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Investigations on the Binary Systems of Boron with Chromium, Columbium, Nickel, and Thorium, Including a Discussion of the Phase "TiB" in the Titanium-Boron System

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Preliminary investigations on the binary systems columbium-, nickel-, and thorium-boron have been carried out at this institute. The results, though incomplete, may be of interest in connection with other investigations on this subject, published by one of the authors [1–5]. These papers include an initial report on the chromium-boron system, a sequel to which is given here. The system titanium-boron has been investigated by Ehrlich [6], who proposed the existence of a phase "TiB" with zincblende structure (*B* 3). However, a critical study, given below, shows that the structure probably is that of a face-centred titanium lattice with boron in the octahedral interstices.

The alloys were prepared and investigated as reported elsewhere [1,3]. No analyses of the alloys were carried out; the composition of the intermediary phases was determined from the amount of boron in the starting mixtures.

THE CHROMIUM-BORON SYSTEM

A report on the phase analysis and structures of two (ζ and Θ) of the five intermediary phases has been published. Some additional data on the δ- and η-phases have since been obtained.

The δ-phase. This phase, with a boron content of about 33 atomic%, is orthorhombic or very nearly orthorhombic with axes:

$$a = 14.7 \text{ Å}, \; b = 7.34 \text{ Å}, \; c = 4.29 \text{ Å}, \; V = 463 \text{ Å}^3.$$

The intensities of a few reflections on the single crystal photographs were not consistent with Laue symmetry *mmm* but with *2/m*. The possibility of a monoclinic cell with β equal or nearly equal to 90° thus can not be excluded. The lengths of the axes are about the same as for the corresponding axes of the δ-phase in the manganese-boron system. The phases are not isomorphous, however. If the chromium boride is orthorhombic the probable space groups are *Abmm* or *Abm*, whereas the manganese boride belonged to *Fddd*.

The η-phase. A complete structure determination of this phase showed it to be isomorphous with Ta_3B_4 and Mn_3B_4, thus belonging to space group *Immm*. The axes of the orthorhombic unit cell were found to be:

$$a = 2.984 \text{ Å}, \; b = 13.02 \text{ Å}, \; c = 2.953 \text{ Å}, \; V = 114.7 \text{ Å}^3.$$

The chromium atoms are situated in 4:(g) + 2:(c) and the boron atoms in 4:(g) + 4:(h). A satisfactory agreement between observed and calculated $|F|$-values was obtained with parameter values of $y_{Cr} = 0.186$, the same value as for Mn_3B_4, and $y_B = 0.372$ (4:(g)) and 0.442 (4:(h)). The boron atoms thus form double chains with a tendency of boron pair formation (distance boron-boron in the same half of a double chain 1.74 Å, between nearest boron atoms in different halves 1.51 Å).

THE COLUMBIUM-BORON SYSTEM

The phase analysis showed the existence of probably six intermediary phases. At room temperature the phases β, γ (CbB), δ (Cb_3B_4), and ε (extended homogeneity range, ideal composition CbB_2) are stable. Two more phases, β' and β'', probably exist, both stable only at higher temperatures.

The β,β', and β''-phases. Complicated powder photographs were obtained from preparations with compositions between the α-(pure columbium) and the γ-phases. At about 10 atomic% boron, probably two phases exist, one (β) stable at room temperature and the other (β') at higher temperatures. It was impossible to obtain β or β' pure, but a comparison between specimens quenched at 1200° C and specimens prepared at 800° C indicated that β' had a non-centred cubic metal lattice with $a = 4.210$ Å. All reflections corresponding to this parameter were observed. It was impossible to decide, however, whether all these reflections belonged to β' or some to β and some to β'. In the range 25—35 atomic% boron a third system of interferences sometimes appeared in quenched specimens. This indicates the existence of a third phase β'', stable only at higher temperatures.

The γ-phase. This phase, with composition CbB, was found to be isomorphous with CrB and TaB. It is thus orthorhombic, belonging to space group *Cmcm*. The axes were found to be:

$$a = 3.298 \text{ Å}, \; b = 8.724 \text{ Å}, \; c = 3.166 \text{ Å}, \; V = 91.09 \text{ Å}^3.$$

Both columbium and boron are in 4:(*c*) and a satisfactory agreement between observed and calculated $p|F|^2$-values was obtained for $y_{Cb} = 0.146$, the same as for CrB and TaB. From space considerations y_B was found to be 0.444.

The δ-phase. This phase was found to be isomorphous with Ta_3B_4, Cr_3B_4 and Mn_3B_4, thus belonging to space group *Immm*. The axes of the orthorhombic unit cell are:

$$a = 3.305 \text{ Å}, \; b = 14.08 \text{ Å}, \; c = 3.137 \text{ Å}, \; V = 146.0 \text{ Å}^3.$$

Satisfactory agreement between observed and calculated $p|F|^2$-values was obtained with the metal atoms in 4:(*g*) + 2:(*c*) and the parameter $y_{Cb} = 0.180$, the same value as for Ta_3B_4. From space considerations the parameters for boron were found to be 0.376 (4:(*g*)) and 0.444 (4(*h*)).

