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The above elements form with each other binary compounds which are very interesting from the point of view of their structure and their chemistry and which are important for technology. The present investigation is concerned with the three-component system and the behavior of the binary compounds occurring in it. Investigations employing various techniques, such as X-ray, chemical analysis, microscopy and fusion experiments showed that no ternary phase exists within the boundary of the ternary system. There is no compound with a higher abrasion capacity than boron carbide. The probable phase field divisions at two isothermic intersections and the fusion isotherms are indicated.
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Non-oxide ceramic materials which are becoming increasingly interesting in technology belong mainly to the boron-carbon-nitrogen-silicon system. They include the compounds SiC, Si₃N₄, B₄C, BN and boron silicide. A precise knowledge of the system and its phases is only partly available, which may be attributed to difficulties arising in research technology.

This article will contribute to supplement the data and specifically it concerns one of the four three-component systems in this field. Reference is made to an earlier work /1/ which dealt with the silicon-carbon-nitrogen system.

1. The Marginal Elements

On one hand because they belong to the same group, and on the other because of the so-called oblique relationship in the periodic system of elements, the three elements exhibit a number of similar chemical and physical properties. They are all metalloids of low density and great hardness (for carbon, diamond; they have a somewhat different, but relatively high melting point, are very inert chemically and form compounds with similar physical and chemical properties, for example the hard and refractory borides, silicides and carbides of the transition metals. They also react with each other, forming extremely hard compounds, which constitute the object of this study.

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*Partial extract from the thesis of G. Leimer, Technical University of Vienna, 1970; Professor Dr. R. Kieffer, Dr. G. Leimer and Lecturer Doctor P. Ettmayer, Institute of Chemical Technology of Inorganic Materials of the Vienna Technical University, A-1060, Vienna, Getreidemarkt 9; Dr. E. Gugel, Research Institute of the Cremer Group, D-8633, Roedenthal, Postfach 44.

**Numbers in the margin indicate pagination in the foreign text.
Carbon

occurs, apart from the amorphous form, in two monotropic forms: as graphite, which crystallizes hexagonally in a particular type of lattice with $a=2.461 \text{ Å}$ and $c=6.708 \text{ Å}$ and as diamond which crystallizes cubically, $/4/$ also with its own type of lattice, with $a=3.567 \text{ Å}$. Its melting point is about 3,800 °C.

Boron

occurs in several allotropeic forms, of which four were identified structurally and specifically two rhombohedric and two tetragonal forms $/2,3/$. Its melting point is 2,150 °C.

Silicon

melts at 1,410 °C and shows no sign of allotropeic conversion above 20 °C. It crystallizes cubically in the diamond type of lattice with $a=5.429 \text{ Å} /4/$.

2. The Marginal Systems

2.1 Silicon-Carbon $/1/$

The system contains a compound with cubic and hexagonal crystallization in many polytypical structural variants, SiC. It has no range of homogeneity and decomposes at 2,760 °C forming the silicon-rich gas phase and graphite. There is no eutectic present, that is, the lowest melting point occurs at 100 % Si.

2.2 Boron-Carbon $/2/$

This system also contains only one compound, $B_4C$, which can take boron instead of carbon in its rhombohedric lattice and form a compound corresponding to $B_{6.5}C$. It melts congruently at about 2,460 °C. Other, often described, compounds are nonexistent. The system has a eutectic on both sides of $B_4C$, one very close to boron at a temperature...
which may be just below the boron melting point, the other at 26 atomic % carbon and 2,400 °C.

2.3 Silicon-Boron

This system was included within the framework of the present investigation (Fig. 1) to provide a foundation for the newer data /5/. Equilibrium systems were established by Knarr /6/ and Samsonov et al /7/. According to the, the system has a eutectic at 19 atomic % boron and about 1,350 °C. On the boron side, the liquidus curve rises sharply up to the melting point of boron. In this region there are three compounds undergoing peritectic fusion.

