

X-Ray Investigations on Me-Si-B Systems

(Me = Mn, Fe, Co)

I. Some Features of the Co-Si-B System at 1 000° C. Intermediate Phases in the Co-Si-B and Fe-Si-B Systems

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Some features of the Co-Si-B system at 1000°C have been determined with X-ray methods. It is found that the homogeneity ranges of the intermediate phases are small. The crystal structure of the ternary phase $\text{Co}_{4.7}\text{Si}_2\text{B}$ (isomorphous with $\text{Fe}_{\sim 4.7}\text{Si}_2\text{B}$) has been established from single crystal data and is closely related to the $\text{W}_3\text{Si}_3(T1)$ structure.

The Fe-Si-B system contains several ternary phases, the most remarkable of which is a cementite (Fe_3C) type phase, while the crystal structures of Fe_2SiB_2 and Mn_2SiB_2 are shown to be of the $\text{Cr}_2\text{B}_2(T2)$ type.

Since there are many similarities in the crystal chemistry of the borides and silicides of the transition metals, it seems very likely that a systematic study of the intermediate phases of Me-Si-B systems will give valuable information about both groups of compounds.

Investigations on Me-Si-B systems have been made by Nowotny and co-workers^{1,2} who have been particularly interested in the Me_5X_3 phases ($\text{X} = \text{B}, \text{Si}$). At this Institute studies on Me-Si-B systems with Me = manganese, iron, and cobalt are in progress. This paper will deal with the Co-Si-B system and will also give some preliminary information about the intermediate phases of the Fe-Si-B and Mn-Si-B systems. In a second paper a more detailed account of the Fe-Si-B system will be given.

Our primary interest has been the crystal structures of the intermediate phases, and our investigations have been carried out chiefly by means of X-ray methods. However, no accurate determinations of the phase diagrams have been made. Before proceeding to the results of the present study of the Co-Si-B system, some reference to previous work on the Co-B and Co-Si systems will be given.

Table 1. Crystallographic data on intermediate phases in the Co-Si and Co-B systems.

	Lattice parameters (in Å)			Structure type	Ref.
	<i>a</i>	<i>b</i>	<i>c</i>		
Co ₂ B	4.408	5.225	6.629	<i>D</i> O ₁₁ (Fe ₃ C)	4
Co ₂ B	5.016		4.220	<i>C</i> 16 (CuAl ₂)	3
CoB	5.253	3.043	3.956	<i>B</i> 27 (FeB)	3
Co ₂ Si	4.918	3.737	7.109	<i>C</i> 23 (PbCl ₂)	5,6
CoSi	4.447			<i>B</i> 20 (FeSi)	7
CoSi ₂	5.366			<i>C</i> 1 (CaF ₂)	8,9

PREVIOUS WORK ON THE Co-B and Co-Si SYSTEMS

Reported crystallographic data on the intermediate phases of the binary Co-Si and Co-B systems are collected in Table 1. Bjurström³ determined the structures of Co₂B and CoB to be of the *C* 16 (CuAl₂) and *B* 27 (FeB) types, respectively. Co₂B was recently discovered by Rundqvist^{4,5}. Borén⁶ determined the unit cell dimensions of Co₂Si and CoSi and found that the structure of the latter was of the *B* 20 (FeSi) type. Borén *et al.*⁷ also gave a structure for Co₂Si, and this has recently been corrected by Geller⁸. The correct Co₂Si structure, which Geller⁸ has shown to be isomorphous with δ-Ni₂Si¹⁰, has been pointed out⁹ to be indeed that of the *C* 23 (PbCl₂) type. Finally, CoSi₂ is of the *C* 1 type (Schubert and Pfisterer¹¹, Bertaut and Blum¹²). A high-temperature modification of Co₂Si has been reported^{13,14}, as well as a phase with the composition Co₂Si^{13,14}. None of these phases is stable below 1170°C and no crystallographic constants have been published for them. The solid solubility of silicon in cobalt has not been determined accurately but Hashimoto¹⁴ reported a solubility of about 10 at % Si at 1000°C.

No studies on ternary Co-Si-B alloys have been noted in the literature.

EXPERIMENTAL

The following chemicals were used:

Cobalt (99.2 %, containing 0.45 % Ni) kindly donated by Société Générale Metallurgique de Hoboken.

Silicon (99.9 %) obtained from Pechiney & Cie, Paris.

