DIAGRAM OF STATE OF THE CHROMIUM-BORON SYSTEM

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There is a great deal of contradictory information on the chromium-boron system. A number of papers note the existence of polymorphic transformations in chromium [1]. The review article [2] advances the view that β-Cr [3] is evidently the Cr_2N. Careful investigations using high-temperature radiography [4-6] have shown the absence of any transformations in chromium, which up to the melting point is in the α-Cr state (body-centered cubic). However, a group of investigators [7] have again confirmed (based on the metallographic method) the point of view of the existence of polymorphic transformations in chromium. In [7] there is no discussion of the results of the high-temperature radiography of chromium.

The most stable crystal form of boron, in which there is observed no transition to other forms, is β-rhombohedral boron ("β" -B) [8]. The published results of [9] furnish a basis to assume that "amorphous boron" is the microcrystalline state of "β "-boron. It must be noted that the authors of [10] did not observe a microcrystalline structure in "amorphous boron" precipitated at 1200°C. In a consideration of the metal-boron system we take β-rhombohedral boron, which forms after heating "amorphous boron" up to 1100°C and higher.

In the chromium-boron system the existence of the boride phases Cr_4B, Cr_2B, Cr_5B_3, CrB, Cr_3B_4, CrB_2, CrB_6 (Table 1) has been observed by x-ray methods.

In [12], on the basis of an investigation of alloys of the chromium-boron system obtained by arc melting followed by long-term annealing, it was shown that in alloys containing up to 33 at.%, there exists only one boride phase, Cr_2B with the structure Mn_4B. The existence of phases with the composition $(Me^{I}Me^{II})_2B$ with the structure of Mn_4B is confirmed in [13]. In [14] it was reported that the compound "CrB_6" contains a considerable amount of oxygen and is probably chromium oxyboride. Efforts to synthesize CrB_6 from the elements have not been crowned with success.

The commonly known diagram of state of the chromium-boron system in the region up to 70 at.% boron [15] was constructed on the basis of a study of the melting of compositions with hot pressing. In [16] there is given a diagram of state of the system which seems more probable (Fig. 1). Still another variant of the diagram [17] is based on a thermographic and metallographic study of the alloys. In this diagram regions are

TABLE 1. Crystallographic Data of Chromium Borides [1, 11, 15]

Borides	System	Structural type	Space group	M*	Lattice constants, Å: a	b	c
Cr_2B	Orthorhombic	Mn_4B	*Fddd*	8	14,71	7,41	4,25
Cr_5B_3	Tetragonal	$D8_l$	*I4/mcm*	4	5,46 (5,44)	—	10,64 (10,07)
CrB	Orthorhombic	*Bf*	*Cmcm*	4	2,969	7,858	2,932
Cr_3B_4	»	$D7_b$	*Immm*	2	2,984	13,02	2,953
CrB_2	Hexagonal	*C*32	*P6/mmm*	1	2,969	—	3,066
Cr_4B?	Orthorhombic	Mn_4B	*Fddd*	8	14,71	7,382	4,262
Cr_2B?	»	—	*Abmm* or *Abm*2	—	14,7	7,34	4,29
Cr_2B?	Tetragonal	*C*16	*I4/mcm*	4	5,185	—	4,316
CrB_6	»		—	—	5,468	—	7,152

* M is the number of formula units in a cell.

Moscow. Translated from Poroshkovaya Metallurgiya, No. 4 (76), pp. 51-57, April, 1969. Original article submitted December 19, 1967.

