

## X-Ray Investigations on Me-Si-B Systems (Me = Mn, Fe, Co)

### II. Some Features of the Fe-Si-B and Mn-Si-B Systems

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The main features of the Fe—Si—B system at temperatures around 1 000°C have been determined using X-ray diffraction methods. Four ternary phases exist in the metal-rich part of this system.  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  is isomorphous with  $\text{Co}_{4.7}\text{Si}_2\text{B}$  but has a more metal-rich composition.  $\text{Fe}_5\text{SiB}_2$  has the  $\text{Cr}_5\text{B}_2$  ( $D8_7$ )-structure, while the structure of a phase with the approximate composition  $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$  has not been solved. There is also a ternary Fe—Si—B phase that crystallizes in the cementite-structure, but the equilibria in which this phase is involved have not been clarified.

In the Mn—Si—B system, which seems to be quite complicated, particularly in the metal-rich part, a phase  $\text{Mn}_6\text{SiB}_2$  (isomorphous with  $\text{Fe}_6\text{SiB}_2$ ) has been identified.

In the previous communication<sup>1</sup> on Me—Si—B systems, the Co—Si—B system was dealt with and, in addition, some crystallographic data on intermediate phases in the Fe—Si—B and Mn—Si—B systems were reported. In this paper we shall present the main features of the Fe—Si—B system at temperatures around 1 000°C and, in particular, discuss the structures and homogeneity ranges of the phases with the composition  $\text{Fe}_5\text{X}_3$  (X = Si, B). We shall also give some qualitative information on the Mn—Si—B system.

Except for phases with compositions around  $\text{MnSi}_2$  and in the metal-rich part of the Mn—Si system, intermediate phases in the boundary binary systems Fe—B, Fe—Si, Mn—B and Mn—Si are crystallographically well characterized. Information on these binary phases may be found in a recent review article<sup>2</sup> and, therefore, will not be repeated here. No systematic studies on the ternary systems Fe—Si—B and Mn—Si—B seem to have been made previously.

## EXPERIMENTAL

The alloys were prepared from the following chemicals,

*Iron rods*, from Johnson, Matthey and Co., London, claimed to contain about 0.03 % carbon, 0.01 % oxygen, 0.01 % nitrogen and a few p.p.m. of other elements.

*Iron sponge*, from Johnson, Matthey and Co., analyzed to contain 95.3 % iron, 2–3 % oxygen (this figure is probably too low), less than 0.001 % nitrogen and about 0.002 % carbon. According to the manufacturer the content of other elements is very low (a few p.p.m.).

*Manganese* (electrolytic), kindly donated by AB Ferrolegeringar, Stockholm, claimed purity 99.8 %.

*Silicon powder*, from Pechiney, Paris, claimed purity 99.9 %.

*Boron powder*, kindly donated by Borax Consolidated, London, claimed purity 99.0–99.7 %.

In some preliminary experiments we also used,

*Iron powder*, from Baker, Phillipsburg, New Jersey, analyzed to contain 97.8 % iron, ~1.1 % oxygen (this figure is probably too low) less than 0.001 % nitrogen and about 0.004 % carbon.

*Carbonyl iron powder*, analyzed to contain 98.5 % iron, 0.18 % oxygen, 0.69 % nitrogen and 0.77 % carbon.

Those iron-silicon-boron samples which have been chemically analyzed were prepared from three master alloys:

$\text{Fe}_3\text{B}$ , analyzed to contain 90.38 % iron and 9.33 % boron, most of the remainder very probably being oxygen, was prepared by repeated sintering and arc-melting mixtures of iron sponge (Johnson, Matthey & Co) and boron, the ferro-magnetic iron boride being magnetically separated after each treatment.

$\text{FeSi}_{\sim 0.25}$  was prepared by reacting iron rods with silicon powder in a high-frequency furnace under vacuum so as to obtain a reasonably brittle iron-rich master alloy.

$\text{FeSi}_2$ , analyzed to contain 46.71 % iron and 52.68 % silicon, most of the remainder very probably being oxygen, was prepared in the same way as  $\text{FeSi}_{\sim 0.25}$ .

The samples were synthesized by arc-melting or sintering mixtures of the master alloys and, depending on the composition of the samples, they were given different heat-treatments as reported in the following paragraph.

In the preliminary studies of the Fe–Si–B system we prepared alloys by sintering mixtures of the elements for 7–10 days at  $975 \pm 20^\circ\text{C}$  in evacuated and sealed silica tubes which were subsequently quenched in oil. After this time no further changes were observed in the powder photographs of the samples on continued sintering and it was concluded that equilibrium had been attained. Several samples were made in each of the three-phase regions shown in Fig. 1, using the iron sponge, Baker's iron powder and the carbonyl iron powder, and within the experimental error ( $\pm 0.05$  %) the same l.p. (lattice parameter) of the phases were found. Samples containing  $\alpha(\text{Fe},\text{Si})$  were recovered for two hours at  $700^\circ\text{C}$  before the exposure in the powder camera.