Boron (99 %) kindly donated by Borax Consolidated Ltd., London.

When a rough knowledge of the system had been obtained from arc melted and sintered alloys, 2–3 g samples of suitable compositions were prepared by sintering pressed pellets of the elements in evacuated silica tubes at 1000°C. After four days, each sample was crushed, thoroughly mixed, then sintered for another two days and finally quenched in oil. After this treatment, all samples gave very sharp powder diffraction lines and the l.p. (lattice parameters) of the phases in a three phase region were found to be the same in different samples from this region. Therefore, it was concluded that equilibrium had been attained.

The powder photographs were taken in a Guinier-type powder camera using CrK α radiation and employing CaF₂ ($\alpha = 5.4630$ Å at 21°C) as a calibration standard. The l.p. are estimated to be accurate to ± 0.03 %.

The oxygen content (weight percent) of two 2–3 g samples, determined by a vacuum fusion technique, was found to be 0.211 and 0.212, respectively. Since the composition of all samples was approximately Co₂Si₂B and the method of preparation was the same, the oxygen content of all samples has been assumed to be 0.21 % by weight. The analyses for cobalt and boron were carried out by Dr. L. Gustafsson at the Analytical Department of this Institute. For the cobalt analyses, the samples were dissolved in a mixture of nitric and hydrofluoric acid. The hydrofluoric acid was then removed by evaporating with sulfuric acid and the cobalt content (including traces of other heavy metals) was subsequently determined by titration with EDTA. For the boron determinations, the samples were first dissolved in dilute hydrochloric acid plus chlorine (0.3 g samples were

completely dissolved within 7–10 h). Cobalt was removed from the acid solution by passing the solution through a cationic exchanger (Dowex 50) and the cobalt-free solution was then neutralized to pH 6.80. After addition of mannitol, the solution was again titrated to pH 6.80. The results of the chemical analyses are given below (weight %).

Sample	Co *	B	Si as difference	Σ (see text)
1	79.75 \pm 0.17	2.99 \pm 0.20	16.7	99.4
2	77.51	4.61	17.3	99.4
4	83.30	5.33	10.8	99.4
6	82.45	3.34	13.6	99.4
9	79.58	2.13	17.7	99.4

* Traces of nickel and iron computed as cobalt are included in the values of this*column.

The accuracy of the cobalt analyses is estimated to be $\pm 0.2\%$, and that of the boron analyses $\pm 0.4\%$. The impurities of the original chemicals (except oxygen and nickel) amounted to about 0.4% by weight. By adding 0.2% oxygen, a total of 0.6% impurities is obtained. The silicon content has been obtained as the difference between 99.4% and the sum of the cobalt and boron contents. This procedure was unsatisfactory, but any direct analysis for silicon would not give more reliable results unless much larger samples were available. However, very accurate analytical figures are of questionable value since the form in which oxygen is present in the sample is unknown. Oxygen may be bound to boron and silicon, and this would slightly reduce the amounts of the latter elements which actually participate in the Co-Si-B equilibria. Therefore, an alloy for which the analytical composition has been found to be $\text{Co}_{4.60}\text{Si}_2\text{B}$ plus traces of oxygen should rather be written $\text{Co}_{4.65}\text{Si}_2\text{B}$ plus traces of B_2O_3 and SiO_2 . In addition, a spectrographic analysis of one sample revealed the presence of traces of nickel and iron. Small amounts of these metals can probably substitute for cobalt in the different alloys and therefore should be added to the cobalt content.

The densities of two samples which contained 80–90% of the ternary phase $\text{Co}_{4.7}\text{Si}_2\text{B}$ were determined by weighing in air and benzene. The amounts of other phases present in the samples were estimated from the powder photographs, while the density of the ternary phase could be calculated. The values were reproducible to within 0.5% and a test of the method on some known substances proved satisfactory. The results of the determination of the densities are given below:

	Density of sample	Calculated density of $\text{Co}_{4.7}\text{Si}_2\text{B}$
Sample 36 (arc melted, contained $\text{Co}_{4.7}\text{Si}_2\text{B} + \text{CoB}$)	7.27 g/cm ³	7.26 g/cm ³
Sample 10 (sintered, contained $\text{Co}_{4.7}\text{Si}_2\text{B} + \text{Co}_2\text{B} + \text{Co}_2\text{Si}$)	7.21 g/cm ³	7.16 g/cm ³
	Average	7.21 g/cm ³

