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Abstract

Full Text

Chemistry

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PREPARATION AND PROPERTIES OF SCANDIUM DIBORIDE

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Numerous studies carried out in recent years have thoroughly investigated the compounds of the transition metals of the first period (titanium, vanadium, chromium, manganese, etc.) with boron, which are hard and refractory compounds finding ever broader use in various branches of technology ([1]). The compound with boron of the first element of the first transition period—scandium—remains completely unstudied; its atom, with the electronic configuration $3s^2 3p^6 3d^1 4s^2$, has the least filled $3d$ shell, with one electron.

Fig. 1. Physical properties of Sc, Ti, V, Cr and their diborides. $\alpha_t \cdot 10^6$ (MeB_2)—coefficient of thermal expansion of the diborides, $\frac{1}{\text{deg}}$; T_m (MeB_2)—melting temperature of the diborides, °C; H_m (MeB_2)—microhardness of the diborides (under a load of 30 g), kg/mm^2; ε_1(Me)—first ionization potentials of the metal atoms, eV; $1/Nn$ (Me)—factor of the degree of incompleteness of the d shell of the metal atom; $\frac{R_{MeB_2}}{R_{Me}}$—ratio of the values of the specific resistivities of the diborides and the corresponding metals.

Therefore it is of interest to compare the physical properties of scandium compounds with the compounds of other transition metals of the first period, in particular the physical properties of the compounds with boron.

Individual samples of scandium diboride ScB_2 were obtained by us earlier; however, they were heavily contaminated with boron carbide, from which they were separated by specific gravity in heavy liquids. On the preparations obtained in this way, N. N. Zhuravlev and A. A. Stepanova ([2]) determined the crystal structure of ScB_2, which proved to be hexagonal (structural type AlB_2), identical with the structures of the diborides of other transition metals of groups IV–VI of the periodic system, including the diborides of titanium, vanadium, and chromium. According to this work, the identity periods of ScB_2 are: $a = 3.140 \pm 0.002$; $c = 3.510 \pm 0.002$ kX, $c/a = 1.118$, calculated from this ···

density $\delta_x = 3.67$ g/cm^3. In subsequent work, carried out by us jointly with B. M. Tsarev, G. A. Kudintseva, and V. S. Neshpor, an attempt was made to determine the principal parameters of thermionic emission of scandium diboride; however, on the basis of X-ray analysis data it was established that in the course of heating in vacuum ScB_2 loses part of the metal, transforming into scandium hexaboride, which has a cubic lattice of the CaB_6 type with period $a = 4.355$ kX. The electron work function for this compound was found to be 2.96 eV, and the constant A in the Richardson equation was 4.6 A/cm$^2 \cdot$ deg^2; the secondary-emission coefficient was 0.58 and the radiation coefficient at 1600° was 0.6.

In the present work a systematic investigation was carried out of the conditions for obtaining scandium diboride by the reaction between Sc_2O_3 and boron in vacuum, with evolution of the volatile lower boron oxide of composition BO or B_2O_2:

$$Sc_2O_3 + 7B = 2ScB_2 + 3BO.$$

It was thereby established that the maximum completeness of the reaction is attained at 1800–1850° and holding at this temperature for 1 h; the product thus obtained contains 32.6% boron, as compared with 32.5% boron in ScB_2 by calculation. The pycnometric density of the diboride powder, equal to 3.65 g/cm^3, agrees well with the X-ray density.

To determine the physical properties of ScB_2, specimens were sintered from its powder by hot pressing in graphite molds without a specially created protective atmosphere at 2000–2050° for 7–10 min, under a load providing a pressure on the sintered powder of 100 kg/cm^2. The microhardness of sintered ScB_2, measured under a load of 50 g, is 1742 ± 337 kg/mm^2; the average density of the hot-pressed specimens is 3.56 g/cm^3; the specific electrical resistivity is 7 –15 $\mu\Omega \cdot$ cm; the thermal coefficient of the thermo-e.m.f. is -7.7 μV/deg; the thermal expansion coefficient at 20–800° is $9.48 \cdot 10^{-6}$; the radiation coefficient, measured in the range from 1035 to 1770° by the method of ([3]), proved to be practically unchanged and equal (at $\lambda = 650$ mμ) to 0.89. Finally, the melting point of ScB_2, determined by the method described in ([4]), is 2250°. Table 1 gives a comparison of some physical properties of the diborides of scandium, titanium, vanadium, and chromium.

