Solid state equilibria in the Cr-Fe-B system at the temperature of 1373 K

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Abstract
The isothermic section of the Cr-Fe-B system with a boron content between 30 and 50 at% was studied at the temperature of 1373 K. In particular the values of the limit boride lattice constants, the extent of the solid solutions $(Fe,Cr)_2B$, (Fe,Cr)B, γ $(Cr,Fe)_2B$, δ $(Cr,Fe)_5B_3$ and ε (Cr,Fe)B and the variation in the relative lattice constants according to composition were defined.
In the two-phase fields of the system it was confirmed that there was preferential distribution of chromium (an element with a lower atomic number) in the phase richest in boron. This was in accordance with what had already been pointed out in the study of the ternary systems Fe-Mn-B, Co-Mn-B and Co-Fe-B.

Riassunto
Equilibri allo stato solido nel sistema Cr-Fe-B alla temperatura di 1373 K
È stata studiata, alla temperatura di 1373 K, la sezione isotermica del sistema Cr-Fe-B con un contenuto di boro compreso tra il 30 ed il 50% at. In particolare sono stati definiti i valori delle costanti reticolari dei boruri limite, l'estensione delle soluzioni solide $(Fe,Cr)_2B$, (Fe,Cr)B, γ $(Cr,Fe)_2B$, δ $(Cr,Fe)_5B_3$, ε (Cr,Fe)B e la variazione delle relative costanti reticolari in funzione della composizione.
Nei campi bifasici del sistema è stato constatato che il cromo, elemento con numero atomico inferiore, si inserisce preferenzialmente nella fase più ricca di boro, in accordo con quanto già evidenziato nelle precedenti ricerche sui sistemi ternari Fe-Mn-B, Co-Mn-B e Co-Fe-B.

A previous study (1) examined the relationship of co-existence in the solid state between the phases which appear in the Fe-Cr-B system at 1250° C. In the zone up to 50 at% boron, the extent of the solid solution derived from iron and chromium borides and the related two and three-phase fields were defined. In particular, in the two iron borides Fe_2B (tetragonal) and FeB (orthorhombic) about 24 and 50% respectively of the iron atoms could be substituted with chromium. In the phases Cr_2B (orthorhombic), Cr_5B_3 (tetragonal) and CrB (orthorhombic) the chromium-iron substitution reached respectively 72, 20 and 40 at%.
This system is still the subject of investigation (2,3): Gorbunov (2) in particular has recently defined the

