ISSN 1087-6596, Glass Physics and Chemistry, 2015, Vol. 41, No. 3, pp. 324–328. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © D.V. Kolovertnov, I.B. Ban'kovskaya, 2015, published in Fizika i Khimiya Stekla.

Kinetics of Oxidation of the Zirconium Boride–Silicon Carbide Composition in the Air Medium

D. V. Kolovertnov and I. B. Ban'kovskaya

Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, 199034 Russia
e-mail: inbankov@isc1.nw.ru

Received April 4, 2014

Abstract—Heat-resistant ceramic materials have been prepared based on the zirconium boride–silicon carbide composition during oxidation in the air atmosphere. The effect of the evaporation of boric oxide on the oxidation kinetics has been revealed experimentally. The electrical resistivity and dilatometric properties of the composites were determined.

Keywords: zirconium boride, silicon carbide, evaporation of boric oxide, electrical resistivity, thermal coefficient of linear expansion

DOI: 10.1134/S1087659615030104

INTRODUCTION

Recently, increasing attention is paid to the elaboration and studies in the field of ultra-high-temperature ceramics (UHTC). Due to its unique properties to withstand oxidation in the air medium at temperatures higher than 2000°C, UHTC is applied in such fields as rocket production, metallurgy, and power engineering [1–7]. The ZrB_2–SiC system is the most promising for the elaboration of the new-generation materials. This work is a continuation of the earlier research [8–15]. In [8, 9] the optimal composition of (wt %) $70ZrB_2 \cdot 30SiC$ was determined and it was shown that it can serve as the basis of the high-temperature protective coating on graphite. Thus, this work is aimed at studying the oxidation processes and properties, such as the thermal coefficient of linear expansion (TCLE) and electrical resistivity of compact samples based on the ZrB_2–SiC composition.

EXPERIMENTAL

The $70ZrB_2 \cdot 30SiC$ composition was chosen as the object of the studies. The size of the particle powders d_{50} for zirconium boride was 12 μm and for silicon carbide it was 5 μm. A 2% water solution of carboxymethylcellulose (CMC) was used as a binder and suspending compound. CMC burns away in the thermal treatment process. Samples were prepared by the slip casting method. The size of the samples was 5 × 10 × 15 mm. The samples were dried at room temperature for 2–3 days. The preliminary thermal treatment of the samples was performed in an electric furnace with silit heaters in the air medium. To this end, the samples were placed in the furnace on supports of fused zirconium dioxide and heated in accordance with the given mode. In the case of the isothermal mode the samples were placed in the furnace preliminarily heated to the given temperature, and in the case of the nonisothermal mode the samples were heated from room temperature to the given temperature at the rate of 7 degrees/min. After annealing the samples were taken from the furnace and cooled in air.

A setup of continuous weighing modernized by the authors, which records the variation of the mass due to the oxidation and evaporation of boric oxide, was used for studying the oxidation kinetics of the samples. The setup was equipped with a corundum tube with a temperature gradient over the length, which was used as a trap for the boric oxide vapors, for measuring the evaporation of boric oxide from the surface sample (Fig. 1).

The electrical resistivity was measured in the electric furnace with nichrome heaters using a ceramic measuring cell by the two-contact method (Fig. 2). The experimental technique is described in [16].

The TCLE was measured on an automated quartz dilatometer of the system of the Institute of Silicate Chemistry, Russian Academy of Sciences [17, 18]. Samples for the measurements in the shape of bars with a size of 5 × 10 × 15 mm were treated thermally according to the isothermal and nonisothermal modes at 1350°C for 6 h.

