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CERTAIN PROPERTIES OF BORIDE ALLOYS OF REFRACTORY TRANSITION METALS

BY: G. A. Layerson, et. al.

English Pages: 26

CERTAIN PROPERTIES OF BORIDE ALLOYS OF
REFRACTORY TRANSITION METALS
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VESTRNOUSTI MESTALOV)
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H. I. Kalina

In the aviation, metallurgical, and chemical industries as well as in
other fields of technology, there is a need for materials possessing a high
degree of corrosion and heat resistance, chemical stability, special electrical
properties, hardness, etc. Such materials, in particular, are the compounds of
refractory, transition metals with light metalloids such as nitrides, carbidies,
borides, silicides and others. In this connection, studies of the properties
of such compounds have recently been expanded.

Great attention is being paid to the study of borides, which until re-
cently were studied less than the carbidies and nitrides.

In various and corrosion resistance borides surpass carbidies and also
possess comparatively small density, and are good conductors of heat and electricity, etc.
The fields in which borides of refractory, transition metals can be applied are quite varied. In the literature there are reports of their use in the production of hard alloys for making gas turbine parts, in the manufacture of nozzles for metallized equipment, exhaust pipes for engines, centrifuge parts, pistons for automatic presses, crucibles for fusion of refractory metals, protective pipes for thermocouple immersion pyrometers, etc. [1 through 4].

Borides of refractory transition metals are also of interest from the viewpoint of the theory of the structure of metal compounds. The uniqueness of borides lies in the fact that by possessing a number of characteristics which are typical of the so-called "interstitial phases", they do not have the ordinary "interstitial" structure due to the large size of the boron atom.

The boride alloys are of significant practical and theoretical interest, despite the fact that their study is in the beginning stage.

In the present work, TiB2 - CrB2, TiB2 - ZrB2, and ZrB2 - CrB2 systems were studied. After taking into account the properties of the initial borides and the possible technical use of their alloys, the research was conducted along the following basic lines:

1) The study of the phase composition and structures of the products of the diffusion reaction of the initial borides.
2) The study of the microhardness of the phases and of the combination of the borides, each having high corrosion resistance.
3) The study of the corrosion resistance and the structure of scales of various compositions.

Alloys TiB2 - CrB2 and ZrB2 - CrB2 were interesting from the viewpoint of the combination of the borides, each having high corrosion resistance.
borides and, if only for that reason, alloys on this base deserve more serious study.

Comparison of these systems also had a certain interest from the viewpoint of experimentally checking the conditions of the formation of a continuous series of solid solutions [3].

The system TiB₂ - W₂B₅ is analogous to the carbide system TiC - WC, which found wide application in the production of hard alloys, and thus it was possible in the present case to expect a certain increase in the micro-hardness of the phases.

The literature contains a number of indications regarding the existence of titanium boride Ti₂B₅, which is isomorphous with the tungsten boride W₂B₅. On this basis it was possible to presume the existence of considerable solubility of titanium boride in W₂B₅, due to the transformation of the structure of TiB₂ into Ti₅B₂ (similar to tungsten carbide alloys having a hexagonal structure alloyed with carbides with a cubic lattice [7, 8]).

Obtaining Borides

Starting powdered borides TiB₂, ZrB₂, CrB₂, W₂B₅ were obtained by a vacuum-thermal method from their respective metal oxides (TiO₂, ZrO₂, Cr₂O₃ and WO₃), boron carbides and calcined soot, in the laboratory vacuum resistance furnace of a retort type with a graphite heater [18]. The calcination methods are given in Table 1.

The obtained borides were ground in a ball mill, in a water medium, and the iron impurities washed out by diluted acid.

Table 2 shows the results of a chemical, x-ray diffraction, and gravimetric analysis of these borides.
As seen from Table 2, the chemical composition of powdered borides is nearly stoichiometric, and the spacing of the crystal lattices, determined within the limits of accuracy of the study, correspond to data in the literature. The density determined by the micropycnometric method [11] agrees with the density calculated from x-ray diffraction data.

