

The Effect of Boron on the Formation of σ -FeCr at 700° C

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Iron-chromium-boron alloys with the atomic ratio Fe/Cr = 54/46 and containing varying amounts of boron (0–26 at %) have been melted twice in an arc-furnace and subsequently annealed for 40–48 days at 700°C in evacuated silica tubes. It has been found that chromium is concentrated in the $(\text{Cr, Fe})_2\text{B}$ phase, thereby lowering the amount of Cr available for the formation of σ -FeCr. In the presence of >8 at % B no sigma phase is found in the samples. The solubility of boron in σ -FeCr is probably very small. Thus, the influence of boron on the formation of σ -FeCr is analogous to that of carbon and nitrogen.

It has been assumed^{1,2} that the bonding strength between a transition metal (Me) and one of the nonmetals boron, carbon or nitrogen (X) decreases with increasing atomic number of the transition metal in a given transition period. This assumption has been useful when systematizing general features and properties of systems containing the mentioned elements. The decreasing stability of the binary borides, carbides and nitrides of the transition metals with increasing group number of the metal is in accordance with this assumption as are the observations that in $\text{Me}_1\text{—Me}_2\text{—X}$ systems (Me_1 and Me_2 from the same transition period) the lower atomic number metal is always concentrated in the phase richest in nonmetal³⁻⁶.

The influence of carbon on the formation of σ -FeCr is one example of this general behaviour. In the metal rich part of the Fe-Cr-C system (15–43 weight % Cr). Shortsleave and Nicholson⁷ found that Cr-rich $(\text{Cr, Fe})_{23}\text{C}_6$ carbide is formed, thereby lowering the amount of chromium available for sigma formation. The higher the carbon content of the Fe-Cr-C alloy, the higher the *total* chromium content which is necessary for σ -FeCr to be found. The effect of nitrogen on sigma formation in Fe-Cr-Ni steels is quite analogous, Cr-rich nitrides being formed⁸.

The present investigation has been undertaken in order to study if the effect of boron on the formation of σ -FeCr could be explained as depending on higher affinity of B for Cr than for Fe. We also wanted to know if boron, like silicon^{9,10}, could be dissolved in σ -FeCr to any considerable extent.

EXPERIMENTAL

The metals used in this investigation had a claimed purity of 99.7 %. The boron was analysed and found to contain 94 % B. 2–3 g samples were melted twice in an arc furnace. The samples contained 0, 4.0, 8.5, 13.2, 16.9, 22.5 and 26.0 atomic % B, and within 2 % the Fe/Cr atomic ratio was 54/46 in all of them. The melts were cold worked by hammering with a sledge and subsequently annealed in evacuated silica tubes for 40 days at 700°C and quenched in oil. After this annealing time the powder photographs showed sharp lines and no changes were observed after annealing another 8 days. Filings of the samples were recovered for 1–2 h at 600°C in vacuum. X-Ray photographs were taken in a Guinier type powder camera using $\text{CrK}\alpha$ radiation and NaCl as calibration standard. (a_{NaCl} has been assumed to be = 5.6400 Å at 21°C.) Measurements of the cube edge of the α -phase could be reproduced within ± 0.01 %. The accuracy of the l.p. (lattice parameters) of the other phases present is estimated to be 0.02–0.03 %.

The samples were chemically analysed for B, Fe and Cr. After dissolving in HCl (under reflux) boron was determined by titration with sodium hydroxide after addition of D-mannitol. Iron and chromium were determined with standard volumetric methods. The result of the chemical analyses (in weight %) is given in Table 1.

Table 1.

Sample No.	% B	% Fe	% Cr	Σ
0		55.2	43.2	98.4
1	0.82	54.8	43.1	98.7
2	1.83	53.5	42.6	97.9
3	2.92	53.1	42.5	98.5
4	3.85	52.9	41.3	98.0
5	5.40	51.5	41.1	98.0
6	6.40	50.5	40.9	97.8

In order to identify the expected boron-rich phases, some alloys in the Cr–B system (≤ 33 at % B) were prepared by arc-melting. They were investigated with X-ray powder methods both in the unannealed state and after annealing in vacuum for 3–4 weeks at 1150°C.

RESULTS

I. *The Cr-B system.* Only one intermediate phase was observed in the region 0–33 at % B. Its composition was approximately Cr_2B . The positions and intensities of all the X-ray powder lines could be explained assuming the crystal structure to be isomorphous with that of Mn_4B^{11} . Sufficiently small single crystals gave very nice Weissenberg photographs which definitely showed that the Cr_2B phase in our samples had the Mn_4B structure. "Our" Cr_2B is evidently identical with the Cr_4B phase reported by Bertaut and Blum¹² but as we found the composition to be much nearer to $\text{CrB}_{0.50}$ than to $\text{CrB}_{0.25}$ it will be referred to as Cr_2B in the following. Two additional phases with the composition Cr_2B have earlier been reported, namely one orthorhombic¹³ (space group $A b m m$ or $A b m 2$) and one having the CuAl_2 structure¹². Neither of these phases were observed in this investigation.

II. Except the ferrite (α) and sigma phases, only Cr_2B (with some dissolved Fe) was found in the Fe-Cr-B alloys. (Two or three very weak lines from samples 1, 2 and 3 probably originate from impurities.) The phases observed in the different samples and the l.p. of the α and Cr_2B phases are collected in

Table 2.