DISCUSSION OF RESULTS

When heated in air, zirconium boride oxidizes with the formation of zirconium dioxide and boric oxide according to the reaction

$$ZrB_2 + 2.5O_2 = ZrO_2 + B_2O_3.$$

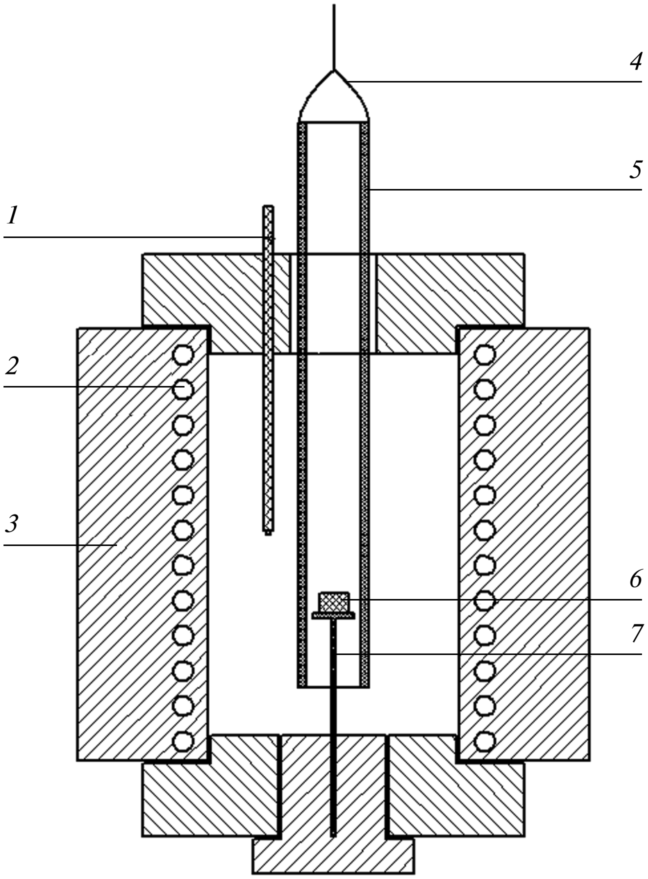

Fig. 1. Setup for continuous weighing with a B_2O_3 trap. *1*—thermocouple, *2*—platinum winding, *3*—ceramic insulator panel, *4*—platinum suspension (to scales), *5*—corundum tube (trap), *6*—sample, *7*—platinum support with a hafnium dioxide cushion.

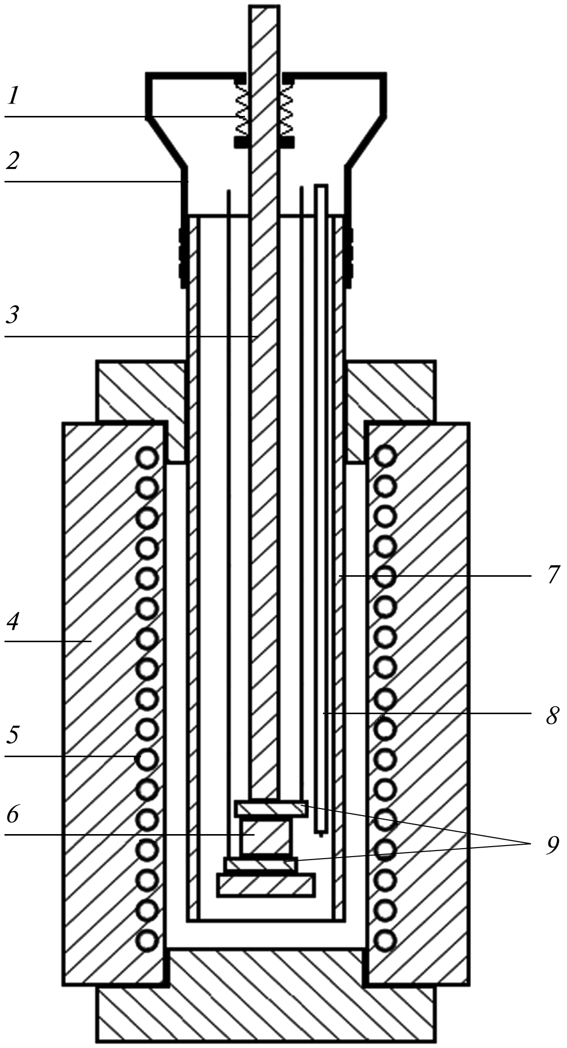

Fig. 2. Setup for measuring the electrical resistivity. *1*—tension clip, *2*—rest plate, *3*—ceramic punch, *4*—furnace insulator panel, *5*—nichrome winding, *6*—sample, *7*—ceramic cell frame, *8*—thermocouple, *9*—platinum or graphite electrodes.

