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The Borides of Tantalum

ROLAND KIESSLING

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

This investigation is part of a study on binary alloys between transition elements and boron. The system tantalum-boron is of special interest as its ratio r_B/r_{Me} is very close to the critical value 0.59, given by Hägg [1, 2].

Only one boride of composition TaB_2 has been mentioned before [3, 4].

GENERAL METHODS

Starting materials were tantalum (Fansteel Met. Corp., North Chicago) and boron, prepared by the reduction of boron tribromide with hydrogen and with a purity of 98—99 % [5]. The alloys were prepared in two ways. Part of the alloys were prepared by sintering mixtures of tantalum and boron in a high frequency vacuum induction furnace at 1800—1900° C for about half an hour. The other method was to heat mixtures in evacuated silica tubes for 100—150 hours at about 1150° C. Selected alloys were analyzed, according to the method, given by Andrieux [3]. It was not possible to melt the alloys. Some experiments on the solubility of boron in tantalum at higher temperatures were made, using quenched specimens. The silica tubes were quenched in water and crushed at the moment of immersion.

The system was investigated by X-ray powder methods. Observed and calculated $p|F|^2$ values were obtained by the method described in a previous publication [6]. The indexing of the two orthorhombic intermediary phases (γ, δ) exclusively from powder data was possible because of the fact that one of them (γ) was found to be isomorphous with a phase in the chromium-boron system, previously indexed by single crystal methods, and the other (δ) had two axes of about the same length as corresponding axes of the γ-phase. The hexagonal ε-phase was indexed by fil. kand. Rolf Hesse, using his method for indexing of powder photographs [7].

All intensity calculations are based solely on the metal lattice, the scattering power of the boron atoms, compared with that of the tantalum atoms, being too low, to be effective. The position of the boron atoms was determined from space considerations.

GENERAL SURVEY OF THE SYSTEM

The system contains four intermediary phases, β, γ, δ and ε, all of which have metallic properties.

The solubility of boron in the body-centred tantalum lattice (α) is low at room temperature, but at higher temperatures the range of solubility is extended.

The β-phase seems to be stable only at lower temperatures. The composition of the phase is impossible to determine because of the slow reaction rate. It always appears together with α-phase.

The boron content of the γ-phase was 50 atomic % and of the δ-phase 57 atomic %. The ε-phase, finally, exists in a homogeneity range of about 64—72 atomic % with the ideal composition TaB_2.

THE α-PHASE

It was found, that the body-centred tantalum lattice could take up small amounts of boron. The amount increased with temperature. An alloy with a boron content of 10 atomic % was quenched at different temperatures and the value of the parameter, which for pure tantalum is 3.303 Å* was increased to 3.309 Å for specimens quenched at 950° C, 3.313 Å at 1170° and 3.321 at 1270°. An attempt to determine the α-phase boundary gave results, which were not reproducible. This probably results from the slow reaction rate and the small variation of the parameter.

THE β-PHASE

When the boron content of the alloys increased, lines of a new phase, the β-phase, appeared. It was not possible to obtain this phase in a pure state. For boron content up to about 14 atomic % the interferences of the β-phase always occurred together with those of the α-phase, even if the alloys were prepared at 1800—1900° C. For higher boron content, lines of the γ-phase appeared and the powder photographs now showed interferences of the three

* True Ångström units = 10^{-8} cm.

Table 1. Ta-B, β-phase, Cr-K radiation.

h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.*	$p\|F\|^2$ calc. $x=1/6$	h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.*	$p\|F\|^2$ calc. $x=1/6$
1 1 0	0786	0785	m	2	7	3 1 2	6141	6141	m	45	62
2 0 0	1573	1570	st	21	24	4 0 0	6281	6280	w−	14	15
0 0 2	2215	2216	st	37	45	2 1 3	6948	6948	m	98	131
2 1 1	2515	2516	st +	160	195	3 3 0	7063	7065	m	49	57
1 1 2	3001	3001	w	8	10	4 1 1	7225	7226	m	98	128
2 2 0	3135	3140	w−	6	5	4 2 0	7851	7850	w−	9	7
2 0 2	3786	3786	m	41	38	4 0 2	8492	8496	w +	30	26
3 1 0	3920	3925	m	44	37	0 0 4	8865	8864	w +	26	25
2 2 2	5355	5356	w−	7	8	3 3 2	9275	9281	st	79	99
3 2 1	—	5656	—	0	0	1 1 4	9661	9649	w	9	6

phases $\alpha + \beta + \gamma$. As the boron content increased, the system $\alpha + \beta$ gradually disappeared. The confusing results from the phase analysis may be explained, if the β-phase is supposed to exist only below a certain temperature and if the reaction rate below this temperature is too slow to permit complete equilibrium to be established.

