

The Binary System Chromium-Boron

I. Phase Analysis and Structure of the ζ - and θ -phases

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This investigation is part of a study on binary alloys between transition elements and boron, carried out at this institute. A phase analysis of the system chromium-boron and structure determinations of two of the intermediary phases have been made. An attempt to determine the structures of the remaining phases is presently carried out, and the result will appear in a later communication.

Few investigations on the chromium-boron system have been reported. According to older works¹⁻⁵ borides of composition Cr_3B_2 and CrB exist. At the moment of publication of this work, a paper »Properties of Chromium Boride and Sintered Chromium Boride» by S. J. Sindeband⁶ appeared. Some X-ray data on the boride CrB are mentioned, which are in accordance with those obtained for the ζ -phase. The conclusion, that only one phase exists in the range 12—20 weight % boron (39.5—54.5 atomic %) seems to be wrong, perhaps resulting from the unsatisfactory method for preparing the alloys.

GENERAL METHODS

Starting materials were chromium, deposited electrolytically, and with a purity of 99.4 % and boron with a purity of 98—99 % prepared by reduction of boron tribromide with hydrogen⁷. The alloys were prepared in two different ways. The first method was to heat and melt mixtures of chromium and boron in a high frequency vacuum induction furnace at about 1600° C. The second method was to sinter weighed mixtures of chromium and boron in evacuated silica tubes, usually for 48—72 hours at 1150° C. Single crystals were obtained, however, from mixtures sintered for about 20 days at 1150° C.

Selected alloys were dissolved in perchloric acid or fused with sodium peroxide or nitrate-carbonate mixture. In the solutions chromium and boron were determined by the usual methods.

The phase analysis was carried out by X-ray powder methods as was the structure determination of the Θ -phase. The structure of the ζ -phase was determined, using single crystal methods. The determination was based on Weissenberg photographs taken with Mo- K radiation. The estimation of the intensities was carried out visually, starting from 4 : 2 : 1 as relative values of the intensities of Mo- $K\alpha_1$, Mo- $K\alpha_2$ and Mo- $K\beta$ radiation. Correlation between the intensity scales of different Weissenberg photographs was obtained according to the Weissenberg oscillation method, described by Magnéli⁸. Relative values of F_{hkl}^2 were obtained by multiplying the intensity values with the factor $\cos^2\mu \times \sin Y \times (1 + \cos^2 2\Theta)$ utilizing the curves given by Chia-si Lu⁹. The temperature factor was neglected.

The calculations of Patterson cuts and electron density function projections were carried out by means of the electric machine for the summation of Fourier series, constructed by Hägg and Laurent¹⁰.

GENERAL SURVEY OF THE SYSTEM

Five intermediary phases, δ , ε , ζ , η and Θ were found, all of which had metallic properties. The hardness was remarkable and all the phases seemed to be rather resistant against chemical attack. Of the more common acids, only perchloric acid was able to dissolve them.

The solubility of boron in the chromium lattice was very low, as no displacements of the interferences of the chromium lattice were observed as the boron content increased.

The δ -phase was found to have a probable content of 33 atomic % boron. It crystallized in very thin hexagonal plates.

The ε -phase had a content of 40 atomic % boron.

The ζ -phase was found with a content of 50 atomic % boron. The homogeneity range was narrow and the crystal structure of this phase will be discussed below. It crystallized in needles or rods with a square transverse section.

The η -phase had a content of about 55 atomic % boron, and the crystals were similar to those of the ζ -phase.

The Θ -phase had the composition CrB_2 and crystallized in hexagonal plates. The structure of this phase will be discussed below.

THE ζ -PHASE

This phase appeared pure in powder photographs of alloys with boron content of 50 atomic %. The homogeneity range was narrow, as no displacements of the interferences of the ζ -phase were observed in alloys of different boron content in the range between the ϵ - and η -phases. A well defined single crystal was investigated. Laue photographs showed the Laue symmetry to be D_{2h} - mmm . Rotation and Weissenberg photographs were taken around $[0\ 0\ 1]$, the needle axis, using Cu- K and Mo- K radiation. Accurate cell dimensions were obtained from powder photographs, giving the axes of the orthorhombic cell:

$$a = 2.969 \text{ \AA}, b = 7.858 \text{ \AA}, c = 2.932 \text{ \AA}.$$

The volume of the unit cell is $V = 68.40 \text{ \AA}^3$. The density found was 6.05, corresponding to a cell content of 4 CrB (calculated density 6.11).

