

**RESEARCH STUDY TO DETERMINE THE
PHASE EQUILIBRIUM RELATIONS OF SELECTED
METAL CARBIDES AT HIGH TEMPERATURES**

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FOREWORD

This report was prepared by the Research Laboratory of National Carbon Company, Division of Union Carbide Corporation, under USAF Contract No. AF 33(616)-6286. This contract was initiated under Project No. 7350, "Ceramic & Cermet Materials", Task No. 73500, "Ceramic & Cermet Materials Development." The work was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Lt. John R. Giancola and Capt Ray H. Wilson acting as project engineers.

This report covers work conducted from January 1959 through March 1960.

The writer has served as spokesman for the work reported. Contributions to the technical effort have been made by R. P. Goton, C. E. Lowell, W. J. Kroenke, J. D. Ruggiero, R. V. Sara and F. J. Beodray. Acknowledgment is made for guidance and helpful suggestions to J. C. Bowman and N. R. Thielke.

WADD TR 60-143

ABSTRACT

The work here reported is the result of an investigation of phase equilibria in the ternary system, silicon-boron-carbon. Techniques for extending the high temperature range of measurements have been developed. Accurate phase diagrams for the silicon-carbon and the boron-carbon binaries have been obtained and details of the ternary system have been determined in the high carbon content region. The data were obtained by high temperature differential thermal analysis and by photoelectric thermal analysis, both supplemented by metallographic, X-ray and chemical techniques.

Results for the boron-carbon binary system indicate that boron melts at $2130 \pm 10^\circ\text{C}$ and that B_4C has a congruent melting point of $2470 \pm 20^\circ\text{C}$. Boron and B_4C form a eutectic at $2080 \pm 20^\circ\text{C}$, whereas carbon and B_4C form a eutectic at $2390 \pm 20^\circ\text{C}$.

Results for the silicon-carbon binary indicate a eutectic between silicon and SiC at $1402 \pm 5^\circ\text{C}$. SiC melts incongruently at $2540 \pm 40^\circ\text{C}$. The peritectic point is located at 27 per cent carbon.

Results for the ternary system indicate a eutectic between B_4C , SiC and carbon at $2250 \pm 20^\circ\text{C}$. No compound formation has been observed in the high carbon region of the ternary system.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RAMKE

Chief, Ceramics and Graphite Branch
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Materials Central

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RESEARCH STUDY TO DETERMINE THE
PHASE EQUILIBRIUM RELATIONS OF SELECTED
METAL CARBIDES AT HIGH TEMPERATURES

by

R. T. Dolloff

I. INTRODUCTION

A. Objective

The need for rapid advances in high temperature technology, precipitated by the onset of the space age, has created great interest in refractory metal carbide systems. The work reported here has, therefore, been directed to the determination of accurate phase equilibrium relations of selected refractory metal carbides at high temperatures. Considerable effort has been applied to the attainment of quality results and to the extension of reliable experimental techniques to the necessary high temperatures.

At the start of this program it was apparent that very little literature on the phase equilibria existed in the area of metal-carbon systems in the carbon-rich composition range. On the other hand, refractory metal-carbide structures, used as aggregated carbide, as inclusions in fabricated graphite shapes, or as coatings for protection of formed graphite articles, are very promising high temperature structural elements. The production and fabrication of structures of predictable composition requires a knowledge of phase relations since changes in phase at forming or operating temperatures produce physical property modifications. Lattice dilatation, brought about by composition change, can cause a catastrophic volume change; precipitation from a solid solution can embrittle; melting of a single component can seriously weaken. Thus, a detailed knowledge of phase relations is a primary requisite to the acceptable fabrication of a composite body.

B. Silicon-Boron-Carbon System

Selection of the silicon-boron-carbon system as the object of this program permitted the detailed investigation of an important area of interest with a minimum of research devoted to modification of existing experimental techniques. For convenience of reporting, the research areas have been

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presented in three individual sections consisting of: the boron-carbon binary, the silicon-carbon binary and the high carbon region of the silicon-boron-carbon ternary.

The binary systems, silicon-carbon and boron-carbon, are both of great interest in the development of refractory aggregates. These have shown promise both as composites and as coating materials for graphite. Compositions within the boron-carbon system are characterized by extreme hardness and high corrosion resistance and thus are of considerable value in modern ceramics. However, the boron-carbon system is not published for carbon contents above the composition B_4C and there has been much controversy about the existence and configuration of this stable carbide phase. Moreover, prior to this program, very little work had been done on the silicon-carbon binary, yet silicon carbide has excellent refractory properties. It is commonly fabricated into high temperature resistance heating elements and kiln furniture, and is often employed as an oxidation-resistant coating for graphite.

The high carbon region of the silicon-boron-carbon ternary is of interest because of the useful refractory properties exhibited by typical ternaries and because of the possible existence of new stable compounds possessing superior high temperature properties. Aggregates of the silicon-boron-carbon ternary are characterized by extreme hardness, high temperature stability and good thermal shock and oxidation resistance. They often exhibit the properties of high temperature semiconductors.

C. High Temperature Technology

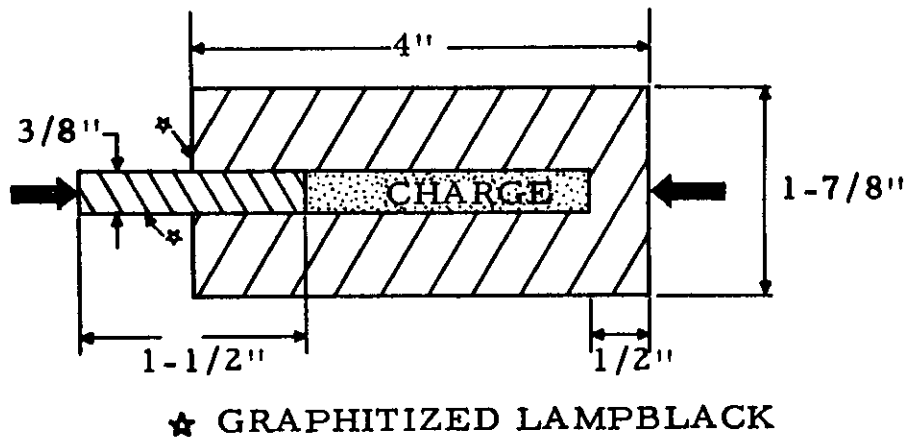
The scarcity of information concerning phase relations in the area of metal-carbide systems can be attributed to the very high temperatures required for the preparation of samples and to the lack of reliable observational methods in the required temperature ranges. Special techniques for obtaining the high temperatures necessary for equilibrating refractory metal-carbides have been developed in previous work at this Laboratory. The present facilities make possible the dynamic determination of phase changes to temperatures as high as $2800^{\circ}C$. These unique facilities greatly reduce the time necessary for the complete and accurate determination of a phase diagram. Most of the furnacing equipment utilizes resistively-heated carbon or graphite to supply the high temperature environments. The presence of these materials has no effect on samples already containing excess carbon. In the special cases where carbon content must be maintained constant however, suitable, nonreacting crucible materials have been employed to contain the specimens.