The Mn–Si–B alloys, which were also prepared by sintering or arc-melting weighed amounts of the elements, were not chemically analyzed.

Powder photographs were taken in cameras of the Guinier type using  $\text{CrK}\alpha$ - and  $\text{CrK}\alpha_1$ -radiation with silicon ( $a = 5.4306 \text{ \AA}$ ) or  $\text{CaF}_2$  ( $a = 5.4630 \text{ \AA}$ ) as internal standards for the l.p. determinations. Because of the low background and the sharp lines on the powder photographs obtained in Guinier cameras, quite small amounts of well-crystallized phases present in a sample can be detected. By mixing small amounts of  $\text{Fe}_{4.88}\text{Si}_2\text{B}$  in  $\text{Fe}_3\text{SiB}_2$ , we found that less than 0.5 % of the former phase was sufficient for its identification in  $\text{Fe}_3\text{SiB}_2 + \text{Fe}_{4.88}\text{Si}_2\text{B}$  samples. Since the powder photographs of phases involved in this study have a rather similar complexity, it may be assumed that when the diffraction lines of a well-crystallized phase are not discernable on a powder film, the sample does not contain more than about 0.5 % of that phase.

The chemical analyses of the Fe–Si–B samples were carried out by Dr. Lilly Gustafsson at the analytical department of this Institute. For the determination of iron, a sample was dissolved in  $\text{HF} + \text{HNO}_3$ , the hydrofluoric acid being subsequently removed by evaporation with sulfuric acid. After reduction in a cadmium-reductor, iron was determined through titration with cerium sulphate. The accuracy of this analysis is estimated to be  $\pm 0.1$  %.

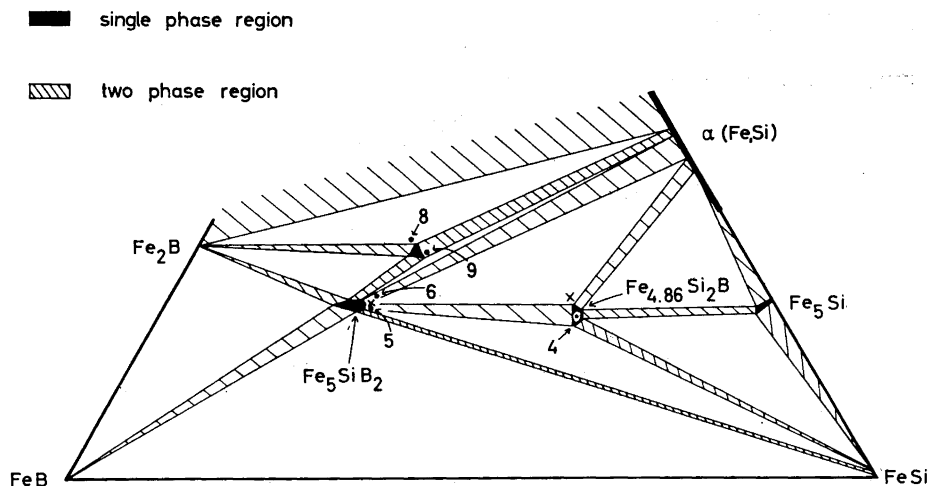


Fig. 1. The Fe—Si—B system in the composition range 50–70 atom per cent iron at temperatures around 1 000°C. The numbers refer to those samples the compositions and heat-treatments of which are given in Table 6. For clarity the narrow  $\alpha(\text{Fe,Si,B})$  single phase region is only represented by a line. The compositions  $\text{Fe}_5\text{SiB}_2$  and  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  are marked with x. Error in figure:  $\text{Fe}_5\text{Si}$  should read  $\text{Fe}_5\text{Si}_3$ .

For the determination of silicon and boron, a sample was melted with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  in a platinum crucible and the melt was dissolved in diluted hydrochloric acid. Silicon was determined gravimetrically as  $\text{SiO}_2$  after the boric acid had been removed by evaporation with methanol. The small amounts of silicon present in the filtrate were determined colorimetrically. For the boron analysis, the acid solution was passed through a hydrogen saturated ion exchanger and, after addition of mannitol, the solution was titrated with sodium hydroxide. The accuracy of the silicon and boron analyses is estimated to be  $\pm 0.5\%$ .

The oxygen and nitrogen content of the samples was determined by a vacuum fusion technique. These analyses were carried out at the analytical department of Avesta Jernverk, where also the carbon content was determined by standard methods.