Reflections $h\ k\ l$ were observed only for $h + k = 2n$, $0\ k\ l$ for $k = 2n$, $h\ 0\ l$ only for $h = 2n$ and $l = 2n$ and $h\ k\ 0$ for $h + k = 2n$. Probable space groups are thus D_{2h}^{17} - $Cmcm$, C_{2v}^{12} - Cmc and C_{2v}^{16} - Ama .

Chromium positions. From space considerations, the only possible positions for the four metal atoms are: *

in C_{2v}^{12} - Cmc the fourfold position 4: (a)

in C_{2v}^{16} - Ama the fourfold position 4: (b)

in D_{2h}^{17} - $Cmcm$ the fourfold position 4: (c).

The investigation was started by examining whether the structure was consistent with 4: (c) in D_{2h}^{17} , having the highest symmetry. (The axes, given above, have been chosen so, that the International tables may be used directly for D_{2h}^{17} - $Cmcm$.)

$$4: (c) \ 0\ y\ 1/4; \ 0\ \bar{y}\ 3/4; \ 1/2\ 1/2 + y\ 1/4; \ 1/2\ 1/2 - y\ 3/4.$$

In order to determine the parameter y , the Patterson-Harker method was used. The space group contains a glide plane perpendicular to the b -axis and thus the section $P(0\ v\ 1/2)$ in the Patterson space was investigated. The only strong maximum appeared at $v = 0.292$. This corresponds to a value of the parameter y in 4: (c) of $v/2 = 0.146$. With this parameter value, the metal

* Notations according to *International tables for the determination of crystal structures*, Berlin 1935.

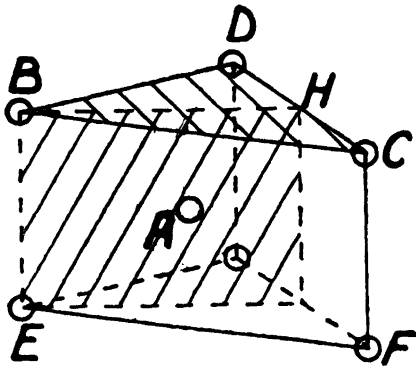
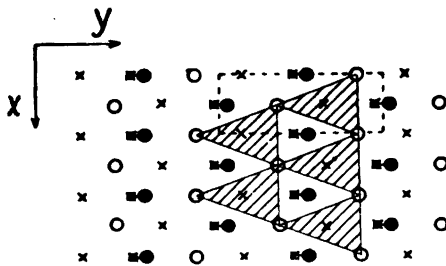


Fig. 1. Trigonal prism of metal atoms in the ζ -phase.

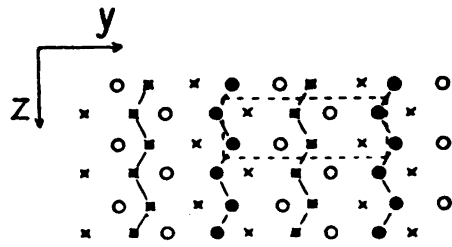
atoms form a lattice, built up of trigonal prisms (Fig. 1) in a manner indicated by Fig. 2. Every metal atom is surrounded by six nearest neighbours, lying at the corners of the trigonal prism, four at distances A—F = 2.65 Å and two at distances A—E = 2.72 Å.

Boron positions. The boron atoms must be situated in holes of the metal lattice. The only holes large enough are situated at the centre of a trigonal prism of metal atoms. These holes are connected to channels, running parallel to the c -axis, and their centres occupy the position $4 : (c)$ in D_{2h}^{17} with a value of the parameter $y = 1/2 - c^2/16 b^2 y_{Mc} = 0.440$. A boron atom placed in such a hole



- × -metal atoms in $xy \frac{1}{4}$
- -metal atoms in $xy \frac{3}{4}$
- -boron atoms in $xy \frac{1}{4}$
- -boron atoms in $xy \frac{3}{4}$

Fig. 2 a. The lattice of the ζ -phase, projected on (001).



- × -metal atoms in Oyz
- -metal atoms in $\frac{1}{2}yz$
- -boron atoms in Oyz
- -boron atoms in $\frac{1}{2}yz$

Fig. 2 b. The lattice of the ζ -phase, projected on (100).