II. PROCEDURES AND EQUIPMENT

A. Sample Preparation

1. Hot-Pressing

Hot-pressing techniques were used for preparing homogeneous samples. Powders of boron, silicon or silicon carbide of the highest available quality were mixed with high purity graphite to the required compositions. After mixing, the samples were hot-pressed in lampblack molds in a carbon tube furnace with argon protection. Pressing temperatures ranged between 2000 and 2600°C and pressures between 2000 and 10,000 psi were utilized. Cylindrical specimens 3/8 inch diameter and 1-1/2 inches in length were consistently prepared in the various compositions by means of the assembly shown in Figure 1. Chemical analyses and photomicrographs of typical samples showed that homogeneous, high density samples were obtained. The compositions closely approximated the original mixtures as shown in Table I.



☆ GRAPHITIZED LAMPBLACK

Figure 1. Hot-Pressing Assembly

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TABLE I
ANALYSIS OF HOT-PRESSED SAMPLES

Starting Composition, At. % C	Final Composition, At. % C	Phases
50	50.0	α SiC
55	54.7	α SiC + C
60	60.4	"
65	65.2	"
70	69.8	"
75	75.1	"
80	80.6	"
85	84.3	"
90	90.3	"
95	94.5	"

2. Arc Image Melting

Samples containing less than 20 atomic per cent carbon were not always amenable to hot-pressing since solution of carbon from the walls of the mold could affect the specimen composition. Low carbon compositions were, therefore, sintered and melted by the arc image technique using a protective argon atmosphere to prevent oxidation. The melting was carefully controlled to minimize evaporation losses. Chemical analyses of the resultant melts agreed well with analyses of the initial composites.

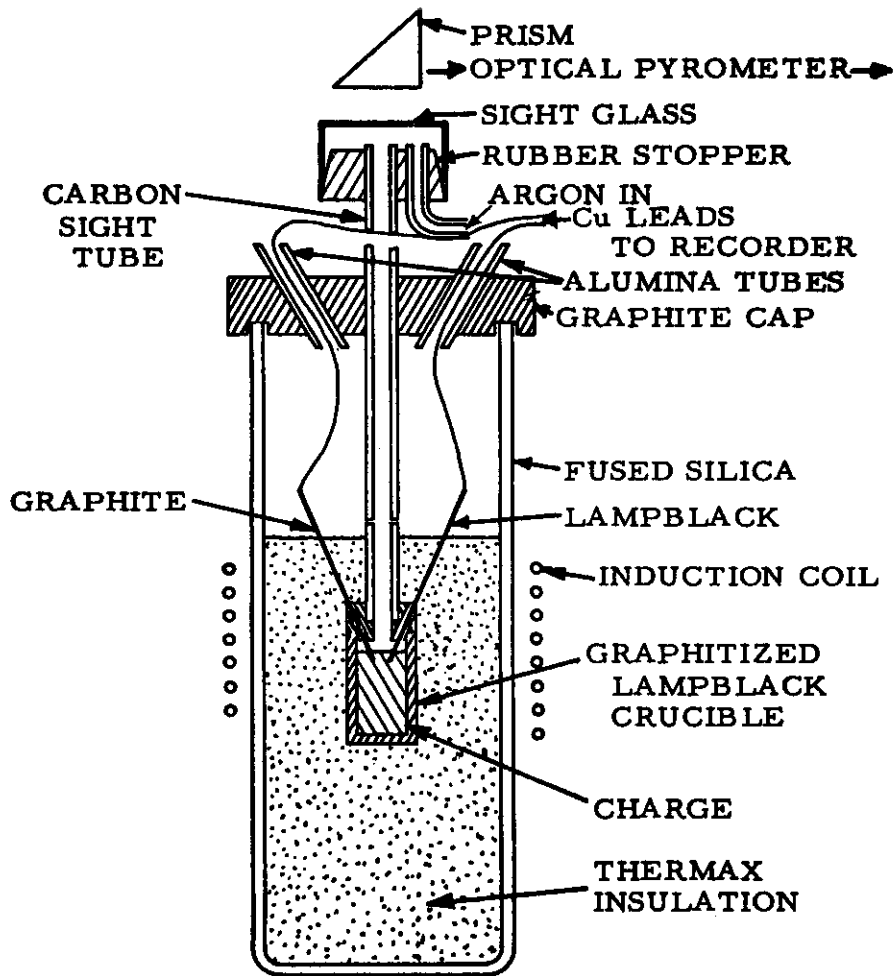
3. Induction Melting

When phase relationships could be determined by standard thermal analytical techniques, simplified preparation methods were used. In these cases, the mixtures were placed in the thermal analysis system and the entire assembly was inductively heated to the desired temperature. After equilibration at temperature, routine thermal analyses were conducted.

B. Thermal Analysis

1. Modified Classical Method

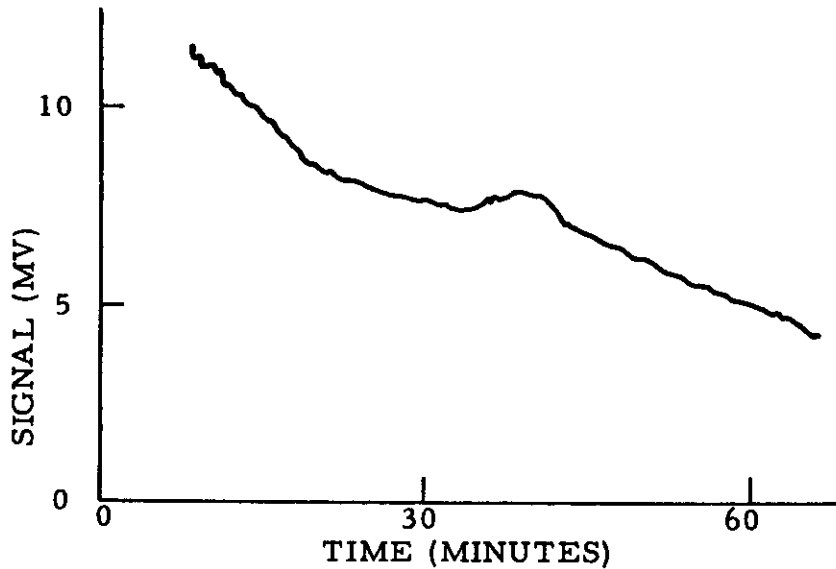
The important element of this method is the heating chamber assembly shown in Figure 2. The combination crucible and susceptor, machined from lampblack base stock, was selected because of its impermeability to liquid silicon and because it introduced no new components into the system. For similar reasons, a thermocouple, made of graphite and lampblack components and with a useful upper temperature limit of 2400°C, was employed for detecting phase changes. Samples were placed in the lampblack crucible, inductively



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Figure 2. Heating Chamber Assembly

heated to temperature and allowed to equilibrate. The thermal analysis-- a record of the thermocouple output versus cooling time--was then carried out. True temperature was determined by optical pyrometry at two-minute intervals during cooling. Figure 3 depicts a typical result for a hypereutectic silicon-silicon carbide composition.