RESULTS

*The Fe—Si—B system.* In Figs. 1 and 2 the Fe—Si—B system at 1 000°C is outlined. (The samples containing less than 50 atomic per cent iron were synthesized by sintering mixtures of the elements at 1 100°C.) The system is characterized by four ternary metal-rich intermediate phases with the approximate compositions  $\text{Fe}_3(\text{Si,B})$ ,  $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$ ,  $\text{Fe}_5\text{SiB}_2$  and  $\text{Fe}_{4.86}\text{Si}_2\text{B}$ , respectively. X-Ray powder data of nearly single-phase alloys are presented in Tables 1–4. The powder photographs of all phases, except  $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$ , could be indexed.  $\text{Fe}_3(\text{Si,B})$  has the cementite ( $D0_{11}$ )-structure,  $\text{Fe}_5\text{SiB}_2$  is isomorphous with  $\text{Cr}_5\text{B}_3$  ( $D8_r$ -type), while  $\text{Fe}_{4.86}\text{Si}_2\text{B}$ , similar to  $\text{Co}_{4.7}\text{Si}_2\text{B}$ , crystallizes in the  $\text{W}_5\text{Si}_3$  ( $D8_m$ )-structure. The l.p. of the phases in the different three-phase regions (at  $975 \pm 20^\circ\text{C}$ ) are collected in Table 5.

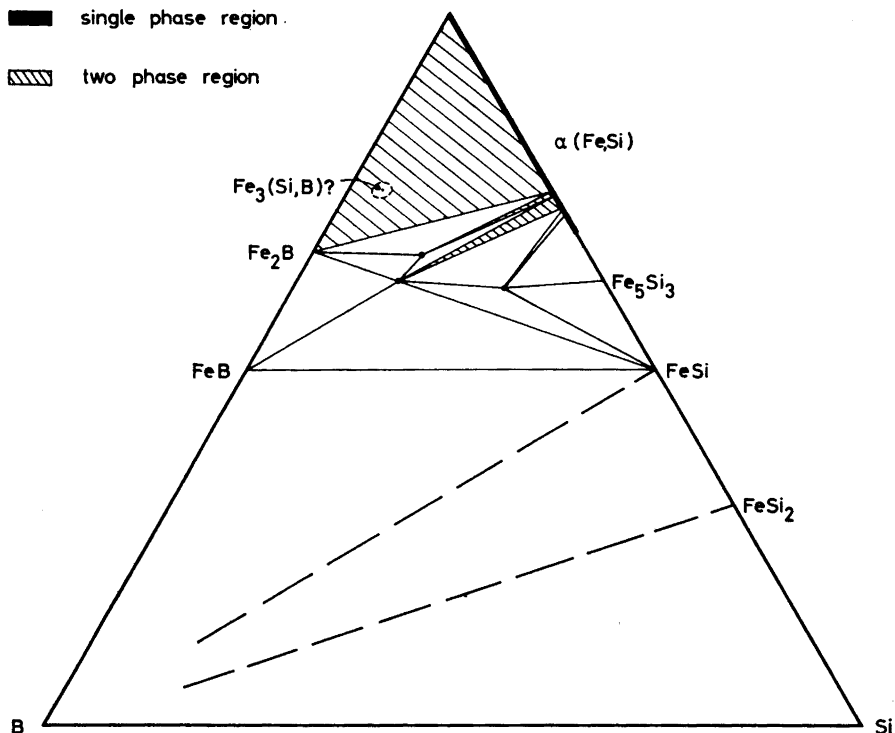


Fig. 2. An outline of the Fe—Si—B system. Most of the two-phase regions are only represented by a line.

Except for  $\text{Fe}_5\text{Si}_3$  the l.p. of the boundary phases are within 0.1 % equal to those reported for the binary iron-borides and -silicides indicating that the two non-metals do not substitute for each other to any appreciable extent in these phases.

In view of the fact that boron is very little soluble in  $\alpha$ - and  $\gamma$ -iron, it seems probable that also its solubility in  $\alpha(\text{Fe},\text{Si})$  is very small. This is supported by the observation that  $\text{Fe}_2\text{B}$  is present in metal-rich alloys containing very small amounts of boron. Thus, no great error is likely to be made if the composition of the  $\alpha(\text{Fe},\text{Si})$  phase, present in Fe—Si—B alloys, is derived from the l.p. *vs.* composition curve, which Farquhar *et al.*<sup>3</sup> have determined for solid solutions of silicon in  $\alpha$ -iron. The composition of  $\alpha(\text{Fe},\text{Si})$  in the three-phase equilibria involving this phase are given below

Three phase range	l.p. of $\alpha(\text{Fe},\text{Si})$	iron content (atom %) of $\alpha(\text{Fe},\text{Si})$
$\text{Fe}_2\text{B} + \text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6} + \alpha(\text{Fe},\text{Si})$	$a = 2.826_3 \text{ \AA}$	74.9
$\text{Fe}_5\text{SiB}_2 + \text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6} + \alpha(\text{Fe},\text{Si})$	$a = 2.826_1 \text{ \AA}$	74.5
$\text{Fe}_2\text{SiB}_2 + \text{Fe}_{4.86}\text{Si}_2\text{B} + \alpha(\text{Fe},\text{Si})$	$a = 2.821_6 \text{ \AA}$	72.6
$\text{Fe}_{4.86}\text{Si}_2\text{B} + \text{Fe}_5\text{Si}_3 + \alpha(\text{Fe},\text{Si})$	$a = 2.820_3 \text{ \AA}$	72.0