TABLE 2. Characteristics of Alloys of the Chromium-Boron System

No. of alloy	Boron content at.%	Boron content wt.%	t^{start}_{melt}, °C	t^{end}_{melt}, °C	Phase composition*	Microstructure
1	1	0,21	1750	1820	α-Cr	α-Cr + melted eutected
2	3	0,64	1610	1800	α-Cr	α-Cr + eutectic
3	5	1,07	1610	?	α-Cr, (Cr_2B)	The same
4	10	2,26	1600	1700	α-Cr, (Cr_2B)	Mainly eutectic
5	15	3,53	1620	1640	α-Cr, Cr_2B	Cr + B + eutectic
6	20	4,94	1650	1690	α-Cr, Cr_2B	Cr_2B + eutectic
7	22	5,55	1660	1690	α-Cr, Cr_2B	The same
8	25	6,48	1640	1700	Cr_2B, α-Cr	Nonhomogeneous
9	30	8,19	1650	1720	Cr_2B, (α-Cr)	Mainly Cr_2B
10	33	9,20	1700	1900	Cr_2B	—
11	33,3	9,42	1870	1920	Cr_2B	Mainly Cr_2B, nonhomogeneous
12	34	9,69	1870	1900	Cr_2B, (Cr_5B_3)	—
13	37,5	11,08	1880	1900	Cr_5B_3, (CrB)	Mainly Cr_5B_3
14	40	11,83	1900	1920	Cr_5B_3, CrB	Two phases
15	43	13,10	1900	1920	CrB, Cr_5B_3	—
16	45	14,81	1900	2030	CrB, Cr_5B_3	—
17	48	16,50	1900	2050	CrB	CrB + melted peritectics
18	50	17,24	—	2100	CrB	One phase
19	51	17,9	—	2090	—	—
20	53	19,4	2070	2100	—	Nonhomogeneous
21	54	20,22	2050	?	CrB, (Cr_3B_4)	—
22	57	21,6	2060	2070	Cr_3B_4, (CrB)	Mainly one phase
23	60	23,8	2070	2080	Cr_3B_4	Peritectic character of crystallization
24	64,5	29,6	2070	2100	—	—
25	65	29,9	2100	2130	CrB_2, (Cr_3B_4)	—
26	66,7	32,3	2100	2180	CrB_2	Mainly one phase
27	70	32,7	2150	2200	CrB_2	One phase
28	72	34,5	2075	2140	CrB_2	—
29	77	40,4	1850	1970	—	CrB_2 + eutectic
30	80	42,9	1850	?	—	—
31	83	51,6	1850	1900	—	Eutectic
32	85	54,2	1840	?	—	Mainly eutectic
33	85,7	55,5	1840	1950	CrB_2, («β»-B)	—
34	87	59,0	1850	2100	CrB_2, («β»-B)	—
35	90	65,2	1820	1950	—	Eutectic + excess isolated "β"-B
36	93	73,5	1800	?	—	"β"-B + eutectic
37	95	78,7	1900	2140	«β»-B, (CrB_2)	—
38	98	91,2	2000	2140	«β»-B	Mainly "β"-B

* In parenthesis are shown phases whose content is insignificant.

TABLE 3. Crystal Lattice Constants of the Phases of the Chromium-Boron System

Phase	Lattice constant, Å a	b	c
α-Cr	2,8843	—	—
Cr_2B*	14,76	7,428	4,287
Cr_5B_3	5,48	—	10,10
CrB	2,9685	7,8587	2,928
Cr_3B_4	2,988	13,01	2,949
CrB_2	2,972	—	3,066

* Structural type corresponds to Mn_4B.

marked out corresponding to the postulated transformations of chromium, "β-Cr," Cr_4B, and CrB_6, the probability of whose existence is open to doubt. Papers have recently been published which give insufficiently reliable data on the chromium-boron system; for example, the authors of [18] regard alloys of chromium with 20 and 40 at.% boron as single-phase, which is insufficiently convincing. There is evidently required further work on making more precise the diagram of state of the chromium-boron system.

The authors have made a new investigation of the chromium-boron system using the method of thermal analysis, which has already been reported earlier [19]. In addition, alloys were synthesized in a vacuum higher than 2×10^{-5} mm Hg at 1400°C for 2 hours. For the investigation there were used chromium powders with a purity of ~99.7% (main impurities: Fe–0.1, Ni–0.02, C–0.08, O_2–0.04, N_2–0.006%) and amorphous boron with a purity of > 99.4%, obtained by the pyrolysis of its volatile compounds. After melting and crystallization, the samples for radiographic investigation were held

TABLE 4. Melting Temperature of the Phases and Eutectics of the Chromium-Boron System °C

Phase, eutectic	[15]	[16]	[17]	Present work	Mean and most probable values
Cr	1890	1890	1860	1840	>1875
$Cr+Cr_2B$	1580—1680	1560	1570—1650	1610—1650	1600
«Cr_4B»	1680	—	1650	—	—
Cr_2B	1840	1760	1740	1870	1850
Cr_5B_3	1900	1860	1880	1900	1890
CrB	2050	2090	2050	2100	2090
$CrB+Cr_3B_4$	~1850	~2060	2040	2050	2050
Cr_3B_4	1960	2090	1940	2070	2080
CrB_2	>2100	2150	—	2200	2200
$CrB_2+\beta$-B	—	—	—	1830	1830
β-B	—	—	2050	2080—2150	not less than 2150