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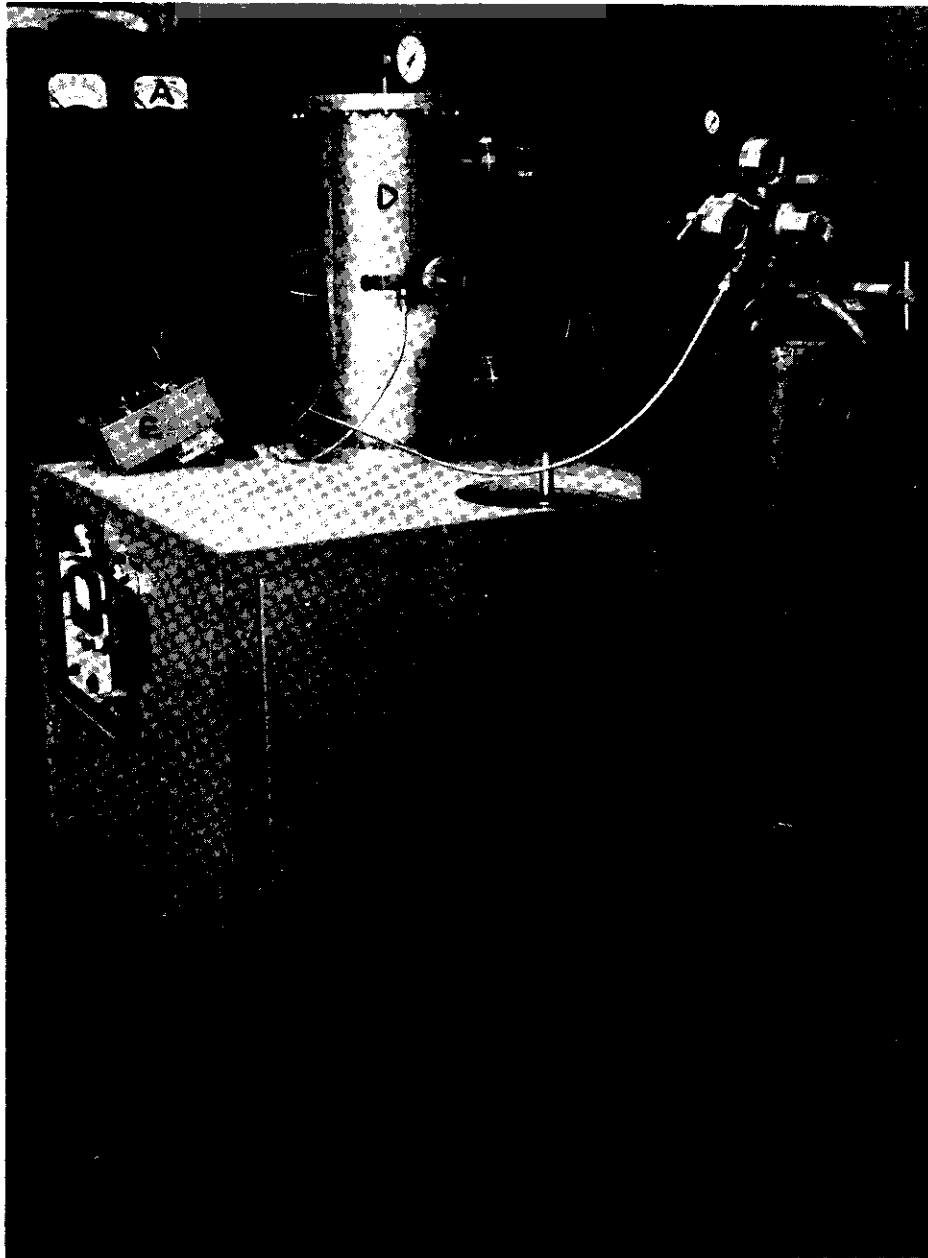
Figure 3. Typical Cooling Curve

2. Photoelectric Thermal Analysis

Thermal analysis is a direct method of determining phase changes, but for temperatures greater than 2000°C, highly sensitive techniques for continuous temperature measurement are generally unavailable. A photoelectric method was therefore evolved at this Laboratory for surmounting this difficulty.

The essential elements of the apparatus are depicted in Figures 4, 5, and 6. The heating chamber of Figures 5 and 6 provides a means of selecting a carefully controlled atmosphere or of operating in vacuum to pressures as low as 5×10^{-7} mm Hg. The sample, surrounded by graphite and molybdenum radiation shields, is heated by passing a current through it and the two graphite electrodes. The temperature is monitored by an optical pyrometer sighted through one side of the radiation shields. Radiation from the other side of the sample is focused on a phototube, the output of which is highly sensitive to small temperature changes. The phototube current, recorded as a function of heating or cooling time, produces the required temperature arrests or accelerations indicative of changes in phase.

Figure 7 shows a plot of phototube output versus time for a mixture of SiC and graphite which had been hot-pressed at 2550°C and 10,000 psi. The temperature arrest is the result of the sample crossing the SiC-C peritectic line.



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- A - Power Control Panel
- B - Argon Supply
- C - Vacuum System and Control
- D - Heating Chamber
- E - P-T Circuit

