PHYSICOCHEMICAL INVESTIGATION OF THE
SiC-B4C SECTION OF THE Si-B-C SYSTEM

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-USSR-
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PHYSICOCHEMICAL INVESTIGATION OF THE SI-C-B\textsubscript{4}C SECTION OF THE SI-B-C SYSTEM

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[Following is a translation of the article "Fiziko-khimicheskie issledovaniya rascheta SiC-B\textsubscript{4}C sistema Si-B-C" by A.A. Kalinina and P.I. Shamray in Doklady Institute Metalurgii imeni A.A. Baykova (Works of the Institute of Metallurgy imeni A.A. Baykova), No 5, Production Methods of Research, Moscow, 1960, pages 151-155.]

It is generally known that compounds of silicon and boron with carbon (silicon and boron carbides) are widely used by industry as refractory and wear-resisting abrasive materials.

Boron carbide is at present employed in the nuclear industry, and silicon carbide is acquiring great importance as a base for the manufacture of heat-resistant parts of gas-turbine and jet-plane motors. Articles without binder (self-sintering) (1) and with a binder of silicon nitride or boron nitride or carbide are made of it (2). However, these compounds are not the best materials of the Si-B-C system for these areas of use. This is to be explained by the inadequate study made of the Si-C, Si-B, B-C and especially the Si-B-C systems.

Of these dual systems, the B-C system has been studied most thoroughly (3-12).

In 1953, Post, Glazer and Moskovets, on the basis of an X-ray examination, and also as a result of the study of the electric resistance and specific weight of boron and carbon alloys conjectured the presence in the system of solid solutions of carbon in boron. In the investigations made by Zhdanov, Zhuravlev and Zevin in 1953, and especially in the works of Zhdanov, Zhuravlev and Samsonov (1951) it was assumed that B\textsubscript{4}C dissolves boron, the solubility being
being realized through the substitution of boron for the
carbon atoms (central) of the linear chain C-C-C-B\textsubscript{12}C\textsubscript{3} with
formation of boron carbide of the composition B\textsubscript{13}C\textsubscript{2} in case
of full substitution.

As a result of investigation (13) the first experiment in
constructing a phase diagram of this system was proposed.
However, the main questions relating to this diagram remained
unsolved. There was no definitive solution of the questions
of the amount and composition of the compounds of the system,
or the nature and limits of the solid solutions based on
these compounds.

The B-Si and Si-C systems have been poorly studied. The
small amount of data in the literature and their contradic-
toriness are to be explained by the immense difficulties
encountered in making such investigations.

The high melting points of the refractory metals and the
alloys, the consequent difficulties due to volatilization
of the several components and the alteration of the composi-
tions considerably complicate the methods of experimenta-
tion and render difficult the application of N.S. Kurnakov's
thermal analysis in its classic form.

The present work was done for the purpose of studying the
Si-C-B\textsubscript{4}C section of the triple system Si-B-C. In preparing
the samples, a press oven of the design worked out at the
VNIIASH (14) was used (Fig. 1). This permits samples with
\% porosity not exceeding 10\% to be obtained by the hot-press-
ing method. Powdered silicon, boron and, in addition, sil-
cicon and boron carbides were used as the basic materials.

The amorphous boron obtained magnesium-thermally, con-
tained 95.5\% B. The silicon content in the silicon powder
was 99.7\%. The quantity of admixtures in the silicon and
boron carbide powders did not exceed 1\%. In view of the fact
that, owing to the volatilization of silicon and boron, sin-
tering produced a change in the composition of the alloy,
the prescribed composition was insured by the choice of charge.
Fig. 1. Experimental Press Oven:

1. water-cooled body; 2. roof with water cooling; 3. carbon heater; 4. hood for pumping out gases; 5. lever; 6. pillar for fastening lever; 7. carbon punch; 8. sump; 9. inspection window; 10. weight.

Legend: A - gas exhaust.
The samples were prepared in the press oven by a double sintering of the mixtures of the initial components with subsequent roasting of the obtained samples at 2000° for 15 minutes and hardening. In this matter, 21 mixtures were sintered, with 5-10 samples of each composition. The compositions of the alloys studied are shown on the concentration triangle (Fig. 2). Investigation of the samples obtained was done by physicochemical analysis methods. The thermal analysis of the alloys was done by two methods. The first consisted in determining the melting point of the alloys from their deformation. For this purpose, the finished sample in the form of a hollow ring was placed in the heating tube of the press oven, forced down to the lower contact by pressing the lever and was heated by passing a current through it.