### Table 1

**Method of Obtaining Borides**

<table>
<thead>
<tr>
<th>Method Indices</th>
<th>TiB₂</th>
<th>ZrB₂</th>
<th>CrB₂</th>
<th>W₂B₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>1540</td>
<td>1770</td>
<td>1670</td>
<td>1340</td>
</tr>
<tr>
<td>Soaking, min</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Content of melt in the furnace charge as % of the calculated quantity</td>
<td>100</td>
<td>95</td>
<td>55</td>
<td>90</td>
</tr>
</tbody>
</table>
### TABLE 2

Characteristics of Powdered Borides

<table>
<thead>
<tr>
<th>Indices</th>
<th>TiB₂</th>
<th>ZrB₂</th>
<th>CrB₂</th>
<th>W₂B₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal content, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>found</td>
<td>69.4</td>
<td>80.2</td>
<td>70.1</td>
<td>90.7</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>68.9</td>
<td>80.8</td>
<td>70.6</td>
<td>89.2</td>
</tr>
<tr>
<td>Boron content, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>found</td>
<td>30.6</td>
<td>19.3</td>
<td>29.9</td>
<td>9.8</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>31.1</td>
<td>19.2</td>
<td>29.4</td>
<td>10.8</td>
</tr>
<tr>
<td>Carbon content, % C (total)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>found</td>
<td>0.7</td>
<td>0.1</td>
<td>0.05</td>
<td>0.9</td>
</tr>
<tr>
<td>Iron content, %</td>
<td>1.0</td>
<td>0.8</td>
<td>0.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>found</td>
<td>4.52</td>
<td>6.05</td>
<td>5.22</td>
<td>11.0</td>
</tr>
<tr>
<td>calculated</td>
<td>4.52</td>
<td>6.15</td>
<td>5.26</td>
<td>13.0</td>
</tr>
<tr>
<td>mean grain size, μ</td>
<td>2.0</td>
<td>4.0</td>
<td>2.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Lattice spacing, Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>3.015±0.004</td>
<td>3.150±0.006</td>
<td>2.966±0.011</td>
<td>2.96±0.01</td>
</tr>
<tr>
<td>from literary data</td>
<td>3.022±0.002</td>
<td>3.163±0.002</td>
<td>2.963</td>
<td>2.976</td>
</tr>
<tr>
<td>b</td>
<td>3.216±0.015</td>
<td>3.502±0.006</td>
<td>3.06±0.015</td>
<td>13.8±0.1</td>
</tr>
<tr>
<td>from published data</td>
<td>3.22±0.002</td>
<td>3.52±0.002</td>
<td>3.060</td>
<td>13.83</td>
</tr>
<tr>
<td>e/a</td>
<td>1.666</td>
<td>1.114</td>
<td>1.035</td>
<td>4.66</td>
</tr>
<tr>
<td>found</td>
<td>1.066</td>
<td>1.114</td>
<td>1.033</td>
<td>4.76</td>
</tr>
<tr>
<td>from published data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- According to Kiesling [1]: Al₂ by has a defective lattice, and the actual composition of the product corresponds to formula Al₂₂±0.6₄±0.1. The composition for Al₂±0.6₂ is given.
Compact samples of alloys were obtained from mixtures of powdered borides by the method of hot pressing in graphite molds on the laboratory press with a lever mechanism for loading. A series of samples were prepared, differing by 10% mole of each component (and with 5% \( W_2B_5 \) for alloys TiB\(_2\) - \( W_2B_5 \)). The samples for the metallurgical study, for determination of the compressive strength and for the study of oxidation processes, were 14 mm in diameter and about 4 mm in height. To determine the electrical conductivity and the coefficient of linear expansion, samples 8 mm in diameter and 15 to 20 mm in height were prepared. The porosity of the samples did not exceed 2 - 3%. The optimum temperature for hot pressing the borides was (in °C):

\[
\begin{align*}
TiB_2 & \quad 2500 \\
ZrB_2 & \quad 2500 \\
CrB_2 & \quad 2130 \\
W_2B_5 & \quad 2370
\end{align*}
\]

Above these temperatures, the samples melted, losing their metallic luster and turning black. This was evidently due to the reaction of the borides with the carbon of the dies and with the formation of comparatively low-melting eutectics.