At a temperature above 1000°C the B_2O_3 vapor has a noticeable pressure leading to its evaporation [19]. Figure 3 shows the kinetic curves of the oxidation of zirconium boride at 1300°C. It can be seen from the figure that in 60 min at 1300°C the mass loss of the sample due to the evaporation of boric oxide is 50% of the total gain in weight (curve *3*).

The introduction of silicon carbide in the system favors a decrease by a factor of five in the gain of the weight during oxidation (Fig. 4, curve *1*), and also the decrease in the evaporation of boric oxide (curve *2*), because it participates in the formation of the borosilicate glass-forming melt.

It can be seen from the comparison of Figs. 3 and 4 that the resultant gain in weight during the oxidation of ZrB_2 and ZrB_2–SiC is 47 and 8 mg/cm^2 (curves *3*), respectively, and the losses due to the evaporation of boric oxide are 24 and 2.5 mg/cm^2 (curves *2*), respectively.

The results of the thermogravimetric analysis and the measurements of the electrical resistivity of “raw” (with the preliminary thermal treatment) samples are combined for the detailed study of processes affecting the electrical resistivity of compact ZrB_2 samples (Fig. 5). The graphite plates of the GMZ grade (graphite fine-grained) were used as electrodes. Graphite electrodes were chosen because they are inert with respect to the studied material to 700°C, which made it possible to reveal the beginning of the oxidation of zirconium boride.

It can be seen from the plot that in the temperature interval of 600–700°C both curves have an analogous shape associated with the formation of reaction products as a result of the oxidation of zirconium boride by air oxygen. Above 700°C the graphite electrodes start to loosen, increase in volume, merge as a result of

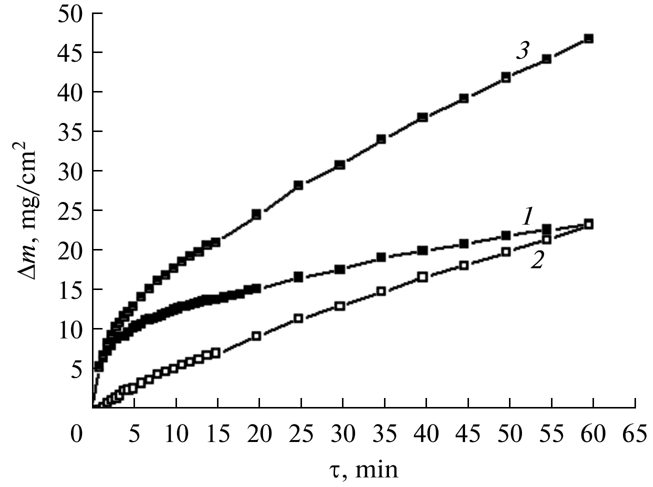

Fig. 3. Kinetic oxidation curves of ZrB_2 at the temperature of 1300°C: disregarding the evaporation of boric oxide (*1*), evaporation of boric oxide (*2*), and with allowance for the evaporation (the total variation of the mass) (*3*).

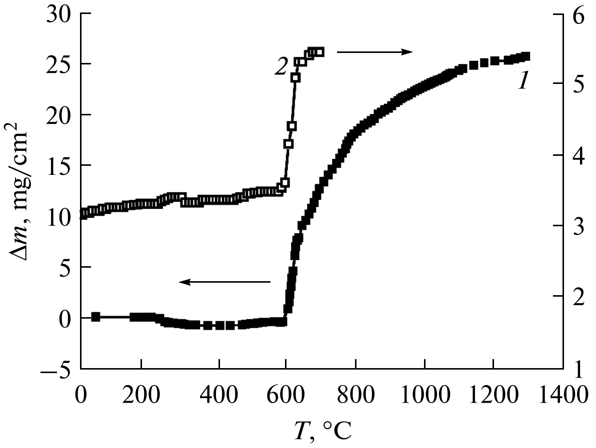

Fig. 5. Temperature dependence of the specific electrical resistivity (*2*) and the variation of the mass (*1*) of the initial ZrB_2 samples.

burning away, and as a consequence, the experiment is terminated (curve *2*).