Sample	at % B	obs. phases	Lattice parameters in Å			at % Cr in α -phase	
			Cr ₂ B		α		
Fe	—	α			2.8662		
Cr	—	α			2.8857		
0	—	σ			—		
1	4.0	$\alpha + \sigma + \text{Cr}_2\text{B}$			2.8736	29	
2	8.6	$\alpha + \text{Cr}_2\text{B}$	$a = 14.63 \quad b = 7.37 \quad c = 4.23$			2.8731	24
3	13.2	$\alpha + \text{Cr}_2\text{B}$	14.63	7.36	4.23	2.8729	22
4	16.9	$\alpha + \text{Cr}_2\text{B}$	14.61	7.36	4.22	2.8721	16
5	22.5	$\alpha + \text{Cr}_2\text{B}$	14.60	7.34	4.22	2.8697	7
6	26.0	$\alpha + \text{Cr}_2\text{B}$	14.58	7.33	4.21	2.8681	3
Cr ₂ B	33	Cr ₂ B	14.71	7.41	4.25		

Table 2. The l. p. of the Fe and Cr used in the preparation of the samples 0—6 and those of pure Cr₂B are also given in the table.

The variation of the l. p. of the α -phase with the Cr content has been determined by Preston¹⁴ (Fig. 1). From Fig. 1 the Cr content of the α -phase of the different samples has been determined and is given in Table 2.

The following observations should be made. With no boron present only the sigma phase is found in the 54/46 (Fe/Cr) sample; with 4 at % B present so much Cr has been bound in the Cr₂B boride that both ferrite (α) and sigma are found. At higher boron concentrations too little Cr is available for any sigma phase to be formed at all, and the α -phase is gradually depleted of Cr with further increasing boron content. The composition of the α -phase at the $\alpha/(\alpha + \sigma)$ boundary (700°C) obtained from sample 1 is 29 at. % Cr in good agree-

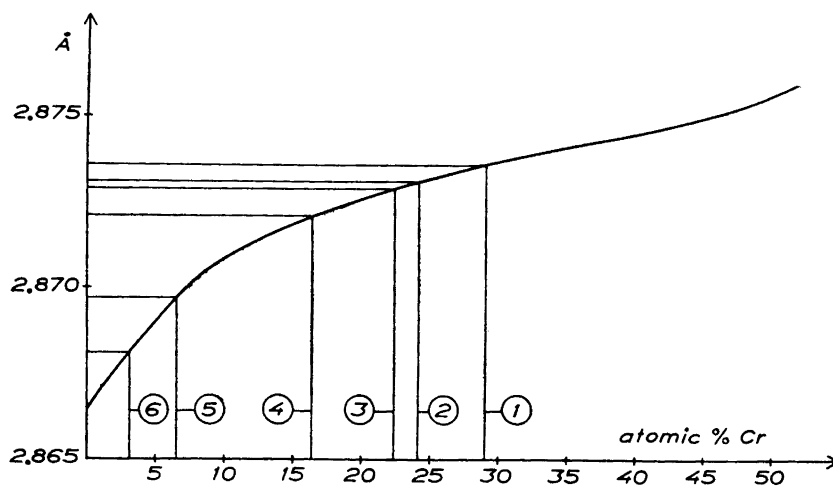


Fig. 1. Cube edge of α -phase as function of Cr content¹⁴. The numbers in circles refer to samples.

ment with the value of 31 at. % Cr which Cook and Jones¹⁵ give for the binary Fe-Cr system. Thus, boron seems to have very little influence on the position of this boundary. In the samples 2—6 the l. p. of the (Cr, Fe)₂B phase are smaller than those of pure Cr₂B showing that considerable amounts of Fe are dissolved in this phase. The atomic ratio Cr/(Cr + Fe) is estimated to be about three times as great in Cr₂B as in the α -phase.

If there is any appreciable solubility of boron in σ -FeCr it should influence the l. p. of this phase, and a closer study of these parameters is appropriate. The l. p. of the sigma phases in the samples 0 and 1 together with those earlier given by Lundström and Aronsson¹⁰ are collected in Table 3.

Table 3.

Sample	Composition	l.p. of the sigma phase	
0	Fe _{0.504} Cr _{0.496}	$a = 8.798 \text{ \AA}$	$c = 4.558 \text{ \AA}$
1	Fe _{0.551} Cr _{0.449}	$a = 8.787 \text{ \AA}$	$c = 4.560 \text{ \AA}$
	Fe _{0.56} Cr _{0.44}	$a = 8.784 \text{ \AA}$	$c = 4.562 \text{ \AA}$

The compositions have been obtained from chemical analyses except for sample 1. Cook and Jones¹⁵ have found that the Fe-rich $\sigma/(\sigma + \alpha)$ limit in the Fe-Cr system occurs at 43.5—44 at % Cr (700°C). We have assumed that the composition of the sigma phase of sample 1 (containing both ferrite and sigma) is the same as at the $\sigma/(\sigma + \alpha)$ boundary of the binary Fe-Cr system.

The l. p. of the different sigma phases show that the a -axis of σ -FeCr decreases and the c -axis increases with increasing Fe content. The l. p. vary in the same directions when Si is dissolved in σ -FeCr¹⁰. These similarities are not unexpected as it has been assumed the Si and Fe are similarly distributed in the sigma structure. We think that the differences in l. p. of the sigma phases are entirely explained by the variations in Fe content and that they are not due to the solubility of boron in σ -FeCr. This solubility is likely to be very small.

CONCLUSIONS

We have found that the influence of boron on the formation of σ -FeCr is similar to that of carbon and nitrogen. With increasing boron content of a Fe-Cr-B alloy (the atomic ratio Fe/Cr = 54/46), increasing amounts of Cr-rich (Cr, Fe)₂B are formed and less Cr is available for sigma formation. We have found no evidence that there is any appreciable solubility of boron in σ -FeCr.

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