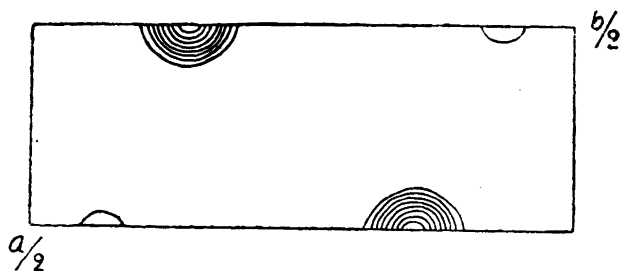


Fig. 3. Projection of the electron density of the ζ -phase on (001).

would be surrounded by six chromium atoms at a distance of 2.19 Å. The boron atoms would be connected to zig-zag chains, running parallel to the c -axis and with a distance boron-boron of 0.86 Å. This value is in close agreement with those previously observed. A comparison between observed and calculated $|F|$ values assuming the positions above for the chromium and boron atoms, is given in Table 1. The agreement is satisfactory. In Fig. 2 the structure is projected on (0 0 1) and (1 0 0). A further support for the positions of the boron atoms is given by the projection of the electronic density on (0 0 1) (Fig. 3). As the position of the heavy chromium was determined from the Patterson cut, the signs of the observed $|F|$ values could be calculated for all reflections. The value of the parameter for the boron atoms, obtained from this projection, was 0.437. The error of this parameter value, however is rather large because of the limited number of reflections and the comparatively small boron maximum. For this reason, the value 0.440 is considered to be more correct. It is of interest to note that the boron chains are parallel to the needle axis of the single crystals.

The ζ -phase, CrB, thus crystallizes in space group $D_{2h}^{17}\text{-Cmcm}$ with the metal as well as the boron atoms in:

$$4 : (c) \ 0 \ y \ 1/4; \ 0 \ \bar{y} \ 3/4; \ 1/2 \ 1/2 + y \ 1/4; \ 1/2 \ 1/2 - y \ 3/4.$$

The values of the parameters are $y_{\text{Me}} = 0.146$ and $y_{\text{B}} = 0.440$.

This structure may be compared with the δ -phases in the molybdenum and tungsten-boron systems (ideal composition MeB)¹¹. The metal atoms of the latter phases have the same coordination as the ζ -phase in the chromium-boron system. The prisms of metal atoms, however, are connected in a different way, giving channels in two directions at right angles. The characteristic zig-zag chains of boron atoms also appear, now running in two directions.

Table 1. ζ -phase. Weissenberg photographs with Mo-K radiation. Comparison between observed and calculated $|F|$ values.

$h k l$	$ F $		$h k l$	$ F $		$h k l$	$ F $	
	obs.	calc.		obs.	calc.		obs.	calc.
2 0 0	60	62	0 2 1	48	61	0 6 2	24	26
4 0 0	41	38	0 4 1	28	36	0 8 2	—	13
6 0 0	31	27	0 6 1	34	40	0 10 2	32	35
0 4 0	52	55	0 8 1	35	34	0 12 2	—	2
0 6 0	29	31	0 10 1	—	11	0 14 2	29	24
0 8 0	21	17	0 12 1	—	2	1 1 2	28	23
0 10 0	39	39	0 14 1	—	2	1 3 2	46	46
0 12 0	—	2	1 1 1	53	54	1 5 2	—	7
0 14 0	31	32	1 3 1	28	29	1 7 2	48	42
1 1 0	36	43	1 5 1	40	41	1 9 2	—	10
1 3 0	62	64	1 7 1	—	9	1 11 2	16	20
1 5 0	—	8	1 9 1	27	33	1 13 2	17	20
1 7 0	45	50	1 11 1	20	23	2 0 2	56	50
1 9 0	—	9	1 13 1	—	20	2 2 2	—	6
1 11 0	27	22	2 2 1	56	42	2 4 2	43	35
1 13 0	21	21	2 4 1	31	29	2 6 2	18	22
2 2 0	—	7	2 6 1	35	34	2 8 2	—	12
2 4 0	42	41	2 8 1	23	30	2 10 2	36	32
2 6 0	31	27	2 10 1	—	10	2 12 2	—	2
2 8 0	—	13	2 12 1	—	2	2 14 2	16	24
2 10 0	38	35	2 14 1	—	10	3 1 2	19	26
2 12 0	—	2	3 1 1	40	34	3 3 2	42	34
2 14 0	22	25	3 3 1	21	20	3 5 2	—	6
3 1 0	24	20	3 5 1	31	30	3 7 2	34	34
3 3 0	49	40	3 7 1	—	7	3 9 2	—	6
3 5 0	—	6	3 9 1	26	28	3 11 2	—	16
3 7 0	41	37	3 11 1	—	19	4 0 2	48	34
3 9 0	—	7	4 2 1	29	30	4 2 2	—	4
3 11 0	—	18	4 4 1	20	20	4 4 2	23	25
4 2 0	—	4	4 6 1	23	24	4 6 2	16	16
4 4 0	30	27	4 8 1	28	22	4 8 2	—	8
4 6 0	20	18	4 10 1	—	8	4 10 2	22	26
4 8 0	—	9	5 1 1	21	22	5 1 2	—	11
4 10 0	31	28	5 3 1	—	14	5 3 2	25	22
5 1 0	—	12	5 5 1	20	20	5 5 2	—	4
5 3 0	31	27	5 7 1	—	5	5 7 2	18	26
5 5 0	—	4	6 2 1	—	20	6 0 2	22	26
5 7 0	31	27	6 4 1	—	15	6 2 2	—	2
6 2 0	—	2	0 2 2	—	8	6 4 2	16	18
6 4 0	22	19	0 4 2	38	41	0 2 3	40	36

