-boron metal boride

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on which it must grow. Thus, because of the existent kinetics of the production of boron, various monotropes rather than allotropes of boron are produced. (Webster defines monotropy as "the relation of two different forms of the same substance which have no definite transition point, since one only is stable.")

Detailed X-ray diffraction data for tetragonal and β -rhombohedral boron are tabulated by Hoard and Newkirk⁽⁵⁾ and by Decker and Kasper⁽⁶⁾ for α -rhombohedral boron.

B. The Boron-Carbon System

The first boron-carbon equilibrium diagram was published by Ridgway⁽⁷⁾ in 1934. He concluded that "results indicate that the boron-carbon system consists of three phases: boron, a compound in the neighborhood of B_4C , and graphite." There was no evidence to indicate a range of solubility for the compound. An indication of the melting point of the carbide was given in that the reacted products were liquid at 2500-2600°C. Prior to the investigation of Ridgway, as a result of the work of Moissan,⁽⁸⁾ it was commonly believed that boron carbide had the formula B_6C .

The crystal structure of boron carbide has been determined to be rhombohedral.⁽⁹⁻¹²⁾ The lattice parameters on the basis of the equivalent hexagonal indexing are $a_0 = 5.60\text{\AA}$ and $c_0 = 12.12\text{\AA}$.

A more comprehensive determination of the equilibrium in the boron-carbon system was made by Meerson and Samsonov.⁽¹³⁾ Compositions in the range 10-50 weight per cent carbon were produced by sintering boron carbide with either carbon or elemental boron. On the basis of metallographic, X-ray diffraction and thermal analytical techniques, it was concluded that the carbide B_4C was formed by the peritectic reaction $L + B \rightarrow B_4C$ at 2250°C. On the basis of a range of parametric values, it was suggested that the carbide might have a range of solubility. A eutectic reaction $L \rightarrow B_4C + \text{Graphite}$ at 2150°C

and 30.2w/o carbon was reported. If the thermal data of these authors are extrapolated, a melting temperature of approximately 2500°C is indicated for elemental boron.

Considerable amount of research has been done on the alloying characteristics of boron carbide. Clark and Hoard⁽¹²⁾ point out that by interstitial substitution of boron in holes in the boron carbide structure a range of solid solutions from $B_{4.67}C$ to B_4C (17.7 to 20a/o C) is possible. Russian investigators⁽¹⁴⁻¹⁶⁾ have shown that solid solution formation occurs by substitution with covalent bonding forming $B_{13}C_2$ (12.3a/o C). This has been verified by Allen.⁽¹⁷⁾ On the basis of linear variation of X-ray diffraction lines Post et al.⁽¹⁸⁾ conclude that the solid solubility region of boron carbide exists from at least 4 to 28a/o carbon.

Samsonov et al.⁽¹⁹⁾ have presented a boron-carbon phase diagram based on microscopic and X-ray diffraction data of hot pressed compacts. The thermal data, peritectic reaction, and eutectic reaction of Reference 13 were incorporated. These investigators accept 2075°C as the melting point of boron. In order that this be consistent with their peritectic reaction, it is necessary for them to postulate that two boron carbides exists--solid solutions based on the stoichiometric compositions B_4C and $B_{13}C_2$. No metallographic or diffraction evidence is presented to substantiate the bifurcation of the boron carbide solid solution. A third carbide B_nC_m existing at approximately 52w/o carbon formed by peritectic reaction is reported. The eutectic reaction thus is re-evaluated to be $L \rightarrow B_4C\text{-solid solution} + B_nC_m$. No experimental evidence is given to support the eutectic reaction $L \rightarrow B + B_{13}C_2\text{-solid solution}$ at approximately 2w/o carbon.

Zhuravlev⁽²⁰⁾ proposes that a single carbide, which congruently melts, exists in the composition range 5-24w/o carbon. The carbide previously designated B_nC_m is positioned at 68-69w/o carbon. Samsonov⁽²¹⁾ rejects the proposal for a single carbide in the range 5-24 per cent on the basis of previous peritectic melting data.

Figure 1(a) depicts the boron-carbon phase diagram as determined by Russian investigators and as summarized by Samsonov.^(21,22)

The complete boron-carbon diagram has been reported by Dolloff.⁽²³⁾ This diagram, Fig. 1(b), shows but a single carbide melting congruently and having eutectics with boron and graphite. The determination was by photoelectric and differential thermal analysis; metallographic and X-ray diffraction techniques were used to supplement these data. The diagram presented by Dolloff is not documented with experimental data; it is therefore difficult to adjudge the quality of the determination. With respect to the boron-carbon diagram in Fig. 1(b), the following should be noted: (1) The eutectic composition at 1-2 per cent carbon was determined by extrapolating the liquidus to the eutectic temperature. The microconstituents taking part in the eutectic reaction were established by micrographic and X-ray techniques. (2) The melting point of boron was determined as $2130 \pm 20^\circ\text{C}$; however, the purity of the boron was only 98.9%. (3) The restricted solubility of boron carbide at temperatures below 1800°C is not discussed. (4) The high boron solubility limit of the boron carbide is stated in the text to be approximately 10a/o, but indicated on the diagram as approximately 14a/o.

The two different versions of the boron-carbon phase diagram suggested by the above data are shown in Figure 1. That presented in Fig. 1(a) is based on melting point determinations in the range 10-50 per cent and on a large amount of speculation with regard to alloying characteristics of boron

carbide. The boron-carbon diagram of Fig. 1(b) is apparently a complete experimental determination of the equilibrium; however, the lack of documentation of the data does not allow its validity to be established. The definitive investigation of the equilibrium as determined by the present study was very much needed.

III. EXPERIMENTAL PROCEDURES

A. Compositions and Alloys

A combination of experimental techniques are required for a definitive delineation of phase equilibria. For the determination of the boron-carbon system a combination of metallographic, X-ray diffraction, and thermal analytical techniques was used. Both sintered compacts and arc-melted specimens were required.

In general, the purity of boron that has been used by previous investigators has been less than 99%. For a definitive determination of the phase equilibria high-purity components are necessary. Two sources of powder were used for production of working alloys. Analyses were supplied as follows:

	<u>Cooper Metallurgical</u>	<u>Shieldalloy</u>
Boron	99.6 %	99.65%
Carbon	0.09	--
Iron	0.12	0.15
Silicon	--	0.10

Very high purity boron was obtained for the determination of the solubility limit of carbon in boron and for the investigation of allotropy of boron. A quantity of high purity boron was obtained from the General Electric Company. This material, which had been produced under contract, ⁽²⁴⁾ had the following analysis:

Oxygen	<0.01%
Hydrogen	0.02
Nitrogen	<0.003
Carbon	0.05
Tantalum	0.02
<u>Other</u>	<u>0.01</u>
Boron + Carbon	99.93 % (difference)

A small quantity of super-pure, zone-refined boron was purchased from the Eagle-Picher Lead Co. This material by spectrographic analysis showed no contamination, although the manufacturer estimated it to be contaminated to the extent of a total of 10 parts per million.

Spectroscopically pure graphite was obtained from the National Carbon Co. This material contains 0.001% ash.

Attempts to arc melt compacts of boron and graphite were unsuccessful. It was necessary to sinter prior to arc melting.

Ten-gram alloys were weighed from boron powder and graphite. Powders were then thoroughly blended by mixing in a mortar and pestle and subsequently ball-milled for twelve hours. Compacts were made by cold pressing in a 1/2 in. diameter die with a load of 20,000 psi. Compacts were wrapped in tantalum foil and sintered for ten minutes in a dynamic vacuum which was maintained at 0.1 micron. Routinely a sintering temperature of 1600°C was employed, although for X-ray determination of phase boundaries compacts were sintered at 2000°C. It was established by visual inspection and X-ray examination that sintering would not take place at 1200°C. No vigorous exothermic reactions were observed during the sintering operation. There was no indication of contamination from the tantalum wrapping.

Sintered compacts were arc melted on a water-cooled copper crucible in an argon atmosphere. Since the sintered compacts were of uniform composition, it was unnecessary to melt repeatedly as is ordinarily done to insure homogeneity.

Weight losses occurring in the arc melting operation were difficult to evaluate accurately since, in part, this represented material that was lost mechanically as a result of the extremely brittle nature of the charged and melted compositions.

A series of dilute alloys were made for the determination of the solubility limit of carbon in boron. These alloys were made with high-purity boron and a 5% master alloy.

Chemical analyses were used to verify that arc-melted compositions did not grossly differ from the nominal compositions. Carbon analyses were made by standard combustion techniques in which the resulting CO₂ is either weighed or its volume determined under known conditions. Boron was determined by precipitation of the Mannitol-borate complex from boric acid formed by the fusion of the boron-carbon sample in sodium carbonate. Carbon which interferes with such a determination is expelled as carbon dioxide.

Chemical analyses of arc-melted compositions are presented in Table I. In general, analyses verify that there is not a great loss of the charged constituents. Carbon analyses for the dilute alloys in general are unreliable. For compositions containing greater than 0.2w/o carbon the agreement is generally good. On the basis of the general qualitative and occasional precise agreement of the carbon analyses with the nominal compositions it is concluded that the analytical method is the source of error and that in reality the true composition is very close to the nominal composition. Carbon and boron analyses for the compositions in the range of boron carbide are further subject to error as a result of sampling since gross segregation often occurs in arc casting.

B. Heat Treatment

Isothermal heat treatments were performed at temperatures from 900° to 2300°C. In the temperature range 900°-1200°C specimens were sealed in quartz

bulbs and annealed in wound-resistance tube furnaces in which the temperature is controlled $\pm 2^\circ\text{C}$. A partial pressure of argon or helium was used to prevent collapse of the bulb. Heat treatments at 1400°C and above were performed in tantalum tube resistance furnaces; specimens are suspended by tungsten or tantalum wire or supported in a refractory metal basket in the hot zone of the furnace. Temperature is controlled and monitored optically. After initial evacuation to 0.05 microns an atmosphere of argon was maintained in the furnace chamber in order to minimize vaporization of the specimen. (Preliminary experimental work established that both sintered and cast specimens volatilized excessively when heated in a vacuum for long periods of time.)

Except for the quartz-encapsulated specimens, isothermal heat treatments of multiple specimens were not water quenched. Specimens cool to a black heat in approximately seven minutes.

C. Metallography

Metallographic specimens were made by the conventional technique of mounting in bakelite or lucite. Preliminary studies were made to determine a satisfactory method of polishing. The conventional procedure employing a succession of silicon carbide grits followed by diamond and alumina, all on a Buehler "Automet," was unsatisfactory. There was excessive chipping of the second phase of a two-phase structure; even more distressing was the inability to obtain a flat surface by such processing.