A small single crystal of the $\text{Co}_{4.7}\text{Si}_2\text{B}$ phase was picked out of an arc melted alloy that contained $\text{Co}_{4.7}\text{Si}_2\text{B}$ and small amounts of CoB. The l.p. of $\text{Co}_{4.7}\text{Si}_2\text{B}$ of this alloy were found to be $a = 8.615 \text{ \AA}$ and $c = 4.250 \text{ \AA}$. These values are intermediate between those found in the neighbouring three-phase triangles. Weissenberg photographs were taken around the tetragonal axis by use of $\text{MoK}\alpha$ radiation, and intensities of 92 nonequivalent reflexions from the layer lines 0–4 were visually estimated. An empirical correction for thermal movement and Θ -dependent absorption was obtained by plotting $\log F_o/F_c$ against $\sin^2\Theta$. The Fourier summations were made on the Hägg-Laurent¹³ machine.

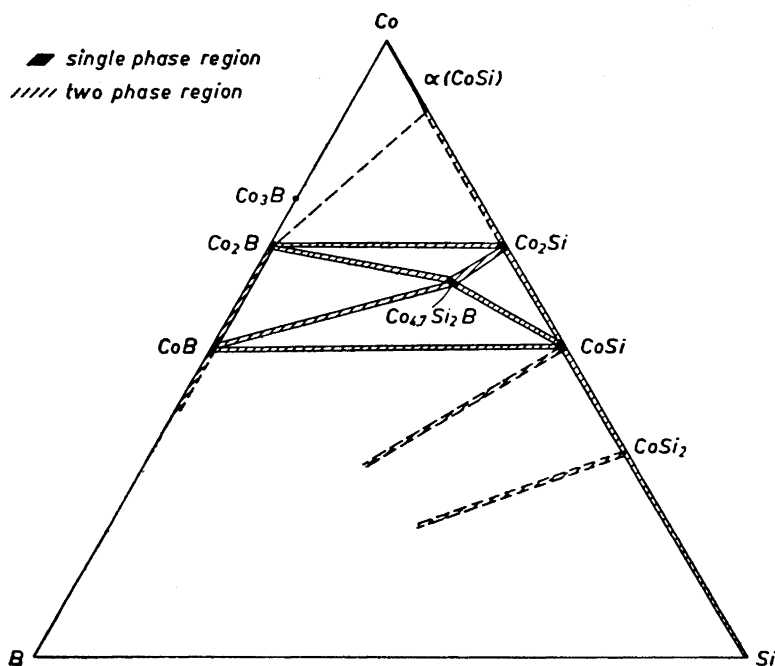


Fig. 1. Some features of the Co-Si-B system at 1 000°C. The one- and two-phase regions are greatly exaggerated for clarity.

RESULTS

The Co-Si-B system at 1 000°C. The results of the present investigation have been used for the construction of a partial isothermal section of the Co-Si-B system at 1 000°C (Fig. 1). The quasi-binary systems $\text{Co}_2\text{B-Co}_2\text{Si}$ and CoB-CoSi divide the section into three parts. The main interest has been devoted to the $\text{Co}_2\text{X-CoX}$ ($\text{X} = \text{Si}, \text{B}$) region, which was found to contain a ternary phase.

The l.p. (lattice parameters) reported for the binary phases Co_2B , CoB , Co_2Si and CoSi are given in Table 1. In ternary Co-Si-B alloys, the l.p. of these phases differ only slightly (not more than 0.2 %) from the values of Table 1, indicating that at 1 000°C the homogeneity ranges of Co_2B , CoB , Co_2Si and CoSi are small in the ternary Co-Si-B system.

In the metal-rich part of the system (> 66.7 at % Co) hexagonal cobalt with dissolved silicon was found. This phase will be called $\alpha(\text{CoSi})$ in the following. (It has not been determined if the hexagonal $\alpha(\text{CoSi})$ phase is stable up to 1 000°C or if it is formed during quenching.) The three-phase region $\text{Co}_2\text{B-Co}_2\text{Si}-\alpha(\text{CoSi})$ and the two-phase region $\text{Co}_2\text{B}-\alpha(\text{CoSi})$ were established. In $\text{Co}_2\text{B-Co}_2\text{Si}-\alpha(\text{CoSi})$ alloys the l.p. of the hexagonal $\alpha(\text{CoSi})$ phase were found to be $a = 2.502 \text{ \AA}$ and $c = 4.062 \text{ \AA}$. These values are smaller