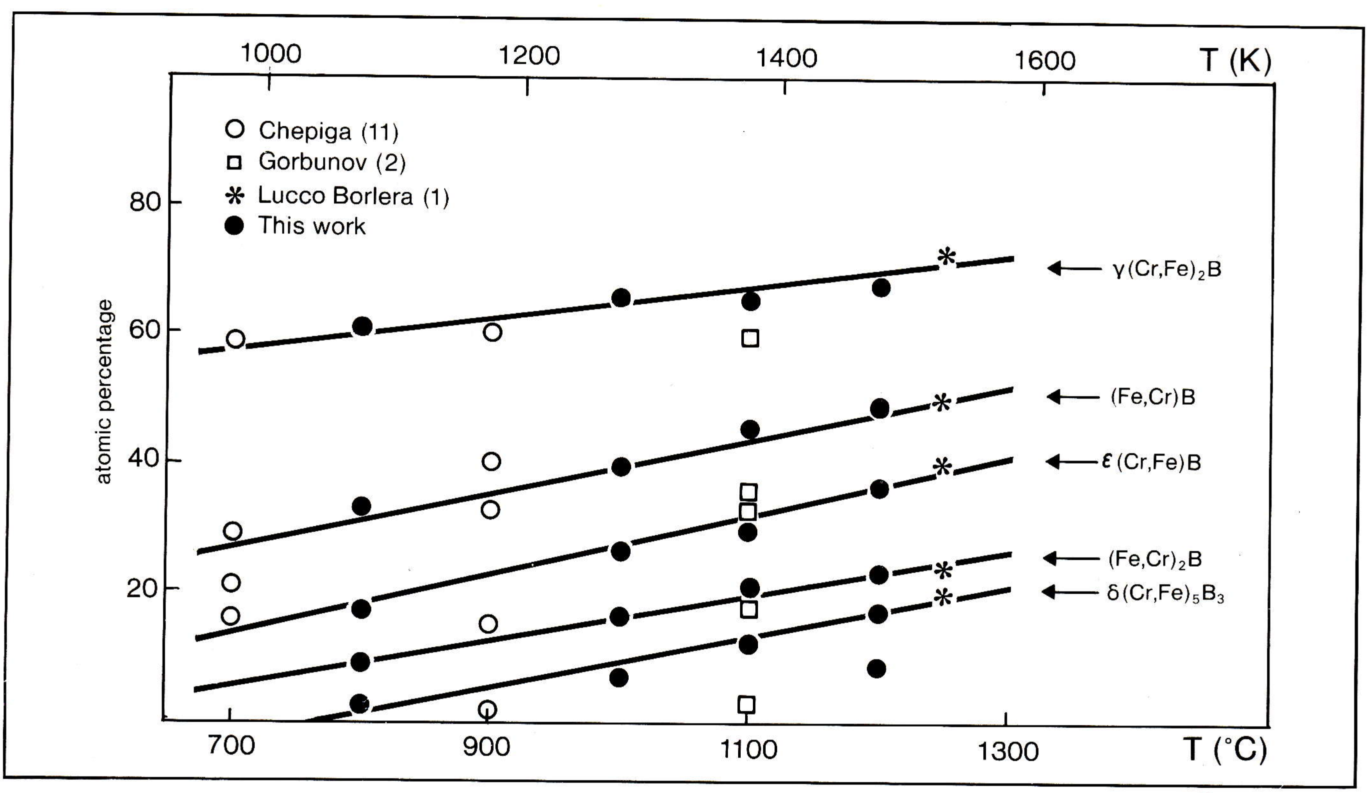


Fig. 1 - Variation with temperature of maximum Cr-Fe replacement in borides belonging to Cr-Fe-B system.

isothermic sections at the temperatures of 700 and 900 °C, in which, as far as the extent of the solid solution and the amplitude of two and three-phase fields are concerned, there are no substantial differences from our previous findings, bearing in mind the different temperature of the experiment. Indeed, using both the data supplied by the literature and that obtained in the course of our research, in Fig. 1 we have recorded in graph form the maximum solubility of chromium and iron respectively (in iron and chromium borides for solid solutions of the Cr-Fe-B system) in the temperature interval included between 700 and 1250 °C. The graph shows that our experimental values fit in perfectly with those of the literature and, in addition, it confirms a progressive increase in the extent of these phases with temperature.

Another subject of research is the definition of the physical characteristics (in particular the lattice constants) of the phases which appear in the system, which we are studying, with reference to the limit iron and chromium borides (4-11). The values recorded in literature present differences which are sometimes considerable and, in addition, as regards the variation of the lattice constants of iron and chromium borides with the reciprocal substitution of the metallic atoms; information is obtainable only for the rhombic phase γ $(Cr,Fe)_2B$ (11) (12).

For the purpose of supplying a homogeneous and complete set of experimental data, we felt it opportune to continue the study of the Cr-Fe-B system, defining the variation in particular, according to the composition, of the phases $(Fe,Cr)_2B$, (Fe,Cr)B, γ $(Cr,Fe)_2B$, δ $(Cr,Fe)_5B_3$ and ε (Cr,Fe)B.

This information will also make it possible to carry out a correct characterisation of the boride layer obtainable on steel containing chromium: since a sample surface, after a boronising treatment, is predominantly composed of M_2B (tetragonal) and MB (orthorhombic) type borides, a preferential insertion of chromium in MB boride is predictable, located in the outermost part of the layer. Indeed, in the course of previous works (13, 14) related to the distribution equilibria which occur between solid solutions of Co-Fe-B, Fe-Mn-B and Co-Mn-B systems, we have ascertained that a preferential insertion of the element with the lower atomic number in the phase richest in boron is achieved between the borides present in the two-phase fields. We believe, therefore, that this behaviour is of a general nature, and must also occur in two-phase samples Cr-Fe-B.

An additional aim of this research was to check again the istothermic section of the Cr-Fe-B system, at the temperature of 1373 K, principally for the part relating to the three-phase field $\gamma(Cr,Fe)_2B + \delta(Cr,Fe)_5B_3 + \varepsilon(Cr,Fe)B$, since the above-mentioned considerations lead us to foresee a different orientation because of the preferential distribution of chromium in the two-phase samples $\gamma(Cr,Fe)_2B + \varepsilon(Cr,Fe)B$, $\gamma(Cr,Fe)_2B + \delta(Cr,Fe)_5B_3$ and $\delta(Cr,Fe)_5B_3 + \varepsilon(Cr,Fe)B$. This specification will also enable us to obtain information concerning the definition of the distribution equilibria between the phases M_2B and MB present in the ternary systems M-M'-B (M,M' = Co,Cr,Fe,Mn). This research is still in progress in this Department.

Experimental procedure

On the basis of what we explained above, in the course of this research we studied the part of the ternary system Cr-Fe-B with a boron content up to 50 at%, in order to check the extent of solid solutions and of two-phase and three-phase fields included in this area of the system.