With the assistance and suggestions of personnel of Adolph Buehler, Ltd., a satisfactory process has been developed. The following grinding and polishing is on automatic polishing equipment:

1. Grind with 320 grit "Norbide" boron carbide on cast iron wheel (no cloth) oil vehicle, 30 minutes.
2. Grind with 30 μ diamond on bakelite disc (no cloth) oil vehicle, 60 minutes.
3. Final polish with Linde A alumina on silk, water vehicle, 45-60 minutes.

This procedure has enabled a flat surface to be obtained without excessive fragmentation and chipping away of the non-matrix phase. Even with special polishing procedures there is a degree of relief etching. No etching medium has been found to delineate satisfactorily the grain boundaries. However, by etching with equal parts of nitric acid, hydrofluoric acid, and water for three to four minutes it is possible to delineate more precisely multiphase specimens. Alloys richer in carbon than the carbide do not require etching.

D. X-Ray Diffraction

Sintered or arc cast alloys were crushed to -200, + 325 mesh for X-ray examination. Straumanis type cameras of 114.59 mm diameter were used throughout the program with nickel-filtered copper radiation. A limited number of X-ray studies were made with a Norelco diffractometer, but these were not as useful as the powder patterns.

E. Melting Temperature Determination

Because of the reactive nature of boron and boron-carbon alloys with refractory materials and metals, the determination of accurate melting temperatures was exceedingly difficult. Optical techniques are used for the determination of the melting temperatures. A specimen is placed in a high-temperature resistance furnace and slowly heated as it is observed through an optical pyrometer. The temperature of initial melting is usually easy to observe since sharp corners become rounded; the determination of the temperature of complete melting is less reliable.

Specimens were supported in the furnace either suspended on a refractory wire, or supported in a crucible of graphite or boron nitride, an extremely refractory and inert substance.

Boron nitride cannot be produced in solid forms unless approximately 5w/o boron oxide is used as a binder. Prior to using the boron nitride, the boron oxide was reduced by heating for eight hours in a hydrogen atmosphere at 1500°C. The boron nitride was then further outgassed by heating slowly to 2000°C in vacuum.

Melting point determination of elemental boron was done either in boron nitride or suspended by wire since it was not desired to contaminate with carbon. Graphite crucibles were satisfactory for the determination of the incipient or first melting temperature in the compositional ranges between boron and boron carbide, and between boron carbide and graphite.

Determination of melting temperatures of the carbide was extremely difficult. Boron nitride could not be used since it formed a liquid phase which sweated out at temperatures above 2200°C. (This phenomenon could possibly result from residual boron oxide binder that had not been decomposed.) Specimens tended to carburize from the graphite crucible, and the melting temperature characteristic of the graphite-carbide eutectic would then be observed rather than the true melting temperature of the alloy. Boron carbide reacts with molybdenum and tantalum at these temperatures. The most accurate measurements of the melting temperature of the boron carbide were made by heating rapidly to minimize the effect of alloying with the crucible or metal support. In this way an indication of a lower limit of the true melting temperature was determined.

The determination of melting temperatures by techniques in which the temperature is continuously increased may be termed "dynamic". In contrast,

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a limited number of cross checks were made by "static" methods. In such a procedure several compositions bracketing the solidus or liquidus are isothermally heated in a small crucible containing multiple cavities. Subsequent to the annealing, macro- or microscopic examination of the specimen will ascertain whether it was all liquid, all solid, or liquid plus solid during the isothermal treatment. The solidus or liquidus boundary may thus be bracketed if suitable compositions are chosen. Because of the extreme reactivity of boron-carbon alloys, such a technique could only be used to distinguish melting from non-melting.

IV. THE PHASE DIAGRAM

A. Allotropy

On the basis of extensive isothermal heat treatment of elemental boron, it must be concluded that β -rhombohedral boron is stable. These experiments are summarized in Table II. If either α -rhombohedral or tetragonal boron are true allotropes, the transformation is certainly extremely sluggish. Any crystalline form of boron other than β -rhombohedral as a consequence need not be considered in regard to the boron-carbon system. A typical pattern of β -rhombohedral is compared to a published standard pattern in Table III.

B. Phase Equilibria

The nature of the phase diagram of the boron-carbon system was established by metallographic investigation of three series of arc-melted alloys.

The first series of alloys made from Shieldalloy boron consisted of compositions at 2a/o intervals up to 30a/o C, plus the compositions 40, 50, and 75a/o C. From the microstructures of these compositions, as cast and

annealed at 1500° and 1950°C, the features of the boron-carbon diagram were established. The observed microconstituents are summarized in Table IV.

As-cast alloys up to 18a/o showed carbide and a boron matrix in coexistence. The amount of carbide microconstituent reached a maximum at 18a/o. No evidence of either eutectic or peritectic freezing was observed. Alloys from 20 through 28a/o carbon showed decreasing amounts of pro-eutectic carbide in a carbide-graphite eutectic matrix; alloys containing 30, 40, 50, and 75a/o carbon showed pro-eutectic graphite. From the cast alloy structures it was concluded that there was but one compound in the boron-carbon system and that the carbide and graphite formed a eutectic at approximately 29a/o carbon.

X-ray diffraction studies confirmed that the microconstituents were boron, carbide, and graphite, respectively.

The arc-melted alloys in the composition range 0-10a/o carbon showed segregation on casting. This segregation made subsequent annealing and melting point determinations difficult since the average composition in small portions of cast ingots would deviate appreciably from the nominal composition. Segregation was most pronounced in the more dilute alloys.

Figures 2, 3, and 4 show the cast microstructure of the nominal 2a/o carbon alloy at magnifications of 25, 100, and 1000 diameters. At 25X the complete cross section of the metallographic sample is shown. The segregation of the microconstituents is apparent. The photomicrographs at 100X and 1000X show the equilibrium between the carbide and boron matrix. It should be noted especially that there is absolutely no indication of either peritectic or eutectic reaction.

Figures 5-9 show typical microstructures of cast alloys of compositions containing 6, 16, 20, 28, and 40a/o carbon. The microstructures of

Figures 3 and 6 (2 and 6a/o carbon) are noticeably similar; however, the micro-constituents of the 6a/o alloy are fairly uniformly distributed while those of the 2a/o alloy are grossly segregated. The 16a/o alloy is typical of alloys in the range 10-20a/o carbon in which there are large quantities of the gray carbide surrounded by a matrix of cream-colored boron. The 20a/o alloy shows carbide with grain boundary carbide-graphite eutectic formation. The solubility extent of the carbide phase is difficult to delineate precisely by metallographic means. The graphite-carbide eutectic tends to degenerate when it is present in small amounts. Such a degenerate eutectic consisting of tiny graphite flakes is difficult to distinguish from normal cracking.

The composition of the carbide-graphite eutectic is positioned at 29a/o carbon; cast structures containing 28 and 30a/o carbon showed pro-eutectic carbide and graphite, respectively. Figure 8 is typical of carbide in a matrix of the eutectic. Pro-eutectic graphite grows into a plate structure, giving a needle appearance in cross section, Figure 9.

Microexamination of specimens annealed at 1950° and 1500°C revealed that the carbide has an extended range of solid solubility. Other than for equilibrating the non-equilibrium co-existent phases in the composition range of approximately 10-20a/o carbon, heat treatment did not alter the microstructures. There was no spheroidization of carbides or precipitation of carbide from the boron solid solution. Figure 10 is typical of the homogenized alloys in the range of 10-20a/o carbon. It is noted that there is excessive cracking in this specimen. It was suspected that this cracking resulted from mounting in bakelite; however, subsequent specimens in this composition range were mounted in lucite with no diminution in cracking. It must be presumed that the cracking arose from the annealing operation.

A second series of boron-carbon alloys was melted and annealed in order to study more carefully the solidification of boron carbide. These alloys were prepared at 1/2a/o intervals between 9 and 21a/o carbon. The metallographic examination of these alloys, as presented in Table V, enabled the composition of congruent melting to be established as 18.5-19.0a/o C. Alloys from this series, supplemented with alloys from the first series, were annealed at 1200°, 1600°, 1950°, and 2300°C to establish carbide solubility limits. Although such data are not best suited for the determination of solubility limits because of the segregation on casting, it is clearly indicated that the solubility limits do not vary appreciably as a function of temperature.

A third series of dilute carbon alloys was prepared in order to evaluate the solubility limit of carbon in elemental boron. The observed microconstituents of these alloys, listed in Table VI, establish that the solubility limit is between 0.1 and 0.2a/o carbon. Typical microstructures of the carbide in the boron matrix are given in Figures 11 and 12 for 0.3 and 0.6a/o carbon. Again, it is noted that there is no sign of peritectic or eutectic reaction.

Alloys in the range 10-20a/o carbon at times showed a very small amount of a white microconstituent, usually at grain boundaries. Attempts were made to identify this by the use of a microprobe analyzer, but only with very limited success: because of the poor electrical conductivity of the boron carbon sample, the unidentified phase was soon burned away when the microbeam was focused on it. A higher scattered electron image indicated that the unidentified material was composed of elements other than boron and carbon and hence was unrelated to the phase diagram.

The observed metallographic data are presented graphically in Figure 13.

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C. Melting Temperatures

Melting data for the boron carbon alloys are summarized in Table VII and plotted in Figure 14. From these data 2075°C is taken as the temperature of the three-phase equilibrium between boron, liquid, and boron carbide; the temperature of the eutectic reaction $L_{29a/o} C \rightarrow \text{Carbide} + \text{Graphite}$ is established as 2375°C.

The extreme reactivity of boron carbide with other refractory metals prevented an accurate determination of the melting temperature of boron carbide. From the trend of the liquidus a melting temperature of 2450°C is indicated. This is consistent with incipient melting temperature of 2420-2430°C in Table VII.

Melting temperature experiments gave no indication of a eutectic reaction at a composition of 1-2a/o carbon. Sintered alloys with nominal composition 1, 2, 4, 6, and 8a/o were heated slowly in a boron nitride crucible in an attempt to observe if one composition would melt at a lower temperature than the others. With the exception of the 8a/o composition, all melted at 2075°C.

No evidence, either metallographic or melting, substantiates the eutectic reaction between boron, liquid, and the carbide phase at a composition of 1-2a/o carbon and at a temperature appreciably lower than the melting point of boron as has been reported by others.^(22,23) The experimental evidence of this investigation supports a degenerate eutectic-peritectic reaction in which the liquid composition is the same as the solid (boron) and in which the temperature of the reaction is identical with the melting temperature of boron.

D. Solubility Limits of Boron Carbide by X-ray Diffraction

In a method similar to that used by Post et al.,⁽¹⁸⁾ the solubility limits of boron carbide were established by X-ray parametric means. In this

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method the Bragg angle of sintered compacts are plotted as a function of composition; the angle varies continuously in the single-phase field and is constant in the two-phase fields.

Preliminary investigations with the low angle lines used by Post et al. yielded inconclusive data. Attempts to refine the data by the use of an X-ray diffractometer to measure the angle and least-squares solution to calculate the parameters were also unsuccessful in delineating the solubility limits.