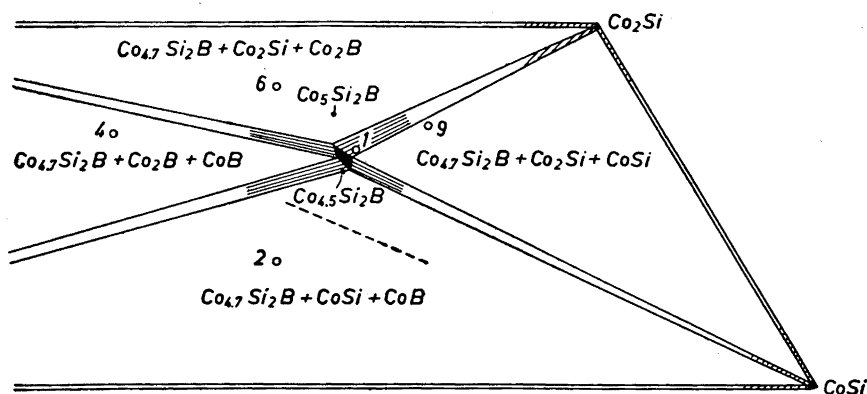


Fig. 2. The Co-Si-B system around $\text{Co}_5\text{Si}_2\text{B}$. The numbers refer to samples the analyses of which are given in the text.

than those reported for pure $\alpha\text{-Co}$ ($a = 2.507 \text{ \AA}$, $c = 4.069 \text{ \AA}$)¹⁶ and show that the $\alpha(\text{CoSi})$ phase in equilibrium with Co_2B and Co_2Si contains considerable amounts of silicon. The existence of Co_3B was confirmed in binary Co-B alloys. No attempt was made to determine the equilibria in the Co-Si-B system in which this phase was involved. Evidently, the phase appears only in silicon-poor alloys.

The composition of the ternary phase could be determined quite well from analysed samples of approximate composition $\text{Co}_5\text{Si}_2\text{B}$ (Fig. 2). The two-phase sample 1 (the l.p. of the $\text{Co}_{4.7}\text{Si}_2\text{B}$ phase in this sample) were intermediate between those found in neighbouring three-phase regions) contained only small amounts of Co_2Si ($\sim 5\%$). The limit between the two phase range $\text{Co}_{4.7}\text{Si}_2\text{B}-\text{Co}_2\text{Si}$ and the three-phase region $\text{Co}_{4.7}\text{Si}_2\text{B}-\text{Co}_2\text{Si}-\text{CoSi}$ was obtained from samples 1 and 9. These facts established the composition of the ternary phase to be $\text{Co}_{4.6}\text{Si}_2\text{B}$ (Fig. 2). This composition was further supported by the observation (from the intensities of the powder lines) that samples 6 and 9 were situated nearer to the ternary single-phase range than samples 2 and 4. As pointed out in the preceding paragraph, some boron and silicon are probably bound to oxygen and the amounts of these elements which actually participate in the Co-Si-B equilibria are slightly smaller than the analytically obtained values used in the construction of Fig. 2. Therefore, we have assigned the formula $\text{Co}_{4.7}\text{Si}_2\text{B}$ to the ternary phase. This composition gives a better agreement between observed and calculated densities than does $\text{Co}_{4.6}\text{Si}_2\text{B}$. The calculated density of $\text{Co}_{4.7}\text{Si}_2\text{B}$ is 7.24 g/cm^3 and that of $\text{Co}_{4.6}\text{Si}_2\text{B}$ is 7.09 g/cm^3 as compared with the observed value of 7.21 g/cm^3 . The results of the single crystal investigation are also more consistent with the formula $\text{Co}_{4.7}\text{Si}_2\text{B}$ rather than with the formula $\text{Co}_{4.6}\text{Si}_2\text{B}$.

The l.p. of $\text{Co}_{4.7}\text{Si}_2\text{B}$ (Table 2) are nearly the same in the different three-phase regions indicating a small homogeneity range of this phase. It seems reasonable to assume that the homogeneity range depends on a variation in

Table 2. Lattice parameters of the $\text{Co}_{4.7}\text{Si}_2\text{B}$ phase. (Estimated accuracy $\pm 0.03\%$.)