The samples were obtained by the diffusion and reaction in the solid state of mixtures of suitable composition of Merk reduced iron (Fe = 99,5 weight%), ICN chromium (Cr = 99,9 weight%), Research boron (B = 98 weight%) and alloys Fe-B (B = 16,2 weight%) and Cr-B (B = 11,1 weight%). Compacted under a pressure of 200 atm, the samples were heated at 1073, 1273, 1373 and 1473 K for periods of time sufficient (100-1000 hours) to reach conditions of equilibrium. For the sake of brevity, we only tell in this work about the isothermal section of 1373 K; one can infer the highest Fe-Cr replacement, at the above mentioned temperature, from Fig. 1. The samples were then subjected to chemical and radiographic analysis to check and define the composition and constitution of the solids: alloys with a chromium content higher than 50 weight% were analysed with Cr K_{α_1} (λ = 228,96 pm) radiation, while the others were analysed with Fe K_{α_1} (λ = 193,60 pm) radiation.

Results

Table 1 indicates the weight percentage composition and the phases present (obtained by radiographic analysis) of some alloys prepared at 1373 K by the previously described procedures. For chromium borides which actually present a varying field of composition, notations will be adopted which, for the sake of simplicity of writing, correspond to those in previous works. That is, for a growing boron content γCr_2B, δCr_5B_3 and εCrB.

Table 2 records the lattice constant values for the limit terms of the solid solutions obtained at 1373 K, from iron and chromium borides, by substitution of the metallic atoms of one type with those of another. The

TABLE 1 - Weight composition and phases present in Cr-Fe-B- alloys

Specimen	Weight composition %Cr	%Fe	%B	Phases
1	4,14	84,39	11,47	$(Fe_{0,92}Cr_{0,08})B + (Fe_{0,96}Cr_{0,04})_2B$
2	9,69	78,80	11,51	$(Fe_{0,80}Cr_{0,20})B + (Fe_{0,92}Cr_{0,08})_2B$
3	15,29	73,15	11,56	$(Fe_{0,67}Cr_{0,33})B + (Fe_{0,88}Cr_{0,12})_2B$
4	20,94	67,45	11,61	$(Fe_{0,59}Cr_{0,41})B + (Fe_{0,83}Cr_{0,17})_2B$
5	28,06	60,27	11,67	$(Fe_{0,80}Cr_{0,20})_2B + \gamma(Cr_{0,35}Fe_{0,65})_2B + (Fe_{0,58}Cr_{0,42})B$
6	35,26	53,01	11,73	$(Fe_{0,55}Cr_{0,45})B + \varepsilon(Cr_{0,70}Fe_{0,30})B + \gamma(Cr_{0,38}Fe_{0,62})_2B$
7	42,53	45,68	11,79	$\varepsilon(Cr_{0,75}Fe_{0,25})B + \gamma(Cr_{0,40}Fe_{0,60})_2B$
8	49,88	38,27	11,85	$\varepsilon(Cr_{0,90}Fe_{0,10})B + \gamma(Cr_{0,49}Fe_{0,51})_2B$
9	45,31	40,56	14,13	$(Fe_{0,55}Cr_{0,45})B + \varepsilon(Cr_{0,70}Fe_{0,30})B + \gamma(Cr_{0,38}Fe_{0,62})_2B$
10	61,10	24,61	14,29	$\varepsilon(Cr_{0,85}Fe_{0,15})B + \gamma(Cr_{0,54}Fe_{0,46})_2B$
11	64,81	23,21	11,98	$\varepsilon(Cr_{0,89}Fe_{0,11})B + \delta(Cr_{0,88}Fe_{0,12})_5B_3 + \gamma(Cr_{0,55}Fe_{0,45})_2B$
12	69,13	16,50	14,37	$\varepsilon(Cr_{0,89}Fe_{0,11})B + \delta(Cr_{0,88}Fe_{0,12})_5B_3 + \gamma(Cr_{0,55}Fe_{0,45})_2B$
13	77,24	8,30	14,46	$\varepsilon(Cr_{0,91}Fe_{0,09})B + \delta(Cr_{0,90}Fe_{0,10})_5B_3$
14	80,07	7,82	12,11	$\varepsilon(Cr_{0,91}Fe_{0,09})B + \delta(Cr_{0,90}Fe_{0,10})_5B_3$
15	61,01	29,12	9,87	$\gamma(Cr_{0,63}Fe_{0,37})_2B + \delta(Cr_{0,90}Fe_{0,10})_5B_3$
16	68,13	21,95	9,92	$\gamma(Cr_{0,70}Fe_{0,30})_2B + \delta(Cr_{0,94}Fe_{0,06})_5B_3$
17	75,32	14,71	9,97	$\gamma(Cr_{0,79}Fe_{0,21})_2B + \delta(Cr_{0,97}Fe_{0,03})_5B_3$
18	82,59	7,39	10,02	$\gamma(Cr_{0,90}Fe_{0,10})_2B + \delta(Cr_{0,98}Fe_{0,02})_5B_3$
19	16,86	78,47	4,67	$\alpha(Cr_{0,17}Fe_{0,83}) + (Fe_{0,80}Cr_{0,20})_2B$
20	10,20	87,68	2,12	$\gamma(Cr_{0,10}Fe_{0,90}) + (Fe_{0,87}Cr_{0,13})_2B$
21	12,26	85,62	2,12	$\alpha(Cr_{0,13}Fe_{0,87}) + (Fe_{0,86}Cr_{0,14})_2B$
22	15,36	82,51	2,13	$\alpha(Cr_{0,16}Fe_{0,84}) + (Fe_{0,83}Cr_{0,17})_2B$
23	22,57	72,74	4,69	$(Fe_{0,80}Cr_{0,20})_2B + \gamma(Cr_{0,35}Fe_{0,65})_2B + \alpha(Fe_{0,82}Cr_{0,18})$
24	28,33	66,96	4,71	$\gamma(Cr_{0,40}Fe_{0,60})_2B + \alpha(Cr_{0,24}Fe_{0,76})$
25	20,56	77,30	2,14	$\gamma(Cr_{0,35}Fe_{0,65})_2B + \alpha(Fe_{0,82}Cr_{0,18})$
26	25,80	72,05	2,15	$\gamma(Cr_{0,41}Fe_{0,59})_2B + \alpha(Cr_{0,25}Fe_{0,75})$
27	36,86	46,48	16,66	$(Fe_{0,54}Cr_{0,46})B$
28	56,91	26,19	16,90	$\varepsilon(Cr_{0,70}Fe_{0,30})B$
29	18,00	73,18	8,82	$(Fe_{0,80}Cr_{0,30})_2B$
30	78,10	10,68	11,22	$\delta(Cr_{0,88}Fe_{0,12})_5B_3$
31	29,82	61,28	8,90	$\gamma(Cr_{0,34}Fe_{0,66})_2B$