The ε-phase. This phase was found to be of the AlB_2-type (*C* 32) with axes of the hexagonal cell (at the composition CbB_2):

$$a = 3.089 \text{ Å}, \; c = 3.303 \text{ Å}, \; c/a = 1.07.$$

An extended homogeneity range for this phase was noted, extending on both sides of the ideal composition CbB_2.

THE NICKEL-BORON SYSTEM

According to Giebelhausen [7], phases Ni_2B, Ni_3B_2, NiB, and Ni_2B_3(?) exist. Bjurström [8] has determined the structure of Ni_2B being of $CuAl_2$-type (*C* 16).

A brief phase analysis showed the existence of at least four intermediary phases, γ existing pure in preparations with 25—30 atomic% boron, δ(Ni_2B), ε at about 40 atomic% boron and ζ at about 50 atomic% boron. Intensity variations were also noted for preparations with a higher boron content than 60 atomic%, but it was not possible to decide whether they were caused by a new phase. It was not possible to interpret the powder photographs of the γ, ε or ζ-phases. Especially noteworthy is the existence of the intermediary phase γ with a boron content lower than that of Ni_2B. This phase has not been reported by previous investigators.

THE THORIUM-BORON SYSTEM

Solubility of boron in the face centred thorium lattice was observed. In addition to the phase ThB_6, previously known, a phase at about 50 atomic% boron was found, giving complicated powder photographs. It was not possible to interpret them, and attempts to prepare single crystals were not successful.

THE TITANIUM-BORON SYSTEM

According to Ehrlich [6] three intermediary phases exist, and solubility of boron in the α-titanium lattice is also noted. A superlattice closely related to the α-titanium lattice was found in the range $TiB_{0.1}$-$TiB_{0.8}$. Two other phases "TiB" and TiB_2 exist, TiB_2 being of the AlB_2-type (*C* 32). "TiB" is reported to have zincblende structure (*B* 3). In the authors' opinion, however, the boron atoms are situated in other positions than in the tetrahedral interstices of the titanium lattice, corresponding to the sulfur positions of ZnS.

If "TiB" has *B* 3 structure, the titanium atoms occupy the positions of the unit cubic cell ($a = 4.202$ Å) with coordinates $000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$, and $\frac{1}{2}\frac{1}{2}0$. These are the positions of a face-centred lattice. The distance between adjacent titanium atoms is 2.97 Å. If the atoms are assumed to be spherical and in contact, this gives a value of 1.49 Å for the radius of the titanium atom in close agreement with values given before. In this face-centred titanium lattice there are two types of holes, respectively tetrahedrally and octahedrally surrounded by titanium atoms. The tetrahedral interstices which would be occupied in a structure of the zincblende type have room for atoms with $r < 0.34$ Å, the octahedral for atoms with $r < 0.62$ Å. Boron, with its radius of 0.87 Å is too great for both types of interstices. It is most probable, however, that it occupies the largest (octahedral) interstices. As the main contribution to the intensities is given by titanium, it is not possible to decide between these two alternatives from the rough intensity data given, but a careful intensity study would perhaps permit a choice. Ehrlich's attempts to obtain "TiB" in a pure state were not successful, interferences from "TiB", α-titanium and TiB_2 always being obtained together. Ehrlich's explanations of this fact, too low a reaction temperature or a supposed transition TiB (zincblende) — TiB_2 (with incomplete networks) seem unlikely. The present authors think that the most probable explanation would be that "TiB", in which even the octahedral interstices are too small for boron atoms at room temperature, will be stable only at higher temperatures. On cooling, part of "TiB" is decomposed into the stable phases α-titanium and TiB_2 whereas another part is retained at room temperature in a metastable condition.

The bonds within "TiB" thus probably are of the same nature as in the other borides of the transition elements, and the titanium-boron system with its radius ratio r_B/r_{Ti} near 0.59 has an intermediate position between simple and complicated systems. This will be discussed in greater detail in a paper, soon appearing in this journal.

SUMMARY

Investigations on the binary systems chromium-, columbium-, nickel-, and thorium-boron are reported. The titanium-boron system is discussed, and it is shown that the phase "TiB", previously assumed to have zincblende structure, probably has a face-centred titanium lattice with boron in the octahedral interstices.

In the chromium-boron system, the structure of the η-phase has been determined. It has the composition Cr_3B_4 and is isomorphous with Ta_3B_4 and Mn_3B_4. Some data for the δ-phase are also given.

For the columbium-boron system, a phase analysis has been carried out. The structures of three of the intermediary phases, CbB, Cb_3B_1 and CbB_2 (with extended homogeneity range) have been determined. They are isomorphous with corresponding phases of the tantalum- boron system.

A brief phase analysis of the nickel-boron system showed the existence of a phase with lower boron content than Ni_2B, which has not been previously reported.

In the thorium-boron system a new phase, probably with a complicated structure, was found with a boron content of about 50 atomic%.

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