The compounds, \( \text{SiB}_3 \) and \( \text{SiB}_4 \), often described in the literature, belong to a phase with rhombohedral crystallization, for which the formula \( \text{SiB}_{3+x} /5/ \) may apply. The phase has a corresponding phase of homogeneity and undergoes peritectic decomposition at 1,350 °C into a fusion, rich in silicon, and \( \text{SiB}_6 \) which undergoes orthorhombic crystallization; the latter has no range of homogeneity or only a very small one. It is stable up to 1,900 °C. Finally, the literature also describes compounds with high boron content with the composition from \( \text{SiB}_{12} \) to \( \text{SiB}_{20} \). Presumably, we have here also a compound with corresponding range of homogeneity, which can undergo orthorhombic crystallization and may be given the designation \( \text{SiB}_{12+x} /5/ \).

3. Literature Survey of the B-C-Si System

The first systematic investigations in the B-Si-C system, especially the pseudobinary section of boron carbide-silicon carbide were carried out by Tone /8/. According to the latter, SiC is dissolved by molten boron carbide and in the solidification a solid solution of chemical compounds are formed. SiC decomposes at 2,200 to 2,300 °C but is stabilized by boron carbide. Metallographic investigations showed that boron carbide dissolves 35 % SiC. Tone assumed that the constitution diagram is of a eutectic nature, with eutectic components
of very different hardness. Pulverized alloys in this system show a higher grinding force than SiC. Tone also produced alloys in the boron-carbide-silicon and boron-silicon-carbide systems, but made no statements regarding the structure of the systems.

Tone's data are confirmed by the studies of Kalinina and Shamray /9/. According to these authors, the eutectic lies at 35 weight % SiC with a melting point of 2,070 °C. At this temperature, according to their data, the solid solution of B₄C and SiC consist of 2 to 2.8 % B, 68 % Si and 28 % C, whereas the solution of SiC in B₄C contains 64 to 66 % B, 12 to 13 % Si and 22 to 23 % C.

For grinding purposes Ormont et al /10/ produced alloys in this system by reduction of boron oxide and quartz which they called "borund". The grinding force was much greater than that of boron carbide. From this and from density measurements the conclusion may be drawn that we must be dealing with a ternary compound or a mixed crystal.

The properties of materials consisting of 85 % Si plus 15 % B were studied by Ganlger /11/ and Bobrowski /12/. According to them, the resistance to temperature change as a result of a slight thermal expansion coefficient is better than that of many refractory oxides and silicates.

In patents by Finlay /13/, Abbey /14/ and Lipp /15/, methods are described to produce alloys in the B-Si-C system resistant to changes in temperature and oxidation.

Accountis et al /16/ and Nicholson /17/ showed the high resistance to oxidation of alloys from the B-Si-C system and TiC or ZrC.

On the basis of metallographic studies in the boron carbide-silicon system, Portnoy et al /18/ believed that they had found a new compound
with high grinding strength and high resistance to oxidation up to 1,200 °C. They proposed for it the formula $B_5SiC_2$ with a microhardness of 7,000 km/mm² and describe its production conditions /19/. They also found, in the silicon carbide-boron system a ternary compound of very great hardness, to which they ascribe the formula $B_3SiC_2$. The raw materials mentioned are "very pure powders".

Meerson et al /20/ gave as maximum solubility of B in SiC 7.8 weight % and emphasized that B with C is soluble even in the non-cubic SiC forms. They indicated 9.7 weight percent as maximum solubility of Si in $B_4C$. Alloys in the $B_4C$-SiC system are assumed to be bi-phased and consist of solid solutions of $B_4C$ and SiC, presumably with extreme hardnesses, which should range up to 8,500 kp/mm² for boron carbide. Dispersion hardening by formation of submicroscopic separation is considered responsible for the "superhardness". Meerson et al reported, that metallographic analyses in the central region of the ternary system show mostly bi-phase (SiC, $B_4C$) compounds and three-phased compounds only for excessive silicon. They were unable to confirm the formation of ternary compounds.

![Figure 1: Position of the studied specimens.](image-url)
Furthermore, Meerson et al /21,22/ reported on the production of SiC and alloys with boron through the gas phase. Metallographic and X-ray studies showed accordingly a solubility of 13.2 weight % of boron in β-SiC.

Meerson et al /23/ reported moreover on alloys in the B₄C-B₄Si system and show a continuous formation of mixed crystals with extreme hardness of 7,100 kp/mm² for 60 mol % B₄C. The alloys should be highly resistant to oxidation because of the formation of a protective layer of borosilicate.