TABLE 2 - Cell parameters of end members present in Cr-Fe-B system solid solutions (1373K)

	a_0	b_0	c_0	V (pm · 10^{-5})
Fe_2B	511,6 pm	—	425,5 pm	1.113,7
$(Fe_{0,80}Cr_{0,20})_2B$	512,4 pm	—	422,6 pm	1.109,6
FeB	406,4 pm	550,3 pm	294,6 pm	658,8
$(Fe_{0,55}Cr_{0,45})_2B$	413,5 pm	556,0 pm	292,6 pm	672,7
γCr_2B	1,456 nm	732,0 pm	420,8 pm	4.485,8
$\gamma(Cr_{0,35}Fe_{0,65})_2B$	1,428 nm	727,5 pm	414,7 pm	4.305,2
δCr_5B_3	548,0 pm	—	1,001 nm	3.006,0
$\delta(Cr_{0,88}Fe_{0,12})_5B_3$	541,4 pm	—	1,016 nm	2.978,0
εCrB	297,0 pm	786,5 pm	293,6 pm	685,8
$\varepsilon(Cr_{0,70}Fe_{0,30})B$	298,2 pm	787,2 pm	293,7 pm	689,4

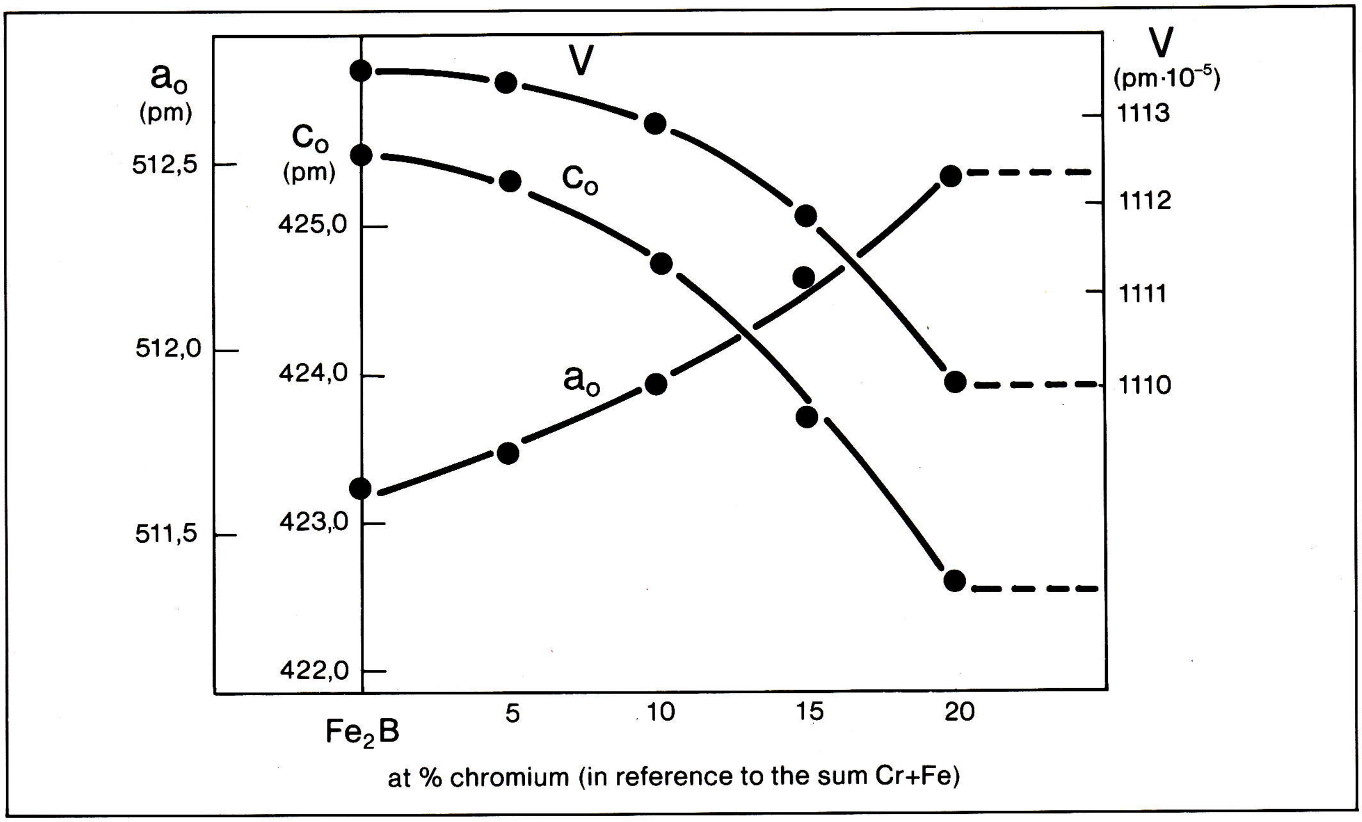
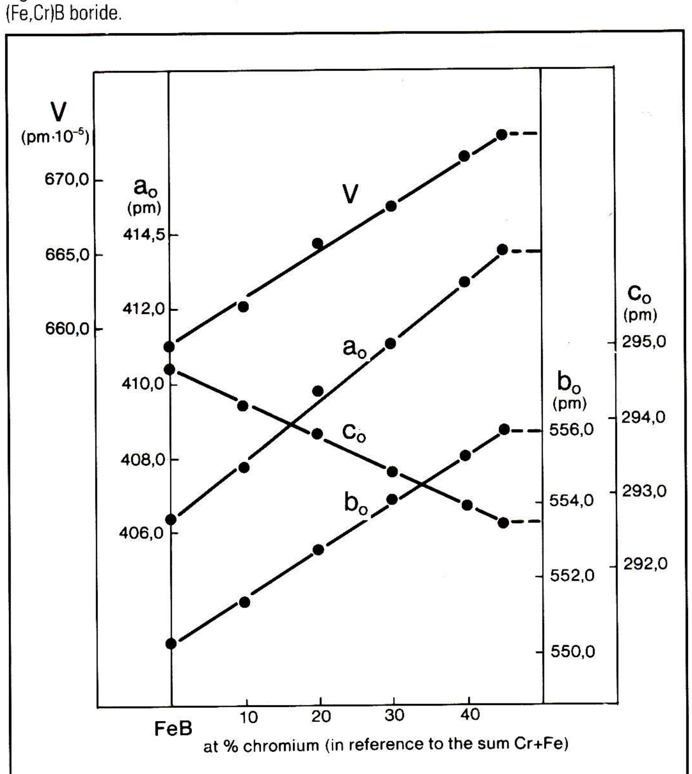


Fig. 2 - Relation between composition and lattice parameters of the tetragonal $(Fe,Cr)_2B$ boride.

Fig. 3 - Relation between composition and lattice parameters of the orthorhombic (Fe,Cr)B boride.



chromium boride lattice constant values refer to the terms of the solid solutions of composition closest to that corresponding to the stoichiometric formula and, therefore, respectively to $\gamma(Cr_{0,675}B_{0,325})$, $\delta(Cr_{0,625}B_{0,375})$ and $\varepsilon(Cr_{0,50}B_{0,50})$; in addition, careful checking of the lattice constant values has shown that no significant differences exist between the terms of extreme composition relative to each chromium boride. The variation in lattice constant values according to composition for the phases $(Fe,Cr)_2B$ (tetragonal), (Fe,Cr)B (orthorhombic), $\gamma(Cr,Fe)_2B$ (orthorhombic), $\delta(Cr,Fe)_5B_3$ (tetragonal) and ε (Cr,Fe)B (orthorhombic) has been recorded in Figures 2-6.
In Figure 7 the isothermal section of 1373 K of the Cr-Fe-B system is traced. This was achieved on the basis of results obtained in this research.
As regards the existence of the above-mentioned fields, there are no differences between our results (present and past) and those recently proposed by Gorbunov; on the other hand, there are considerable differences (both of extent and orientation) in these fields, as appeared in examining the isothermic section of the Cr-Fe-B system proposed by the above-mentioned researcher (2) (11).