Table 1. Powder photograph of a sintered alloy, containing  $\text{Fe}_2\text{B}$  and the Fe—Si—B phase isomorphous with cementite. (CrK $\alpha$ -radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>	$pF_{\text{calc}}^2 \times 10^{-2}$ for $\text{Fe}_3\text{C}$ (Ref.7)
011	—	0.0953	—	0.27
( $\text{Fe}_2\text{B}$ )	0.1006		st	
101	—	0.1119	—	0.04
020	~0.118	0.1180	vw	0.16
111	—	0.1414	—	0.16
200	—	0.1845	—	1.2
( $\text{Fe}_2\text{B}$ )	0.2011		vst	
210	0.2140	0.2140	w+	7.4
121	0.2299	0.2300	st	7.8
201	0.2502	0.2503	m—	6.3
002	0.2630	0.2632	vw	8.2
211	0.2794	0.2798	st	24.8
( $\text{Fe}_2\text{B}$ )	0.2906		vst	
220	0.3025	0.3025	st+	24.8
102	0.3093	0.3093	st	28.1
( $\text{Fe}_2\text{B}$ )	0.3240		vvst	
031	0.3313	0.3314	st+	49.0
112	0.3388	0.3388	st	21.1
221	0.3684	0.3683	st	25.9
131	0.3775	0.3775	m	18.3
022	—	0.3812	—	0.92
( $\text{Fe}_2\text{B}$ )	0.3916		st	
( $\text{Fe}_2\text{B}$ )	0.4027		m	
122	0.4276	0.4274	st	11.4
202	—	0.4477	—	0.25
230	0.4503	0.4501	w+	7.5
040	0.4721	0.4722	vw	3.4
212	—	0.4772	—	5.9
301	0.4809	0.4809	m	14.6
( $\text{Fe}_2\text{B}$ )	0.4916		vst	

The l.p. of  $\text{Fe}_5\text{Si}_3$  are slightly larger in ternary Fe—Si—B alloys than in binary Fe—Si (or ternary Fe—Si—O) alloys, indicating that a small number of boron atoms may be interstitially accommodated in  $\text{Fe}_5\text{Si}_3$ . As pointed out earlier<sup>4</sup>, the iron-silicon skeleton of  $\text{Fe}_5\text{Si}_3$  ( $\text{Mn}_5\text{Si}_3$  ( $D8_8$ )-type) contains octahedral holes of convenient size for small non-metal atoms and it seems likely that the boron atoms are located in these holes. (It was recently shown<sup>5</sup> that in the isomorphous  $\text{Mn}_5\text{Si}_3$ , the distances from the centre of the "hole" to the surrounding metal atoms is 2.03 Å, which is a short but not unreasonably short Fe—B distance.)

The l.p. variations observed for FeSi and  $\text{FeSi}_2$  in ternary Fe—Si—B alloys are not greater than those reported for binary FeSi and  $\text{FeSi}_2$ , and thus may be explained as depending on a variation of the Fe/Si ratio in these phases.

As reported in the previous paper<sup>1</sup> a Fe—Si—B phase isomorphous with cementite and tentatively denoted as  $\text{Fe}_3(\text{Si},\text{B})$  has been identified in metal-rich alloys, sintered at 975°C. A powder photograph of a  $\text{Fe}_3(\text{Si},\text{B}) + \text{Fe}_2\text{B}$  alloy is given in Table 1. The exact composition of  $\text{Fe}_3(\text{Si},\text{B})$  and the equilibria

Table 2. Powder photograph of a sintered alloy, containing  $\text{Fe}_3\text{Si}_{0.4}\text{B}_{0.6}$ ,  $\text{Fe}_2\text{B}$  and  $\alpha(\text{Fe},\text{Si})$ . (CrK $\alpha$ -radiation).

$I_{\text{obs}}$	$\sin^2\theta_{\text{obs}}$	$I_{\text{obs}}$	$\sin^2\theta_{\text{obs}}$
vw	0.1256	vw	0.3044
w—	0.1351	vw	0.3058
vw	0.1626	m+	0.3130
m	0.1968	w+	0.3242 ( $\text{Fe}_2\text{B}$ )
w	0.2119	st+	0.3287 ( $\alpha(\text{Fe},\text{Si})$ )
w	0.2147	m—	0.3380
m	0.2402	st	0.3443
m	0.2459	st+	0.3592
m	0.2732	m—	0.3917
m+	0.2828	m	0.4208
		w+	0.4424

in which this phase are involved have not been clarified. The relation between the composition and the l.p. variations displayed by  $\text{Fe}_3(\text{Si},\text{B})$  is also unknown, although it has been observed<sup>2</sup> that the unit volume increases as the boron content increases.