The metallurgical study was made on sections prepared in the usual way. In order to expose the structure, sections of alloys TiB\(_2\) - CrB\(_2\) were treated with a mixture of HF + H\(_2\)SO\(_4\) + glycerine (1 : 1 : 1), sections of alloy ZrB\(_2\) - CrB\(_2\) with a mixture of HF + H\(_2\)SO\(_4\) (1 : 1), and sections of TiB\(_2\) - \( W_2B_5 \) by a mixture of HCL + H\(_2\)SO\(_4\) (1 : 1), or a concentrated solution of Na\(_2\)HPO\(_4\) in H\(_2\)SO\(_4\).

Alloys TiB\(_2\) - CrB\(_2\) in the entire range of compositions have a single-phase structure. The structure of alloys TiB\(_2\) - \( W_2B_5 \) and ZrB\(_2\) - CrB\(_2\) is a two-phase structure.
Fig. 1 shows the dependence of the mean grain size of alloys CrB₂-TiB₂ and CrB₂-ZrB₂ on the composition. As seen from this Fig., the dependence curve of the grain size on the alloy composition of TiB₂-CrB₂ has a clearly expressed maximum in the region of high chromium-boride content. The increase in grain size of alloys TiB₂-CrB₂ with an increase in CrB₂ content is evidently explained by the lower melting temperature of chromium boride. Therefore the annealing of alloys rich in chromium boride occurred at a comparatively higher temperature, and the conditions for the growth of the grains were more favorable. The considerable decrease in the grain size during transition to the pure chromium boride can probably be explained by the nearness of the annealing temperature to the melting point. Under these conditions recrystallization occurred simultaneously around a great number of nuclei, thereby causing a decrease in grain size. A similar phenomenon was observed when during the annealing of tungsten, the temperature approached the melting point.

X-ray diffraction studies were made by the powder method of taking x-ray photographs with copper radiation. As shown in Fig. 2, Vegard's law is closely observed for alloys TiB₂-CrB₂; within the limits of accuracy of our measurements, the points lay on straight lines. The variation in the spacings of the lattice constants in alloys TiB₂-0.3 and ZrB₂-CrB₂ is negligible and is within the accuracy of the measurements.

The electrical conductivity of alloys TiB₂-CrB₂ and CrB₂-CrB₂ was measured by the Thomson bridge. Cylindrical samples 3 mm in diameter and a length of about 40 mm; their porosity fluctuated between 10% and 16%. The resistivity values were reduced to zero porosity by the formula

\[ \rho_{\text{comp}} = \rho_{\text{por}} (1 - \eta) \]

where \( \rho \) is the resistivity of the compact (\( \rho_{\text{comp}} \)) and porous (\( \rho_{\text{por}} \)) material.
\( n \) is the porosity in fractions of one.

**Fig. 1.** Dependence of mean grain size of alloys of chromium diboride with diborides of titanium and zirconium on their composition (after annealing at 2000° for four hours):

1) alloy \( \text{CrB}_2 - \text{TiB}_2 \)
2) alloy \( \text{Cr}_3 \text{B}_2 - \text{ZrB}_2 \)

**Fig. 2.** Data of the x-ray diffraction study of borides:

a - System \( \text{TiB}_2 - \text{CrB}_2 \)

b - System \( \text{TiB}_2 - \text{ZrB}_2 \)

c - System \( \text{CrB}_2 - \text{CrB}_2 \)
The position of the maximum of electrical conductivity and microhardness on the "composition-property" curves coincides in the first approximation (Fig. 3).

The microhardness of the phases was measured on etched sections with a HM-3 instrument under a load of 30 g. As seen in Fig. 3 for alloys TiB₂ - CrB₂, the curve of the dependence of microhardness on the composition is smooth, with a maximum of 4200 kg/m² at 80% mole TiB₂. Corresponding microhardness curves of phases of alloys TiB₂ - 2B₂ and Ti₃B₂ - CrB₂ have a form characteristic of two-phase alloys.

Fig. 3. "Composition-property" diagrams of boride systems
a. System TiB₂ - CrB₂
b. System TiB₂ - 2B₂
c. System Ti₃B₂ - CrB₂
1. Depth of corrosion; 2. Coefficient of linear expansion;
The thermal coefficient of linear expansion of alloy samples was measured in a temperature range of 20 to 700°C by a quartz dilatometer [15]. The general view and diagram of the instrument are shown in Fig. 4.