The use of an intense back-reflection line of the sintered boron-carbon compacts proved to be ideal for such a determination. This line at a Bragg angle of approximately 75° is out of the range of the diffractometer, and so film techniques were 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 so that observation errors are minimized, and (b) the systematic errors arising from absorption are small.

Compacts of boron and graphite containing 0.5, 1.0, 1.5, 2.0, 3, 5, 7, 10, 12, 14, 16, 18, 20, 24, 28, and 30a/o carbon were sintered at 1600° and 2000°C in argon for a half hour. Since sintering does not occur at 1200°C , compacts sintered at 1600°C were annealed at 1200° to provide data pertinent to the latter temperature. A limited number of specimens were also reannealed at 2280°C to provide the solubility limit at a temperature near the graphite-carbon eutectic temperature.

The Bragg angle of the back-reflection line varied linearly with the carbon content in the composition range 10-18a/o carbon. These data are plotted in Figure 15. A least-squares solution of these data yields the following equation:

$$\theta = 0.2607X + 71.22$$

where θ is the Bragg angle and X is the composition of the compact in atomic per cent carbon. In making this solution the datum 18a/o C-1200°C was eliminated since it appeared to have greater experimental error than the other data.

Observed Bragg angles in the boron + carbide and carbide + graphite phase fields were averaged and the composition of the saturation calculated. Data in the carbide + graphite field enabled a very accurate determination of the high-carbon solubility limit to be calculated; interference from β -rhombohedral boron pattern did not permit many data to be averaged to obtain the low-carbon solubility limit.

A comparison of the observed pattern of boron carbide with published data is made in Table VIII.

The observed data for the parametric determination of the solubility limits of boron carbide are plotted in Figure 16. From these data, the following solubility limits were calculated:

	<u>Solubility Limit, a/o C</u>	
	<u>Low Limit</u>	<u>High Limit</u>
2280°C	--	19.9
2000	9.4	19.8
1600	9.1	19.9
1200	8.8	19.8

The Bragg angles of arc-cast alloys also were measured (Fig. 16e). These data are in agreement with the sintered data supporting a maximum solubility of 19.9a/o carbon, at the eutectic temperature.

The solubility data as determined by the X-ray technique are plotted on Figure 13. The phase boundary of the carbide has been drawn through these data. Because of segregation occurring on casting boron-carbon alloys, it is believed that the boundaries determined by X-ray techniques are more accurate

than those determined by metallographic examination. Sintered alloys are homogeneous and will deviate from the nominal composition less than arc-cast alloys. The metallographic determination of the solubility limits must not be minimized, however. Although subject to error arising from the non-equilibrium conditions on casting, the metallographic specimens support a single boron carbide with approximately the same composition limits as determined by X-rays.

V. MECHANICAL PROPERTIES

Boron and boron carbide, both in the sintered and arc-cast condition, are extremely brittle materials. No trend in hardness or friability was observed in the routine handling of the alloys.

Microhardness readings were made of cast alloys. With 100 and 200 gram loads specimens often cracked at the indenter; however, loads less than 100 grams yielded such small indentations that the diagonals could not be determined accurately. Typical values of hardness are recorded in Table IX. It will be noted that hardness readings made with a 200-gram load are less than those made at 100-gram load. This can be attributed to a greater amount of microcracking that exists for the greater load.

VI. DISCUSSION

The phase diagram as determined in this definitive investigation differs from both those diagrams previously published. In general, however, the diagram is very similar to that determined by Dolloff, with the following points of agreement:

- (1) A single carbide melting congruently
- (2) The temperature of the three-phase reaction between boron, carbide, and melt.
- (3) The eutectic temperature between carbide, melt, and graphite; the composition of the eutectic is in approximate agreement.

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The diagram differs from that of Dolloff in the following:

- (1) No eutectic reaction is observed at 1-2% carbon.
- (2) The solubility limits of boron carbide are not restricted to a narrow composition range below 1800°C. This has been verified by X-ray diffraction and metallographic examination (Figure 10.) The solubility limits of boron carbide were determined at even lower temperatures than determined by Dolloff and no restriction was indicated.
- (3) Boron does not dissolve more than 20a/o carbon at the eutectic temperature.

Inasmuch as the diagram published by Samsonov is based mostly on speculation, it is not surprising to find points of disagreement, namely:

- (1) A single carbide is observed in the composition range of less than 20a/o C in comparison to two reported by Samsonov.
- (2) No supercarbide B_nC_m is observed.
- (3) The eutectic temperature between carbide and graphite is observed to be 2375°C in comparison with 2125°C for the comparable eutectic observed by Samsonov.

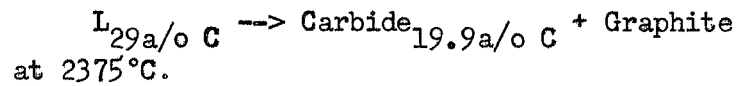
The eutectic composition of 29a/o carbon (31w/o) is in agreement with the eutectic composition determined by Samsonov.

VII. SUMMARY

The phase diagram presented in Figure 17 incorporates the experimental data previously discussed in this paper. Salient features of the diagram are as follows:

- (1) A single carbide of boron exists. This has a rhombohedral structure and an approximate solubility range from 9 to 20a/o carbon. The carbide melts congruently at a temperature of approximately 2450°C at 18.5a/o carbon.
- (2) The solid solubility of carbon in boron is between 0.1 and 0.2a/o. β -rhombohedral boron was found to be stable at all temperatures above 900°C; no allotropy of boron was noted.

- (3) Boron-carbon alloys in the range 0-9a/o carbon freeze by a degenerate eutectic-peritectic reaction at 2075°C.
- (4) Alloys richer in carbon than boron carbide freeze by the eutectic reaction



VIII. PERSONNEL AND LOGBOOKS

The following personnel were associated with this program:

Rodney P. Elliott	Project Leader
Ronald Wibel	Project Technician
James Dvorak	Metallographer
Robert Dragen	Metallographic Technician

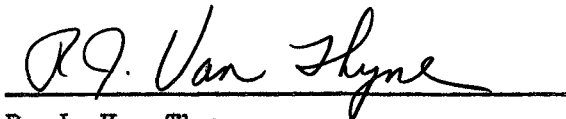
Pertinent experimental data are recorded in ARF Logbooks C 1191 and C 11013.

Respectfully submitted,

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ILLINOIS INSTITUTE OF TECHNOLOGY



Rodney P. Elliott
Senior Metallurgist



R. J. Van Thyne
Assistant Director
Metals and Ceramics Research

REFERENCES

1. E. Weintraub, *J. Ind. Eng. Chem.*, 5, 106, (1913).
2. J. Cueilleron, *Compt. rend.*, 221, 698, (1945).
3. H. S. Cooper, Rare Metals Handbook, 2nd edition, Reinhold, 1961, p. 74.
4. Hooker Electrochemical Co., cited in AEC brochure "Boron and Its Isotopes" 1957.
5. J. L. Hoard and A. E. Newkirk, *J. Am. Chem. Soc.*, 82, 70, (1960).
6. B. F. Decker and J. S. Kasper, *Acta Cryst.*, 12, 503, (1959).
7. R. R. Ridgway, *Trans. Electrochem. Soc.*, 66, 117, (1934).
8. H. Moissan, *Compt. rend.*, 118, 556, (1899).
9. F. Laves, *Neue Folge* 1, 57, (1934).
10. N. G. Sevastianov, *Khim. Referat. Zhur.*, No. 5, 67, (1940).
11. H. S. Zhdanov and N. G. Sevastianov, *Compt. rend. (Doklady) Acad. Sci. U.S.S.R.*, 32, 432, (1941).
12. H. K. Clark and J. L. Hoard, *J. Am. Chem. Soc.*, 65, 2115, (1943).
13. G. A. Meerson and G. V. Samsonov, *Izvest. Sektora Fiz.-Khim. Anal.*, 22, 92, (1953).
14. G. S. Zhdanov and N. G. Sevastianov, *Zhur. Fiz. Khim.* 17, 326, (1943).
15. G. S. Zhdanov, N. N. Zhuravlev, and L. S. Zevin, *Doklady Akad. Nauk. SSSR*, 92, 767, (1955).
16. G. S. Zhdanov, G. A. Meerson, N. N. Zhuravlev, and G. V. Samsonov, *Zhur. Fiz. Khim.* 28, 1076, (1954).
17. R. Allen, *J. Am. Chem. Soc.*, 75, 3582, (1953).
18. F. W. Glaser, D. Moskowitz, and B. Post, *J. Appl. Physics*, 24, 731, (1953).
19. G. V. Samsonov, N. Zhuravlev, and I. G. Annuel, *Fizika Metallov i Metallovedenie* 3, 309, (1956).
20. N. N. Zhuravlev, cited in Boron, its Compounds and Alloys by G. V. Samsonov, L. J. Markovskii, A. F. Zhigatch, and M. G. Valjaschko, Kiev, 1960, p. 164.
21. G. V. Samsonov, *ibid.* p. 165.

22. G. V. Samsonov, Zhur. Fiz. Khim., 32, 2424, (1958).
23. R. T. Dolloff, "Research Study to Determine the Phase Equilibrium Relations of Selected Metal Carbides at High Temperatures". WADD Technical Report 60-143, on Contract No. AF 33(616)-6286, July 1960.
24. A. U. Seybolt, Trans. Am. Soc. Metals, 52, 971, (1960).

TABLE I
CHEMICAL ANALYSIS OF COMPOSITIONS

Nominal Carbon Composition		Analyzed Composition		
		Carbon, w/o		Boron, w/o
a/o	w/o	Outside Firm	ARF	ARF
0.075	0.083		0.332 0.170	
0.1	0.111		0.184 0.347	
0.2	0.222		0.240	
0.3	0.333		0.212	
0.6	0.666		0.886 0.668	
2.0	2.215	2.75		96.6
6.0	6.616	7.02 6.95		
12.0	13.146			84.8
18.5	20.125		17.52	81.76
19.0	20.658		20.44	78.84
19.5	21.190		21.42	78.48
20.0	21.722	21.85		78.34
22.0	23.843	23.08		
28.0	30.151	29.85		72.04
30.0	32.236			68.6 68.5

TABLE II
SUMMARY OF INVESTIGATION
TO ASCERTAIN ALLOTROPY OF BORON

Condition	Time, hr	Temp, °C	Furnace	Container	Structure
<u>Shieldalloy</u>					
As-received powder	--	--	--	--	β-Rhomb.
Loose powder	168	900	Globalar	Quartz tube	β-Rhomb.
Loose powder	48	950	Globalar	Quartz tube	β-Rhomb.
Loose powder	72	1100	Globalar	Quartz tube	β-Rhomb.
Loose powder	4	1100	Globalar	Quartz tube	β-Rhomb.
Arc cast	--	--	--	--	β-Rhomb.
Arc cast	6	1400	Vacuum-resistance	Ta package	β-Rhomb.
Arc cast	6	1500	Vacuum-resistance	Ta package	β-Rhomb.
Arc cast	6	1600	Vacuum-resistance	Ta package	β-Rhomb.
Compacted powder	1/2	2000	Vacuum-resistance	Ta package	β-Rhomb.
<u>Cooper</u>					
As-received powder	--	--	--	--	β-Rhomb.
Compacted powder	1/6	1600	Vacuum-resistance	Ta package	β-Rhomb.
Arc cast	--	--	--	--	β-Rhomb.
<u>General Electric</u>					
As-received solid	--	--	--	--	β-Rhomb.
As-received solid	720	1000	Muffle	Quartz ⁺	β-Rhomb.
As-received solid	720	1100	Muffle	Quartz ⁺	β-Rhomb.
As-received solid	720	1200	Muffle	Quartz ⁺	β-Rhomb.
<u>Eagle-Picher</u>					
As-received solid	--	--	--	--	β-Rhomb.
As-received solid	720	1000	Muffle	Quartz ⁺	β-Rhomb.
As-received solid	720	1100	Muffle	Quartz ⁺	β-Rhomb.
As-received solid	720	1200	Muffle	Quartz ⁺	β-Rhomb.