Table 1

Property	ScB_2	TiB_2	VB_2	CrB_2
Melting point, °C	2250	2980	2400	2200
Microhardness, kg/mm^2	1780	3370	2400	1800

Property	ScB_2	TiB_2	VB_2	CrB_2
Coeff. therm. expans., $\times 10^6$	9.48	6.8	~ 8.0	9.8
Specific electrical resistivity, $\mu\Omega \cdot$ cm	7–15	25.9	16.0	32.2
$R_{MeB_2} : R_{Me}$	(0.13)	0.47	0.62	1.5
First ionization potential, eV	6.7 (Sc)	6.81 (Ti)	6.74 (V)	6.7 (Cr)
Degree-of-unfilledness factor of the d-electron shell $(1/Nn)$	0.333 (Sc)	0.167 (Ti)	0.111 (V)	0.067 (Cr)

These data show that the properties characterizing, to one degree or another, the strength of the crystal lattice pass through an extremum for titanium diboride, with a corresponding decrease in strength both toward scandium diboride and toward the diborides of vanadium and chromium. Since in the structures of diborides the boron atoms are bonded to one another by covalent bonds into flat nets, in which each boron atom is surrounded by three neighbors, the bond between the atomic complexes of boron and the metal atoms is effected chiefly through the latter, as is indicated by the clear correlation between the course of variation of the melting point,

microhardness, and coefficient of thermal expansion of diborides, on the one hand, and the first ionization potentials of the atoms of transition metals, on the other. This observation at the same time shows that the indicated properties are determined mainly by the state of the 4s-electrons, while the d-electrons of the metal atoms take a much smaller part in bonding with the boron complexes, as is shown by the lack of correspondence between the variation of these properties and the variation of the incompleteness factor of the d-electron shells of transition metals. The latter, on the contrary, determine the degree of scattering of conduction electrons, as is shown by the agreement of the values $1/Nn$, where n is the number of electrons in the d-shell and N is the principal quantum number of this shell [5], with values indicating an increase in electrical resistance upon the formation of borides relative to the metal. The value of the specific

electrical resistivity of scandium is unknown; however, extrapolating to ScB_2 the ratio $R_{MeB_2} : R_{Me}$ as a function of $1/Nn$, we obtain $R_{ScB_2} : R_{Sc} = 0.13$, whence the resistance of scandium should lie in the range from 55 to 115 $\mu\Omega \cdot$cm. Thus, the variation of the resistance of diborides as a function of the scattering ability of the *d*-shells confirms the earlier views on this question set forth in [6]*.

Consequently, scandium diboride is a compound whose properties allow it to be placed in the series ScB_2—TiB_2—VB_2—CrB_2 and to be regarded as the end member of this series; moreover, the strength of the crystal lattice of ScB_2 is determined predominantly by the state of the *s*-electrons, while the electrical properties are determined by the state of the *d*-electrons, which also applies to the diborides of the other metals of the first transition period.

In conclusion, it should be noted that the melting temperature, hardness, and coefficients of thermal expansion of ScB_2 and CrB_2 are unusually close, which, together with the high electrical conductivity and, consequently, thermal conductivity of ScB_2, as well as its specific gravity being 35% lower than that of CrB_2, makes the use of ScB_2 promising in light heat-resistant alloys, in which chromium boride is currently used [7]. O. I. Shulishova took part in the experimental portion of the work.

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* Using the data of this work, the specific electrical resistivity of scandium may

be assumed to be $\sim 90\ \mu\Omega\cdot$cm, whence the most probable value of the resistance of ScB_2 proves to be $11.7\ \mu\Omega\cdot$cm.

Note: Figure translations are in progress. See original paper for figures.

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