The instrument consists of a horizontal tubular electric furnace (1) with a nichrome heater, in the center of which is a quartz tube (2). One end of the tube is soldered, and the other is fastened with clamps (3) to the table (4) of the microscope (11).

The test sample (5) (diam 8 mm, length 15 to 20 mm) is placed in a graphite holder (6) for centering and for a more uniform heating of the sample. By means of a flat steel spring (7) the sample is pressed by a quartz rod (9), which in turn abuts against the soldered end of the tube (2).

Spring (7) is fastened to tube (2) by clamps (10). The movement of rod (8) due to the pressure of sample (5) expanding during heating (or due to the pressure of spring (7) when compressed) is measured by a microscope (11) with an ocular microanometer gage (14) of the M9-1 type. Readings are taken from indicator (12), which is a metal frame with an attached cover glass on which fine graduated lines are drawn.

The temperature is measured by a chromel-alumel thermocouple (13), the junction of which is placed in the side opening of the graphite holder (6) to a depth corresponding to the middle of the sample. It was established that at a temperature increase of about 5 to 6°C per minute there was no noticeable drop in temperature between the sample and the thermocouple.

The results of the measurements are given in Fig. 5 (curves 2).

The limit of compressive strength was determined on a 17-ton manual hydraulic press by means of special equipment. Truncoid fragments of the alloy were compressed. The limit of tensile strength was determined by means of
special equipment on a GZhF-5 testing machine. The cylindrical samples 14 mm in diameter and 3 to 4 mm high were bent through their diameter.

Fig. 4. Diagram of a quartz dilatometer installation
(1) Electric tubular furnace; (2) quartz test tube
(3) clamp for fastening test tube; (4) table for microscope;
(5) sample; (6) graphite holder; (7) compression springs;
(8, 9) quartz rods; (10) clamp to hold springs;
(11) microscope; (12) calibrated indicator; (13) thermometer;
(14) ocular micrometer gage.

Results of all measurements are given in Table 3. For comparison, data available in the literature are given in the Table.

On the basis of data from metallographic and x-ray diffraction analyses, and also from the results of measuring the microhardness of alloy phases and electrical conductivity (see Fig. 3), it can be concluded that in the system
TiB₂ - CrB₂ crystallization of a continuous series of solid solutions occurred, but in systems TiB₂ - W₂B₅ and ZrB₂ - CrB₂ only limited solubility was observed. The solubility of TiB₂ in W₂B₅ and W₂B₅ in TiB₂ does not exceed 10 and 5% mole respectively. The solubility of ZrB₂ in CrB₂ is about 20% mole and the solubility of CrB₂ in ZrB₂ is evidently negligible.

**TABLE 3**

Properties of Borides of Titanium, Zirconium, Curium and Tungsten

*(in brackets - published data)*

<table>
<thead>
<tr>
<th>Indicia</th>
<th>TiB₂</th>
<th>ZrB₂</th>
<th>CrB₂</th>
<th>W₂B₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness, kg/cm²</td>
<td>3400±200</td>
<td>2500±200</td>
<td>1500±130</td>
<td>2600±130</td>
</tr>
<tr>
<td></td>
<td>(370)</td>
<td>(2250)</td>
<td>(1800)</td>
<td>(2660)</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ohm⁻¹ cm⁻¹</td>
<td>12</td>
<td>100±1</td>
<td>500</td>
<td>10 600</td>
</tr>
<tr>
<td></td>
<td>(37 700)</td>
<td>(169 000)</td>
<td>(47 600)</td>
<td></td>
</tr>
<tr>
<td>Thermal coefficient of linear expansion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α 10⁻⁶</td>
<td>6.2</td>
<td>5.2</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>Ultimate strength, kgf/mm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in compression</td>
<td>250</td>
<td>170</td>
<td>100</td>
<td>70</td>
</tr>
<tr>
<td>in bending</td>
<td>70</td>
<td>50</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated on the basis of 100% density*
The study of corrosion resistance. The total oxidation process of borides can be expressed by equations:

\[ \text{MeB}_n + \frac{1}{2}(m + \frac{2}{3} n)\text{O}_3 = \text{MeO}_{m+\frac{1}{3}} + \frac{n}{2}\text{B}_2\text{O}_3 \]

According to published data the solubility of the oxides of titanium, zirconium, and chromium in B\(_2\)O\(_3\) at temperatures below 1200\(^\circ\)C is small, and these metals do not form borates (in the present study this assumption was checked and confirmed). Thus, at the first moment of oxidation, at 1000\(^\circ\)C a mechanical mixture of B\(_2\)O\(_3\) and the oxide of the corresponding metal is formed on the surface of the borides.