Dokukina et al /24/ also studied alloys in the boron-silicon-carbon system by means of chemical, metallographic and X-ray methods and found no evidence of the formation of ternary compounds.

In the study of the phase equilibrium in the pseudo-binary B₄C-SiC system, Secrist /25/ also arrived at the conclusion that he was dealing with a eutectic, of composition of 70 weight % B₄C and 30 weight % SiC at 2,300 ± 20 °C. At this temperature the mutual solubility is < 2 weight %. He considered that the ratio of α-SiC to β-SiC depends on the content of boron carbide.

In a reaction of quartz and boric acid with carbon in the electrical arc lamp, Lipp and Roeder /15,26/ obtained a compound which has a very extended boron carbide lattice. On the basis of the chemical analyses they assumed that the carbon of the B₁₂C₃ was replaced not only by silicon, but also by boron in accordance with the formula B₁₂(C,Si,B)₃. Besides this, they found another compound whose X-ray picture was not consistent with any of the compounds occurring with certainty in this system. The composition could not be determined since there were no suitable methods of separation.

Shaffer /27/ found that the solubility of boron in α-SiC from 2,450 to 2,500 °C < 0.2 weight %, whereas the solubility of silicon in
boron carbide is considerable. α-SiC saturated with boron and a phase of formula $B_{12}(C, Si, B)_3$ are in equilibrium with the fusion at the eutectic temperature of $2,245 \degree C$. The eutectic occurs at 30 mol % SiC and 70 mol % boron carbide. No phase harder than $B_4C$ was found.

Niewmisky et al /28/ produced, both through the gas phase and by powder metallurgy, compounds with 74.5 weight % B, 19.9 weight % C and 5.7 weight % Si, which all have properties of boron carbide and may be considered as solution of silicon in boron carbide.

4. Our Own Investigations

Figure 1 shows the position of all the specimens studied in the three-component system. In the Si-C marginal system no investigations were carried out; here, results of an earlier study /1/ were evaluated. The results of the experiments in the C-B system were already communicated in /2/.

4.1 Materials Used

Boron: H. C. Starck Company, Berlin, grain size $< 38 \mu m$; 97.5 % B; Fe, O each $< 1 \%$. Si, C each $< 0.15 \%$; Mg, N each $< 0.05 \%$.

Silicon: Association for Electrometallurgy, Nuernberg; grain size $< 75 \mu m$; $> 99.7 \%$; main impurities: Fe, Al; traces of Mg, Mn, Cu and Sn.

Carbon: Acetylene black; ash content $< 0.01 \%$.

Boron carbide: Electric Melting Works of Kempten; grain size $< 5 \mu m$; impurities: Fe, Si, Al each 0.1 percent; Ca, Na each 0.01 %.

Silicon carbide: Electric Melting Works of Kempten; approximately 99.5 % SiC; grain size $< 5 \mu m$. 

4.2 Methods of Study

4.21 Phase Analysis

X-ray goniometer equipment, CuKα-radiation. The samples were finely pulverized in a hard metal or boron carbide mortar and applied with acetone uniformly on a glass specimen carrier.

4.22 Chemical Analysis

The boron and carbon analysis took place according to the method described in /2/. To determine Si, the electron beam microanalyzer was used. The concentration was obtained by comparison with silicon hexaboride as standard. The percentage contents obtained are averages corrected by absorption according to the method of Philibert /29/ from several point measurements.

4.23 Microscopic Investigation

Examination by optical microscopy of slides whose production was described in /2/.

4.24 Determination of the Melting Point

Direct observation of a pyramid-shaped body in a high temperature furnace, heated with tungsten or carbon resistance heating conductors /2,30/.