+ Boron samples were packed in boron powder to minimize any contamination during annealing.

TABLE III
 COMPARISON OF OBSERVED β -RHOMBOHEDRAL
 BORON PATTERN WITH PUBLISHED DATA

hkl	Published Data*		ARF Data	
	d, Å	I	d, Å	I
101	8.806	<1	**	
003	7.937	40	7.9294	8
012	7.415	24	7.3984	7
110	5.472	21	5.4631	7
104	5.041	100	5.0451	10
021	4.648	56	4.6506	9
113	4.505	28	4.5214	6
202	4.403	18	4.3773	6
015	4.255	25	4.2525	7
006	3.969	17	3.9614	7
024	3.708	23	3.7082	8
211	3.542	28	3.5338	8
122	3.430	17	3.4265	7
205	3.359	2		
116	{ 3.213	1	{ 3.2136	<1
107	{ 3.202	1		
300	3.159	<1		
214	3.074	6	3.0775	5
303	2.935	7	2.9386	6
123	2.863	19	2.8603	8
018	2.840	7		
027	2.763	6	2.7653	1
220	2.736	9	2.7365	6
009	2.646	9	2.6536	5
131	2.613	17	2.6196	6
223	2.587	8	2.5756	5
312	2.567	8		
208	2.520	12	2.5263	7
306	{ 2.472	10	{ 2.4724	9
217	{ 2.467	8		
134	2.405	17	2.4020	6
119	2.382	9		
401	2.360	11	2.3594	6
042	2.324	13	2.3241	6
1.0.10	2.309	1		
315	2.301	2		
128	2.289	3	} 2.2927	<1
226	2.253	5	2.2568	3
404	2.201	8	2.1987	6
321	2.165	2	2.1633	<1
			2.1101	<1
137	2.080	4	2.0823	3

* Reference 5

** (101) is observed in some films, not in others

TABLE IV
SUMMARY OF METALLOGRAPHIC DATA
FIRST ALLOY SERIES

Nominal Composition, a/o C	Microconstituents* Observed		
	As-Cast	1950°-4hr	1500°-2hr (homog. 1950°-4hr)
2	B + C	B + C	B + C
4	B + C	B + C	B + C
6	B + C	B + C	B + C
8	B + C	B + C	B + C
10	B + C	B + C	C
12	B + C	C	C
14	B + C	C	C
16	B + C	C	C
18	B + C	C	C
20	C + E	C + E	C + E
22	C + E	C + E	C + E
24	C + E	C + E	C + E
26	C + E	C + E	C + E
28	C + E	C + E	C + E
30	E	E + G	E + G
40	E + G	E + G	E + G
50	E + G	E + G	E + G
75	E + G	E + G	E + G

* B = Boron Solid Solution
 C = Boron Carbide
 E = Carbide-Graphite Eutectic
 G = Graphite

TABLE V

SUMMARY OF METALLOGRAPHIC DATA, SECOND ALLOY SERIES

Nominal Composition, a/o C	Microconstituents Observed*				
	As-Cast	2300°-1/4 hr	1950°-4 hr	1600°-4 hr (homog. 1900°-4 hr)	1200°-600 hr (homog. 1800°-4 hr)
6.0**					B + C
8.0**					B + C
9.0	B + C		B + C	B + C	B + C
9.5	B + C		B + C	B + C	B + C (mostly C)
10.0	B + C		B + C	B + C	B + C
10.5	B + C		C	B + C (most areas all C)	C
11.0	B + C				
11.5	B + C				
12.0	B + C				
12.5	B + C				
13.0	B + C				
13.5	B + C				
14.0	B + C				
14.5	B + C				
15.0	B + C				
15.5	B + C				
16.0	B + C				
16.5	B + C				
17.0	B + C				
17.5	B + C				
18.0	B + C				
18.5	C		C	C	C
19.0	C	C	C	C + E(?)	C
19.5	C + E		C + E	C + E	C + E
20.0	C + E	C + E	C + E	C + E	C + E
20.5	C + E				
21.0	C + E	C + E			
22.0**		C + E			

* For meaning of Symbols, See Table IV.
 ** Alloys taken from first series.

TABLE VI
SUMMARY OF METALLOGRAPHIC DATA
DILUTE ALLOY SERIES

Nominal Composition, a/o C	As-cast Micronstituents Observed*
0.025	B
0.050	B
0.075	B
0.10	B
0.20	B + C
0.30	B + C
0.60	B + C

* B = Boron solid solution
C = Boron carbide

TABLE VII
SUMMARY OF MELTING TEMPERATURE DETERMINATIONS

Composition	State	Crucible	Incipient* Melting, °C	Complete* Melting, °C	Remarks
G. E. Boron	as-received	W-wire	2050	=	
	as-received	BN	2045	=	
	as-received	Ta-wire	2075	=	
	as-received	BN	2075	=	
B-1a/o C	arc-melted	graphite	2035	=	
	arc-melted	graphite	2010	=	
	arc-melted	BN	2075	ND	
B-2a/o C	arc-melted	graphite	2075	ND	
	arc-melted	BN	2075	2105	
	arc-melted	BN	2075	=	
	sintered	graphite	2050	2075	
	arc-melted	BN	2095	2125	
	arc-melted	BN	2075	ND	
B-4a/o C	arc-melted	graphite	2075	ND	
	arc-melted	BN	2075	ND	
	arc-melted	BN	ND	2210	
	sintered	graphite	ND	2345	
	sintered	BN	2055	2160	
	arc-melted	BN	2050	2200	
	arc-melted	BN	2075	ND	
B-6a/o C	arc-melted	W-wire	2145	ND	most probably a segregated sample
	arc-melted	BN	2055	2235	
	sintered	BN	2050	2275	
	arc-melted	BN	2075	ND	
B-8a/o C	arc-melted	graphite	2085	2395	
	arc-melted	BN	2270	ND	most probably a segregated sample
	arc-melted	BN	2075	ND	
	arc-melted	graphite	2085	ND	
	arc-melted	BN			did not melt at 2075°C

TABLE VII
(Continued)

Composition	State	Crucible	Incipient* Melting, °C	Complete* Melting, °C	Remarks
B-10a/o C	sintered	graphite	2345	2420	did not melt when held iso- thermally at 2250°C
	sintered	graphite			
B-12a/o C	sintered	graphite	2375	2430	did not melt when held iso- thermally at 2250°C
	sintered	graphite	ND	2395	
	sintered	graphite			
B-14a/o C	sintered	graphite	2395	2450	did not melt when held iso- thermally at 2250°C
	sintered	graphite			
B-16a/o C	sintered	graphite	2380	2475	initial melting might be eutec- tic melting
	sintered	graphite	ND	2470	did not melt when held iso- thermally at 2250°C
	sintered	graphite			
B-17a/o C	arc-melted	Ta-wire	--	--	specimen did not melt at 2410°C although specimen re- acted with Ta commercial BN refractory partially melted
	arc-melted	BN	--	--	

TABLE VII
(Continued)

Composition	State	Crucible	Incipient* Melting, °C	Complete* Melting, °C	Remarks
B-18a/o C	sintered	graphite	2420	2450	melting occurred at 2375°C as result of carbon pick-up reacted with floorplate at 2370°C reacted with W at 2365°C fast heat up, reaction with graphite at contact did not melt when held isothermally at 2250°C
	sintered	graphite			
	arc-melted	ZrO ₂ floorplate			
	arc-melted	W-floorplate			
	arc-melted	graphite	2430	=	
	sintered	graphite			
B-18.5a/o C	arc-melted	graphite	2420	2450	
	arc-melted	graphite	2410	=	
B-19a/o C	arc-melted	graphite	2430	2455	
	arc-melted	graphite	2410	2420	
	arc-melted	graphite	2420	=	
B-19.5a/o C	arc-melted	graphite	2395	2410	
B-20a/o C	arc-melted	graphite	2410	=	
	arc-melted	graphite	2365	=	
B-28a/o C	arc-melted	graphite	2380	ND	
B-30a/o C	arc-melted	graphite	2375	ND	
	arc-melted	graphite	2350	ND	
B-40a/o C	arc-melted	graphite	2410	ND	

* Sign, =, signifies complete melting temperature was same as incipient melting temperature; ND. indicates complete melting temperature was not determined.