From the isothermic section of 1373 K, which for the sake of brevity we will not describe, it is particularly interesting to examine the conditions of equilibrium established between the solid solutions present in the two-phase fields.
Indeed a systematic preferential insertion of chromium, which has an atomic number lower than that of iron, could be observed in the boride richest in the latter element, as was similarly found in the systems Fe-Mn-B, Co-Mn-B and Co-Fe-B.
This inequality in distribution is not compatible with the orientation of two-phase fields indicated in the isothermic section of the system proposed by Gorbunov. He does not evaluate the quantitative aspect of the phenomenon, which will be the subject of one of our future studies.
Finally, as regards the three-phase field $\gamma(Cr,Fe)_2B + \delta(Cr,Fe)_5B_3 + \varepsilon(Cr,Fe)B$ our results confirm that, at equilibrium, the terms $\gamma(Cr_{0,55}Fe_{0,45})_2B$, $\delta(Cr_{0,88}Fe_{0,12})_5B_3$ and $\varepsilon(Cr_{0,89}Fe_{0,11})B$ are present in three-phase samples.
The above-mentioned field has, therefore, an orientation and extent in accordance with the facts that emerged with regard to the preferential distribution of chromium between the phases in equilibrium containign iron and chromium in solid solution.

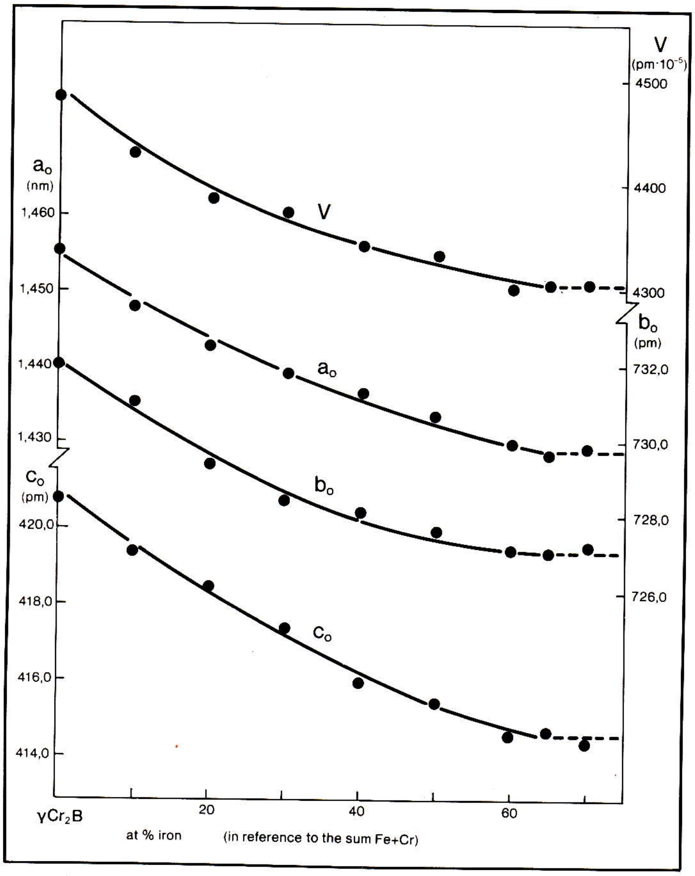
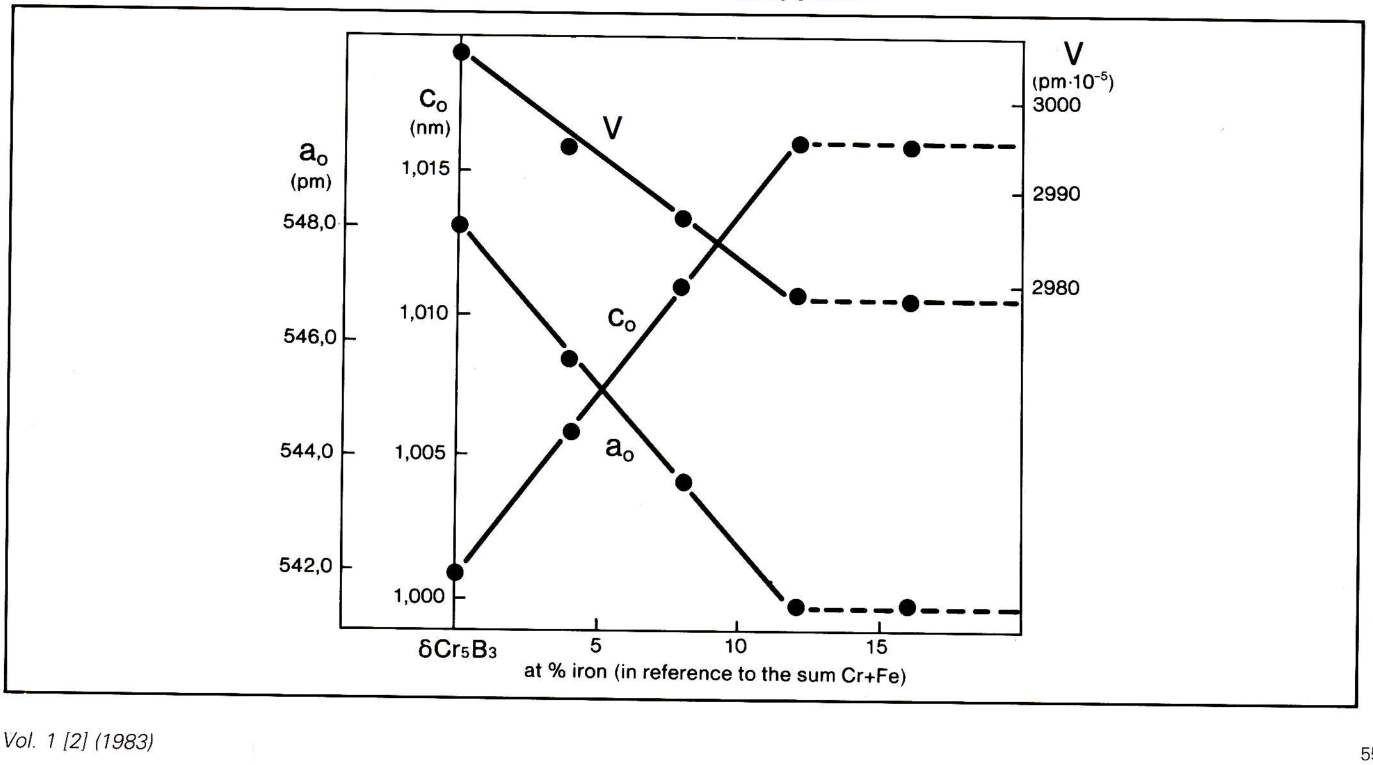