Figure 4. Photoelectric Thermal Analysis Assembly

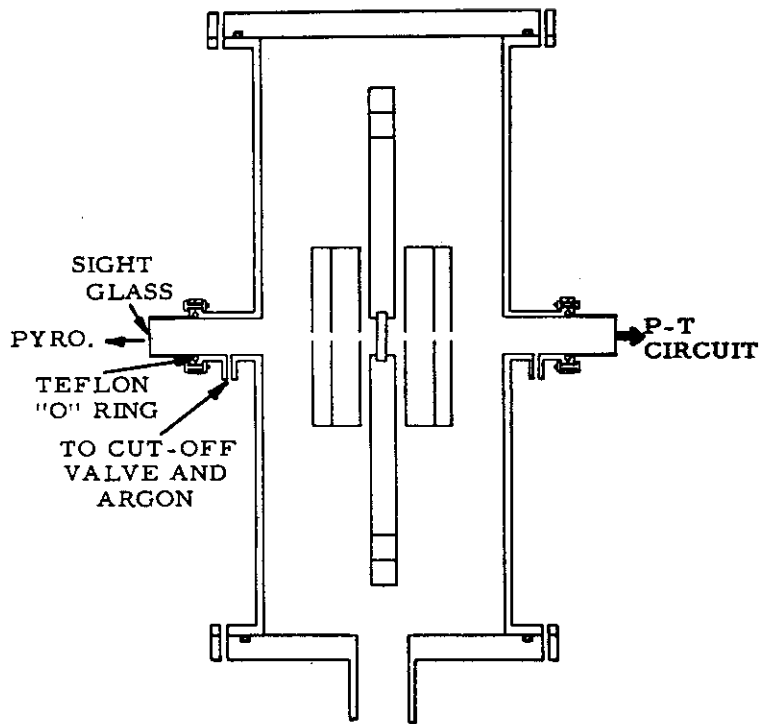
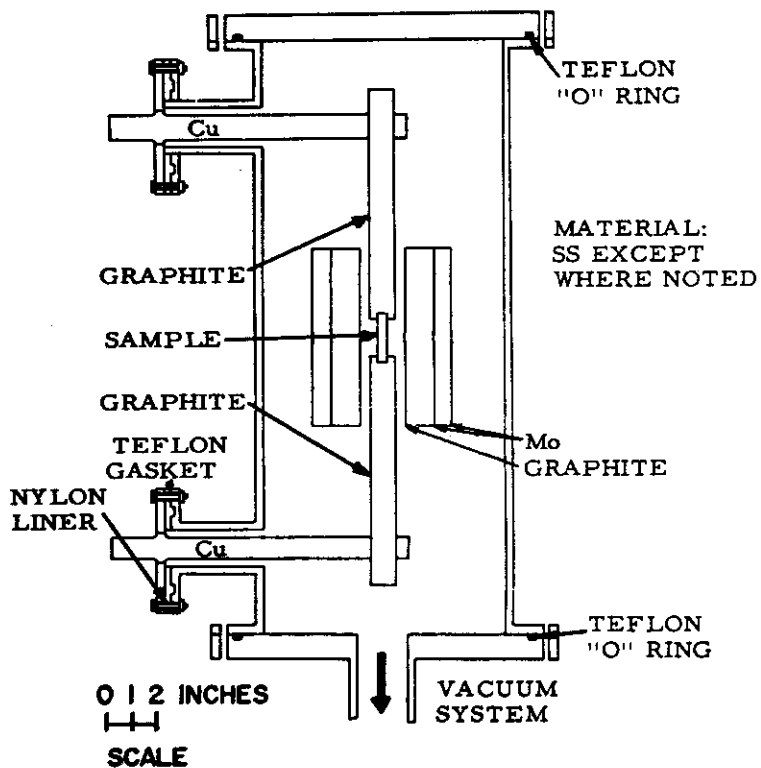
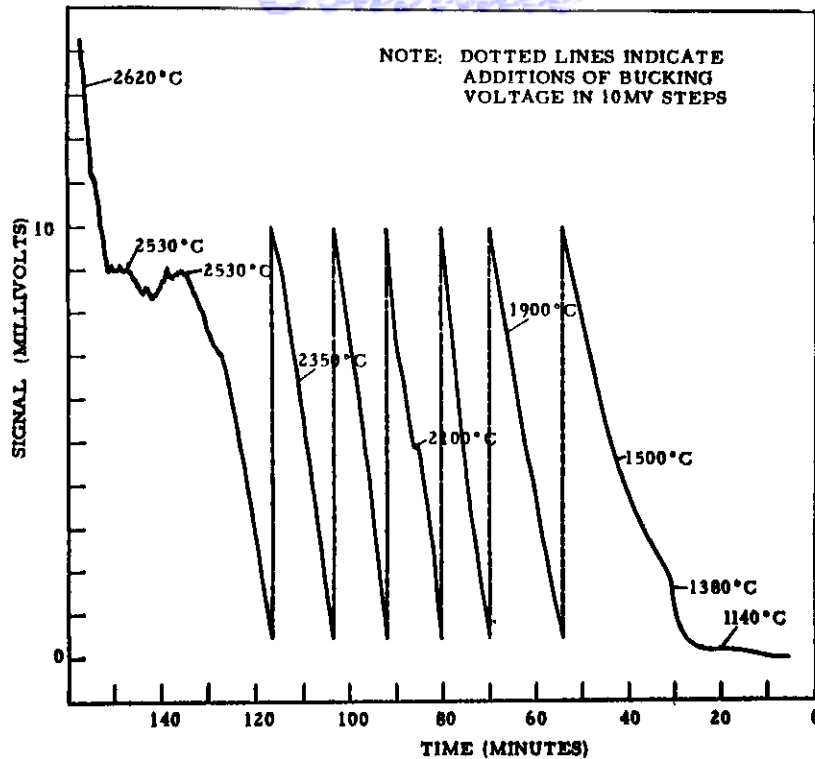


Figure 5.
Cross Section of
Heating Chamber

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Figure 6.
Cross Section of
Heating Chamber
at 90°
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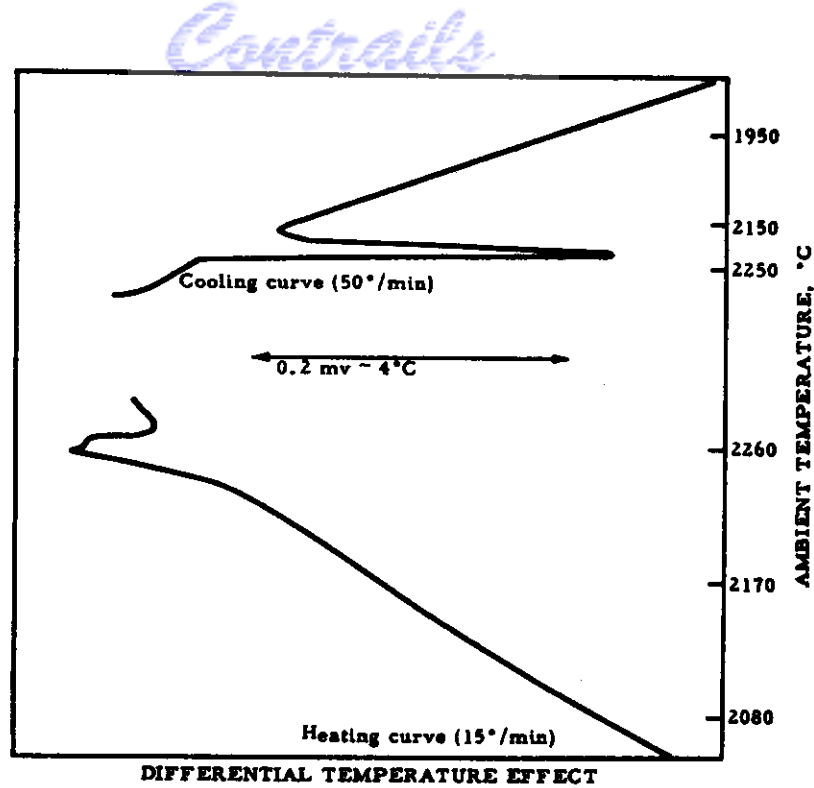
Figure 7. Typical Photoelectric Thermal Analysis Curve

3. Differential Thermal Analysis

A novel, high temperature, differential thermal analysis (DTA) apparatus has been developed in this Laboratory and has been extensively used during the course of this research. The DTA apparatus is capable of detecting phase changes at temperatures approaching 3000°C and, in the present study, has been used to accurately position both eutectic and liquidus lines. The utilization of this technique greatly reduces the effort required to locate phase boundaries since the sensitivity is sufficient for the detection of temperature differences of 0.1°C. A typical DTA thermogram is shown in Figure 8 for a sample composition of 15 per cent silicon, 20 per cent boron and 65 per cent carbon in atomic per cent. The endothermic peak observed at $2250 \pm 20^\circ\text{C}$ crosses the ternary eutectic temperature.