The interpretation of the interferences of the β-phase showed the phase to have tetragonal symmetry, the axes of the elementary cell being:

$$a = 5.778 \text{ Å}, \; c = 4.864 \text{ Å}, \; c/a = 0.842, \; V = 162.4 \text{ Å}^3$$

The value of the length of the axes indicated an isomorphy between the tantalum lattice of this phase and the metal lattices of the borides of the $CuAl_2$-type (*C* 16), Fe_2B, Co_2B, Ni_2B, Mo_2B and W_2B[6, 8–10]. This was verified by further structure analysis.

Reflections *h k l* were observed only for $h + k + l = 2n$, *h k* 0 for $h + k = 2n$, *h h l* for $l = 2n$ and 0 *k l* for $k = 2n$ and $l = 2n$, showing that space group D_{4h}^{18}—*I*4/*mcm* is possible. The structure analysis showed that the tantalum lattice of the phase corresponds to the position of 8 : (*h*) in D_{4h}^{18}. The agreement between observed and calculated $p|F|^2$ values was good with a value of the parameter $x = 1/6$ (Table 1). The metal lattice of the phase thus is isomorphous with the metal lattices of the Me_2B borides mentioned. Each tantalum atom is surrounded by one metal neighbour at 2.72 Å, two at 2.79 Å, four at 3.05 Å and four at 3.10 Å. There are four holes per cell, with

* Referred to α_1 for all lines.

the position 4 : (*a*), which have room for boron atoms. They have place for spherical atoms with a radius less than 1.11 Å and the radius of the boron atom is about 0.86 Å. The isomorphy between the metal lattice of this phase and the metal lattices of the Me_2B-phases suggests that the real composition of the phase should be Ta_2B. The fact that it was impossible to obtain the β-phase pure at this composition may depend on the difficulty to get equilibrium at temperatures, where the β-phase is stable.

THE γ-PHASE

This phase was found homogenous in preparations with a boron content of 50 atomic %. The homogeneity range was narrow, and an inspection of the powder photographs indicated an isomorphy between this phase and the ζ-phase in the chromium-boron system, the structure of which has been determined previously [11]. This was confirmed by further structure analysis. The powder photographs could be indexed from an orthorhombic cell with axes:

$$a = 3.276,\ b = 8.669,\ c = 3.157,\ V = 89.66\ \text{Å}^3.$$

A cell content of 4 TaB per cell would give a calculated density of 14.29, in close agreement with the density found, 14.0.

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*. (The axes have been chosen so that the International tables may be used directly for D_{2h}^{17}.) The further structure analysis showed the phase to be isomorphous with the ζ-phase in the chromium-boron system. The tantalum atoms are thus in 4 : (*c*) of D_{2h}^{17}-*Cmcm* and in Table 2 a comparison between observed and calculated $p|F|^2$ values is given, assuming the parameter $y = 0.146$ (the same value as for the ζ-phase in the chromium-boron system). The agreement is acceptable, except for the reflection 2 0 0, which is too weak compared with the calculated value. The disagreement may be due to some orientation effect. The lattice is fully described elsewhere [11]. Each tantalum atom is surrounded by four metal neighbours at 2.90 Å, two at 2.98 Å, two at 3.16 Å and two at 3.28 Å. The boron atoms occupy the same position 4 : (*c*) with a value of the parameter $y = 0.440$. The distance tantalum-boron is 2.40 Å and boron-boron 1.91 Å. The boron atoms form zig-zag shaped chains, all running parallel to the *c*-axis.