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TABLE VIII
COMPARISON OF OBSERVED PATTERN
OF BORON CARBIDE* WITH PUBLISHED DATA

hkl	Published Data**		ARF Data	
	d, Å	I	d, Å	I
101	4.49	30	4.5016	5
003	4.02	40	4.0251	6
012	3.79	70	3.7713	4
110	2.81	30	2.8026	4
104	2.57	80	2.5603	9
021	2.38	100	2.3762	10
113	2.30	10	2.2999	1
006	2.02	10	1.8930	<1
211	1.82	10	1.8131	2
205	1.714	30	1.7116	6
116	1.637	10		
107	1.628	10	1.6273	1
303	1.505	20	1.4994	5
125	1.463	30	1.4611	5
018	1.446	30	1.4418	6
027	1.407	30		
220	1.403	30	1.4022	6
009	1.345	20	1.3378	4
131	1.342	20	1.3238	4
223	1.326	20	1.3158	3
208	1.286	10	1.2818	1
306	1.261	20	1.2578	5
042	1.191	10	1.2085	1

* 20a/o C

** Reference 17

TABLE IX
MICROHARDNESS OF PHASES
OF THE BORON-CARBON SYSTEM

Composition	Condition	Hardness, DPH
<u>100-gram Load</u>		
Unalloyed Boron	as cast	5150, 4950, 4950
B=0.1a/o C	as cast	4750, 4750, 4750
B=2a/o C matrix	as cast	4750, 4750
B=2a/o C carbide		5150, 5600, 5600
B=12a/o C	annealed	6700, 6400, 6400
B=14a/o C	annealed	7400, 6700, 6700
B=18a/o C	annealed	7400, 7400, 7400
B=18.5a/o C	as cast	6500, 6100, 6100
<u>200-gram Load</u>		
B=8a/o C	as cast	3700
B=12a/o C	as cast	4600
B=14a/o C	as cast	3900
B=16a/o C	as cast	3800, 3900
B=18.5a/o C	as cast	4000, 4100
B=18.5a/o C	annealed	3700
B=19a/o C	as cast	5150, 4850
B=19a/o C	annealed	4350, 4700, 3800
B=19.5a/o C	as cast	5500, 4850, 4600
B=19.5a/o C	annealed	4850, 4700
B=20a/o C	annealed	3550, 3400
B=20a/o C	annealed	5450, 4300, 4850

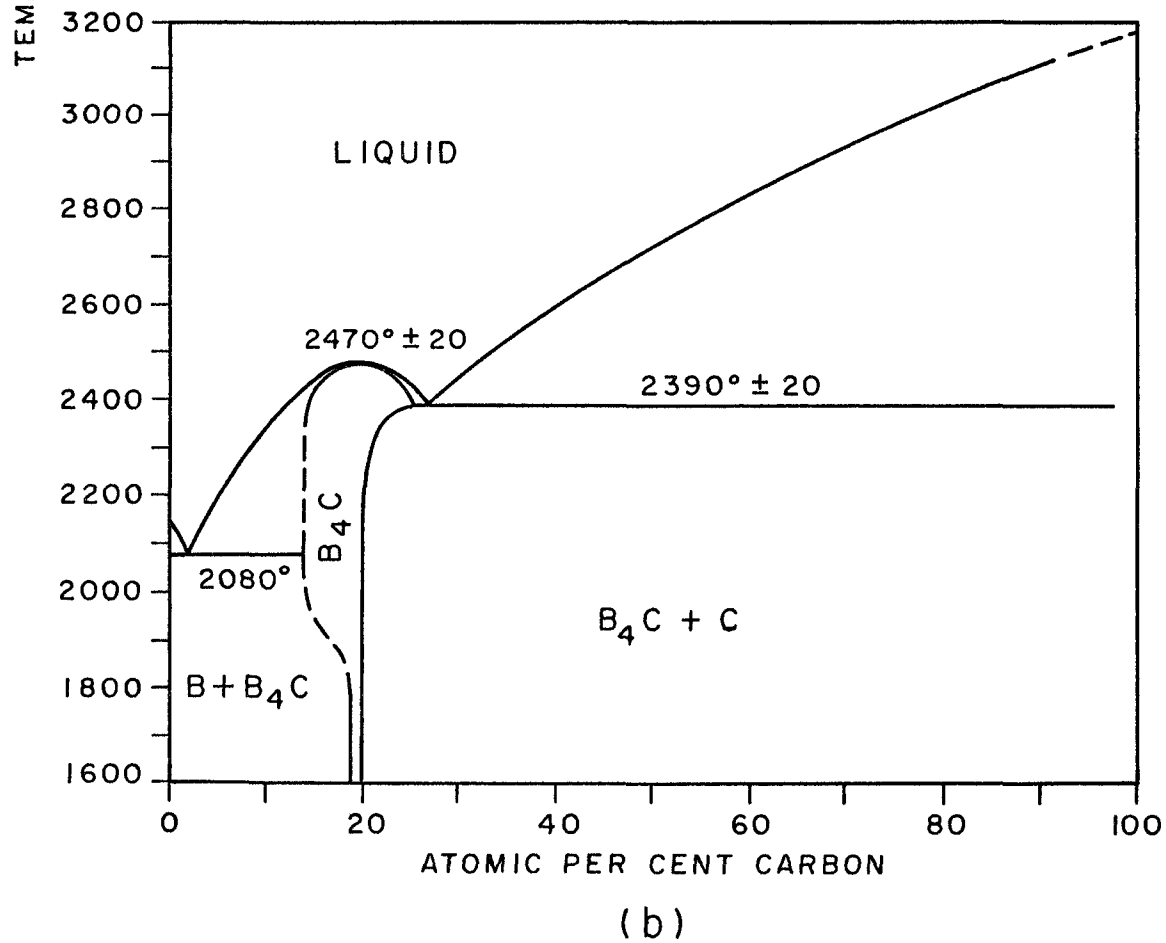
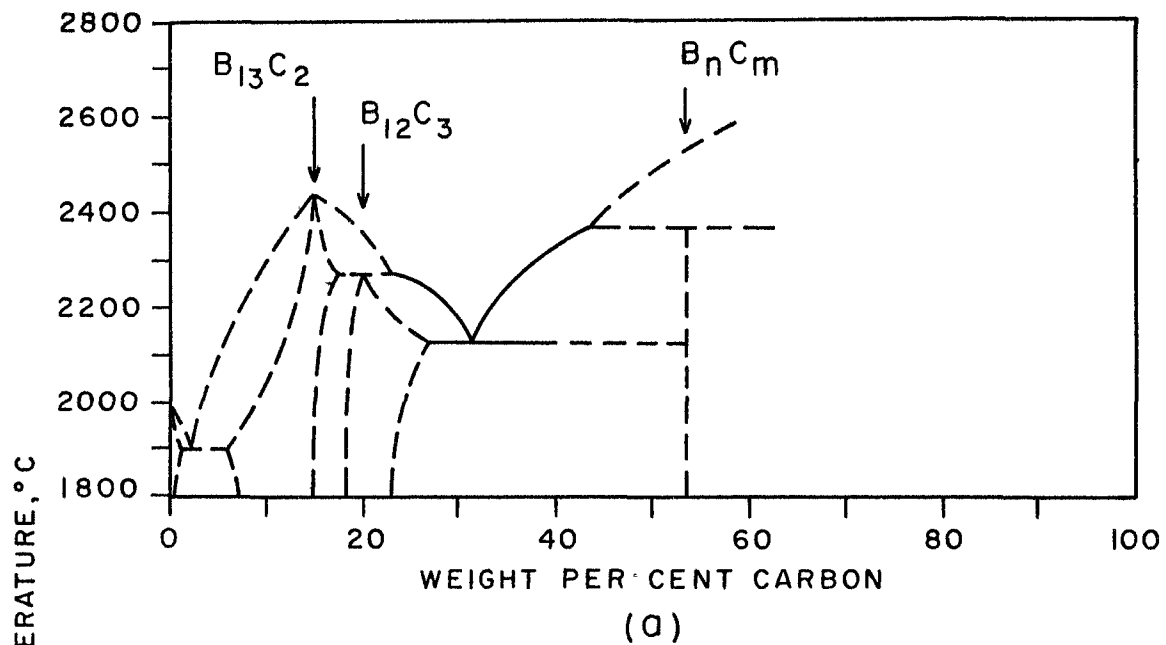


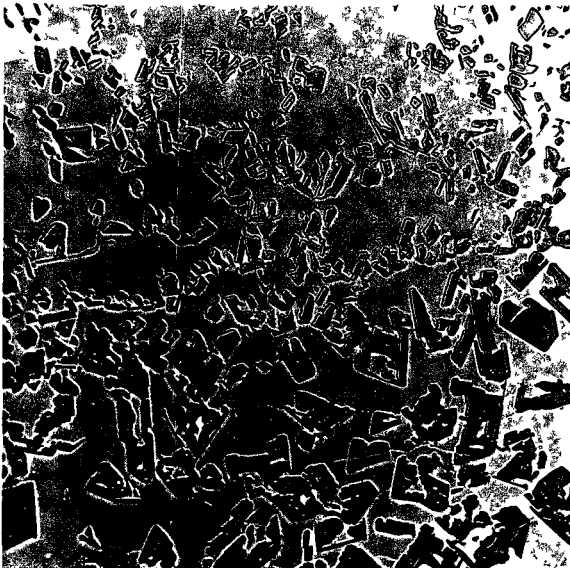
FIG. 1 BORON-CARBON EQUILIBRIUM AS REPORTED BY
(a) Samsonov, and (b) Dolloff.



X 25 Unetched Neg. No. 21195

Fig. 2

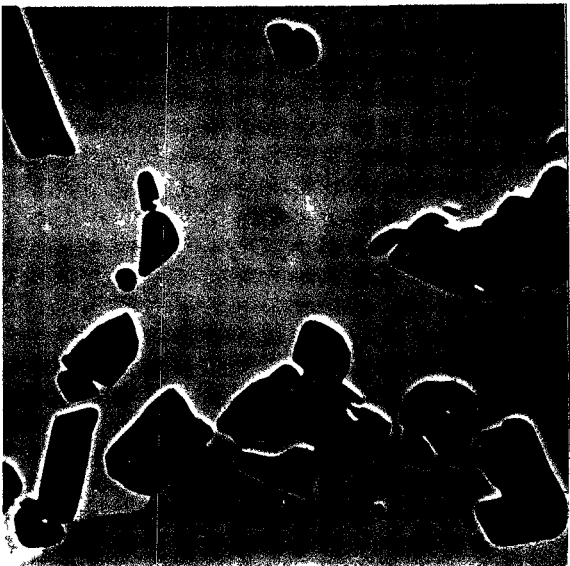
Boron-2a/o Carbon, As-Cast.
Extreme case of segregated boron
carbide crystals in boron matrix.



X 100 Unetched Neg. No. 21191

Fig. 3

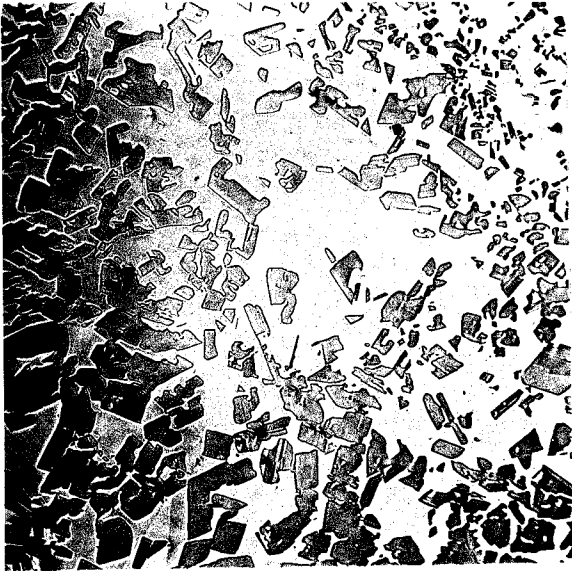
Boron-2a/o Carbon, As-Cast.
Boron carbide in boron matrix.