C. Analytical Techniques

Metallographic data were extensively employed in the interpretation of the results obtained from thermal analysis. Photomicrographs and hardness measurements established the number and character of existing phases and



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Figure 8. Typical Differential Thermal Analysis Curve of a Ternary Mixture

determined the characteristic structures of various compositions. Examination of polished microsections permitted the rapid and accurate identification of eutectic and peritectic compositions.

Phase identification by X-ray techniques was carried out by standard methods using powder photographic and diffractometer methods. In certain special cases it was possible to identify solid phases in a polyphase system by comparing the diffraction patterns with standard patterns representing the individual phases. Solid solution ranges were probed by observing the change in lattice parameter with composition at constant temperature.

Spectroscopic and routine chemical analyses were performed on all raw materials to establish their purities and compositions. Standard wet chemical analyses were utilized to determine final compositions of test specimens subsequent to a variety of experimental test conditions.

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III. BORON-CARBON BINARY SYSTEM

A. Experimental Procedures

1. Boron Melting Point Determination

A primary aim of this project was to accurately determine the melting point of boron since the literature values range from 2000°C to 2350°C.¹ Boron of 98.9 per cent purity was obtained from United States Borax and Chemical Co., a division of Pacific Coast Borax Corp., and was used for all melting point determinations. The melting point was measured by differential thermal analysis on powders and on solid pieces melted by the arc image furnace. Four different containers were used during melting to eliminate any possible thermal effects caused by interaction between the boron and crucibles. The tabulated results of the heating curves are presented in Table II.

TABLE II
BORON MELTING POINT

Lining	Peak Temperature °C	
	Beginning	End
Graphite	2110	2120
Molybdenum	2140	2150
Tantalum	2130	2140
Boron Nitride	2120	2130

An average temperature of 2130°C was measured by means of a calibrated optical pyrometer with emissivity corrections applied. Estimated accuracy of the measurement, which includes the pyrometer calibration and the observed spread in the data, is $\pm 10^\circ\text{C}$. Thus, these measurements indicate that the melting point of boron is $2130 \pm 10^\circ\text{C}$. This number agrees well with the latest reported literature value.²

2. Low Carbon Eutectic Region

Samples were prepared by mixing 98.9 per cent purity boron and high purity B_4C , followed by sintering and melting in the arc image furnace. Differential thermal analysis, using a graphite crucible, indicated a thermal arrest at $2080 \pm 20^\circ\text{C}$. The arrest temperature was observed for all compositions up to 14 per cent carbon. Photomicrographs and X-ray powder photographs indicated a eutectic structure between elemental boron and B_4C .

The liquidus line of this portion of the diagram was determined by controlling the temperature of total fusion of samples placed in lampblack crucibles. The extrapolation of this curve to its intersection with the isothermal eutectic line leads to a eutectic of composition between 1 and 2 per cent carbon.

3. High Carbon Eutectic Region

All samples were hot-pressed at 2300°C and 2000 psi and annealed for two hours at 2000°C in an argon atmosphere. Differential thermal analysis of compositions between 28 and 90 atomic per cent carbon showed an endothermic peak at $2390 \pm 20^\circ\text{C}$ for all samples. Crossing the liquidus line produced sharp changes of slope in the temperature versus time curves. Check points on the liquidus-solidus boundary were obtained by simple crucible melting techniques. X-ray and metallographic analyses revealed a eutectic structure between B_4C and carbon. Extrapolation of the liquidus indicates a eutectic composition of 27 atomic per cent carbon.

A metastable equilibrium was observed during the cooling cycle of all hypereutectics. The cooling curve, at the eutectic composition, produced crystallization peaks approximately 200°C below the eutectic temperature. Seeding experiments verified that the phenomena is caused by supercooling. It is believed that the eutectic composition supercools because of a lack of nucleation sites at the liquid-graphite interface.

4. B_4C and the Solid Solubility Region

The carbide, B_4C , exists in the region between 10 and 27 atomic per cent carbon. This carbide has been the subject of many controversies. Most of the available thermodynamic data refer to the formula B_4C .^{4, 5} Crystallographic and other X-ray considerations^{6, 7} show that the same X-ray pattern is obtained over a wide range of nonstoichiometry.^{8, 9, 10, 11} Specific gravity, resistivity, and microhardness values tend to indicate the presence of a solid solution of either one of the elements in the lattice.