Table 2. Ta-B, γ-phase, Cu-K radiation.

h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.*	$p\|F\|^2$ calc. $z = 0.146$	h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.*	$p\|F\|^2$ calc. $z = 0.146$
0 2 1	0908	0910	st	10	21	0 6 2	5224	5215	w—	3	5
1 1 1	1225	1227	st	12	26	2 6 1		5642			10
0 4 0	1259	1261	st	12	8	0 8 1	5642	5640	m	36	8
1 3 0		1262			18	3 1 1		5648			13
0 4 1	1855	1856	w +	8	5	0 2 3	5667	5666	m	18	10
1 3 1		1857			5	3 3 0		5682			9
2 0 0	2210	2209	w—	1	9	2 4 2	5859	5848	w	14	15
0 0 2	2378	2378	w +	8	8	1 1 3	5989	5983	w	14	13
1 5 0	—	2523	—	0	0	3 3 1	6295	6278	w—	4	3
2 2 0	—	2524	—	0	1	0 4 3	6619	6612	w	8	2
0 2 2	—	2693	—	0	1	1 3 3		6613			3
0 6 0	2830	2837	w —	1	4	1 7 2	6802	6793	m	26	19
1 1 2	3011	3010	w	8	11	1 9 0	—	6937	—	0	1
2 2 1	3119	3119	st	63	27	3 5 0	—	6943	—	0	0
1 5 1		3118			29	0 8 2		7422			2
0 6 1	3443	3432	w—	3	6	2 6 2	7429	7424	w +	17	9
2 4 0	3480	3470	w	7	10	3 1 2		7430			7
1 3 2	3644	3640	m	33	23	1 9 1	7535	7531	m	31	15
0 4 2		3639			10	3 5 1		7538			18
2 4 1	4067	4065	w—	3	6	1 5 3		7874			17
1 7 0	4420	4415	w	11	12	2 2 3	7880	7875	st	49	16
2 0 2	4603	4587	w	8	11	010 0		7881			4
2 2 2	—	4902	—	0	2	3 3 2	8066	8060	w	15	15
1 5 2	—	4901	—	0	0	0 6 3	8200	8188	w—	5	4
1 7 1	—	5010	—	0	0	010 1	8497	8496	w—	2	1
0 8 0		5044			1	2 4 3		8821			4
2 6 0	5050	5046	w +	13	6	3 7 0	8835	8835	w	15	8
3 1 0		5052			4	4 0 0		8836			4

The γ-phase, TaB, thus crystallizes in D_{2h}^{17}-*Cmcm*, isomorphous with CrB with the tantalum 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 value of the parameters $y_{Ta} = 0.146$ and $y_B = 0.440$.

* Referred to α_1 for all lines.

THE δ-PHASE

When the boron content of the alloys increased above 50 atomic %, lines of a new phase appeared. This phase had the ideal composition Ta_3B_4, as will be shown below. The powder photographs showed similarities with those of the γ-phase, but new lines appeared. The interferences always appeared at fixed angles in alloys with composition between the γ- and ε-phases, showing that the homogeneity range was narrow. The powder photographs could be indexed, assuming the symmetry to be orthorhombic, the axes of the elementary cell being:

$$a = 3.29 \text{ Å}, \; b = 14.0 \text{ Å}, \; c = 3.13 \text{ Å}, \; V = 144.0 \text{ Å}^3 \; *$$

The δ-phase thus has the a- and c-axes of the unit cell of about the same size as corresponding axes of the γ-phase, but the b-axis is longer, the ratio between the b-axes being 1.6. The number of metal atoms in the elementary cell therefore seems to be six.

The density calculated for 2 Ta_3B_4(13.60) is in good agreement with the density found (13.50). Reflections $h\ k\ l$ only appeared for $h + k + l = 2n$, $0\ k\ l$ for $k + l = 2n$, $h\ 0\ l$ for $h + l = 2n$ and $h\ k\ 0$ for $h + k = 2n$. Probable space groups are thus D_{2h}^{25}-*Immm*, D_2^8—*I*222, D_2^9—$I2_12_12_1$ and C_{2v}^{20}-*Imm*.