At low temperatures (Fig. 6) the electrical resistivity of samples containing silicon carbide (curves *2, 3, 4*) is much less than the electrical resistivity of samples containing only zirconium boride. The increase in the temperature of the preliminary thermal treatment of samples leads to the increase in the electrical resistivity.

In the high-temperature region the electrical resistivity samples decreases to 10^6–$10^{2.5}$ Ohm · cm when the temperature increases from 600 to 1000°C.

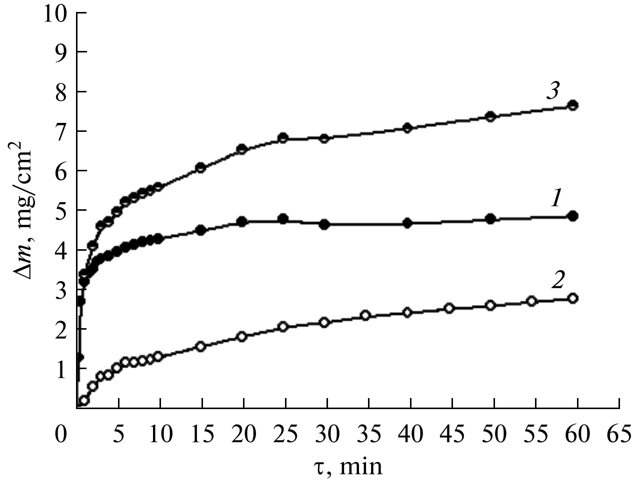

Fig. 4. Kinetic oxidation curves of the $70ZrB_2 \cdot 30SiC$ composition at a temperature of 1300°C (notations to curves, see Fig. 3).

The inflections of curve *1* at the temperatures of 400 and 650°C apparently correspond to the softening of borate glass and the oxidation of zirconium boride. The same inflections are also observed on curves *2, 3,* and *4*. It should be noted that with the increase in the temperature of the preliminary thermal treatment from 1100 to 1300°C the first inflection point is displaced to the higher temperature region from 450 to 600°C.

For dilametric measurements the sticks were pressed from the composition, then they were thermally processed, and then polished for obtaining parallel end-butts. A part of the oxidized surface was stripped, and the further oxidation occurred during the measurement of the elongation in the heating process. It can be seen from Fig. 7 that the heating and cooling curves do not coincide, since the oxidation of the sample continues and the composition of the surface layer varies. As a result of the first cycle, the considerable elongation of the sample to 350 μm at 650°C (650°C corresponds to the temperature of the oxidation of zirconium boride) is observed. The elongation becomes less expressed in the subsequent cycles, which indicates the formation of a film that is more stable to oxidation.

At a temperature of 300°C the elongation of the sample is observed, which is associated with the thermal expansion of boric oxide (Fig. 8). In the fifth cycle heating and cooling curves almost coincide, and the TCLE values of 95×10^7 K^{-1} for the interval of 350–450°C and 43×10^7 K^{-1} for the interval of 550–800°C were calculated from these data.

Curves *2, 4,* and *5* coincide in the interval of 450–650°C (Fig. 9). In this interval the TCLE value is 74.6×10^7 K^{-1}. The elongation of the sample is associated with the thermal expansion of the glass matrix.