The composition of the other three ternary phases could be fairly well determined from samples prepared from the master alloys. The compositions

Table 3. Powder photographs of alloys, containing  $\text{Fe}_3\text{SiB}_2$  and  $\text{Mn}_3\text{SiB}_2$ , respectively \*. (CrK $\alpha$ -radiation).

$hkl$	$\text{Fe}_3\text{SiB}_2$			$\text{Mn}_3\text{SiB}_2$			Calculated for $\text{Fe}_3\text{PB}_2$ **	
	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$	$pF^2 \times 10^{-4}$
002	—	0.0491	—	—	0.0481	—	0.02	0.01
110	0.0850	0.0852	w	0.0833	0.0833	w	0.51	0.61
112	0.1342	0.1342	w+	—	0.1314	—	0.95	1.64
200	0.1703	0.1703	w—	0.1666	0.1667	w—	0.41	0.88
004	0.1963	0.1964	m	0.1926	0.1926	m	1.90	4.66
202	0.2193	0.2194	m—	0.2148	0.2149	m—	1.35	3.68
211	0.2251	0.2252	st	0.2205	0.2204	st	10.2	27.8
114	0.2815	0.2816	st—	0.2759	0.2760	st	7.45	22.0
213	0.3234	0.3234	vst	0.3167	0.3167	vst	21.1	64.4
220	0.3406	0.3406	m+	0.3333	0.3334	m	4.6	13.7
204	0.3669	0.3668	st—	0.3594	0.3593	st	16.0	46.2
222	—	0.3897	—	—	0.3815	—	0.11	0.34
310	0.4423	0.4420	m—	0.4337	0.4334	m—	3.30	7.26

\* Only the diffraction lines originating from  $\text{Fe}_3\text{SiB}_2$  and  $\text{Mn}_3\text{SiB}_2$  are given in the table. The iron-boron-silicon alloy was a two-phase alloy and contained, besides  $\text{Fe}_3\text{SiB}_2$ ,  $\alpha(\text{Fe},\text{Si})$  with an observed  $\sin^2\theta$ -value for the 110-line of 0.3292. The manganese-boron-silicon alloy was a three-phase alloy, containing  $\text{Mn}_3\text{SiB}_2$ ,  $\text{Mn}_3\text{Si}_3$  and  $\text{MnB}$ .

\*\* As silicon and phosphorus as well as iron and manganese have very similar scattering factors, we have compared the observed intensities of  $\text{Fe}_3\text{SiB}_2$  and  $\text{Mn}_3\text{SiB}_2$  with those calculated for  $\text{Fe}_3\text{PB}_2$ . The structure of the latter phase has been refined from single crystal data by Dr. Rundqvist<sup>6</sup> who was so kind as to put his values at our disposal. In the computations of the  $p|F|^2$ -values of  $\text{Fe}_3\text{PB}_2$ , the following atomic parameters were used (space-group  $I 4/mcm$ ):

$$\begin{aligned}
 &16 \text{ Fe in } 16(l), & x = 0.169_0, & z = 0.140_5 \\
 &4 \text{ Fe in } 4(c) \\
 &8 \text{ B in } 8(h), & x = 0.37_5 \\
 &4 \text{ P in } 4(a)
 \end{aligned}$$

and heat-treatments of these samples are given in Table 6. On basis of this information, Fig. 1 has been constructed and the compositions of the ternary phases have been found to be well represented by the formulæ  $\text{Fe}_2\text{Si}_{0.40}\text{B}_{0.60}$ ,  $\text{Fe}_5\text{Si}_{1-x}\text{B}_{2+x}$  ( $x \sim 0.0-0.1$ ) and  $\text{Fe}_{4.86}\text{Si}_2\text{B}$ , respectively.

(Because of the presence of oxygen the amounts of iron, silicon and boron that participate in the Fe—Si—B equilibrium are not likely to be precisely proportional to the total concentration of these elements in a sample as has been assumed in the construction of Fig. 1 and in the determination of the compositions of the ternary phases. The uncertainties in these compositions are larger than the errors in the chemical analyses.)

X-Ray data for  $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$  are given in Table 2. We did not succeed in indexing the powder photograph of this phase and attempts to prepare single crystals were also unsuccessful.  $\text{Fe}_2\text{Si}_{0.4}\text{B}_{0.6}$  decomposes at temperatures  $\sim 1100^\circ\text{C}$  and above this temperature there exists a three-phase region  $\text{Fe}_2\text{B} + \text{Fe}_5\text{SiB}_2 + \alpha(\text{Fe},\text{Si})$ .

