HIGH TEMPERATURE INTERACTION OF BORON OXIDE WITH ALUMINUM FLUORIDE
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High-temperature interaction of Boron Oxide with Aluminum Fluoride has been studied by infrared spectroscopy and derivatography. The formation of volatile Boron Fluoride, and some complex Aluminum-Boron Oxides has been found, which have a stabilizing effect on Boron at a molar ratio of Boron Oxide to Aluminum Fluoride 1:2 and lower.

For production of Aluminum pre-alloys in-situ by electrolysis of cryolite melts, oxides of the alloying elements (SiO₂, TiO₂, B₂O₃,...) are added to the melt [1]. However, oxides of Boron and Silicon interact with Aluminum Fluoride with a formation of volatile fluorides BF₃ and SiF₄ [2,3]. In the present work, we studied in detail the interaction of Boron Oxide with Aluminum Fluoride by derivatography of the B₂O₃·AlF₃ system. Infrared spectra of the rapidly quenched B₂O₃·AlF₃ salts heated to different temperatures were also taken. Information obtained can also be used for developing an in-situ electrochemical synthesis method for producing Titanium Diboride cathodic layer from cryolite based melts.

Thermodynamic Calculations

Thermodynamic calculations are performed for exchange reactions between Boron Oxide and Aluminum Fluoride, with formation of simple Al₂O₃ and also with formation of complex Aluminum-Boron oxides with different molar ratios of B₂O₃ to Al₂O₃ (hereinafter called "complex molar ratio" or CMR) of 1:2 and 2:9. Thermodynamic properties of phases are taken from handbooks [4,5]. Results of calculations are given in Table 1. As Table 1 shows, the change of standard Gibbs energies of the exchange reactions are positive at low temperatures, and become negative at higher temperatures (the temperature at which the standard Gibbs energy becomes zero is called hereinafter as "zeroG temperature"). As activities of all the solid and liquid phases given in Table 1 can be taken as approximately 1, the vapor pressure of the product Boron Fluoride will reach the outside pressure of 1 bar at the zeroG temperature. Hence, at this temperature, massive losses of Boron in the form of Boron Fluoride are expected. As shown in Table 1, the zeroG temperature is 850 K when the complex oxide product has the highest complex molar ratio (1:2), and becomes higher at lower complex molar ratios, being 910 K.
for a complex molar ratio of 2:9, and 970 K for a complex molar ratio of 0:1
(actually for simple \( \text{Al}_2\text{O}_3 \)).

Table 1. Change of standard Gibbs energy of possible reactions in the \( \text{B}_2\text{O}_3-\text{AlF}_3 \) system at different temperatures

| Reaction | \( T \)/K | \( \Delta \text{G}^\circ / \text{k} \) |
|----------|--------|------------------|
| reaction A | 773 | 95 |
| \( 2\text{AlF}_3(s) + \text{B}_2\text{O}_3(l) = \text{Al}_2\text{O}_3(s) + 2\text{BF}_3(g) \) | 873 | 40 |
| | 970 | 0 |
| | 973 | -2 |
| | 1073 | -33 |
| reaction B | 773 | 53 |
| \( 4\text{AlF}_3(s) + 3\text{B}_2\text{O}_3(l) = \text{Al}_4\text{B}_2\text{O}_9(s) + 4\text{BF}_3(g) \) | 850 | 0 |
| | 873 | -8 |
| | 973 | -51 |
| reaction C | 773 | 385 |
| \( 18\text{AlF}_3(s) + 11\text{B}_2\text{O}_3(l) = \text{Al}_{18}\text{B}_4\text{O}_{33}(s) + 18\text{BF}_3(g) \) | 873 | 98 |
| | 910 | 0 |
| | 973 | -185 |
| | 1023 | -324 |

Experimental Techniques

Chemically pure \( \text{H}_3\text{BO}_3 \) and \( \text{AlF}_3 \) were used for experiments. The amounts of the two components were taken such, that the molar ratio of \( \text{B}_2\text{O}_3 \) (to be formed at higher temperature from the originally used \( \text{H}_3\text{BO}_3 \)) to \( \text{AlF}_3 \) was 2:1, 1:1 and 1:2 (this ratio is called hereinafter "experimental molar ratio", or EMR). The sample powders were carefully mixed before experiments. Derivatogramms were taken on a derivatograph OD-102 with a heating rate of 10 °C/min, to the maximum temperature of 1000 °C. Pure alumina was used as reference material in the derivatograph. Other samples were heated to different temperatures (up to 950 °C), kept at the given temperature for 30 minutes, then quenched. Quenched samples were pressed into disks made of Potassium Bromide. Infrared spectra of the samples were measured on a spectrometer SPECORD M-80 in a range of 200-4000 cm\(^{-1}\). Characteristic frequencies for some molecules of importance for this study are given in Table 2.