Tantalum positions. The investigation was started by examining, whether the structure was consistent with space group D_{2h}^{25}, the space group with the highest symmetry. From space considerations, the six metal atoms must be situated in one twofold and one fourfold position and only the two fourfold positions 4 : (*g*) and 4 : (*h*) are possible. 4 : (*g*) may be combined with one of the positions 2 : (*a*), 2 : (*b*), 2 : (*c*) or 2 : (*d*). A comparison between observed and calculated $p|F|^2$ values for some reflections $h\ 0\ l$ makes it possible to exclude 2 : (*a*) and 2 : (*d*) (Table 3). 2 : (*b*) may be excluded if the intensities of some $0\ k\ l$ and $h\ k\ l$ reflections are compared (Table 3). To make the influence of a variation of the parameter y in 4 : (*g*) as small as possible, small k-values have been chosen. From space considerations, the value of the parameter y must be situated between 0.170 and 0.186. The value 0.180 has been chosen for the calculations.

The remaining possibility for placing six tantalum atoms in D_{2h}^{25} thus is 4 : (*g*) + 2 : (*c*) (or, which will be the same, 4 : (*h*) + 2 : (*a*))

4 : (*g*) 0 y 0; 0 $\bar{y}$ 0; 1/2 1/2 + y 1/2; 1/2 1/2 − y 1/2.
2 : (c) 1/2 1/2 0; 0 0 1/2.

* The axes are given with less accuracy than for the other phases because of the rather diffuse reflections and the great number of coincidences (see Table 4).

Table 3. Calculated $p\,|F|^2$ values for different positions of the metal atoms in the δ-phase.

$h\ k\ l$	$p\,\|F\|^2$				
	obs.	calc. for 4 : (*g*) +			
		+ 2 : (*a*)	+ 2 : (*b*)	+ 2 : (*c*)	+ 2 : (*d*)
1 0 1	70	478	53	53	478
2 0 0	210	193	193	193	193
3 0 1	0	238	26	26	238
1 0 3	0	228	25	25	228
0 1 1	0	211	211	2	2
2 1 1	0	260	260	2	2
0 1 3	0	89	89	1	1

The agreement between observed and calculated $p|F|^2$ values is satisfactory for a value of the parameter $y = 0.180$ (Table 4). The interferences were rather broad and α_1 and α_2 were not separated even at high glancing angles. The limits of error for y seems to be $0.175 < y < 0.186$ (Table 5). The distances between the different atoms thus may be slightly altered, but the fundamental building of the structure is not influenced.

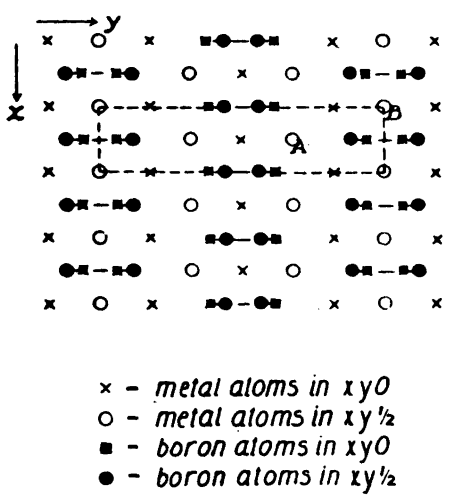

Fig. 1a. Structure of the δ-phase, projected on (001). The elementary cell and the double-chains of boron atoms are indicated.

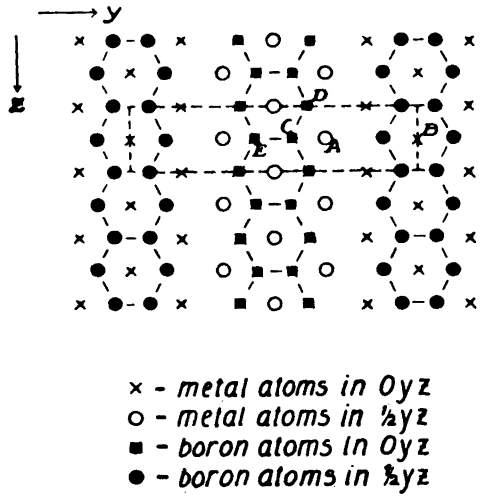

Fig. 1b. Structure of the δ-phase, projected on (100).