The powder photograph of a  $\text{Fe}_5\text{SiB}_2 + \alpha(\text{Fe},\text{Si})$  alloy is given in Table 3 and by assuming  $\text{Fe}_5\text{SiB}_2$  to possess the  $\text{Cr}_5\text{B}_3$ -structure (as does<sup>6</sup>  $\text{Fe}_5\text{PB}_2$ ) good agreement between observed and calculated intensities is obtained. It seems probable that (similar to the situation in  $\text{Mo}_5\text{SiB}_2$ <sup>4</sup> and  $\text{Fe}_5\text{PB}_2$ <sup>6</sup>) the non-metal atoms are ordered in  $\text{Fe}_5\text{SiB}_2$ , the silicon atoms occupying the 4(*a*)-positions and the boron atoms the 8(*h*)-positions. The observed l.p. variations (Table 5) are compatible with the assumption that the homogeneity

Table 4. Powder photograph of an arc-melted alloy with the analyzed composition  $\text{Fe}_{4.858}\text{Si}_{2.043}\text{B}_{1.000}$  (sample 4), ( $\text{CrK}\alpha_1$ -radiation).

<i>hkl</i>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	<i>I</i> <sub>obs</sub>	<i>I</i> <sub>calc</sub> (relative) *			<i>pF</i> <sup>2</sup> × 10 <sup>-4</sup> *		
				$\text{Fe}_{4.67}\text{Si}_2\text{B}$	$\text{Fe}_{4.86}\text{Si}_2\text{B}$	$\text{Fe}_5\text{Si}_2\text{B}$	$\text{Fe}_{4.67}\text{Si}_2\text{B}$	$\text{Fe}_{4.86}\text{Si}_2\text{B}$	$\text{Fe}_5\text{Si}_2\text{B}$
110	—	0.0339	—	6.1	0.3	0.8	0.23	0.01	0.03
200	—	0.0677	—	0.6	0.1	0.2	0.05	0.01	0.13
220	0.1354	0.1354	m—	15	9	6	2.52	1.63	1.09
211	0.1548	0.1548	w+	6	6	6	1.15	1.15	1.15
310	0.1693	0.1693	st	43	57	63	9.21	12.08	14.45
400	0.2707	0.2709	w	0.9	2.3	3.7	0.28	0.66	1.05
002	0.2808	0.2808	st	65	59	55	19.44	17.71	16.42
321	0.2902	0.2903	vst	141	141	141	42.82	42.82	42.82
330	0.3047	0.3047	st	27	32	36	8.16	9.83	11.16
112	0.3147	0.3146	st—	23	30	36	7.06	9.30	11.10
420	0.3386	0.3386	st+	56	67	76	17.22	20.61	23.26
202	0.3485	0.3485	st	41	50	57	12.22	15.06	17.31
411	0.3579	0.3580	vvst	300	300	300	88.06	88.06	88.06
222	0.4162	0.4162	st+	93	108	120	23.58	27.29	30.20
510	0.4404	0.4402	w—	5.7	2.7	1.1	1.35	0.63	0.28
312	—	0.4501	—	1.4	0.1	0.5	0.31	0.002	0.11
431	0.4937	0.4937	w	16	16	16	3.13	3.13	3.13

\* It has been assumed that the metal position in 4(*b*) is occupied to 67, 86 and 100 %, respectively, in  $\text{Fe}_{4.67}\text{Si}_2\text{B}$ ,  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  and  $\text{Fe}_5\text{Si}_2\text{B}$ , and that the atomic parameters are the same as in  $\text{Co}_{4.7}\text{Si}_2\text{B}$  (Ref.<sup>1</sup>).

Table 5. Lattice parameters (in Å) of the various phases in different three-phases regions. The alloys have been prepared by sintering mixtures of the elements at 975°C for 7–10 days.