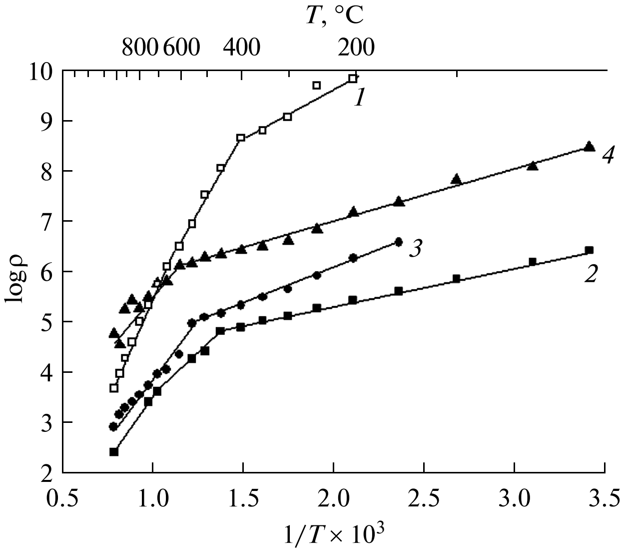

Fig. 6. Dependence of the specific electrical resistivity in the inverse temperature of samples preliminarily treated thermally at 1100, 1250 and 1300°C for 20 h.

1—ZrB_2 (1250 °C), *2*, *3*, *4*—ZrB_2–SiC (1100, 1250, 1300°C, respectively).

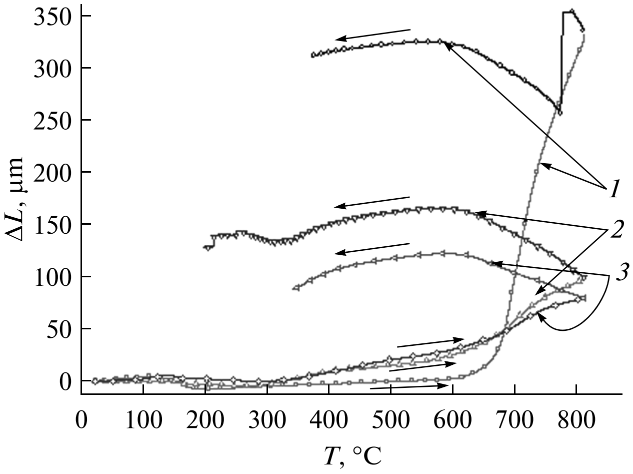

Fig. 7. Dilatometric curves of the ZrB_2–SiC sample preliminarily treated thermally according to the isothermal mode at 1300°C for 3 h.

1, *2*, *3*—heating and cooling cycles.

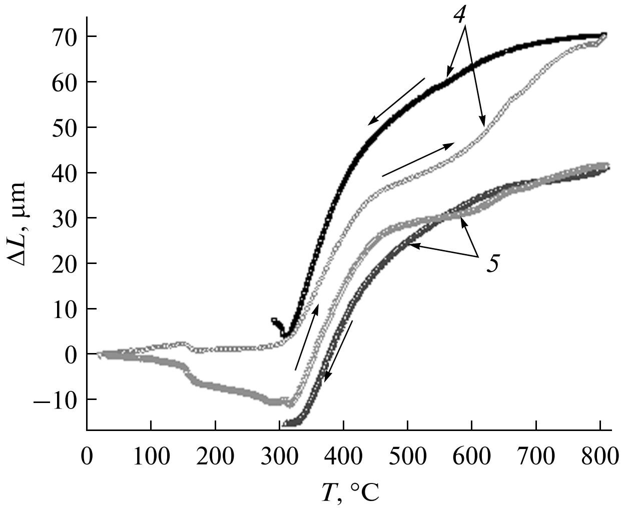

Fig. 8. Dilatometric curves of the ZrB_2–SiC sample preliminarily treated thermally at 1300°C for 3 h.

4 and *5*—heating and cooling cycles.