Table 4. Ta-B, δ-phase, Cu-K radiation.

h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.	$p\|F\|^2$ calc. $z = 0.180$	h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.	$p\|F\|^2$ calc. $z = 0.180$
0 2 0	0123	0121	w—	0.11 *	0.3	1 11 0	4216	4213	w	26	28
0 4 0	0489	0485	w—	1*	2	0 11 1	4288	4270	w—	9	3
1 1 0	0576	0579	st	19*	22	2 7 1		4288			8
0 1 1	—	0636	—	0	0	0 8 2	—	4361	—	0	2
1 3 0	0823	0822	w	4*	5	0 12 0	—	4361	—	0	6
0 3 1	0871	0879	st	61*	50	1 7 2	—	4456	—	0	4
0 6 0	1090	1090	w	20*	20	2 0 2	4626	4621	m	34	26
1 0 1	1149	1155	w—	7*	5	2 2 2	—	4742	—	0	1
1 2 1	1271	1276	st	48	54	2 4 2	—	5106	—	0	3
1 5 0	1305	1306	st	26	36	3 3 0		5218			2
0 5 1	1369	1363	—	0	2	2 10 0	5245	5226	w	26	8
1 4 1	1633	1640	w+	7	5	2 9 1		3257			32
0 8 0	—	1938	—	0	2	1 9 2	—	5425	—	0	1
1 7 0	—	2033	—	0	3	0 10 2	5450	5451	w—	6	8
0 7 1	2085	2090	w+	5	6	0 1 3	—	5482	—	0	0
2 0 0	2198	2198	st	21	19	1 12 1	—	5516	—	0	0
1 6 1	2253	2245	w—	1	5	3 0 1	—	5551	—	0	3
2 2 0	—	2319	—	0	0	1 13 0	5669	5667	w	30	0
0 0 2	2426	2423	m	14	19	3 2 1		5672			27
0 2 2	—	2544	—	0	0	3 5 0		5702			18
2 4 0	—	2683	—	0	2	2 6 2	5714	5711	st	120	39
2 1 1	—	2834	—	0	0	0 3 3		5725			23
0 4 2	—	2908	—	0	2	0 13 1		5724			12
1 1 2		3002			25	0 14 0	—	5937	—	0	1
1 9 0	3011	3008	m	25	1	1 0 3	—	6001	—	0	3
0 10 0		3028			5	3 4 1	6027	6036	w—	8	9
0 9 1		3059			22	1 2 3	6123	6122	w +	35	26
2 3 1	3081	3077	st +	158	64	0 5 3	—	6209	—	0	1
1 8 1		3093			61	3 7 0	—	6429	—	0	2
1 3 2	—	3245	—	0	6	2 11 1	6470	6468	w—	11	5
2 6 0	3290	3288	w	15	26	1 4 3		6486			8
0 6 2	3516	3513	w	18	26	2 8 2		6559			4
2 5 1	—	3561	—	0	3	2 12 0	6620	6559	w	19	10
1 5 2	3733	3729	m	45	46	1 11 2	(dif-	6636			5
2 8 0	—	4136	—	0	2	3 6 1	fuse)	6641			3
1 10 1	—	4183	—	0	1	0 12 2	6801	6784	w—	8	9

* The interferences, marked *) have been obtained in a camera with a bent monocromator of Guinier type.

Table 4 (cont.).

h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.	$p\|F\|^2$ calc. $z = 0.180$	h k l	$\sin^2\Theta$ obs.	$\sin^2\Theta$ calc.	I obs.	$p\|F\|^2$ obs.	$p\|F\|^2$ calc. $z = 0.180$
0 7 3	—	6936	—	0	3	0 9 3		7905			13
1 6 3	7095	7091	w +	39	3	2 3 3	7923	7923	st	111	37
1 14 1		7092			39	2 13 1		7922			20
1 15 0	—	7363	—	0	1	1 8 3		7939			36
3 1 2		7398			15	1 13 2	—	8090	—	0	0
3 9 0	7413	7398	w	19	0	3 5 2	8124	8125	w +	36	30
0 15 1		7420			5	2 14 0		8135			2
3 8 1	7484	7489	w +	39	37	0 14 2	—	8360	—	0	2
3 3 2		7641	w	19	4	2 5 3	—	8407	—	0	2
2 10 2	7650	7649			13	3 10 1	—	8579	—	0	0
2 11 3	—	7680	—	0	0	3 11 0	8616	8609	w +	22	19
0 16 0	7770	7753	w—	9	7	4 0 0	8803	8790	w	7	9
						3 7 2	—	8852	—	0	3