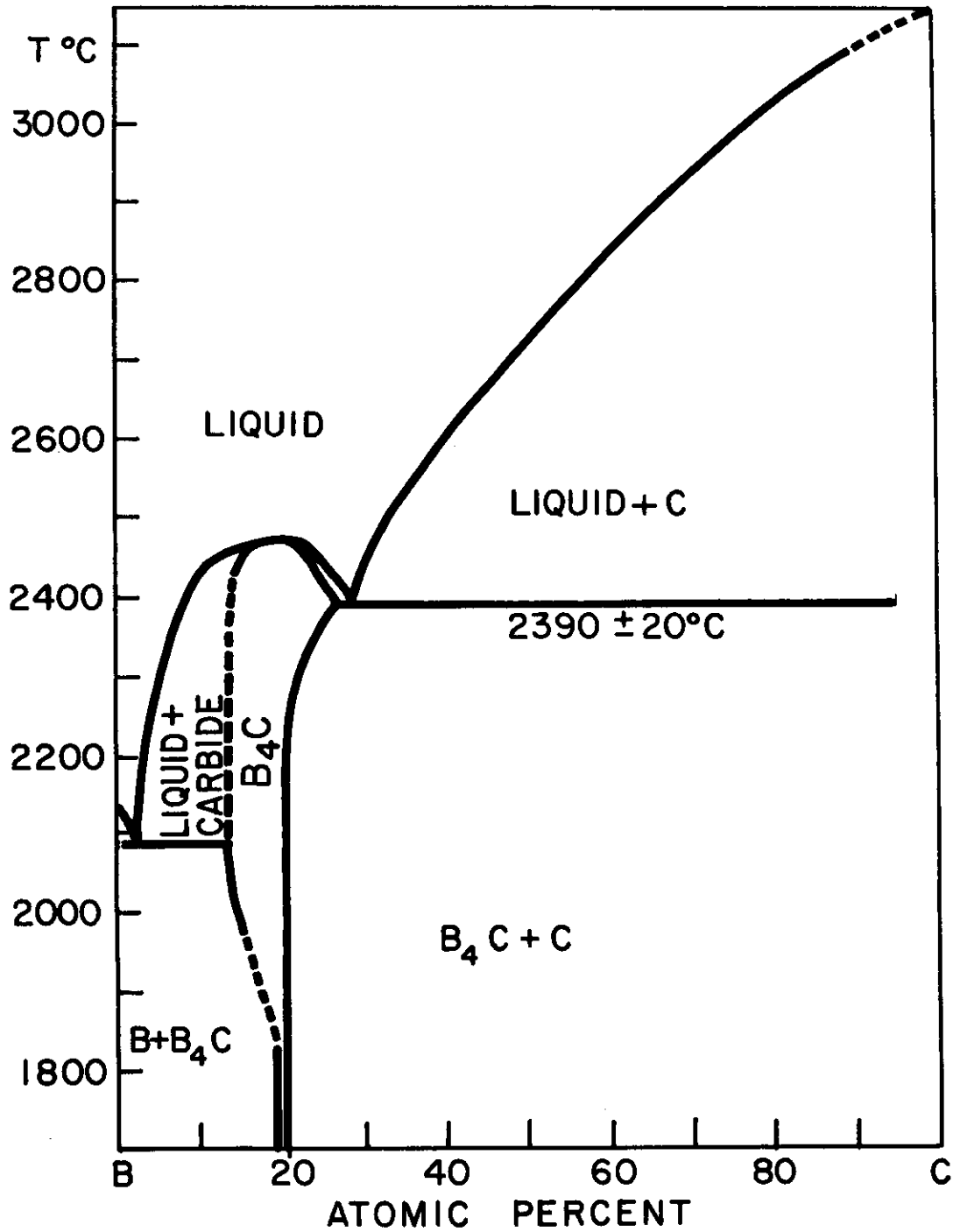
The solubility of boron in boron carbide was investigated by the arc melt preparation of composition ranges from $\text{B}_{3.95}\text{C}$ to $\text{B}_{4.10}\text{C}$ followed by differential thermal analysis. Peaks, representing the boron- B_4C eutectic temperatures of $2080 \pm 20^\circ\text{C}$ were found to vanish at a composition of 10 atomic per cent carbon. From these observations it is concluded that the boron carbide lattice may dissolve as much as 10 atomic per cent boron above 2000°C .

The solubility of carbon in boron carbide was investigated with samples quenched from 2300 to 2350°C . Metallographic and X-ray examinations established that carbon is dissolved to a maximum of 6 atomic per cent at the eutectic temperature.

B. Summary of Boron-Carbon Binary Results

By means of differential thermal analysis, X-ray, metallographic and microhardness techniques, the phase diagram for the boron-carbon binary system has been established. In some respects the results differ from the published literature. The present findings are believed to be reliable and complete. Eutectic temperatures and liquidus curves have been drawn from

experimental data and several solubility limits have been investigated. The resultant phase diagram is shown in Figure 9. The basic findings may be



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Figure 9. Proposed Boron-Carbon Phase Diagram

summarized as follows:

1. The melting point of boron is $2130 \pm 10^\circ\text{C}$.
2. A eutectic between boron and B_4C occurs at $2080 \pm 20^\circ\text{C}$, a composition between 1 and 2 atomic per cent carbon.
3. A eutectic between B_4C and carbon occurs at $2390 \pm 20^\circ\text{C}$ at a composition of 27 atomic per cent carbon. This eutectic temperature disagrees with the 2150°C reported by Russian authors.³
4. Metastability exists at the eutectic between B_4C and carbon during the cooling of all hypereutectics. It is believed that recrystallization of the carbide is impeded by the relatively high solubility of carbon in B_4C .
5. B_4C is the only carbide which has been positively identified. It melts congruently at $2470 \pm 20^\circ\text{C}$.
6. Boron carbide can dissolve as much as 10 atomic per cent boron above 2000°C . It can dissolve a maximum of 6 atomic per cent carbon at the 2390°C eutectic.
7. The phase region above 90 per cent carbon content was not investigated in this work because of the very high vapor pressures of the components.

IV. SILICON-CARBON BINARY SYSTEMA. Experimental Procedures1. The Eutectic Region

The initial step in this section of the investigation was a study of the silicon-silicon carbide eutectic by the modified classical method of thermal analysis described in Section II B. of this report. Various compositions prepared from 99.999 per cent pure silicon and 99.99 per cent pure silicon carbide, were mixed, placed in a graphite crucible and inductively heated to temperature. Temperatures from 1600 to 2200°C were employed, the values increasing with the carbon content of the samples. Thermal analyses were performed after equilibration.

A definite thermal arrest was observed in the cooling curves of all compositions between 5 and 50 atomic per cent carbon. Analysis of this arrest showed it to be an isothermal between silicon and silicon carbide occurring at $1405 \pm 5^\circ\text{C}$. The melting point of silicon is reported to be $1412 \pm 5^\circ\text{C}$.¹² The melting point value measured in the present work, by means of photoelectric thermal analysis, is $1415 \pm 5^\circ\text{C}$. From this, and the observed arrest temperature, it is concluded that the isothermal arrest between silicon and silicon carbide is the result of a eutectic reaction.

Additional proof of the existence of a eutectic was obtained by means of metallographic and X-ray analyses. Polished microsections, microradiograms and X-ray diffraction patterns of representative samples showed primary silicon carbide clustered around large grains of silicon. Embedded in the silicon were silicon carbide platelets. This phenomenon is characteristic of a eutectic reaction. A quantitative examination of the metallographic data places the composition of the eutectic at less than 5 atomic per cent carbon. Extrapolation of the liquidus to 1405°C gave a eutectic composition of 0.75 ± 0.5 atomic per cent carbon.

2. The Liquidus

The modified classical method of thermal analysis was not sufficiently sensitive to accurately locate the liquidus line. Hence, additional experiments were necessary to determine the solubility of silicon carbide in liquid silicon. This was accomplished by the standard method of crucible melting.

Silicon and excess silicon carbide were placed in graphite crucibles contained in a graphite capsule and heated to temperatures between 1500 and 2600°C in a carbon tube furnace. All samples were subsequently analyzed for carbon and selected specimens were also analyzed by X-ray diffraction to establish the phases present.