Three-phase region	Fe <sub>2</sub> B	α(Fe <sub>2</sub> Si)	Fe <sub>3</sub> SiB <sub>2</sub>	FeB	Fe <sub>4.88</sub> Si <sub>2</sub> B	FeSi	Fe <sub>3</sub> Si <sub>3</sub>	FeSi <sub>2</sub>	Si
Fe <sub>2</sub> B + Fe <sub>3</sub> Si <sub>10.4</sub> B <sub>0.8</sub> + α	a = 5.109 c = 4.249	a = 2.826 <sub>3</sub>							
Fe <sub>2</sub> B + Fe <sub>3</sub> Si <sub>10.8</sub> B <sub>0.8</sub> + Fe <sub>3</sub> SiB <sub>2</sub>	a = 5.108 c = 4.250		a = 5.546 c = 10.321						
Fe <sub>2</sub> B + Fe <sub>3</sub> SiB <sub>2</sub> + FeB	a = 5.109 c = 4.248		a = 5.532 c = 10.300	a = 5.500 b = 2.947 c = 4.057					
Fe <sub>2</sub> Si <sub>10.4</sub> P <sub>0.8</sub> + α + Fe <sub>3</sub> SiB <sub>2</sub>		a = 2.826 <sub>1</sub>	a = 5.547 c = 10.332						
Fe <sub>3</sub> SiB <sub>2</sub> + Fe <sub>4.88</sub> Si <sub>2</sub> B + α		a = 2.821 <sub>6</sub>	a = 5.552 c = 10.339		a = 8.817 c = 4.338				
Fe <sub>3</sub> SiB <sub>2</sub> + Fe <sub>4.88</sub> Si <sub>2</sub> B + FeSi			a = 5.552 c = 10.338		a = 8.806 c = 4.325	a = 4.489			
Fe <sub>3</sub> SiB <sub>2</sub> + FeB + FeSi				a = 5.499 b = 2.947 c = 4.057		a = 4.486			
Fe <sub>4.88</sub> Si <sub>2</sub> B + Fe <sub>3</sub> Si <sub>3</sub> + α		a = 2.820 <sub>2</sub>			a = 8.826 c = 4.345		a = 6.766 c = 4.726		
Fe <sub>4.88</sub> Si <sub>2</sub> B + Fe <sub>3</sub> Si <sub>3</sub> + FeSi					a = 8.818 c = 4.337	a = 4.488	a = 6.770 c = 4.730		
FeSi + FeB + ? *				a = 5.500 b = 2.947 c = 4.058		a = 4.486			
FeSi + FeSi <sub>2</sub> + ? *						a = 4.484	a = 2.695 c = 5.137		
FeSi <sub>2</sub> + Si + ? *							a = 2.688 c = 5.128	a = 5.425	
L.p. of binary phases (ref. 2)	a = 5.109 c = 4.249			a = 5.506 b = 2.952 c = 4.061		a = 4.488 – 4.483	a = 6.755 c = 4.717	a = 2.698 – 2.683 c = 5.141 – 5.127	

\* Alloys sintered at 1 100°C.



Table 6. Composition and heat-treatment of samples prepared from the master alloys.

Sample	Composition	Heat-treatment	Observed phases
4	% Fe: 79.62 % Si: 16.82 Fe <sub>4.866</sub> Si <sub>2.043</sub> B <sub>1.000</sub> % B: 3.18 Σ*: 99.62	arc-melted	Fe <sub>4.86</sub> Si <sub>2</sub> B (and perhaps a trace of α(Fe,Si))
5	% Fe: 83.60 % Si: 8.54 Fe <sub>4.923</sub> Si <sub>1.001</sub> B <sub>2.000</sub> % B: 6.58 Σ*: 98.72	arc-melted, annealed in evacuated tubes for three days at 1 060°C	Fe <sub>5</sub> SiB <sub>2</sub> and a small amount of Fe <sub>4.86</sub> Si <sub>2</sub> B. The ratio Fe <sub>4.86</sub> Si <sub>2</sub> B/Fe <sub>5</sub> SiB <sub>2</sub> is estimated to be not greater than 1/99.
6	% Fe: 84.04 % Si: 8.51 Fe <sub>5.152</sub> Si <sub>1.038</sub> B <sub>2.000</sub> % B: 6.32 Σ*: 98.87	as sample 5	Fe <sub>5</sub> SiB <sub>2</sub> + small amounts of α(Fe,Si)
8	% Fe: 85.65 % Si: 8.19 Fe <sub>2.000</sub> Si <sub>0.381</sub> B <sub>0.607</sub> % B: 5.03 Σ*: 98.87	sintered in evacuated silica tubes for 11 days at 1 050°	Fe <sub>2</sub> Si <sub>0.4</sub> B <sub>0.6</sub> + Fe <sub>2</sub> B + α(Fe,Si)
9	% Fe: 84.90 % Si: 9.27 Fe <sub>4.000</sub> Si <sub>0.435</sub> B <sub>0.594</sub> % B: 4.88 Σ*: 99.05	arc-melted, annealed in evacuated silica tubes for 8 days at 1 040°	Fe <sub>2</sub> Si <sub>0.4</sub> B <sub>0.6</sub> + α(Fe,Si)

\* Samples prepared in exactly the same way as those above were analyzed to contain 0.1 weight % oxygen (arc-melted) to 0.5 weight % oxygen (arc-melted and annealed in silica tubes for 7–10 days), while the carbon content was found to be 0.02–0.03 weight % and the nitrogen content less than 0.001 %. We believe that the figures obtained for the oxygen content are too low (as was also found to be the case when different iron powders were analyzed) and that most of the impurity in the samples is oxygen.

range of Fe<sub>5</sub>SiB<sub>2</sub> is associated with a B/Si substitution, the l.p. decreasing with increasing boron content. As the B/Si ratio in silicon-rich Fe<sub>5</sub>SiB<sub>2</sub> (as determined from sample 5) is 2.05/1.00, this ratio is greater than 2.00 for all compositions of Fe<sub>5</sub>SiB<sub>2</sub>. This indicates that the boron atoms may substitute for a fraction of the silicon atoms in the 4(*a*)-positions (which correspond to anti-prismatic holes in the metal atom skeleton) whereas the 8(*h*)-positions (which correspond to smaller triangular prismatic holes in the metal atom skeleton) are only occupied by boron atoms over the whole homogeneity range. The composition of Fe<sub>5</sub>SiB<sub>2</sub> may thus be represented by the formula Fe<sub>5</sub>Si<sub>1-x</sub>B<sub>2+x</sub> (*x* ~ 0.0–0.1).