The tantalum lattice (Fig. 1) contains two kinds of metal atoms. One kind, (A), has its six nearest neighbours at the corners of a surrounding trigonal prism, two at distances 2.97 and four at distances 3.00 Å. These atoms, lying in 4 : (*g*), thus have the same coordination as the tantalum atoms of the γ-phase. The other kind, (B), in the twofold position 2 : (*c*) is surrounded by four neighbours at 2.97 Å, two at 3.13 Å and two at 3.29 Å.

Boron positions. The boron atoms must be situated in holes of the tantalum lattice. The only holes, large enough, are in the centre of a trigonal prism of metal atoms. These holes are connected to channels, all being parallel to the

Table 5. Limits for the parameter of the δ-phase.

h k l	$p\|F\|^2$ obs.	$p\|F\|^2$ calc. $z =$ 0.175	0.180	0.186
0 12 2	77	161	94	34
0 16 0	92	29	70	97
3 11 0	220	160	186	183

c-axis. There are 8 such holes per cell, and in D_{2h}^{25} they possess the two fourfold positions 4 : (g) and 4 : (h) with parameters $y = (1-y_{Me})\,{}^1/_2 - c^2/8\,b^2\,y_{Me} = 0.375$ in 4 : (g) and $y = (1-y_{Me})\,{}^1/_2 + c^2/8\,b^2\,y_{Me} = 0.444$ in 4 : (h).

Boron atoms, placed in these holes, would be connected to double-chains (Fig. 1). Each doublechain may be regarded either as consisting of two usual single chains (compare the γ-phase) or of hexagonal boron rings (compare the ε-phase). The distance boron-boron in the same halfchain (C-D) will be 1.85 Å and the distance between two adjacent boron atoms in different half-chains (C-E) 1.57 Å (assuming the atoms to be spherical and in contact). The distance boron-boron in chains or nets obtained from other determinations has been about 1.72—1.74 Å. The holes in the tantalum lattice, however, are great enough to make a symmetrical arrangement with distances 1.72 Å between adjacent boron atoms in the same doublechain possible.

The boride thus will have the formula Ta_3B_4. It crystallizes in space group D_{2h}^{25}-$Immm$ with two formula units per cell and the tantalum atoms in 2 : (c) and 4 : (g).

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

The value of the parameter $y = 0.180$.

The eight boron atoms are placed in the two fourfold positions 4 : (g) and 4 : (h).

4 : (h) 0 y 1/2; 0 $\bar{y}$ 1/2; 1/2 1/2 + y 0; 1/2 1/2−y 0.

with the parameters $y = 0.375$ for 4 : (g) and $y = 0.444$ for 4 : (h). The lattice will be further discussed below in connection with the ε-phase.

THE ε-PHASE

In preparations with a boron content of more than 58 atomic % lines of a new phase, the ε-phase, appeared. This phase showed an extended homogeneity range. The powder photographs could be indexed, assuming a hexagonal cell with axes (at the ideal composition TaB_2):

$$a = 3.078 \text{ Å}, \; c = 3.265 \text{ Å}, \; c/a = 1.06.$$

The homogeneity range was determined by studying the variation of the axes with the boron content. The lower limit was at about 64 atomic % ($a = 3.099$ Å, $c = 3.224$ Å), the upper at about 72 atomic % ($a = 3.057$ Å, $c = 3.291$ Å). The agreement between observed and calculated $p|F|^2$ values was satisfactory, assuming the metal atoms to form a simple hexagonal lattice.

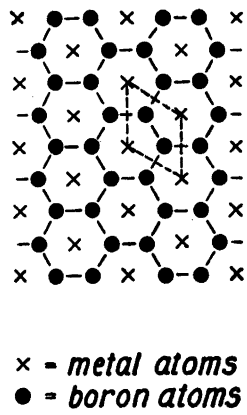

Fig. 2. Structure of the ε-phase, projected on (001). The elementary cell and net of boron atoms are indicated.