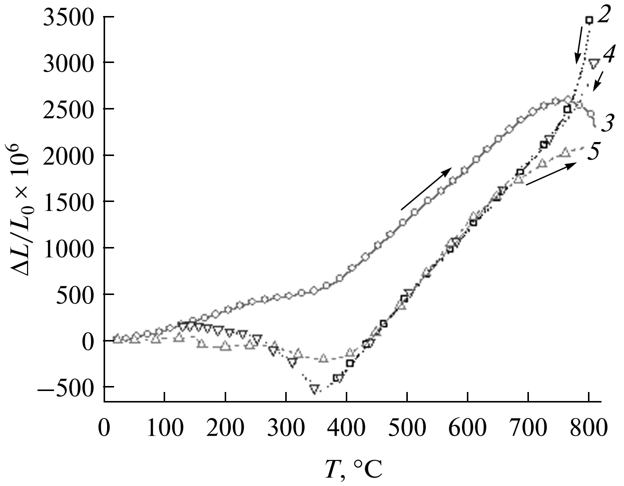

Fig. 9. Dilatometric curves of the ZrB_2–SiC sample, preliminarily treated thermally according to the nonisothermal mode 20–1300°C at a rate of 10°/min.

1, *2*, *3*, *4*—heating and cooling cycles.

No elongation associated with the oxidation of zirconium boride is observed, since the oxidation occurred at a larger depth in this mode.

CONCLUSIONS

The kinetics of the oxidation of compact samples of the ZrB_2–SiC composition in the isothermal heating mode at 1300°C was studied.

—It was shown that during the introduction of silicon carbide in the composition of samples the electrical resistivity in the low-temperature region decreases by three orders of magnitude and in the high-temperature region by the order of magnitude that is associated with the difference of the composition of the surface layer. The electrical resistivity increases with the increase in the temperature during the measurement of the electrical resistivity of samples not preliminarily treated thermally, which indicates the formation of the reaction products. The electrical resistivity decreases during the heating of samples after the preliminary thermal treatment that is associated with the softening of the borate and borosilicate glass and the continuation of the oxidation process of zirconium boride.

—The dilatometric properties of samples after different modes of the preliminary thermal treatment were studied: in the nonisothermal mode the thermal broadening of the sample is observed to be associated with the broadening of the glass matrix, and in the isothermal mode also with the oxidation of zirconium boride. The TCLE value is 95×10^7 K^{-1} for the interval of 350–450°C, 74.6×10^7 K^{-1} for the interval of 450–650°C, and 43×10^7 K^{-1} for the interval of 550–800°C.

ACKNOWLEDGMENTS

We are grateful to V.P. Klyuev, Cand. Sci. (Chem.), for his help in dilametric measurements.