4.25 Hardness and Grinding Capacity

The microhardness (Vickers, 50 and 100 g) was determined. Moreover the grinding hardness was studied according to equipment described in /31/. The criterion used for the grinding hardness was the abrasion of a hard metal cutting disk in a suspension of 10 g of the test substance<75 μm in 30 g glycerine. The speed of revolution of the disk was 60 rpm, while the cutting disks which were loaded with 300 g were moved back and forth radially over 6 cm on the disk in 75 s.
4.3 Results of the Investigations

4.3.1 Pseudobinary $B_4C$-SiC System

Mixtures with compositions varying each time by 10 percent were exposed to hot compression at about 2,000 °C and under a pressure of 100 kp/cm$^2$, and tempered in a carbon tube furnace under 400 mm argon pressure for 17 hours at 1,800 °C; for 10 hours at 2,000 °C and for 4 hours at 2,100 °C. Independently of the sintering conditions, X-ray analysis gave in all cases the two phases SiC and $B_4C$. The interference (001 for the hexagonal case, 333 for the cubic case) occurring for all polytypical SiC systems at $2\theta=133.5$ degrees C was constant to within ±0.2° C, so that the incorporation of boron in the SiC lattice is unlikely.

The lattice constants of the $B_4C$ show a relatively wide spread between $a_0=5.58$ and 5.61 Å and $c_0=11.99$ and 12.11 Å. The lower values tend to occur with increasing sintering temperature and increasing SiC content in the initial mixture. Since the lattice constants lie below the minimum values of $a=5.595$ and $c=12.05$ /2/ found for the B-C system, and the lower values tend to occur on the SiC side, the conclusion may be drawn that a certain formation of mixed crystals exists (SiC in $B_4C$), which was confirmed later. Such a solubility was excluded in the more recent literature /25/, but considered possible in the older works /9/.

Fig. 2 shows the result of the determination of the melting point as compared with the literature data /25/. According to it, the eutectic is somewhat closer to $B_4C$ (about 64 mol % $B_4C$) and at a lower temperature (about 2,240 °C).
Fig. 2: Liquidus curve in $\text{B}_4\text{C}$-SiC system. ⭕ C tube furnace; ○ W tube furnace.

Fig. 3: Grinding force of various materials in the $\text{B}_4\text{C}$-SiC system and boron. 1- $\text{B}_4\text{C}$; 2- 60 mol % $\text{B}_4\text{C}$ and 40 mol % SiC; 3- boron (99.8 %); 4- 80 mol % $\text{B}_4\text{C}$ and 20 mol % SiC; 5- SiC; 6- 40 mol % $\text{B}_4\text{C}$ and 60 mol % SiC. Key: (1) abrasion; (2) time.

On specimens sintered at 1,800 °C etching tests were conducted, which showed an absolute resistance to cold and hot HF, HNO$_3$, chromosulfuric acid, chlorine and bromine vapors; as well as against alkaline solutions and NaOH fusion. Samples rich in SiC may be etched electrolytically with aqueous oxalic acid, on the other hand chromic acid plus acetic acid /32/ showed no effect. The most favorable substances proved to be soda and borax fusion, and in particular, the thermal etching at 800 °C in the air, to obtain good grinding pictures.

The ground surfaces showed a uniform grain structure. Measurements of microhardnesses gave the values common for SiC and $\text{B}_4\text{C}$ from 3,100 to 3,300 and from 5,400 to 6,000 kp/mm$^2$. Investigations by microprobes showed the uniform distribution of the Si.
The B$_4$C-SiC eutectic could have a favorable grinding force because of the higher viscosity to be expected. Therefore grinding experiments were conducted according to the above-described method, which gave the results shown in Fig. 3.

Surprisingly the most pure boron provided to be superior even to pure boron carbide. SiC proved to be most unfavorable. Against expectation, there was a clear classification according to the SiC-B$_4$C proportions. In the B$_4$C-SiC system there is no specimen with higher grinding force than B$_4$C.

4.32 Pseudobinary B$_4$C-Si System

Investigations were conducted on specimens undergoing hot compression, and those which were hot compressed and tempered for 8 hours at 1,800 °C, or 6 hours at 2,000 °C in a carbon tube furnace in argon atmosphere. It was possible to establish B$_4$C and SiC by X-rays in all cases, on the other hand Si was still present only in the untempered specimens. Microscopic examination showed the additional stoichiometrically required presence of boron silicides.

A solubility of 2.16 weight % and 4.3 atomic % of Si in B$_4$C was established by means of the microprobe, from the pulse rates corrected according to the method of Philibert /29/; unlike the values of 5.7 /28/ and 9.7 weight % /20/ previously given in the literature.