Three-phase region	Lattice parameters in Å			
	<i>a</i>	<i>c</i>	<i>c/a</i>	<i>V</i>
$\text{Co}_2\text{B}-\text{Co}_2\text{Si}-\text{Co}_{4.7}\text{Si}_2\text{B}$	8.624	4.248	0.4926	316.0 Å ³
$\text{Co}_2\text{Si}-\text{CoSi}-\text{Co}_{4.7}\text{Si}_2\text{B}$	8.618	4.252	0.4934	315.8
$\text{Co}_2\text{B}-\text{CoB}-\text{Co}_{4.7}\text{Si}_2\text{B}$	8.621	4.247	0.4926	315.6
$\text{CoSi}-\text{CoB}-\text{Co}_{4.7}\text{Si}_2\text{B}$	8.605	4.249	0.4938	314.6

cobalt content (meaning a varying amount of vacancies in the cobalt skeleton) and on a B-Si substitution. Increasing the cobalt content should increase the volume of the unit cell while this should decrease with increasing B/Si ratio. As the unit cell volume is nearly constant for the first three of the three-phase regions shown in Table 2, we have sketched the single-phase range (Fig. 2) so that with increasing cobalt content, the B/Si ratio also increases. With a simultaneous increase of these two parameters, the volume of the unit cell will be very little affected.

Alloys of approximate composition $\text{Co}_5\text{Si}_2\text{B}$ were annealed at temperatures between 950°C and 1150°C, but no transformation of the ternary phase was observed, showing that $\text{Co}_{4.7}\text{Si}_2\text{B}$ is probably stable up to the melting point. Since a phase with the composition $\text{Me}_5\text{Si}_2\text{B}$ has been found both in the Fe-Si-B and in the Mn-Si-B systems, alloys of approximate composition $\text{Co}_5\text{Si}_2\text{B}$ were also annealed between 950°C and 1150°C. However, only the three phases Co_2B , CoB and $\text{Co}_{4.7}\text{Si}_2\text{B}$ were found in the samples and it was concluded that no phase with the composition $\text{Co}_5\text{Si}_2\text{B}$ exists above 950°C.

Some alloys were prepared in the "cobalt-poor" part of the system (< 50 at % Co). CoSi and CoSi_2 were found to be in equilibrium with some very "boron-rich" phase, but no lines from this phase were observed on the powder photographs. The phase is amorphous and possibly is amorphous boron.

The crystal structure of $\text{Co}_{4.7}\text{Si}_2\text{B}$. The powder photograph of $\text{Co}_{4.7}\text{Si}_2\text{B}$ showed that the crystal structure of this phase must be very similar to that found for the tetragonal Me_5Si_3 silicides of the $\text{W}_5\text{Si}_3(T1)$ type¹⁷⁻¹⁹. It was considered important to study the $\text{Co}_{4.7}\text{Si}_2\text{B}$ structure more closely for two reasons. Firstly, it would be of interest to know whether the metal skeleton of $\text{Co}_{4.7}\text{Si}_2\text{B}$ is, in fact, entirely analogous to that of the W_5Si_3 type silicides

Table 3. Results of the single crystal investigation on $\text{Co}_{4.7}\text{Si}_2\text{B}$. (Space-group $D_{4h}^{16}-I4/mcm.$)

Atomic parameters		Relative scattering parameters from the $q(xy)$ and $q(xy1/4)$ in W_5Si_3 sections		Corresponding parameters in Cr_5Si_3	
		$q(xy)$ proj.	$q(xy0)$ and $q(xy1/4)$ in sections	$x = 0.074$ $y = 0.223$	$x = 0.075$ $y = 0.224$
16 Co_I in 16(<i>k</i>)	$x = 0.0757$ $y = 0.2036$	27.4	27.0		
2.5-3 Co_{II} in 4(<i>b</i>)		18.0	19.6		
8 Si in 8(<i>h</i>)	$x = 0.162$	14.0		$x = 0.17$	$x = 0.165$
4 B in 4(<i>a</i>)		4.8			

as this situation would imply the existence of Co-Co contacts shorter than 2.13 Å (= $c/2$). Secondly, it would be interesting to know whether or not the boron and silicon atoms are statistically distributed in the structure. A detailed study of the crystal structure of $\text{Co}_{4.7}\text{Si}_2\text{B}$ might also give some explanation for the deviation from stoichiometry.