Table 2. Characteristic frequencies for some molecules (cm\(^{-1}\))

| Molecule      | \( \nu_1 \) | \( \nu_2 \) | \( \nu_3 \) | \( \nu_4 \) | Literature |
|---------------|-------------|-------------|-------------|-------------|------------|
| \( \text{H}_3\text{BO}_3 \) | 1060 | 668-648 | 1490-1428 | 545 | 8 |
| \( \text{B}_2\text{O}_3 \) | - | - | 1330-1310 | - | 9 |
| \( \text{BF}_3 \) | 888 | 718 | 1505 | 482 | 8 |
| \( \text{AlF}_3 \) | - | 544 | 665 | 360 | 7 |
| \( \text{Al}_2\text{O}_3 \) | 860 | 786 | 660-620 | 462 | 12 |
Results of Experiments and Discussion

Derivatograms of mixtures with three different experimental molar ratios are given in Fig. 1. Mass losses in % found from low-temperature and high-temperature parts of the derivatograms are given in Table 3 (columns 3 and 5). Infrared spectra of the quenched samples previously heated to different temperatures are given in Fig. 2.

The low temperature parts of all three derivatograms are identical. One can observe two endothermic processes accompanied by some mass loss at 170 and 236 °C on each derivatogram. These two low-temperature processes are obviously due to loss of water by H$_3$BO$_3$ in the following two steps [6]:

\[
\begin{align*}
H_3BO_3 & = HBO_2 + H_2O & 1. \\
2 HBO_2 & = B_2O_3 + H_2O & 2.
\end{align*}
\]

In columns 2 and 3 of Table 3 the low temperature mass losses are given as calculated for reaction 1 and 2, and as measured from derivatograms of Fig. 1. As follows from comparison of calculated and measured data, the calculated and measured mass losses are identical for low B$_2$O$_3$ content. For high B$_2$O$_3$ content, however, there is a higher mass loss measured than expected, probably due to some extra water content of the initial salts. The nature of low-temperature mass losses can also be understood from comparison of spectrum in Fig. 2.1 (taken without pre-heating) with other spectra (taken with high-temperature pre-heating), showing the disappearance of peaks corresponding to the OH- group and H$_3$BO$_3$. It should be noted, that the peaks disappear only, if the B$_2$O$_3$ is complexed at high temperatures (see details below). Finally we can conclude, that above 236 °C the sample does not contain any more H$_3$BO$_3$ and therefore all the processes above 236 °C refer to interaction between B$_2$O$_3$ and AlF$_3$.

Table 3. Calculated and measured mass losses in % for 3 derivatograms (Fig.1.)
("low T" is calculated from Reactions 1, 2; measured values taken as average between 250 and 600 °C; "high T" is calculated based on Table 4.; measured values taken as the difference between mass at 900 °C and mass at 600 °C; "high T diff." is a difference between measured and calculated data)

| EMR | low T, calc. | low T, meas. | high T, calc. | high T, meas. | high T diff. |
|-----|--------------|--------------|--------------|--------------|--------------|
| 2:1 | -24.4 %      | -30 ± 2 %    | -23.0 %      | -27 ± 4 %    | -4 ± 4 %     |
| 1:1 | -19.0 %      | -21 ± 1 %    | -35.8 %      | -37 ± 2 %    | -1 ± 2 %     |
| 1:2 | -13.2 %      | -13 ± 1 %    | -49.6 %      | -36 ± 2 %    | +14 ± 2 %    |