Studies of the melting point were conducted also in this system on samples were were previously sintered, and whose results fit into the general representation of the three-component system.

4.33 Pseudobinary B-SiC System

X-ray phase analysis on hot compressed samples sintered for 12 hours at 2,000 °C at a vacuum of 10$^{-2}$ Torr gave the two phases SiC and B$_4$C for all mixtures. Here, too, boron silicide must have formed.
To determine the solubility of boron in SiC, in accordance with the data from the study of the B₄C-Si system, B₄C was kept at 1,800 °C in a silicon fusion for 15 hours at 10 atmospheres of argon. Subsequently Si was removed chemically and in the residue, consisting of only β-SiC, 4.9 to 5.2 weight % or 16.8 atomic % boron was determined (that is 9.6 % as B₄C or 6.4 % as SiB₄).

This value is very high as compared with Shaffer's /27/. On the other hand Kalinina et al /9/ and Meerson /21,22/ specify considerable solubility of boron in β-SiC.

The results of the determinations of the melting point are used once again for the general representation of the three-component systems, just like that of the following series of samples.

![Fig. 4: Fusion isotherms in B-C-Si system.](image)

4.34 Pseudobinary B₄C-SiB₄ System

The initial powders used were boron, silicon and carbon, which were made into tablets under cold compression at 1 t/cm2 and, before the heat treatment just below the melting point of Si, underwent heat treatment for 10 hours in argon with subsequent short-term heating to 2,300 °C, so that partly reguline specimens were obtained. X-ray phase analysis of the samples, tempered subsequently for 9 hours at 1,900 °C, gave B₄C in all cases, and in addition, for the initial compounds with 10 to
80% SiB₄, SiC as a second phase; and for the samples with 80 to 90% SiB₄, some SiB₆ as third or second phase. It was impossible to find a ternary compound. The continuous formation of mixed crystals mentioned in /23,34-37/ occurs below 1,350°C if at all. Besides boron carbide, SiC also occurs, SiB₄₋ₓ decomposes above 1,350°C into SiB₆ and Si, which reacts with the B₄C to form SiC. It was impossible to establish a change in the lattice parameters of B₄C in equilibrium with the silicon-boron alloys.

4.35 The Three-Component B-C-Si System

The initial components for the investigations were once again boron, carbon and silicon powder which were compressed into tablets under a pressure of 1 t/cm² and subsequently underwent preliminary sintering for 5 hours at 1,300°C under vacuum in a carbon tube furnace, both for X-ray determinations and for determining the melting point.

The heat treatment at 1,700 and 1,900°C, each for 15 hours, took place in an autoclave heated with a carbon tube under slight excess argon pressure. The support used was heated BN; moreover the samples were surrounded for protection with Mo foil without contact, to prevent the absorption of C.

The phases occurring were Si, SiC, B₄C, SiB₆, SiB₁₂₋ₓ and C. Ternary phases did not occur also in the compositions indicated in the literature /18,19/. Nor could they be established in the enamelled beads after the determination of the melting point. In the silicon-rich region, it was possible to find by microscopic examinations undissolved SiC crystals in the enamelled beads. Therefore, in these cases, the real melting point must occur somewhat higher. The marginal Si-C system also shows that the melting point must increase sharply on the silicon side when even small amounts of carbon are added.
When all the melting points determined in this system are considered, taking into account the marginal systems and possible sources of errors, we arrive at the fusion isotherms shown in Fig. 4.

According to the latter, the ternary eutectic is very close to the binary eutectic of the B-Si system.

The fusion channel coming from the B₄C-SiC eutectic runs near the B-Si two-component system. It was impossible to clarify, within the range of measurement precision, whether the melting channel occurs in the sense of a reaction.

\[
\text{Fusion} + B_4C \rightleftharpoons \text{SiC} + \text{SiB}_6 \quad \text{or in the sense of a reaction} \\
B_4C + \text{fusion} \rightleftharpoons \text{SiC} + \text{SiB}_{12+x}.
\]

The microscopic examination of the samples could not clarify this question clearly either, because in such systems the phenomena which are connected to the solidification of oversaturated fusions, are observed frequently (eutectics, peritectic borders could not be found).