If they are placed in 0 0 0, the only place for boron atoms will be in 1/3 2/3 1/2 and 2/3 1/3 1/2, giving an ideal formula of TaB_2 for this phase. The positions are compatible with space group D_{6h}^1—*C* 6/*mmm* and the boride thus is isomorphous to AlB_2, ZrB_2 and CrB_2 (*C* 32 type)[11—13].

The boron atoms form a plane hexagonal net (Fig. 2) with a distance boron-boron of 1.79 Å. It is of interest to compare the structure of this phase with that of the δ-phase. The similarities between the lattices is great, the δ-phase may be regarded as consisting of parallel sheets of simple hexagonal metal lattices with boron nets in the holes (Fig. 1). The difference in potential energy between the lattices of the δ-phase and the ε-phase must be small, and when boron is added to the δ-phase, linkages between the net fragments are formed. The ε-phase will be stable even if the boron net is not complete as indicated by the extended homogeneity range below 66.7 atomic % boron. The homogeneity range, however, is extended above 66.7 atomic %, where the nets are complete, up to about 72 atomic % boron. There are two possibilities for an ε-phase with more than 66.7 atomic % boron. The first is, that in the lattice of the ε-phase some tantalum atoms are replaced by boron atoms. This possibility may be excluded, as it would result in a decrease of the length of the axes, whereas in reality the *a*-axis is decreased but the *c*-axis increased with increasing boron content. The remaining possibility is therefore that boron atoms are added to the simple hexagonal tantalum lattice with complete boron nets. These additional boron atoms may be taken up between the different nets, probably in the positions 1/3 2/3 0, 2/3 1/3 0. They may also be taken up in the centres of the already existing rings of the nets e. g. in the position 0 0 1/2, giving more or less complete sheets of boron atoms as in the ε-phases of the molybdenum- and tungsten-boron systems[6]. The former

possibility would cause an increase of both the a- and the c-axes. The latter would give an increased c- and a decreased a-axis, the decrease depending on the reduction of the distances boron-boron caused by the forces between the boron atoms of the hexagonal rings and the additional atoms in the ring centres. The last possibility thus seems to be more probable.

GENERAL DISCUSSION

The tantalum-boron system belongs to the group of interstitial compounds. It has a ratio $r_B/r_{Me} = 0.59$, equal to the critical value given by Hägg [1, 2]. Compared with the other binary systems between transition metals and boron, which have been investigated [6, 8–11, 13], it has an intermediate position between simple and complicated systems. The solubility of boron in the tantalum lattice is small at room temperature, but the limit of solid solubility is extended at higher temperature. The intermediary phases partly belong to the more complicated kind of phases (β, γ), in part to the simple type (ε) and in part have an intermediate position between simple and complicated lattice types (δ). Further the tendency of the boron atoms to form first chains and then rings with increased boron content of the phases is remarkable. The same tendency has been observed for other systems, for instance the molybdenum- and tungsten-boron systems. In the tantalum-boron system, the β-phase has isolated boron atoms, the γ-phase has zig-zag shaped chains, the δ-phase doublechains, which may be regarded as fragments of boron nets and the ε-phase plane boron nets, which seem to have a tendency to take up more boron to form complete two dimensional sheets.

SUMMARY

The system tantalum-boron has been studied by X-ray methods. The solubility of boron in the tantalum lattice is low at room temperature, but the solubility range is extended at higher temperatures.

Four intermediary phases exist. Complete structure determinations of all the phases have been carried out.

The β-phase is instable at higher temperatures. The metal lattice of the phase is isomorphous with the metal lattices of the borides of the $CuAl_2$ type (C 16). The composition has not been possible to determine, but the isomorphy suggests the composition Ta_2B.

The γ-phase with composition TaB is isomorphous with CrB and the boron atoms form parallel chains through the lattice.

The δ-phase has the composition Ta_3B_4 and the boron atoms form fragments of nets.

The ε-phase with the ideal formula TaB_2 has an extended homogeneity range and is of the AlB_2 type (C 32).

The system is discussed according to the relation r_B/r_{Me}, and to the tendency of the boron atoms to form chains and nets, a tendency, also found in other systems.

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