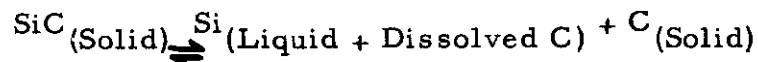
A steeply rising liquidus curve was obtained with the last point indicating an upward break at about 2550°C and 26 atomic per cent carbon.

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The line could not be determined above 2600°C since the excessive vapor pressure of silicon at this temperature would result in prohibitive losses of material.

3. The Peritectic Reaction

While previous investigators¹³ agreed that silicon carbide dissociates at high temperatures, indicating a peritectic reaction, there was some doubt as to the nature of the phases present at the reaction temperature, i. e., two solids and a liquid or two solids and a vapor. For this reason an experiment was carried out in which silicon carbide was photographed at the dissociation temperature by means of a high temperature microscope. Silicon carbide was placed at the focal spot of the arc image furnace and the reaction was simultaneously observed and photographed. An examination of the film showed the existence of a liquid phase. This result indicates the following high temperature reaction:



4. The Peritectic Region

Because of the high temperatures involved in this region, standard methods of thermal analyses were not sufficiently sensitive to accurately locate the peritectic line. This difficulty was overcome by use of the photoelectric method of thermal analysis.

Samples with compositions containing from 50 to 90 atomic per cent carbon were hot-pressed at 7500 psi at temperatures between 2500 and 2600°C. The resultant samples were well compacted, uniform in structure and showed less than 1 per cent variation in composition from the starting materials. Photoelectric thermal analyses of the samples showed a temperature arrest at $2540 \pm 40^\circ\text{C}$ which was attributed to the peritectic reaction. Samples quenched before completion of the reaction showed the separation and agglomeration of two phases which were subsequently identified as a silicon plus silicon carbide phase and a type of graphite usually formed by the decomposition of silicon carbide. This evidence offers further proof of the nature of the reaction observed in the arc image furnace and discussed in the preceding subsection 3.

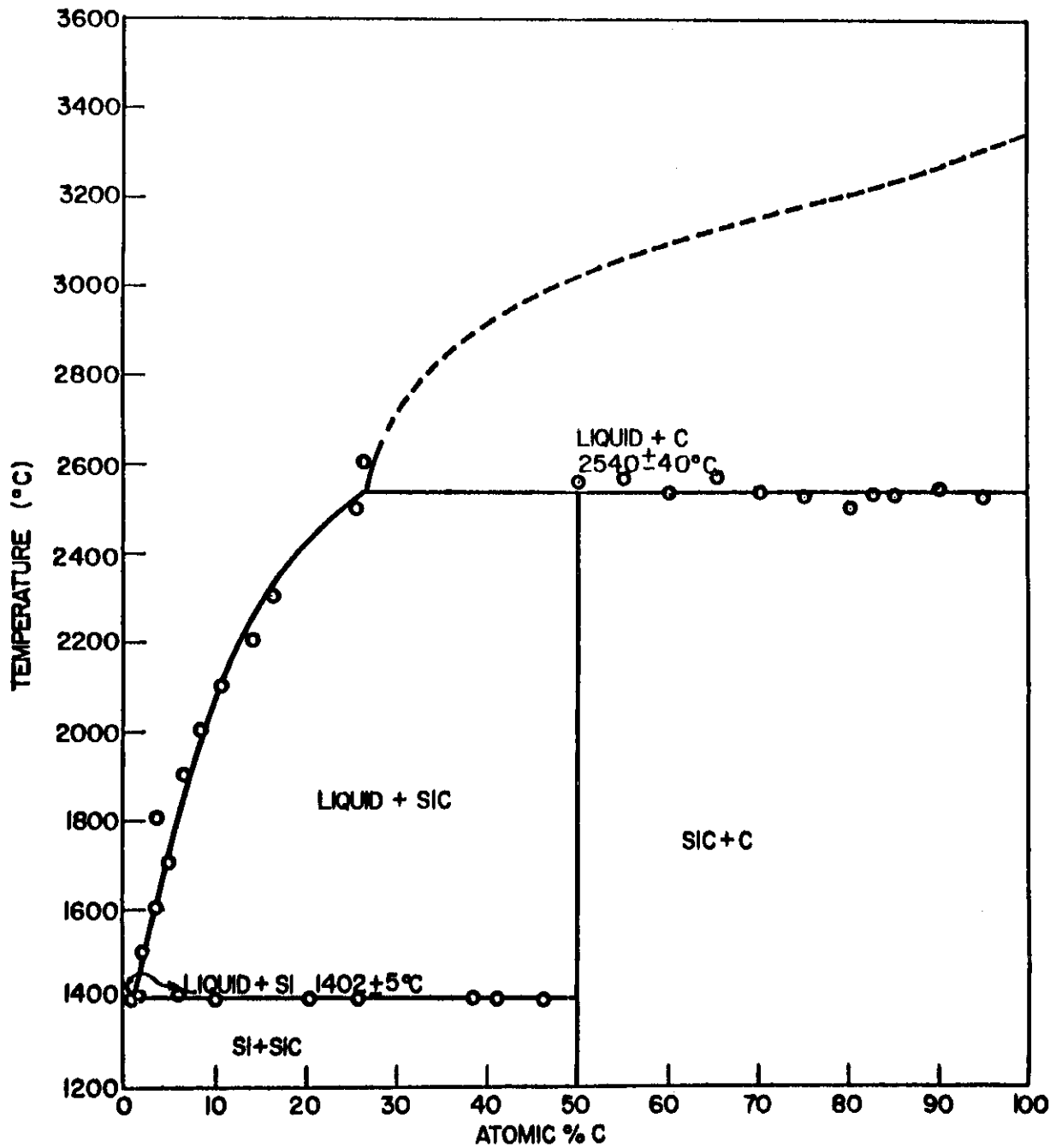
The intersection of the liquidus curve with the isothermal peritectic line leads to a terminal composition of approximately 27 atomic per cent carbon.