Fig. 2. Concentration Triangle of Compositions:
1. compositions; 2. saturated solutions $\alpha$ and $\beta$, secreted chemically; 3. solid $\alpha$-solution; eutectic; 5. productional samples; 6. Gangler data.

Legend: $A = \text{weight}$

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Fig. 3. Diagram of state of SiC-B$_4$C section.

Legend: $A = \{\text{Ridgeway}\}$
$B = \{\text{Meyerson}\}$
Fig. 4. Eutectics: 35--36% SiC, 64--65% B$_4$C

Fig. 5. Solid $\alpha$-solution: 68% Si, 2--3% B, 20% C
Fig. 6. Solid β-Solution: 12--15% Si, 64--66% B, 22--23% C

At the moment when melting began there was a deformation of the sample and a lowering of the lever. The change in the temperature of the sample was determined by an optical pyrometer through the aperture in the heating tube. Continuous measurement of the temperature every 15 seconds permitted us to detect the temperature halt caused by the melting of the alloys. Then the melted samples were subjected to examination in slides. In this way, the melting point of the crystals of the primary phase was established.

The microstructure was studied on polished, etched slides by looking through them in reflected light in metallic microscope MIM-6. The electric resistance was measured with a Wheatstone bridge. The phase X-ray analysis was made by the Debye powder method, and the Zagg reverse reflection method was used in determining the lattice parameters. The phase chemical analysis was based on a selective oxidation of the alloys with subsequent dissolving of the oxidized phase in water acidified with hydrochloric acid.

The investigations permitted us to establish the character of the processes taking place in the interaction of silicon, boron and carbon in the Si--B=C section of the Si B=C system and to construct a diagram of the state of
this section (Fig. 3).

It follows from an examination of the diagram that the SiC-B$_4$C system contains a dual eutectic of the composition 35-36% SiC and 64-65% B$_4$C with a melting point of 2070° ± 20° (Fig. 4). The eutectic composition found confirms Tournier's data obtained by him when using other initial materials (3). The presence of eutectic is observed in the alloys in the composition intervals between 17 and 95% silicon carbide.

In the areas adjacent to boron and silicon carbides lie the fields of the solid α- and β-solutions (Figs. 5 and 6). The solid solutions possess a higher electric resistance than the initial silicon and boron carbides a polygonal structure and altered lattice parameters of the basic initial components.

The supposition that boron carbide can form solid solutions with boron was expressed by Ridgway as early as 1934. Later, this was confirmed by a number of other investigators (Allen, Zhdanov, Sevastiyanov and others). The physico-chemical investigation showed that in the triple system Si-B-C the area of homogeneity of the alloys in the SiC-B$_4$C section extends to an 11-12% (by weight) Si content on the B$_4$C side and to 3% B on the SiC side. In alloys with a silicon content of over 50% by weight, the silicon carbide forming the solid α-solution corresponds in structure to the SiC$_{11}$ of hexagonal modification. In alloys containing less than 50% silicon by weight, the silicon carbide crystallizes in cubic form (β-SiC). The maximum concentration of solid α- and β-solutions for the above cited experimental conditions was determined by phase chemical analysis. The solid α-solution of the saturated concentration has the composition: 68% Si, 2-3% B, 29% C; the solid β-solution: 12-13% Si, 64-66% B, 22-23% C. These data permit one to regard the SiC-B$_4$C section of the Si-B-C system as quasibinary, representing a system of solid α- and β-solutions with limited solubility.

CONCLUSIONS

1. The SiC-B$_4$C section of the Si-B-C system is quasibinary and formed by solid solutions with limited solubility: the solid solution α on the basis of a SiC compound and a α-solid solution on the basis of a B$_4$C compound, forming a eutectic between them when the SiC content is 35-36% and the B$_4$C content 64-65% with a melting point of 2070° ± 20°.
2. at 2070° the $\beta$-solid solution on the basis of a $B_4C$ compound extends in the section to a concentration of 15-17% $SiC$ ($B = 64-66\%$, $Si = 12-13\%$ and $C = 22-23\%$); the solid solution $\alpha$ on a $SiC$ base is considerably lower. In it there is only 4-5% $B_4C$ ($B = 2-2.5\%$, $Si = 63\%$, $C = 20\%$).

LITERATURE

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