Finally Figs. 5 and 6 also show the phase field distributions for two isotherm sections in this system, which are likely on the basis of X-ray, microscopic, analytic and fusion technology investigations.

As may be expected from the comparison of the thermodynamic stability of SiC and B₄C, when the temperatures are not too high, Si fusions are in equilibrium with SiC, but not with B₄C. The ternary phases found by different authors could not be detected in the studied temperature ranges. The solubility of Si in B₄C found with the microprobe, is consistent in order of magnitude with the data of other authors. The powder diagrams of alloys in the range of this solid solution of B₄C + Si did not give any evidence of the existence of a phase with the nature of a ternary compound. But one cannot exclude the possibility that Si is incorporated in the B₄C lattice not statistically, but in certain
positions. This phenomenon is observed most often in the incorporation of foreign atoms in boride lattices /38,39/. The solubility of B in SiC could not be detected by X-rays and the electron beam microprobe could not be used to determine the boron content, but it may be very small. The range of homogeneity of the SiB₆ phase with reference to the three components was not studied in greater detail, nor was the solubility of carbon in SiB₁₂⁺ₓ.

![Diagram](image)

Fig. 5: Distribution of the phase fields in the B-C-Si system at 1,700 °C.  
Fig. 6: Distribution of the phase fields in the B-C-Si system at 1,900 °C.

5. Discussion

Apart from very doubtful data by a Russian researcher, little may be found in the literature regarding studies of the three-component system. This is due to the great difficulties arising in the study of the phase equilibria in systems with nonmetal hard materials.

In the solid state there is mostly only a slight tendency to lattice diffusion, so that the equilibria can be adjusted in most cases only with great difficulty. Therefore it is hard, only on the basis of X-ray and microscopic data, to make statements regarding the position of a phase or to find the distributions of the phase fields.

The X-ray diffraction photographs of several phases are so rich in lines, that it is often impossible to establish the presence of small amounts of other phases.
Further difficulties, especially in the system studied here, are raised by certain properties of the occurring phases. The high melting boron carbide and boron phases occur, along with the low-melting silicon, carbon which does not melt at normal temperature, the silico-borides which decompose under fusion and the silicon carbide which dissociates into vapor and solid. Moreover, for the high temperatures needed for studying the system, silicon has a high vapor pressure, so that shifts in the composition may occur easily. The components boron, carbon and silicon themselves are very reactive at high temperatures and there are hardly any inert sample holding devices. The results or the new phenomena occurring must therefore be interpreted very prudently.

Because of the extraordinary hardness of the substances occurring in this system, the production of the ground phases needed for the metallographic examination is also complicated. Automatic grinding and polishing devices such as diamonds are absolutely necessary as means of grinding and polishing.

For studies in the three-component region, it was primarily necessary to study the marginal systems, regarding which there is still much lack of clarity in spite of repeated studies, especially of the boron-carbon /2/ and boron-silicon systems. The carbon-silicon system /1/ has not been clarified specifically to its smallest details, but the fact that, apart from carbon and silicon, only the compound SiC occurs was sufficient for the purpose of studying the three-component material.

X-ray, microscopic, chemical and fusion technology methods were used to study the system. The results of the investigation may be summarized briefly as follows: in the B-Si system, the SiB\(_{3+x}\), SiB\(_6\), and SiB\(_{12+x}\) phases were confirmed /5/, while in the last case we have \(x \geq 8\).

In the three-component region it was impossible to find any evidence of a ternary compound. Because of the overall results; a phase distri-
bution was conducted for the isothermic sections of 1,700 and 1,900 °C. From fusion technology investigations, insofar as total fusion was obtained, it was possible to establish the fusion isotherms with the fusion channels.

The determination of the solubilities raised difficulties, since the ordinary methods failed and it is hardly possible to achieve the separation needed for a chemical analysis. But the values range generally between the limits given by other authors, and are not too high. A solution of this problem could certainly be achieved only by means of a microprobe able to analyze all three elements.

Contrary to the Russian studies, measurements of microhardness showed no harder phase than that of boron carbide. The grinding force of B₄C is, apart from that of boron, higher than all the other alloys in the three-component system.

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