X 1000 Unetched Neg. No. 21192

Fig. 4

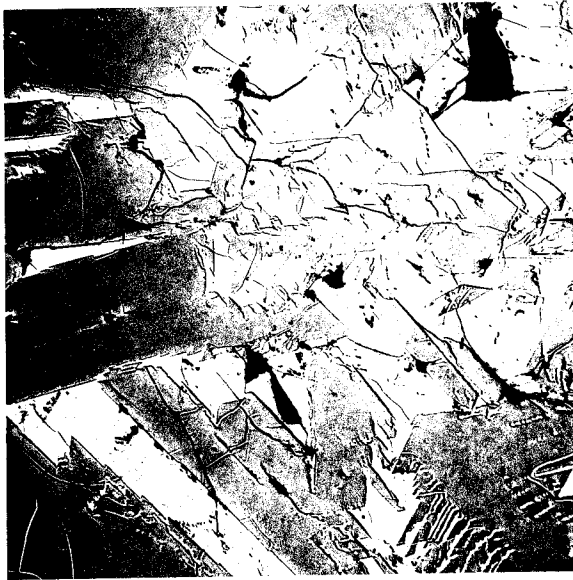
Boron-2a/o Carbon, As-Cast.
Boron carbide in boron matrix.



X 100 Unetched Neg. No. 21190

Fig. 5

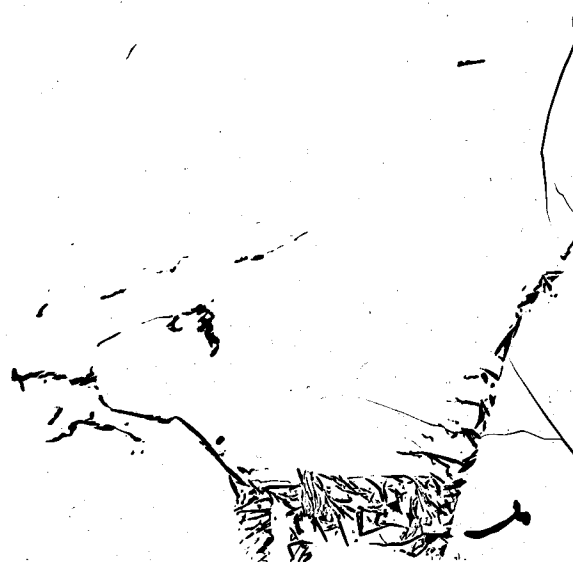
Boron-6a/o Carbon, As-Cast.
Boron carbide in boron matrix.



X 100 Unetched Neg. No. 21188

Fig. 6

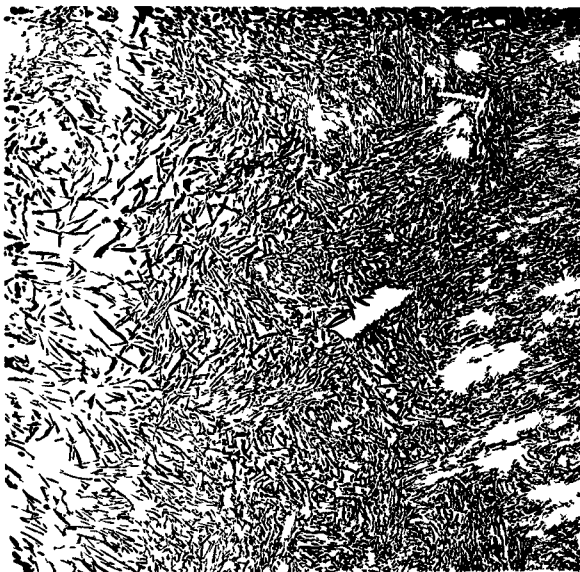
Boron-16a/o Carbon, As-Cast.
Co-existent non-equilibrium phases
of boron carbide (grey) in boron
matrix (light).



X 100 Unetched Neg. No. 21187

Fig. 7

Boron-20a/o Carbon, As-Cast.
Boron carbide with carbide-graphite
eutectic.



X 100 Unetched Neg. No. 21185

Fig. 8

Boron-28a/o Carbon, As-Cast.
Pro-eutectic boron carbide in matrix
of carbide-graphite eutectic.



X 100 Unetched Neg. No. 21186

Fig. 9

Boron-40a/o Carbon, As-Cast.
Pro-eutectic graphite in matrix of
carbide-graphite eutectic.



X 100 Unetched Neg. No. 21189

Fig. 10

Boron-16a/o Carbon, Annealed 1500°C.
Single-phase boron carbide.



X 100 Unetched Neg. No. 21194

Fig. 11

Boron-0.3a/o Carbon, As-Cast.
Boron carbide in boron matrix.



X 100 Unetched Neg. No. 21193

Fig. 12

Boron-0.6a/o Carbon, As-Cast.
Boron carbide in boron matrix.