At higher temperatures (above 650 °C) on derivatograms of Fig. 1. one can observe one (for Fig. 1.1.), or several (Fig. 1.2. and 1.3.) endothermic peaks, accompanied by mass loss. Those peaks obviously correspond to chemical reactions listed in Table 1, leading to formation of gaseous Boron Fluoride. As a simplest
case, amounts of products are calculated in Table 4 supposing reaction A of Table 1 is totally shifted to the right, and no complex formation between Al₂O₃ and B₂O₃ is taking place (i.e. no reaction B or C of Table 1). The high-temperature mass loss calculated based on this simplified model is given in column 4 of Table 3. Column 5 of Table 3 presents the experimental values of high temperature mass losses, measured from derivatogramms of Fig.1. between temperature range of 600 and 900 °C. In the last column of Table 3 the difference between measured and calculated high-temperature mass losses are given. One can see, that for experimental molar ratios of 2:1 and 1:1 the difference is negligible, hence probably indeed reaction A is taking place. This is obvious also from the fact that the first high-temperature endothermic peaks on Figs 1.1. and 1.2 appear at 703 and 700 °C accordingly, while the zeroG temperature of reaction A appears practically at the same temperature (970 K = 697 °C - see Table 1). However, for an experimental molar ratio of 1:2, the measured weight loss is less by 14 % than expected from reaction A (see last column, last row of Table 3). Recalculating the 14 % to the weight of B₂O₃ in the sample, one can find, that about 40 % of B₂O₃ is remaining in the system against 0 % predicted by Reaction A (see last row of Table 4). Then, the molar ratio of remaining oxides in the sample is 1:1.5, which is between the complex molar ratios 1:2 [4] and of 1:1 [11], or single Al₂O₃. Hence, obviously a mixture of complexes (and also pure alumina) is formed, i.e. instead of the single reaction A, in fact, some complex processes involving reaction A, B and C are taking place. This is also obvious from the fact that the first high-temperature peak in Fig.1.3. appears at 675 °C, which is between the zeroG temperatures of reaction A, B and C.

Table 4. Calculation of the products of reaction supposing only reaction A of Table 1 is active and is shifted totally to the right

| EMR | reactants | products | CMR |
|-----|-----------|----------|-----|
| 2:1 | 2 B₂O₃ + 1 AlF₃ | 1.5 B₂O₃ + 0.5 Al₂O₃ + 1 BF₃ | 3:1 |
| 1:1 | 1 B₂O₃ + 1 AlF₃ | 0.5 B₂O₃ + 0.5 Al₂O₃ + 1 BF₃ | 1:1 |
| 1:2 | B₂O₃ + 2 AlF₃ | 0 B₂O₃ + 1 Al₂O₃ + 2 BF₃ (*) | 0:1 |

* in reality, about 0.4 B₂O₃ + 0.6 Al₂O₃ + 1.2 BF₃ + 0.8 AlF₃ is formed (see Table 3, last column, last row), hence the real CMR is 1:1.5.

The above conclusions based on derivatogramms are also verified by infrared spectra. For an experimental molar ratio of 2:1 the spectra are shown in Fig 2.2. and 2.3 for 760 and 950 °C heat treatment. Comparing Fig. 2.2 with Fig.2.2. (received without heat treatment), one can see the followings:

i. the low frequency peak at 360 cm⁻¹ of Fig.2.1. corresponding to AlF₃ disappears;
ii. the high frequency peak above 3000 cm⁻¹, corresponding to OH- group of H₃BO₃, is still present, although with slightly lower intensity;
iii. the peak at 1450 cm⁻¹, corresponding to H₃BO₃, is still present, although with lower intensity;
iv. there is a poorly defined peak between 400 and 900 cm⁻¹, corresponding probably to Al₂O₃ that may be partly complexed by B₂O₃.

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The spectra for the experimental molar ratio of 2:1 with a heat treatment at 950 °C (Fig.2.3) is quite different from the spectra of the same system preheated to 760 °C (Fig.2.2). Before listing differences it should be noted, that there is no peak for AlF₃ in Fig.2.3. either, i.e. the two experiments are identical for the AlF₃ disappearance from the system. Fig.2.3. differs from Fig.2.2. in the following: in Fig.2.3
i. there is no peak for the OH- group;
ii. there is no peak for H₃BO₃;
iii. there are new, very well defined peaks at around 600, 800, and 1300-1350 cm⁻¹ frequency regions, which probably correspond to deformed peaks of Al₂O₃ and B₂O₃.

Hence, at higher temperatures just 0.5 mole of Al₂O₃ seems to stabilize all the 1.5 mole of B₂O₃. This result is surprising, because the well known phases between Boron oxide and Aluminum oxide have complex molar ratios of 1:2 and 2:9 [4], but not 3:1. On the Al₂O₃ - B₂O₃ phase diagram given in [11] one more compound with complex molar ratio of 1:1 is also given (so called "eremeevit"). Therefore, based on our results, we can conclude, that there should be a high-temperature phase with the B₂O₃ to Al₂O₃ molar ratio of 3:1, which might be metastable at room temperature (and therefore not seen on phase diagrams), but still is able to stabilize B₂O₃ if rapidly quenched.