TABLE 5. Values of the Microhardness of Phases of the Chromium-Boron System

Phase	Microhardness, kg/mm²			
	[3], loading 100 g	[11], loading 50 g	[18], loading 50 g	present work, loading 50 g
α-Cr in equilibrium with Cr_2B	500	—	—	330—380
«Cr_4B»	—	1240±60	1350±24	—
Cr_2B	—	1350±100	—	~1800
Cr_5B_3	—	—	—	1420—1520
CrB	1200—1300	2100	2280±36	2100—2220
Cr_3B_4	1400—1500	—	1780±18	1800—1850
CrB_2	2100—2200	2100±80	1600±50	2130—2240
β-B in equilibrium with CrB_2	—	—	—	3700

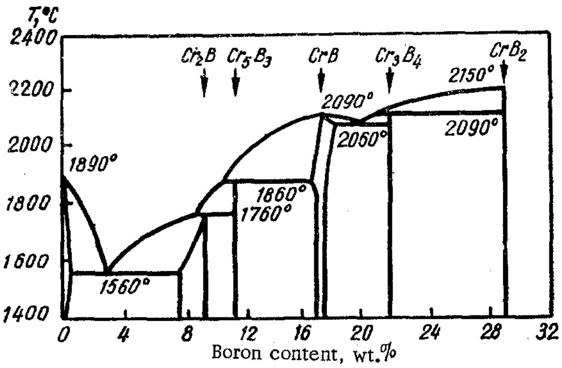

Fig. 1. Probable diagram of state of the chromium-boron system according to [16].

for 2-5 min at a temperature 50-100°C below the melting point. Samples destined for preparation of microslides were held in the liquid state for 2-3 min and were rapidly cooled. In the work, use was made of local x-ray spectral analysis and the microhardnesses of the phase components was measured.

The x-ray analysis was done in CrK_α-radiation. The lattice constants were determined in a type URS-50I diffractometer with an accuracy up to 0.05%. The local x-ray spectral analysis was carried out in type MAR-1 instrument, using a vacuum spectrometer and a type MSTR-4 counter, with respect to the line $L\alpha_3$Cr at a voltage of 35 kV.

The studied compositions of the chromium-boron system, the results of a determination of the temperature of the start and end of their melting (t_{melt}^{start} and t_{melt}^{end}) and of phase analysis and study of the microstructure are given in Table 2, and the values of the lattice constants of the phases of the system in Table 3. On the basis of the results of the investigation, a diagram of state of the system was constructed (Fig. 2).

The compounds Cr_4B, Cr_2B (with a structure different from Mn_4B), Cr_3B_2, and CrB_6 were not observed by the authors in the binary system. The melting and decomposition temperatures of chromium borides and the eutectics they form, according to the data of different authors, are given in Table 4. The authors observed less difference in the melting temperatures of a mixture of α-Cr + Cr_2B in the pre-eutectic and after-eutectic regions, than are given in other papers; this can be explained by the effect of the impurities on the properties of the eutectic. The microstructure of an alloy with 20 at.% B, shown in Fig. 3,a, does not correspond to a single-phase state. Repeated measurements of the temperature of the end of melting of compositions containing from 30 to 35 at.% B, constitute a basis for assuming that the temperature of the

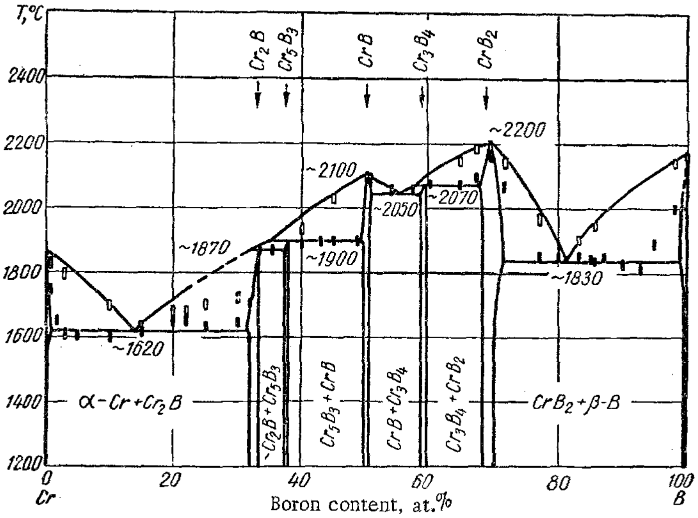

Fig. 2. Diagram of state of the chromium-boron system (authors' data).