Having accepted the diffusion character of oxidation and considering the rate of evaporation of B\(_2\)O\(_3\) as constant and equal to B, we obtain the following equation of the kinetics of boride oxidation (or of other chemical compounds in the oxidized scale of which there are volatile components):

\[ \Delta G = A t^\alpha - B t \]

where

- \(\Delta G\) is change of weight per unit surface of the sample;
- \(A\) is the constant of oxidation rate;
- \(B\) is the evaporation rate of B\(_2\)O\(_3\) per unit surface;
- \(t\) is the time of oxidation.

Since the oxidation rate decreases with time and the evaporation rate of B\(_2\)O\(_3\) can be taken as constant, there will arrive a moment when the evaporation rate will become equal to the oxidation rate and then will exceed it. Therefore, after a certain period of time, almost all the B\(_2\)O\(_3\) in the scale will be evaporated. From that moment the scale will consist mostly of metal oxides.
and the process of oxidation will be described by a parabolic dependence:

$$\Delta G = A t^2$$

(2)

where $A < A_0$.

It follows from this that the oxidation process of borides can be divided into two stages. The kinetic curves of boride oxidation will divide correspondingly into two sectors.

Analysis of Eq. (1) leads to a series of dependences.

The duration of the first stage of oxidation:

$$t_1 = \frac{A - A_0}{a} \frac{\ln[A/(1 - K_1)]}{K_1}$$

(3)

where $K_1$ is the coefficient, showing which portion of the increase in weight is due to the formation of metal oxides.

The value of $K_1$ is determined only by stoichiometric ratios (see the general equation for the reaction of boride oxidation:

$$K_1 = \frac{m}{a + \frac{3}{2} a}$$

(4)

If $K_1 > 0.5$, then during a certain period of time the weight of the sample will decrease in the process of oxidation; i.e., the maximum will appear on the sector of curve $\Delta G = t$ corresponding to the first stage of oxidation. To this maximum corresponds the time:

$$t_i = \left(\frac{A}{a}\right)^3$$

(5)

The period of time $t_1 - t_2$, during which oxidation is accompanied by a decrease in weight, is:

$$t_1 - t_2 = \frac{1}{8} \left(0.5 - K_1\right) (1.5 - K_1)$$

(6)

In order to determine the coefficients $a$ and $b$ in Eq. (1), it is necessary to plot an experimental curve in coordinates $x$ and $1/t_1^2$, where
The angle of slope of the straight line will equal \( \alpha \); the intercept on the axis will correspond to \( B \).

In general the process of oxidation can be described not by a parabolic, but by a step dependence and Eq. (1) will have the form:

\[
\Delta G = A \tau - Bt
\]  

(8)

The curve described by Eq. (8) is rectified when plotting in coordinates \( \log (\Delta G) \) and \( \log t \).

The change in weight of the sample (weight-increase), which is fixed by various weighting methods of testing (without removing the scales), and the change in the outer dimensions of the sample cannot uniquely characterize the oxidation resistance of the material.

Depth corrosion is an indicator comparable for different materials and uniquely characterizing the degree of corrosion and, therefore, the corrosion resistance.

Fig. 5. Diagram of the scale formation.

By examining the dependence between the change in weight \( (\Delta G) \), the
depth of corrosion ($C_L$) and the change in outer dimensions of the sample ($C_1$) in the process of oxidizing (Fig. 5), the following relations can be derived:

\[ \begin{align*}
L &= K_1 G \\
L_1 &= K_2 G \\
1 = L_1 + L &= (K_2 + K_3) G
\end{align*} \]  

(9) \hspace{1cm} (10) \hspace{1cm} (11)

where $C_L$ is the depth of corrosion,

$C_1$ is the change of outer dimensions of sample due to corrosion,

$\mu_1$ is the scale thickness,

$K_2$ is the coefficient equal to the depth of corrosion (in $\mu$ ) during the change in the weight of the sample by $1 \text{mg/cm}^2$

$K_3$ is the coefficient equal to the change in the outer dimensions of sample (in $\mu$ ) during the change in the weight of the sample by $1 \text{mg/cm}^2$.