For an experimental molar ratio of 1:1, the spectra are shown in Fig 2.4, 2.5 and 2.6 for 720, 760 and 950 °C heat treatment. As seen from infrared spectrum of Fig.2.4, at 720 °C the reaction A is not shifted totally to the right, as a medium intensity peak of AlF₃ can still be observed. At slightly higher temperature 760 °C (Fig.2.5) the peak of AlF₃ has practically disappeared. The 0.5 mole of Al₂O₃ formed might form a 1:1 complex oxide with the remaining amount of 0.5 mole of B₂O₃. At higher temperature this 1:1 complex can dissociate to the 3:1 complex (see above) and 1:2 or 2:9 complexes (see [4] and Table 4). The total complex formation of the remaining salt can be well seen in the spectrum (Fig 2.6) of the salt preheated up to 950 °C.

For an experimental molar ratio of 1:2 the spectra are shown in Fig 2.7, 2.8, and 2.9 for 760, 900 and 950 °C heat treatment. As was shown before, in this case the complex formation between Al₂O₃ and B₂O₃ will partially prevent the formation of gaseous Boron Fluoride. The formation of complexes can be well seen on the spectra.

Conclusions

1. The gaseous Boron Fluoride is formed at about 700 °C, or at lower temperature in excess of Aluminum Fluoride.
2. The high-temperature complex oxide phase is found with molar ratios of Boron Oxide to Aluminum Oxide 3:1, which forms at about 900 °C, and is metastable at lower temperatures.
3. The formation of complex Aluminum-Boron oxides can partially prevent Boron losses due to Boron Fluoride formation in excess Aluminum Fluoride. When the Aluminum Fluoride to Boron Oxide molar ratio is 2:1, about 40% of Boron Oxide is kept in the system in form of complex oxides up to 950 °C.

Acknowledgements

This work has been supported by COPERNICUS 1171 and OTKA T016903.

References

1. A.I. Belyaev, Metallurgiya legkikh metallov, p.543, Metallurgiya, Moscow (1944).
2. A.P. Krymov, V.V. Bugaenko, V.V. Nerubashchenko and R.V. Chernov, Elektrokhimicheskie i termodinamicheskie svoistva ionnykh rasplavov, p.69, Naukova Dumka, Kiev (1977).
3. D.V. Pruttskov, Ionnye rasplavy i tverdye elektrolity, 1, 70 (1986).
4. Ih. Barin, Thermochemical Data of Pure Substances, VCH, Weinheim (1993).
5. M.W. Chase et al., JANAF Thermochemical Tables (Third Edition), J. Phys. Chem. Data, 14, Suppl.1 (1985).
6. H. Remy, Lehrbuch der Anorganischen Chemie, p.334, AVG&P, Leipzig (1960).
7. E.N. Jurtenko, G.N. Kustova, S.S. Batsanov, Kolebatel'nye spektry neorganicheskikh soedinenii, p.19, Nauka, Sibirskoe otdelenie, Novosibirsk (1981).
8. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, p. 98, Wiley-Interscience, Second Edition, New York (1970).
9. V.N. Pavlikov and al., Russ. J. Inorg. Chem., 19, 1597 (1974).
10. P. Ramdohr, H. Strunz, Lehrbuch der Mineralogie, p. 564, Ferdinand Enke Verlag, Stuttgart (1967).
11. P.J.M. Gielisse and W.R. Foster, Nature, 195, 69 (1962).
12. V.A. Florinskaya, Infraokrasnye spektry neorganicheskikh stekol i kristallov, p. 113, Khimiya, Leningrad (1972).
Fig. 1. Derivatogramms of $\text{B}_2\text{O}_3$-$\text{AlF}_3$ systems.
2.1. 
$\text{B}_2\text{O}_3: \text{AlF}_3$

2.2. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 2:1$
$T = 760°C$

2.3. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 2:1$
$T = 950°C$

2.4. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:1$
$T = 720°C$

2.5. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:1$
$T = 760°C$

2.6. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:1$
$T = 950°C$

2.7. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:2$
$T = 760°C$

2.8. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:2$
$T = 900°C$

2.9. 
$\text{B}_2\text{O}_3: \text{AlF}_3 = 1:2$
$T = 950°C$

Fig. 2. Infrared spectra of rapidly quenched salts of the $\text{B}_2\text{O}_3: \text{AlF}_3$ system.