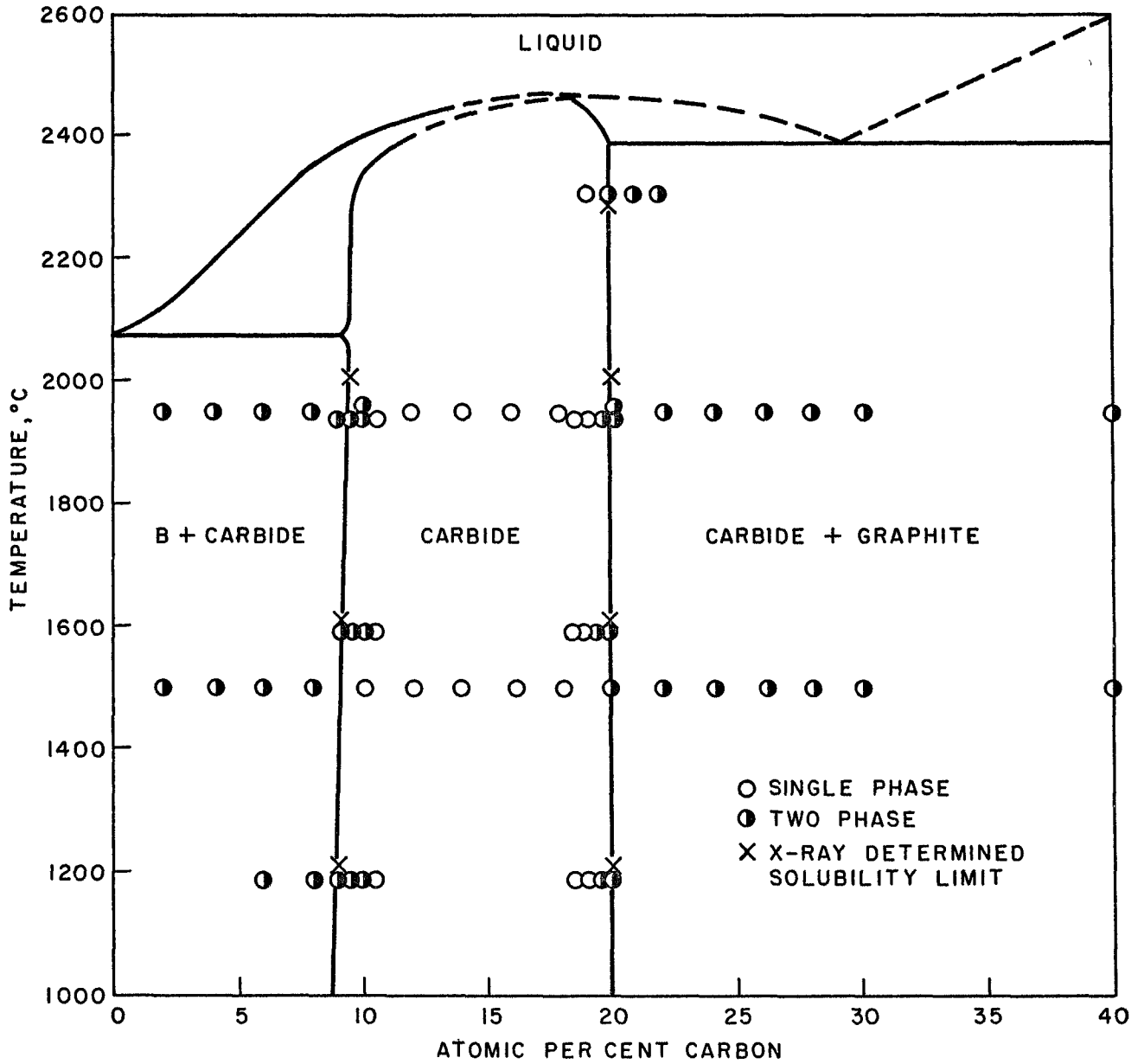


FIG. 13 - DELINEATION OF BORON CARBIDE SOLUBILITY LIMITS

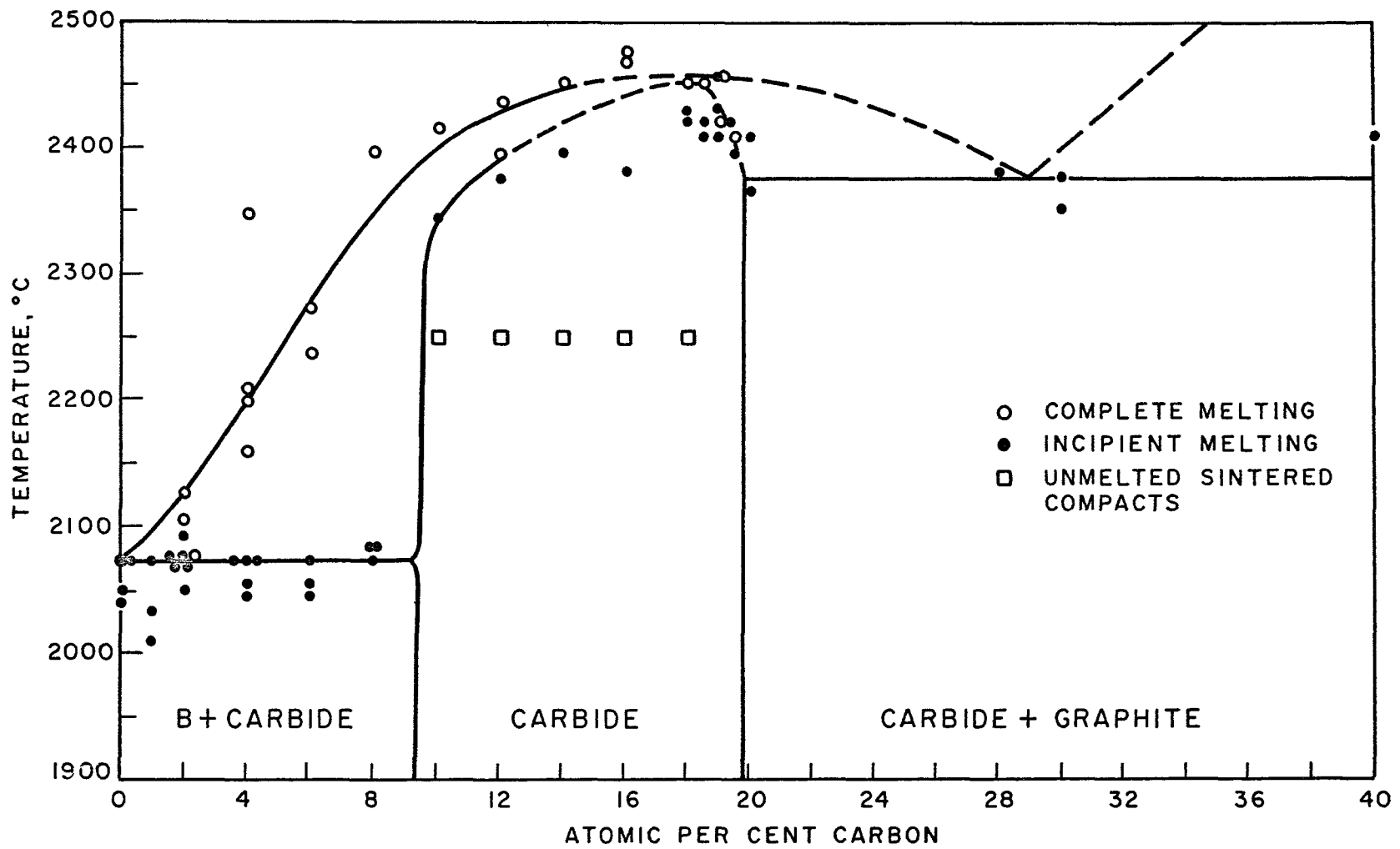


FIG. 14 MELTING TEMPERATURES OF BORON-CARBON ALLOYS.

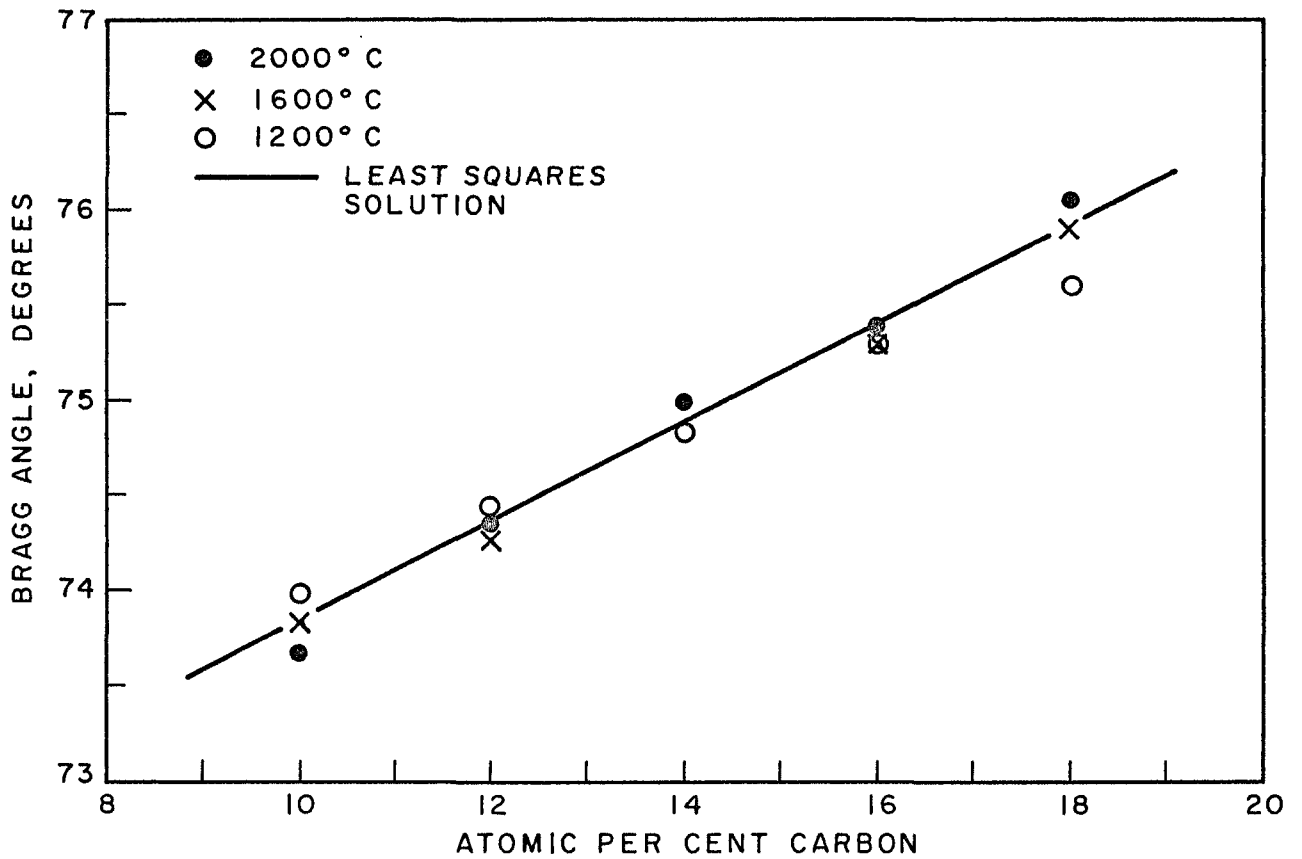


FIG. 15 ANGULAR VARIATION OF STRONG BACK-REFLECTION OF BORON CARBIDE AS A FUNCTION OF CARBON CONTENT.

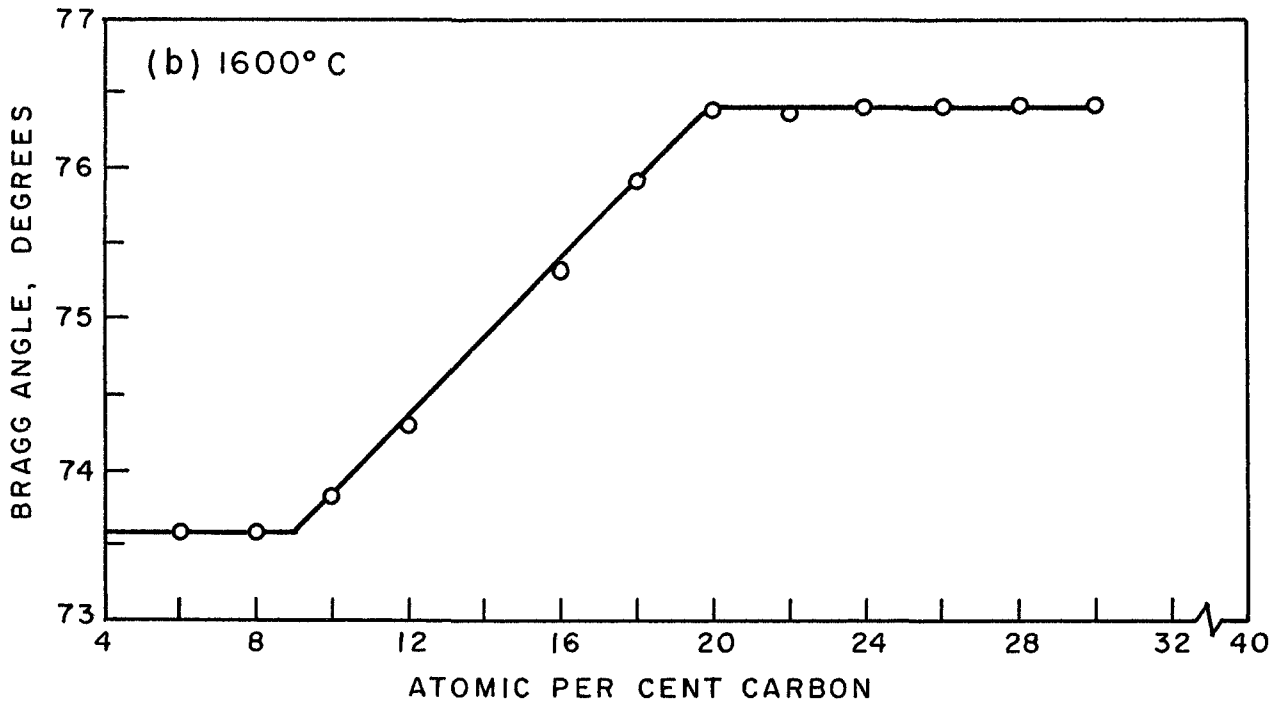
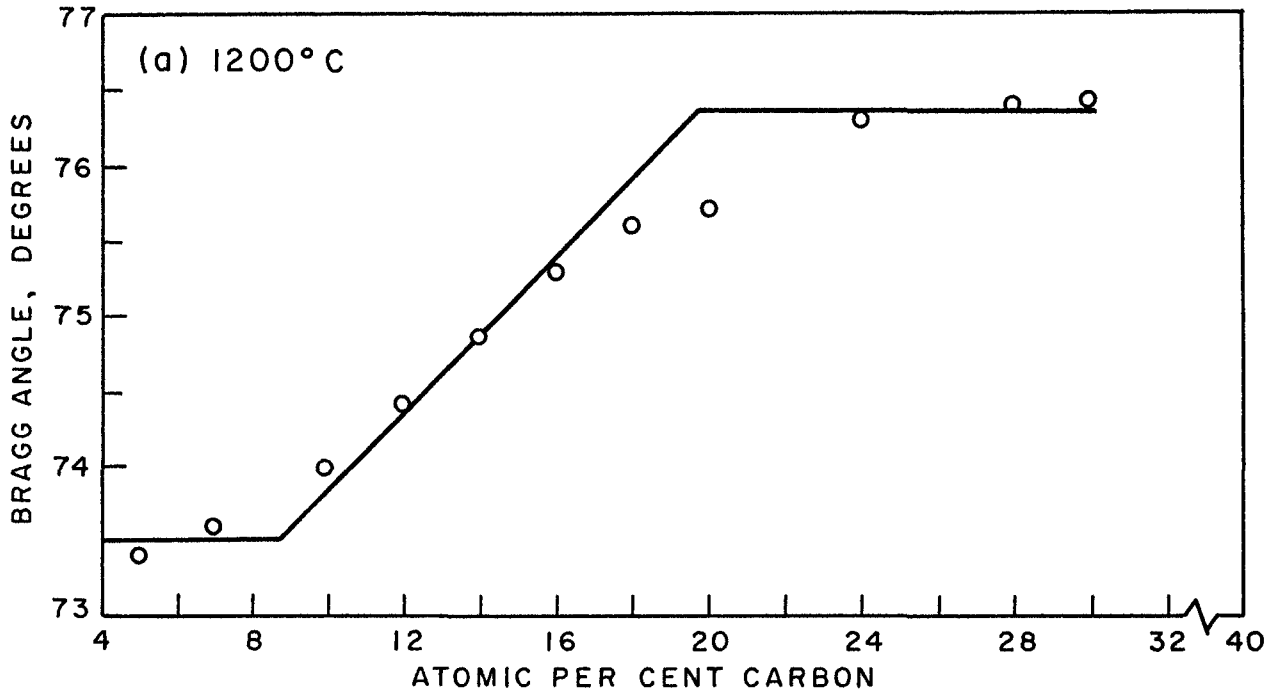


FIG. 16 OBSERVED DATA FOR THE PARAMETRIC DETERMINATION OF THE SOLUBILITY LIMITS OF BORON CARBIDE.