Table 1 (cont.).

<i>h k l</i>	$ F $		<i>h k l</i>	$ F $		<i>h k l</i>	$ F $	
	obs.	calc.		obs.	calc.		obs.	calc.
0 4 3	18	24	1 13 3	—	18	3 9 3	21	25
0 6 3	30	29	2 2 3	30	31	3 11 3	—	17
0 8 3	18	26	2 4 3	22	22	4 2 3	21	23
0 10 3	—	9	2 6 3	26	26	4 4 3	—	8
0 12 3	—	2	2 8 3	20	24	4 6 3	—	21
0 14 3	—	10	2 10 3	—	8	4 8 3	—	19
1 1 3	34	34	2 12 3	—	2	4 10 3	—	8
1 3 3	18	20	2 14 3	—	9	5 1 3	—	20
1 5 3	30	30	3 1 3	25	26	5 3 3	—	12
1 7 3	—	8	3 3 3	18	16	5 5 3	—	18
1 9 3	20	27	3 5 3	23	24	5 7 3	—	5
1 11 3	—	19	3 7 3	—	6			

THE Θ -PHASE

This phase was obtained at a boron content of 66.7 atomic %. As for the ζ -phase the homogeneity range of this phase was narrow. Powder photographs gave a hexagonal cell with unit dimensions:

$$a = 2.969 \text{ \AA}, c = 3.066 \text{ \AA}, c/a = 1.03.$$

The agreement between observed and calculated $p |F|^2$ values is satisfactory, assuming the metal atoms form a simple hexagonal lattice. If they are placed in 0 0 0, the only place for two boron atoms per cell will be in $1/3 \ 2/3 \ 1/2$; $2/3 \ 1/3 \ 1/2$. These positions are compatible with space group $D_{6h}^1-C \ 6/mmm$ and the boride thus is isomorphous to AlB_2^{12} and ZrB_2^{13} (C 32 type). The boron atoms form a plane hexagonal net, similar to that of the carbon atoms in graphite. The distance boron-boron in the same net will be $a\sqrt{3}/3 = 1.72 \text{ \AA}$, giving a radius of the boron atom of 0.86 \AA (assuming the atoms to be spherical and in contact).

SUMMARY

The chromium-boron system has been investigated by X-ray methods. Five intermediary phases with contents of boron of respectively about 33 (δ), 40 (ε), 50 (ζ), 55 (η) and 66.7 (Θ) atomic % have been found to exist

Complete structure determinations of the orthorhombic ζ -phase and the hexagonal Θ -phase have been carried out. In the ζ -phase, the boron atoms form parallel chains running through the metal lattice and the structure is related to the δ -phases of the molybdenum- and tungsten-boron systems. The Θ -phase is of C 32 type and the boron atoms form hexagonal nets.

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