REFERENCES

1. Tripp, W.C. and Graham, H.C., Thermogravimetric study of the oxidation of ZrB_2 in the temperature range of 800 to 1500°C, *J. Electrochem. Soc.*, 1971, vol. 118, no. 7, pp. 1195–1199.
2. Zamora, V., Ortiz, A.L., Guiberteau, F., and Nygren, M., Crystal-size dependence of the spark-plasma-sintering kinetics of ZrB_2 ultra-high-temperature ceramics, *J. Eur. Ceram. Soc.*, 2012, vol. 32, no. 2, pp. 271–276.
3. Pimenoff, J.A., *Coatings and Surface Doping—Nano-Sized Industrial Applications*, Espoo, Finland: Beneq Oy. E-mail: joe.pimenoff@beneq.com, www.beneq.com.
4. Sazonova, M.V. and Efimenko, L.P., Thermal stability of $MoSi_2$–SiC composites in air at temperatures of 1100–1400°C, *Fiz. Khim. Stekla*, 2009, vol. 35, no. 2, pp. 285–292.
5. Sazonova, M.V. and Efimenko, L.P., Thermal stability of $MoSi_2$–SiC composites in air at temperatures of 1100–1400°C, *Glass Phys. Chem.*, 2009, vol. 35, no. 2, pp. 219–224.
6. Sevast'yanov, V.G. Simonenko, E.P., Gordeev, A.N., Simonenko, N.P., Kolesnikov, A.F., Papynov, E.K., Shichalin, O.O., Avramenko, V.A., and Kuznetsov, N.T., Production of ultrahigh temperature composite materials HfB_2–SiC and the study of their behavior under the action of a dissociated air flow, *Russ. J. Inorg. Chem.*, 2013, vol. 58, no. 11, pp. 1269–1278.
7. Chunfeng Hu, Yoshio Sakka, Jinghui Gao, Hidehiko Tanaka, and Grasso, S., Microstructure characterization of ZrB_2–SiC composite fabricated by spark plasma sintering with $TaSi_2$ additive, *J. Eur. Ceram. Soc.*, 2012, vol. 32, pp. 1441–1446.
8. Ban'kovskaya, I.B. and Kolovertnov, D.V., Effect of the thermal treatment mode on the composition and structure of ZrB_2–SiC system composites, *Fiz. Khim. Stekla*, 2013, vol. 39, no. 5, pp. 816–828.
9. Ban'kovskaya, I.B. and Kolovertnov, D.V., Effect of the thermal treatment mode on the composition and structure of ZrB_2–SiC system composites, *Glass Phys. Chem.*, 2013, vol. 39, no. 5, pp. 579–588.
10. Kolovertnov, D.V. and Ban'kovskaya, I.B., Heat-resistant materials based on ZrB_2 with additives of SiO_2, SiC, and Si_3N_4, *Fiz. Khim. Stekla*, 2012, vol. 38, no. 6, pp. 931–933.
11. Ban'kovskaya, I.B., Kolovertnov, D.V., Salikova, A.P., Vasil'eva, I.A., Gonchukova, N.O., and Ratushnyak, S.L., Reaction synthesis of gas-impermeable coatings based on the zirconium boride–silicon nitride system for the protection of carbon materials, *Fiz. Khim. Stekla*, 2012, vol. 38, no. 6, pp. 755–767.
12. Ban'kovskaya, I.B., Vasilyeva, I.A., and Kolovertnov, D.V., Oxidation processes in a silicon–boron–zirconium boride composite in the temperature range 1000–1300°C, *Fiz. Khim. Stekla*, 2012, vol. 38, no. 3, pp. 409–416.
13. Ban'kovskaya, I.B., Vasilyeva, I.A., and Kolovertnov, D.V., Oxidation processes in a silicon–boron–zirconium boride composite in the temperature range 1000–1300°C, *Glass Phys. Chem,* 2012, vol. 38, no. 3, pp. 327–331.
14. Ban'kovskaya, I.B., Kolovertnov, D.V., and Efimenko, L.P., Preparation of composites in the ZrB_2–Si system and investigation of their properties, *Fiz. Khim. Stekla*, 2011, vol. 37, no. 2, pp. 250–258.
15. Ban'kovskaya, I.B., Kolovertnov, D.V., and Efimenko, L.P., Preparation of composites in the ZrB_2–Si system and investigation of their properties, *Glass Phys. Chem.*, 2011, vol. 37, no. 2, pp. 188–197.
16. Tikhonov, P.A., Formation, stability, and electrical properties of fluorite-like solid solutions in the ZrO_2–Y_2O_3–Yb_2O_3, ZrO_2–Y_2O_3–CaO, and ZrO_2–Y_2O_3–MgO systems, *Extended Abstract of Candidate's Sci. Dissertation*, Institute of Silicate Chemistry of the Academy of Sciences of the Soviet Union, Leningrad, 1971.
17. Klyuev, V.P. and Chernousov, M.A., An automated dilatometer with a small measuring force, in *Tret'e Vsesoyuznoe soveshchanie "Metody i pribory dlya tochnykh dilatometricheskikh issledovanii materialov v shirokom diapazone temperature"* (Proceedings of the Third All-Union Conference "Methods and Instruments for Precision Dilatometric Investigations of Materials over a Wide Temperature Range"), Leningrad, 1984, pp. 53–54.
18. *Properties and Structure of Oxide Glasses*, Klyuev, V.P. and Pevzner, B.Z., Eds., Kerala, India: Research Signpost, 2010.
19. Voitovich, R.F., Pugach, E.A., and Men'shikova, L.A., Investigation of high-temperature oxidation of zirconium diboride, *Poroshk. Metall.*, 1967, no. 6 (54), pp. 44–48.

Translated by L. Mosina