The result of the single crystal investigation is shown in Table 3. (For comparison some data on W_5Si_3 ¹⁷ and Cr_5Si_3 ¹⁸ are included.) The systematic extinctions were consistent with the space-group $D_{4h}^{18}-I 4/mcm$. The atomic parameters were refined from successive twodimensional $\rho_o(xy)$ and $\rho_c(xy)$ syntheses with the last backshift-corrections being 0.0003 for the cobalt parameters and 0.001 for the silicon parameter. This procedure gave the final parameters $x_{\text{Co}} = 0.0757$, $y_{\text{Co}} = 0.2035$ and $x_{\text{Si}} = 0.162$ in excellent agreement with the values $x_{\text{Co}} = 0.0758$, $y_{\text{Co}} = 0.2037$, and $x_{\text{Si}} = 0.162$ derived from the threedimensional $\rho_c(xy0)$ section. The scattering parameters were obtained from the $\rho(xy)$ projection. By choosing the scattering parameters proportional to 27.0, 18.0, 14.0 and 5.0 the final ($\rho_o - \rho_c$) synthesis was very nearly zero for all values of x and y . The final R -value of the 26 observed nonequivalent $hk0$ reflexions was 6.1 %. A temperature factor with $B = 0.72 \text{ \AA}^2$ was employed. If the scattering parameters were assumed to be proportional to 27.0, 27.0, 14.0 and 5.0 respectively the R -value did not drop below 16 %.

Evidently, the 16(k) positions are occupied mainly by cobalt atoms; the 8(h) positions, mainly by silicon atoms and the 4(a) positions, mainly by boron atoms. The number of electrons found in the 4(b) positions, however, is much smaller than one would expect if this position was entirely occupied by cobalt atoms. (A reinspection of the $\rho_o(xy)$ projection which was evaluated during the determination¹⁷ of the structure of W_5Si_3 showed that in W_5Si_3 there is no significant difference in the scattering parameters for atoms occupying 16(k) and 4(b), respectively.) The small number of electrons found in the 4(b) position can be explained either by assuming that this position is only partly (to 70 %) occupied by cobalt atoms or that it is occupied by a mixture of cobalt, silicon, and boron atoms. The composition of the ternary phase required for the second alternative is shown by the dotted line in Fig. 2. This line has been constructed with the assumption that the 4(b) positions are occupied

Table 4. Interatomic distances in $\text{Co}_{4.7}\text{Si}_2\text{B}$. (Estimated accuracy $\pm 0.03 \text{ \AA}$.) (Distances have an asterisk when one of the atoms are in the partly occupied position 4(b).)

		Average (Å)	
Co _I	— 9 Co	2.49(2); 2.69; 2.64(2); 2.65(2); 2.84(2) *	2.66
	— 4 Si	2.29; 2.35; 2.53(2)	2.42
	— 2 B	2.15 (2)	2.15
Co _{II}	— 10 Co	2.13(2) **; 2.84(8) *	2.70
	— 4 Si	2.24(4) *	2.24
Si	— 10 Co	2.24(2) *; 2.29(2); 2.35(2); 2.53(4)	2.38
	— 2 Si	3.02(2) †	
B	— 8 Co	2.15(8)	2.15
	— 2 B	2.13(2)	2.13

by a mixture of cobalt, silicon and boron with a weighted mean atomic number of 20. Evidently this alternative is not the correct one. The first alternative corresponds to a composition of $\text{Co}_{4.67}\text{Si}_2\text{B}$, in excellent agreement with the formula $\text{Co}_{4.7}\text{Si}_2\text{B}$ arrived at in the preceding paragraph.

The atomic parameters in $\text{Co}_{4.7}\text{Si}_2\text{B}$ are different from those in W_5Si_3 ¹⁷ and Cr_5Si_3 ¹⁸, which means that the antiprismatic holes of the metal skeleton (where the boron atoms are situated in $\text{Co}_{4.7}\text{Si}_2\text{B}$) are relatively smaller in $\text{Co}_{4.7}\text{Si}_2\text{B}$ than in W_5Si_3 and Cr_5Si_3 . The distance from the centre of the antiprismatic hole to the eight neighbouring metal atoms is only 2.15 Å in $\text{Co}_{4.7}\text{Si}_2\text{B}$ while the corresponding distance in Cr_5Si_3 ¹⁸ is 2.46 Å. The different atomic parameters also imply that Si-Me distances much shorter than in Cr_5Si_3 and W_5Si_3 have been created in $\text{Co}_{4.7}\text{Si}_2\text{B}$. The distance between the silicon atoms and the cobalt atoms in the partly occupied position is only 2.24 Å while the shortest Me-Si contact in Cr_5Si_3 is 2.42 Å¹⁸. The average Co-B and Co-Si distances in $\text{Co}_{4.7}\text{Si}_2\text{B}$ (2.15 Å and 2.38 Å) are very similar to those found in Co_2B^3 (2.15 Å) and Co_2Si (2.42 Å)⁸.