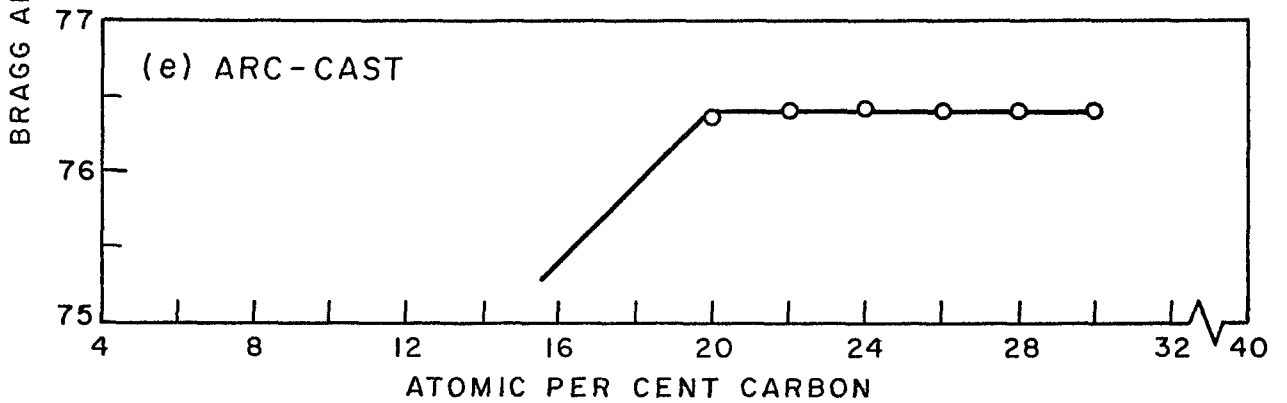
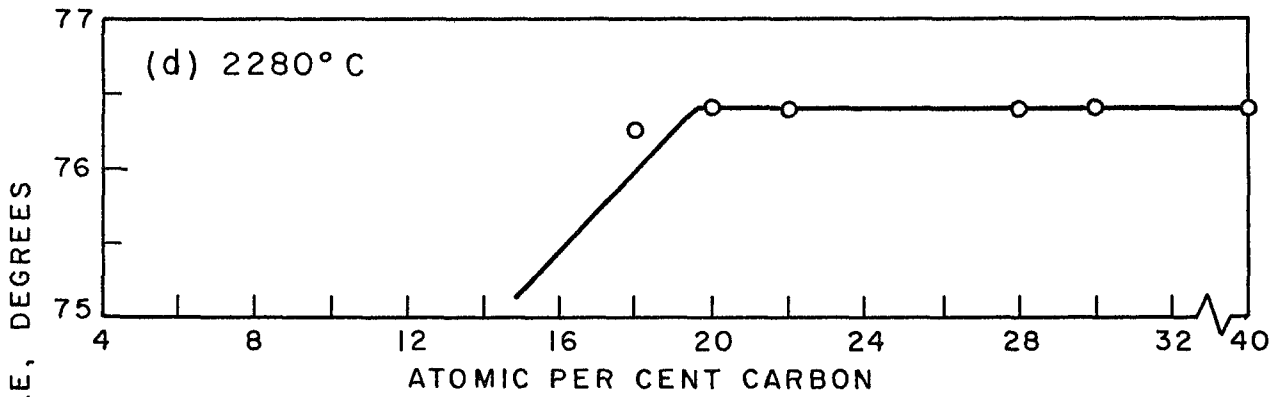
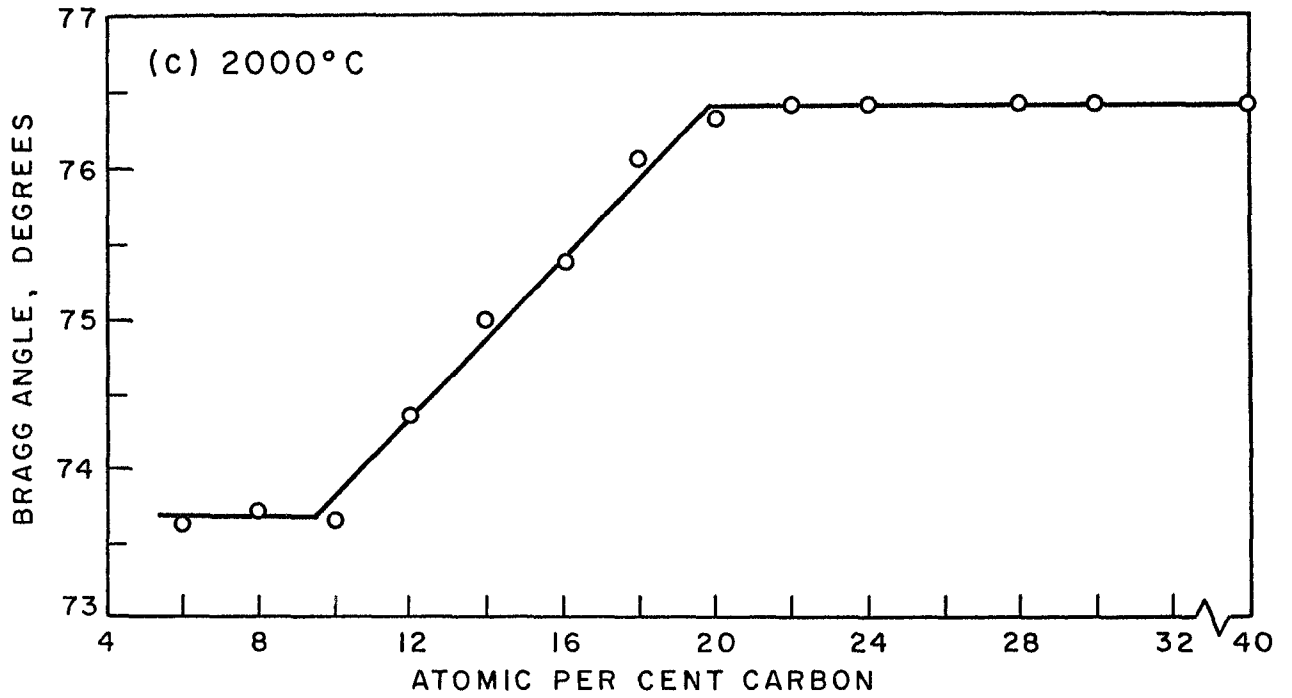


FIG. 16 CONTINUED.

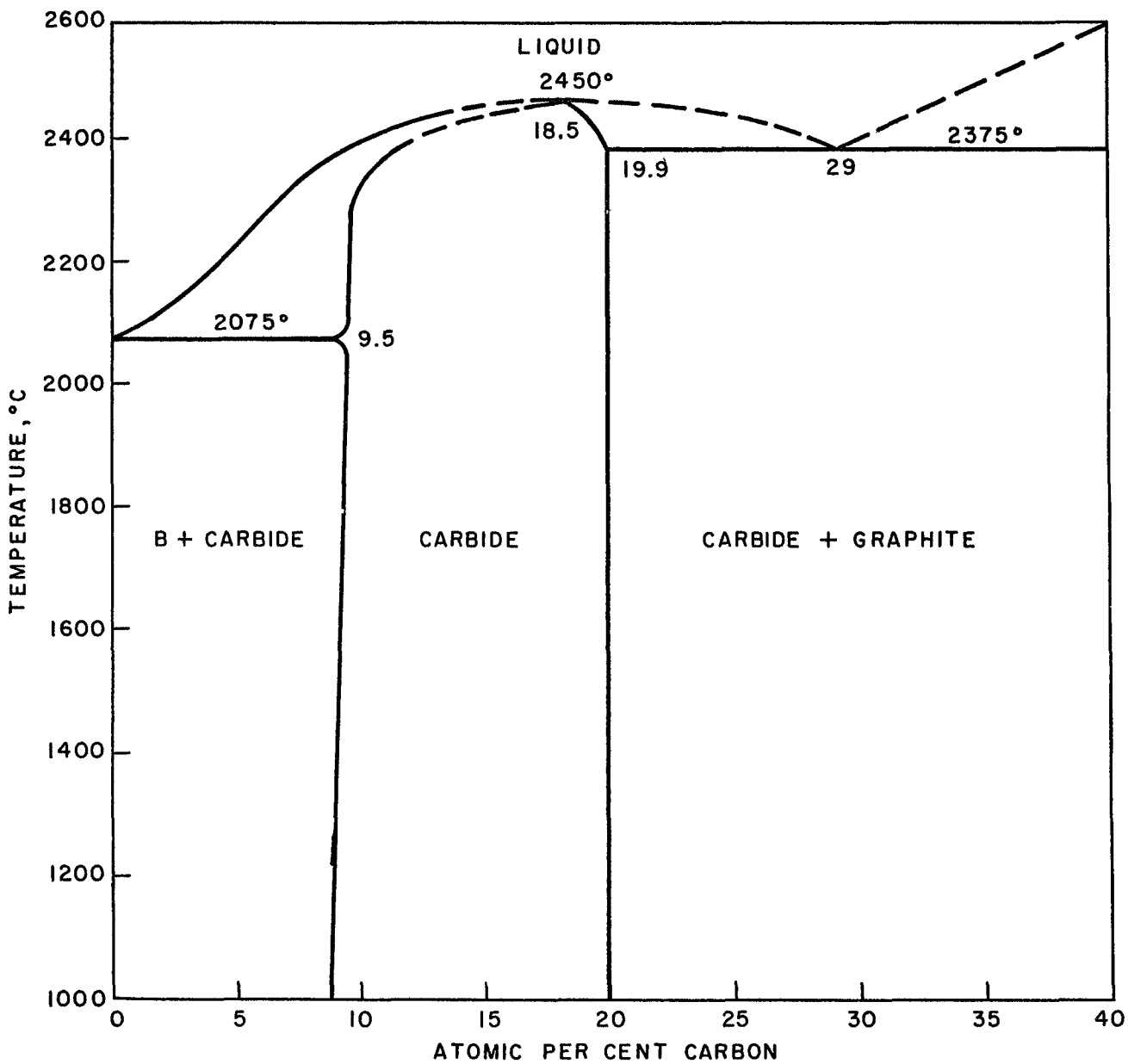


FIG.17 - BORON-CARBON EQUILIBRIUM DIAGRAM