The Binary System Zirconium-Boron

ROLAND KIESSLING

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

As a part of a study of binary systems, composed of a transition element and boron, the zirconium-boron system has been investigated by X-ray methods. Certain studies on alloys between these elements have been reported [1,2]. The phases, however, do not seem to be pure. Mc Kenna has found a boride of the composition ZrB_2[3], which will be discussed below.

The alloys were prepared in a high frequency vacuum induction furnace[4], using a Philips H. F. generator with an output of 5 kW and a frequency of 800 kc/s as a source of energy. Other methods for preparing the alloys were tried, for instance melting in a vacuum furnace with a graphite tube as heating element and sintering in evacuated silica tubes. The inductive melting in vacuum using high frequency currents, however, was found to be the only possible method of preparation for these pure alloys. The starting materials were zirconium (Foote Mineral Co., Philadelphia) and boron with a purity of about 99 %[5].

X-ray investigations by means of powder methods showed, that small amounts of boron were dissolved by the α-zirconium lattice. The unit dimensions of zirconium ($a = 3.229$ Å, $c = 5.139$ Å*) thus increased to the limit $a = 3.249$ Å, $c = 5.203$ Å. The solubility limit of boron in α-zirconium seems to be at about 1 atomic % boron. Small amounts of boron caused a great increase in the hardness of the zirconium phase.

Only one intermediate phase was found. This phase, which had the composition ZrB_2, had metallic properties and a considerable hardness. The homogeneity range was narrow. A boride of the composition ZrB_2, containing 1.09 % carbon as impurity, has been reported[3]. The product has been investigated by X-ray methods and the metal atoms found to form a simple hexagonal lattice, the unit dimensions of the cell beeing $a = 3.15$ and $c = 3.53$ Å.

Powder photographs of the phase ZrB_2 verified the results. A hexagonal cell was found with unit dimensions:

$$a = 3.169 \text{ Å}, \ c = 3.530 \text{ Å}, \ c/a = 1.11$$

The observed density of 5.64 most closely corresponds to a cell content of one formula unit per cell and the agreement between observed and calculated $p\,|F|^2$ values is satisfactory, assuming the metal atoms to form a simple hexagonal lattice.

If the metal atoms are situated in 000, the only place for two boron atoms per cell is in $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2};\ \frac{2}{3}\,\frac{1}{3}\,\frac{1}{2}$. These positions are compatible with space group D^1_{6h} — $C\,6/mmm$ and the boride thus is isomorphous to AlB_2[6] (C 32 type). The boron atoms form a plane hexagonal network, similar to that of the carbon atoms in graphite. The distance boron-boron in the same net will be $a\sqrt{3}/3 = 1.829$ Å, giving a radius of 0.91 Å for the boron atom (assuming the atoms to be spherical and in contact)*. The lattice may be regarded as a sequence of sheets . A H A H A H . . were A are plane hexagonal sheets of zirconium atoms and H are the hexagonal networks of boron atoms. Interpenetrating twins of ZrB_2 were observed, similar to those of AlB_2[6]. The maximum angle between the twins was compatible with ($1\,1\,\bar{2}\,2$) as twin plane. According to the figures, the same twin plane has been accepted for

* All values given in true Ångström units. 1 Å = 10^{-8} cm = 1/1.00202 kX units.

* The value is slightly greater than the probably correct value 0.87 Å[7]. The larger value found here seems to be caused by the metal atoms beeing in contact.

AlB_2, although it has erroneously been written as $(1\,1\,\bar{2}\,1)$.

This system is composed of a transition element and boron, thus belonging to those, discussed by Hägg[8,9]. The ratio r_B/r_{Zr} is 0.54, assuming the radii to be 0.87 Å for boron and 1.60 Å for zirconium (12-fold coordination). It is less than the critical value 0.59 and in fact the system is very simple. A range of solid solubility of boron in the metallic lattice exists. ZrB_2, the only intermediary phase which has been found, is a typical interstitial compound with a lattice of one of the four simple types, given by Hägg, and has metallic properties. It is of interest to compare this system with the chemically related system titanium-boron with the ratio $r_B/r_{Ti} = 0.60$, for wich a short report has been published[10]. According to this report a range of solid solubility of boron in the titanium lattice exists and a phase TiB_2, isomorphous to ZrB_2 and with metallic properties is to be found. In addition a superlattice, closely related to the titanium lattice exists and further a new phase, TiB, appears. This phase is reported to have »zincblende» structure with definite linkages titanium-boron. Thus it does not belong to the typically interstitial compounds. So far as can be judged from the brief report, the system titanium-boron thus has an intermediate position between simple and complicated systems and in fact the radius ratio is very near the critical value.

The existence of phases MeB_2 of the *C* 32 type seems to be rather usual among the transition elements. In addition to ZrB_2 and TiB_2 the borides CrB_2, CbB_2 and TaB_2 are isomorphous to AlB_2 (Kiessling, unpublished). In the systems molybdenum-boron and tungsten-boron, the ε-phases have a lattice, partially composed of a MeB_2 lattice of the type above[7]. This may depend on the tendency of the boron atoms to form plane networks.

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On the Action of *Bacillus macerans* Amylase

K. MYRBÄCK and EBBA WILLSTAEDT

Institute of Organic Chemistry and Biochemistry, University of Stockholm, Stockholm, Sweden

Bacillus macerans contains an amylolytic enzyme which is secreted into the culture medium. This enzyme is different from all the other amylases known to us; it converts starch, glycogen *etc.* into the non-reducing Schardingerdextrins (cyclo-amyloses) which can be determined semi-quantitatively by the Tilden-Hudson iodine test [1]. Since the action of the enzyme on starch paste is accompanied by an extremely rapid decrease in viscosity it must be concluded that the enzyme does not only split off end-chains from the amylopectin molecules (under the formation of cycloamyloses) but also ruptures linkages in interior chains between branching points [2]. The action is there-