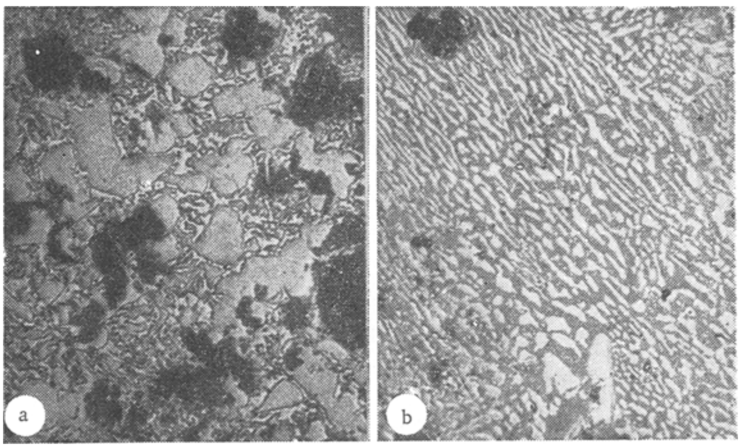

Fig. 3. Microstructure of alloys of the chromium-boron system, 300 magnifications: a) 80 at.% Cr + 20 at.% B; b) 15 at.% Cr + 85 at.% B. Etching agent— 1 part NaOH, 2 parts $K_3[Fe(CN)_6]$, 3 parts water.

the peritectic decomposition of the compound Cr_2B of stoichiometric composition is rather high and reaches ~1870°C. The conditions for the appearance of thermographic effects and fluidity in chromium alloys with 20-30 at.% B need to be made more precise.

In alloys containing more than 70 at.% B, there was observed the formation of a eutectic between CrB_2 and a solid solution of chromium in "β"-boron with a melting temperature of ~1830°C. Fig. 3,b shows the microstructure of an alloy with 85 at.% B, close to the eutectic. An alloy with 98 at.% B was practically single-phase. A comparison of the recording speeds of the x-ray spectral line of chromium in standards, in a eutectic CrB_2 + "β"-boron, and in excess grains of "β"-boron showed that the eutectic contained ~83 at.% Cr.

In an x-ray structural analysis, there were observed no substantial changes in the lattice constants of α-Cr and of the boride phases in alloys with different boron contents. There was a slight change only in the lattice constants of the phases Cr_2B and CrB_2. Alloys synthesized at 1400°C in vacuum, as was shown by radiographic investigation, were analogous with respect to phase composition to alloys obtained by melting. With the synthesis of an alloy with 85.7 at.% B, the CrB_2 and β-boron phases were observed. The phase "CrB_6" (together with CrB_2) was successfully observed only in the case of the synthesis of an alloy at a low vacuum; this is evidence of the fact that this phase is chromium oxyboride.

Values of the microhardness of the phase components of alloys of the chromium-boron system obtained by the authors are compared in Table 5 with the measurements of other authors. It is evident that it is possible to differentiate the boride phases of chromium by the microhardness.

CONCLUSIONS

1. On the basis of new investigations of the chromium-boron system and of a consideration of the literature data there is proposed a more plausible diagram of state of the system.

2. There has been confirmed the absence of the compounds Cr_4B, Cr_2B with a structure of the type $CuAl_2$, Cr_3B_2, and CrB_6.

3. For the compound Cr_2B, with a Mn_4B structure (as the most plausible), there has been determined a temperature of the peritectic decomposition of ~1870°C.

4. Between α-Cr and Cr_2B there is formed a eutectic, whose melting temperature is evidently effected by impurities.

5. The compound CrB_2 is in equilibrium with a solid solution of chromium in β-rhombohedral boron, and forms with it a eutectic containing ~83 at.% boron and melting at ~ 1830°C. The maximum solubility of chromium in boron is ~2 at.%.

6. The compound known as CrB_6 is chromium oxyboron and can be obtained by sintering the components at a not too high vacuum.

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