Fig. 4 - Relation between composition and lattice parameters of the orthorhombic $\gamma(Cr,Fe)_2B$ boride.

Fig. 5 - Relation between composition and lattice parameters of the tetragonal $\delta(Cr,Fe)_5B_3$ boride.



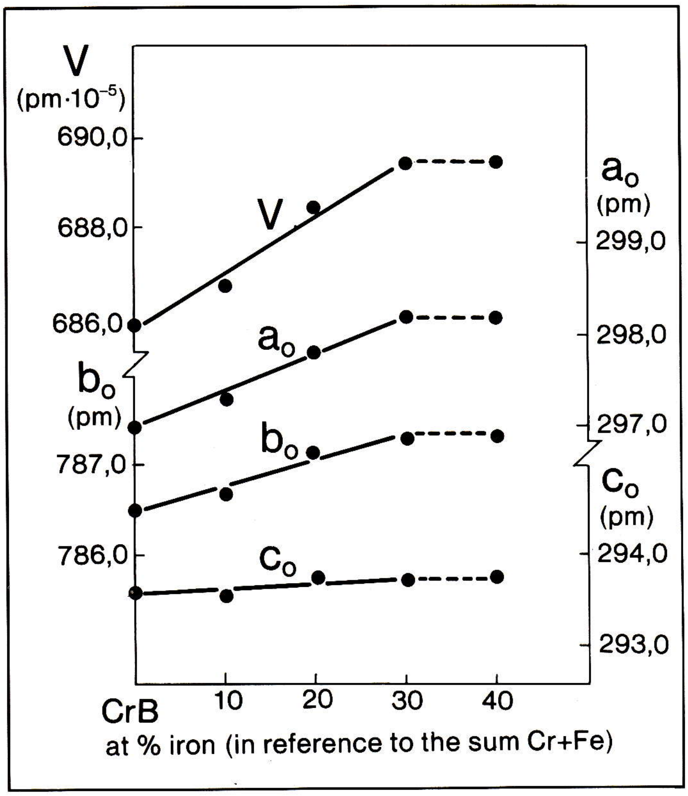
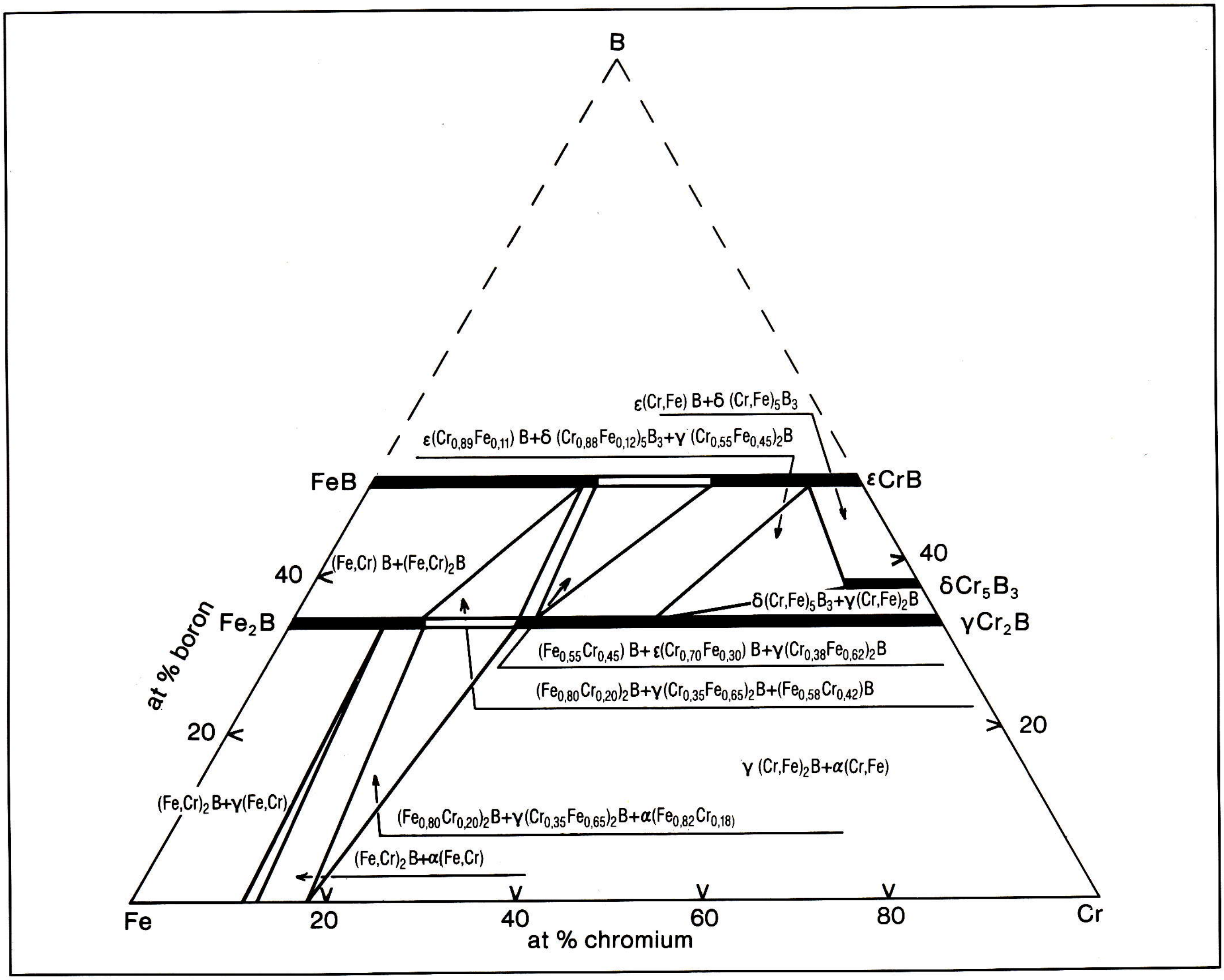


Fig. 6 - Relation between composition and lattice parameters of the orhorhombic ε(Cr,Fe)B boride.

Conclusions

In the ternary system Cr-Fe-B, at the temperature of 1373 K and in the zone up to 50 at% boron, the extent of solid solutions composed of iron and chromium borides was defined, as well as the variation in the lattice constants with composition and the two- and three-phase fields present in the ternary system. The maximum Cr-Fe substitution as an atomic percentage in relation to the sum of the metallic atoms, corresponded to 20 and 45% respectively in the Fe_2B and FeB phases. In the borides γCr_2B, δCr_5B_3 and εCrB it was possible to carry out the substitution of chromium with iron until respectively 65, 12 and 30 at% iron.
For all the phases recorded above, a progressive increase (with temperature) of the Fe-Cr substitution in

Fig. 7 - Isothermal section at 1373K (1100 °C) of Cr-Fe-B system.



chromium or iron borides was verified.
In addition, chromium, metallic element with lower atomic number and higher affinity in respect of boron, was found in the two-phase samples Cr-Fe-B to have preferential insertion in the borides richest in boron. This is in accordance with what was found in the systems M'-M"-B (M'-M" = Co,Fe, Mn): as a result the three-phase field $\gamma(Cr,Fe)_2B + \delta(Cr,Fe)_5B_3 + \varepsilon(Cr,Fe)B$ has an orientation closely related to the quantity of the above-mentioned phenomena of distribution.

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