This detailed inspection of $\text{Co}_{4.7}\text{Si}_2\text{B}$ has revealed some significant differences between the crystal structure of this phase and that of the W_5Si_3 (T1) type silicides. The deviation from stoichiometry for $\text{Co}_{4.7}\text{Si}_2\text{B}$ is dependent upon the fact that the 4(b) positions are only partly (to 65–70 %) occupied by cobalt atoms, thus leaving vacancies in the structure. The difference in sizes of the two types of holes in the metal skeleton is larger in $\text{Co}_{4.7}\text{Si}_2\text{B}$ than in the binary Me_5Si_3 phases of W_5Si_3 (T1) type. The boron and silicon atoms are ordered in $\text{Co}_{4.7}\text{Si}_2\text{B}$ with the boron atoms occupying the smaller holes of the metal skeleton and the silicon atoms, the larger.

INTERMEDIATE PHASES OF THE Fe-Si-B AND Mn-Si-B SYSTEMS

The Fe-Si-B system is more complicated than the Co-Si-B system. In the metal-rich (> 50 at % Fe) part of the system, four ternary phases have been found in alloys sintered at 975°C (Table 5). One of these phases is isomorphous with $\text{Co}_{4.7}\text{Si}_2\text{B}$ and probably has a similar composition. Fe_5SiB_2 crystallizes in the Cr_5B_3 (T2)^{20,19} structure and thus is isomorphous with Mo_5SiB_2 ²¹ and Fe_5PB_2 ²². The crystal structure of a phase with the approximate composition Fe_4BSi is apparently unknown. A cementite (Fe_3C) type phase with slightly varying l.p. has also been found. Since the volume of the unit cell has been found to be smaller for this phase than for $\text{Fe}_3\text{C}_{0.2}\text{B}_{0.8}$ ²³,

Table 5. Intermediate phases in the Fe-Si-B and Mn-Si-B systems at 975°C.

Approximate compositions and lattice parameters (in Å)	Structure type
$\text{Fe}_{4.7}\text{Si}_2\text{B}$	$\text{Co}_{4.7}\text{Si}_2\text{B}$ (T1)
Fe_5SiB_2	Cr_5B_3 (T2)
$\text{Fe}_3(\text{Si},\text{B})$ or $(\text{Fe},\text{Si})_3\text{B}$ (boron-rich)	Fe_3C (cementite)
(boron-poor)	
Fe_4BSi	unknown
Mn_5SiB_2	Cr_5B_3 (T2)

it has been assumed that the formula should be written $(\text{Fe, Si})_3\text{B}$. However, the small unit cell volume could also be explained by assuming the formula to be $\text{Fe}_3(\text{Si, B})$ with vacancies in the iron skeleton.

In the Mn-Si-B system Mn_5SiB_2 (isomorphous with Fe_5SiB_2) has been found but no phase analogous with $\text{Co}_{4.7}\text{Si}_2\text{B}$ seems to exist in this system.

A more detailed account of the Fe-Si-B system will soon appear in this journal.

Acknowledgements. The research described in this paper was sponsored by the *European Commission of Air Research and Development Command* under Contract no. AF61(052)-40. The financial support from this authority is gratefully acknowledged.

We want to thank professor G. Hägg for many valuable suggestions and Dr. S. Rundqvist for stimulating discussions. We want to express our gratitude to Dr. Lilly Gustafsson who devoted much time to the chemical analyses. The oxygen analyses were performed at the Analytical Department of Avesta Jernverk and we are much indebted to Dr. G. Liljekvist and Mr. E. Gunnarsson of this factory. Thanks are also due to Mr. K. Nordgren who carried out the density determinations.

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Received November 7, 1958.