Values $K_2$ and $K_3$ can be calculated by formulas:

\[ K_2 = \frac{10}{\gamma C (M_a - 1)} \]

\[ K_3 = K_2 (n - 1) \]  

(12)

where $\gamma C$ is the specific weight of the oxidizing compound.

$M_a$ is the molecular weight of the oxidizing compound.

$\gamma C$ is the weight of the oxides formed by oxidation of 1 mole of the compound.

$a$ is the ionic-Badeworth ratio (valence of oxidation: valence of compound).

Table 4 shows coefficient values of $\gamma$, $K_1$, $K_2$ and $K_3$ for Ti, Zr, Ba, and Co. For comparison, data is given for some other compounds and alloys.
**Table 4**

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha ) without allowing for the ( \text{B}_2\text{O}_3 )</th>
<th>( \alpha ) allowing for the ( \text{B}_2\text{O}_3 )</th>
<th>( x_1 )</th>
<th>( x_2 )</th>
<th>( x_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{TIB}_2 )</td>
<td>3.70</td>
<td>1.36</td>
<td>0.60</td>
<td>11.8</td>
<td>5.3</td>
</tr>
<tr>
<td>( \text{ZrB}_2 )</td>
<td>3.21</td>
<td>1.22</td>
<td>0.40</td>
<td>7.3</td>
<td>3.9</td>
</tr>
<tr>
<td>( \text{CrB}_2 )</td>
<td>3.73</td>
<td>1.04</td>
<td>0.40</td>
<td>6.0</td>
<td>2.5</td>
</tr>
<tr>
<td>( \text{W}_2\text{B}_3 )</td>
<td>2.95</td>
<td>2.00</td>
<td>0.44</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>( \text{TIC} )</td>
<td>1.60</td>
<td>1.54</td>
<td>1.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>( \text{TIC}-20% \text{Co} )</td>
<td>1.60</td>
<td>1.54</td>
<td>1.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>( \text{Fe} )</td>
<td>1.47</td>
<td>1.17</td>
<td>1.9</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>( \text{NaSi}_2 )</td>
<td>2.95</td>
<td>2.95</td>
<td>2.2</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>( \text{SiAl} )</td>
<td>2.85</td>
<td>2.85</td>
<td>2.2</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>( \text{SiC} )</td>
<td>1.60</td>
<td>1.60</td>
<td>2.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>( 67% \text{SiC}, 33% \text{B}_4\text{C} )</td>
<td>1.81</td>
<td>1.81</td>
<td>2.8</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** When calculating it was understood that the scales consisted of oxides of TiO, CrO, FeO, Al₂O₃, CaO, MgO, MnO, SiO₂.

**Volumetric Rate of Corrosion and Oxide Alloys**

In order to study the volumetric rate during a restricted period (up to 70 hours), a gravimetric method was used with periodic readings of samples.
from the furnace for weighing and measuring. To study the initial oxidation period (2 to 4 hours), the method of periodic weighing was used without removing the samples from the furnace. The samples, placed on porcelain disks, were loaded into a muffle furnace (Fig. 6). Oxidation occurred at 1000°.

Fig. 6. Diagram of loading samples in the furnace when studying the kinetics of oxidations.

- Muffle; 2 - refractory brick; 3 - porcelain disks;
- samples; 5 - thermocouple; 6 - refractory shield.

The kinetic curves of oxidation for certain samples are given in Fig. 7.

Mathematical processing of the experimental data by the above method showed that the oxidation process in all cases can be satisfactorily described by Eq. (5). The value of the exponent $n$ equals 0.5 within the limits of accuracy of the tests.

As an example, data are given in Table 5 on the oxidation rate of Tid$_2$ samples.

The oxidation rate of curcuma dioide and its alloys with a small quantity of Tid and Tid$_2$ is of interest. During short exposure, curcuma dioide, and particularly its alloys containing 15 to 25% of Tid, and 25% remains in weight very slightly. However, during longer oxidation
(longer than 20 to 30 hours) the weight increase of the samples rose sharply (ten of times).