B. Summary of Silicon-Carbon Binary Results

Thermal analysis techniques in conjunction with X-ray, metallographic, radiographic and chemical analyses lead to a statement of the silicon-carbon phase diagram which differs from that proposed by other workers.^{12, 13}

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Analysis of possible experimental errors leads to the conclusion that the phase diagram, as presented in Figure 10, is correct. The main features of the



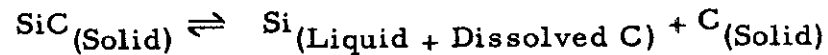
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Figure 10. Proposed Silicon-Carbon Phase Diagram

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silicon-carbon system are these:

1. There is a eutectic between silicon and SiC at $1402 \pm 5^\circ\text{C}$ at a composition of 0.75 ± 0.5 atomic per cent carbon.
2. SiC melts incongruently at 2540°C . The intersection of the liquidus and peritectic lines occurs at 27 atomic per cent carbon.
3. The peritectic reaction involves a liquid rather than a vapor. The reaction has the following form:



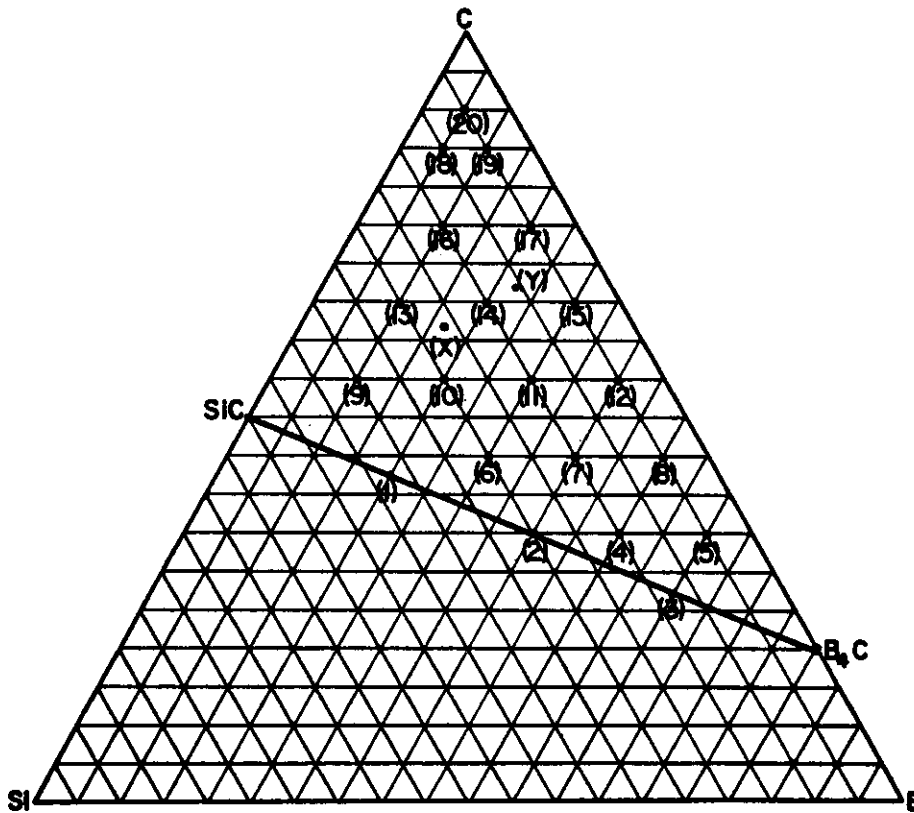
V. SILICON-BORON-CARBON TERNARY SYSTEM

A. Experimental Procedures

1. General Considerations

The terms of the contract indicate a special interest in the study of the high carbon content region of the B-Si-C phase diagram. There are several reasons for this interest, the most important being the general lack of reliable information about this area. Other reasons are concerned with the possibility of undiscovered, refractory compounds and the fact that high temperature apparatus using carbon or graphite components can be used to study such systems without detrimental effects on the reliability of the results.

The investigation of the ternary system has, therefore, been carried out in the interior region of the phase triangle with apices located at the components carbon, boron carbide and silicon carbide. Twenty-two mixtures were selected for analysis from within the defined phase triangle. The compositions chosen are depicted in Figure 11. The line joining SiC and B₄C



R3-1469

Figure 11. Investigation of Mixtures in the Phase Triangle, B₄C-SiC-C

has been arbitrarily drawn to define the area of research. It does not indicate the existence of the pseudobinary system $\text{SiC-B}_4\text{C}$.

2. The Ternary Eutectic

Samples were prepared by hot-pressing silicon carbide, boron carbide and graphite blended in the required proportions. The ideal pressure and temperature for obtaining high densities were found to be 6000 psi and 2200°C, respectively. Since silicon losses caused by the high vapor pressure of silicon above 2000°C could be significant, the percentage weight losses were evaluated for representative samples in the temperature range 2000 to 3000°C. Although the temperature and time dependences were found to be related to the final silicon content, continuous heating at temperatures up to 2200°C produced no significant changes in the sample compositions.

Differential thermal analyses were performed on each of the 22 mixtures. In most cases similar curves were obtained. An endothermic peak was observed at $2250 \pm 20^\circ\text{C}$ during the heating cycle. Since the endothermic peak was both reversible and reproducible, and since X-ray data confirmed the presence of boron carbide, alpha-silicon carbide and carbon, it is apparent that a ternary eutectic exists.

The observation that mixtures (2), (3), and (4)--see Figure 11--had undergone a complete fusion by 2300°C led to the conclusion that the eutectic composition lies within the triangle formed by these three compositions. Detailed studies of the photomicrographs of this region confirmed the presence of the eutectic. Additional samples within the triangle were then investigated. The eutectic composition was thus established to be approximately 15 per cent silicon, 30 per cent carbon and 55 per cent boron in atomic per cent.

B. Summary of Silicon-Boron-Carbon Ternary Results

The results of the study in the region of the ternary system bounded by the phase triangle with apices at carbon, boron carbide and silicon carbide may be summarized as follows:

1. A ternary eutectic between B_4C , SiC and carbon exists at $2250 \pm 20^\circ\text{C}$. The approximate eutectic composition is 15 per cent Si, 30 per cent C and 55 per cent boron in atomic per cent.
2. No evidence of compound formation has been observed in the high carbon region of the ternary system.
3. The ternary eutectic temperature of 2250°C supports the 2390°C eutectic temperature found for the B_4C -carbon binary system. It does not support the 2150°C binary eutectic temperature claimed by the Russian authors.³

The following conclusions are drawn from the experimental work outlined in this report:

1. A proposed phase diagram for the boron-carbon binary system has been established from experimental data. The binary system is characterized by a eutectic between boron and boron carbide, by a stable carbide phase formed by the solid solution of both boron and carbon in boron carbide, and by a eutectic between boron carbide and carbon.
2. A proposed phase diagram for the silicon-carbon binary system has been established from experimental data. The binary system is characterized by a eutectic between silicon and silicon carbide and by a peritectic between silicon carbide and carbon.
3. The phase equilibrium relations for the high carbon region of the silicon-boron-carbon ternary system have been investigated. The system is characterized by a eutectic between carbon, boron carbide and silicon carbide.
4. High temperature differential thermal analysis and photoelectric thermal analysis, used in conjunction with hot-pressing facilities (up to 3000°C at 10,000 psi) and arc image furnace facilities (up to 3800°C) afford a unique opportunity for the establishment of reliable phase equilibria data at high temperatures. These facilities are particularly well suited for the analysis of carbon-rich compositions. Both thermal analysis methods are dynamic, thereby circumventing the need for quenching techniques. When supplemented by chemical, metallographic and X-ray analyses, the methods provide excellent means for clarifying uncertainties in existing experimental data and for providing new data in previously unexplored high temperature areas.

Contrails
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