The arc-melted sample 4 gave a powder photograph on which only the sharp lines originating from Fe<sub>4.86</sub>Si<sub>2</sub>B were observed. As the oxygen content of this sample is very low, it is no doubt that the iron content of Fe<sub>4.86</sub>Si<sub>2</sub>B is lower than that corresponding to the stoichiometric formula Fe<sub>5</sub>Si<sub>2</sub>B. As pointed out in the previous communication <sup>1</sup>, the isomorphous phase Co<sub>4.7</sub>Si<sub>2</sub>B

also has a composition deviating from the ideal formula, depending on the fact that the metal position in 4(b) is only partially occupied. In Table 4 we have calculated the intensities for the  $\text{Fe}_x\text{Si}_2\text{B}$  phase ( $x = 4.67, 4.86, 5.00$ ) assuming that the 4(b) position is occupied by iron atoms to 67, 86 and 100 %, respectively, and that the atomic parameters are the same in  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  as in  $\text{Co}_{4.7}\text{Si}_2\text{B}$ . The marked differences in the observed intensities of 110, 220, 211 and 400 for which  $I_{110} \ll I_{400} < I_{211} < I_{220}$  is in good agreement with the intensities calculated for  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  but hardly with those calculated for  $\text{Fe}_{4.67}\text{Si}_2\text{B}$  and  $\text{Fe}_5\text{Si}_2\text{B}$ . Thus, the X-ray data of  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  are not inconsistent with the assumption that the deviation from stoichiometry of this phase depends on the 4(b) positions being only partially occupied by iron-atoms. The observed l.p. variations of  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  (Table 5) indicates that the homogeneity range of  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  may mainly depend on a variation of the number of vacant 4(b) positions.

The Fe—Si—B system is of interest since it contains one representative for each of the three common  $\text{Me}_5\text{Si}_3$  structure types, in which a number of transition metal silicides and silico-borides have been found to crystallize. These structure types are discussed in a recent review article<sup>2</sup> and, therefore, will not be commented on in this paper. It is noteworthy, however, that the variation in composition displayed by  $\text{Fe}_5\text{Si}_3(\text{B})$ ,  $\text{Fe}_5\text{SiB}_2$  and  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  seems to have quite different causes. In  $\text{Fe}_5\text{Si}_3(\text{B})$  a varying number of boron atoms are interstitially dissolved in the iron-silicon skeleton, in  $\text{Fe}_5\text{SiB}_2$  the extended homogeneity range is mainly associated with a B/Si substitution, while in  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  one of the iron positions is occupied to a varying degree.

*The Mn—Si—B system.* Our qualitative study of the Mn—Si—B system only aimed at seeing to which extent this system displays similarities to the more comprehensively investigated Fe—Si—B and Co—Si—B systems.

The metal-rich part of the Mn—Si—B system seems to be much more complicated than is the case in the Fe—Si—B and Co—Si—B systems. We found no Mn—Si—B phase isomorphous with  $\text{Fe}_{4.86}\text{Si}_2\text{B}$  and  $\text{Co}_{4.7}\text{Si}_2\text{B}$ , but in alloys sintered at 900—1 000°C, a phase with the  $\text{Cr}_5\text{B}_3$  structure was identified (Table 3) and this phase is tentatively denoted as  $\text{Mn}_5\text{SiB}_2$ .

The equilibria in the non-metal-rich part of the Mn—Si—B system are also different from those in the Fe—Si—B and Co—Si—B system. Thus, the boron-rich manganese borides  $\text{Mn}_3\text{B}_4$  and  $\text{MnB}_2$  seem to be in equilibrium with silicon, whereas in the other systems no boride is stable in the presence of silicon.

*Acknowledgements.* We wish to thank Professor G. Hägg for his kind interest in this work and for the facilities put at our disposal. We are also much indebted to the Head of the analytical department of this Institute, Dr. F. Nydahl, and to Dr. Lilly Gustafsson for her courtesy in carrying out the chemical analyses. We want to thank Dr. J. Bäcklund and Mr. E. Gunnarsson at Avesta Jernverk for help with the oxygen, nitrogen and carbon analyses.

Many thanks are due to Miss B. Pettersson and Mr. S. Wahlgren for excellent technical assistance.

We sincerely acknowledge financial support from the *Air Force Office of Scientific Research and the Research and Development Command, United States Air Force*, through its European Office under Contract No. AF 61(052)—40 and from the *Swedish State Council of Technical Research*.

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Received July 1, 1960.