<table>
<thead>
<tr>
<th>Time of oxidation, hrs.</th>
<th>Weight increase</th>
<th>Change in outer dimensions</th>
<th>Calculated depth of corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Calculated</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>6.8</td>
<td>5.2</td>
<td>0.025</td>
</tr>
<tr>
<td>2.8</td>
<td>10</td>
<td>9.2</td>
<td>0.045</td>
</tr>
<tr>
<td>9.3</td>
<td>19</td>
<td>15</td>
<td>0.080</td>
</tr>
<tr>
<td>19</td>
<td>25</td>
<td>20</td>
<td>0.090</td>
</tr>
<tr>
<td>29</td>
<td>20</td>
<td>23</td>
<td>0.135</td>
</tr>
<tr>
<td>40</td>
<td>24</td>
<td>26</td>
<td>0.165</td>
</tr>
<tr>
<td>48</td>
<td>28</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td>63</td>
<td>29</td>
<td>29</td>
<td>0.18</td>
</tr>
<tr>
<td>82.5</td>
<td>32</td>
<td>29</td>
<td>0.17</td>
</tr>
<tr>
<td>102</td>
<td>30</td>
<td>30</td>
<td>0.185</td>
</tr>
<tr>
<td>119</td>
<td>29</td>
<td>29</td>
<td>-</td>
</tr>
<tr>
<td>117</td>
<td>29</td>
<td>29</td>
<td>0.19</td>
</tr>
<tr>
<td>170</td>
<td>31</td>
<td>31</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Several similar jumps could be observed on the kinetic curves of oxidation of pure CrB₂ (Fig. 7). The reason for such abrupt deterioration of the protective qualities of the scale is its insufficient stability, due evidently to the very small values of coefficient $\alpha$ (the ratio of the volume of the forming scale to the volume of the oxidized material, see Table 4).

The data on the weight increase and depth of corrosion, calculated by formula (y) and obtained during oxidation of various alloys, for 150 hours at 1000°, are given in Table 6 and in Fig. 3 (curves 1).

As can be seen in Fig. 3, the depth of corrosion of the intermediate alloys in the Ti₆₆-Cr₃₄ system is considerably less than for the pure components. The scale on these intermediate samples differed substantially from the scale on Ti₆₆ and Cr₃₄. It can be assumed that in the present case the formation of a chemical compound of Ti₆₆ and Cr₃₄ takes place and this compound has the high protective properties characteristic of Cr₂O₃, and at a favorable value of $\alpha$, characteristic also of TiO₂. Such a chemical compound Cr₂O₃, which probably has an ionic-crystalline lattice, was discovered.
by McBride and his colleagues.

TABLE 6

Weight change $\Delta m$ (in mg/cm$^2$) and depth of corrosion $d_1$ (in mm)
during oxidation of borides and their alloys in the air at 1000$^\circ$C
for 150 hours

(in brackets - extrapolated data)

<table>
<thead>
<tr>
<th>Composition, % mole</th>
<th>$\text{TiB}_2 \cdot \text{CrB}_2$</th>
<th>$\text{TiB}_2 \cdot \text{Y}_2\text{B}_3$</th>
<th>$\text{ZrB}_2 \cdot \text{CrB}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>29</td>
<td>0.48</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>60</td>
<td>0.94</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>41</td>
<td>0.63</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>11</td>
<td>0.26</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>12</td>
<td>0.32</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>18</td>
<td>0.56</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>20</td>
<td>0.68</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>37</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>—</td>
<td>1.7</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>35</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* Oxidation during 50 hours.
In the system ZrB₂ - CrB₂ the dependence of the depth of corrosion on the composition is of a complex nature. With an increase in CrB₂ content to 40 to 50% mole, the depth of the corrosion increases somewhat; between 40 to 70% mole it decreases and then again rises sharply.

The corrosion resistance of the investigated borides increases in the following order: W₂B₃ - TiB₂ - ZrB₂ - CrB₂ (at small exposures). The corrosion resistance of TiB₂, ZrB₂, CrB₂, and particularly their alloys, exceeds the corrosion resistance of titanium carbide, but is lower than that of some silicides. The corrosion resistance of the borides, which is lower by comparison with the silicides, is evidently due to the substantial difference between SiO₂ and B₂O₃. The film of boron oxide formed by the oxidation of the borides cannot serve effectively as a protection against oxidation, because of low viscosity and high volatility, and the protective properties of the boride scales are primarily determined by the properties of the metal oxides.

The fact that the corrosion resistance of borides is higher than the resistance of the corresponding carbides, and even more so of the metals, shows however that the presence of boron oxide in the products of oxidation substantially increases corrosion resistance. It is evident that with any oxidation time the content of B₂O₃ in the inner layers of the scale is considerable, whereas in the outer layers B₂O₃ is practically non-existent. Then therefore the borides are oxidised, there occurs continuous diffusion of the water B₂O₃ through the layer of the scale and the subsequent evaporation from the surface, as a result of a certain (though insignificant) mutual solubility of B₂O₃ and H₂O. The presence of B₂O₃ in the scale accelerates the scaling of the metal at high oxidation temperatures (scaling in the presence of a liquid phase). In the oxidation of carbides and nitrides.
the escaping gases (CO, CO₂, N₂) react in the opposite way; they loosen the scale.

Thus it may be presumed that, during oxidation of borides, a process of "self-healing" of the scale occurs, although to a lesser degree than with silicides [17]. Upon the appearance of a small crack or some other defect in the scale, an intensive oxidation of the boride begins; the products of oxidation (CO₂ and B₂O₃), which occupy a large volume, quickly fill the crack, thus preventing the access of oxygen. After that, the greater part of the boron oxide evaporates, leaving a dense layer of metal oxide "welding" the crack.

Scale Structure. The study of the scale structure was made on prepared sections of the scale and also on oblique sections. In some cases, the samples were drenched with polymethylmethacrylate. The change in the outer appearance of the samples during oxidation confirms the assumption that first a mechanical mixture of metal oxides and B₂O₃ forms. After a while, the B₂O₃ content in the outer layers of the scale becomes negligible. In alloys Ti₃B₂ - B₂ and Cr₃B₁ - CrB₁, there evidently forms a mechanical mixture of oxides of the corresponding metals. In alloys Ti₃B₁ - CrB₁, the character of the scale differs considerably from the Ti₃B₂ and CrB₁ scale.

The study of the oblique sections and the prepared sections of the scale showed that in most cases multilayered scales form, the inner layers of which consist of lower oxides (TiO, Cr₂O₃ - Cr₂O₅). The presence of comparatively thick layers of these oxides in the scale of the borides testifies to the decreased partial pressure in the inner layers of the scale.

It is interesting to note the first point of view the results of oxidation of titanium boride, with an increase in partial Ti₂, the
color of the surface of the sample changes from bluish-black through dull-black and gray to grey-white. Simultaneously, the surface character changes from a very smooth, glossy ("lacquered") surface to a dull one. In studying the cross and oblique cuts of the scale (Fig. 5) and the prepared sections, a black layer clearly appears between the boride base and the thick white layer of ZrO₂. All these facts can be explained by the formation of lower oxides of zirconium, probably ZrO, the existence of which has been denied in the majority of studies [18, 19]. However, the conclusion regarding the existence of ZrO₂ (and Zr₂O₃) was confirmed by chemical and x-ray diffraction analyses in subsequent studies [20]. The data obtained in the present work also confirm the presence of lower zirconium oxides.

Fig. 8. Scale on zirconium boride

(A) Boride bases; (B) thin black layers of lower oxides

(probably ZrO); (C) layer of ZrO₂.
Thus it can be assumed that oxidation of zirconium boride at 100°C occurs in the following way. In the initial period (1 to 2 hours) a film forms on the surface of the boride of ZrO which is covered by a layer of semi-liquid boron oxide or having a solution of ZrO in it. In the course of the next 10 to 20 hours, as a result of diffusion of oxygen, ZrO is oxidized to ZrO$_2$. Judging by the outer appearance of the scale at this stage of oxidation, it can be assumed that oxidation of ZrO occurs along the entire thickness of the vitreous layer of boron oxide and the forming particles of ZrO$_2$ form a similar suspension in B$_2$O$_3$. Upon further oxidation, the boron oxide gradually evaporates and on the surface of the sample of ZrO$_2$ it gradually forms a scale. The inner layers of ZrO$_2$ are very dense and hard, and therefore the ZrO layer retains a considerable thickness.

References