

Electrochemical behavior and galvanic treatment of boron carbide in ionic melts



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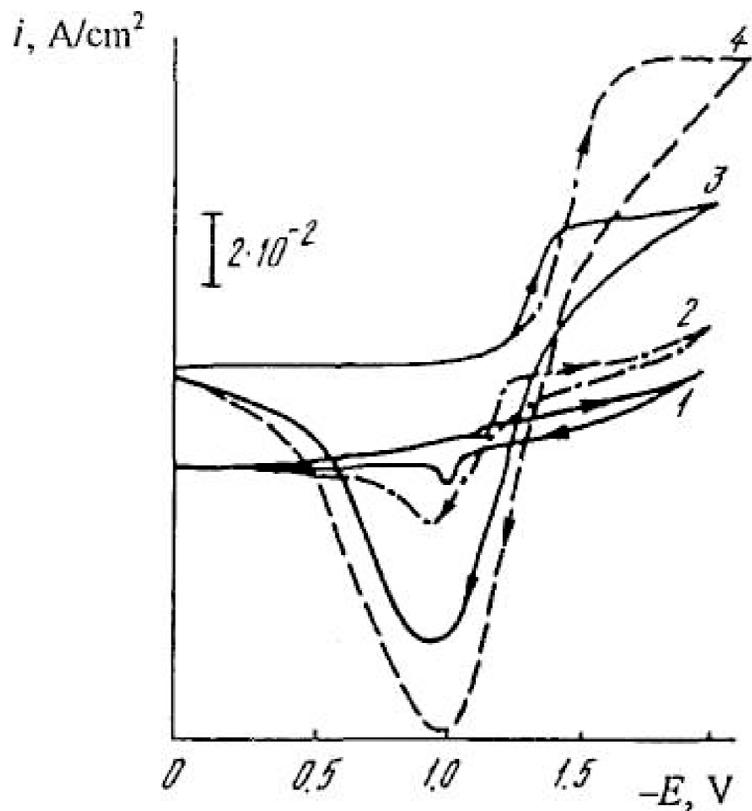
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Introduction and Methods

The concept we developed to explain the generation of electrochemical potential due to redox processes at the semiconductor-melt interface and its dependence on acid-base properties of the melt has been applied recently to silicon carbide [1]. With the aim to extend the range of semiconductive materials involved in the indicated system we undertook the potentiometric and voltammetric study of the electrochemical behavior and corrosion of boron carbide in halide, halide-oxide and oxide melts. The investigation is of current concern in connection with the development of processes to produce articles on the basis of metallized boron carbide [2].

Boron carbide belongs to the class of high-ohmic semiconductors. The sample of B_4C used in the experiments is a mixture of black shiny monocrystals (dispersity 315/250) with a rhombohedral lattice. It is oxidized by oxygen at a temperature above 1373 K and slowly degrades in contact with hydrofluoric, sulfuric or nitric acid. Alkalis easily decompose boron carbide to give borates. When heated with Group IV or VI refractory metal oxides, B_4C reduces them to the corresponding borides. We used two electrochemical techniques in the study, i.e., potentiometry and linear scan voltammetry.

Results and Discussion



The thermodynamic analysis was carried out of possible reactions between boron carbide and oxygen-containing compounds of the Group IV and VI elements usually used to modify acid-base properties of melts in electrodeposition and synthesis of refractory metal carbides and borides.

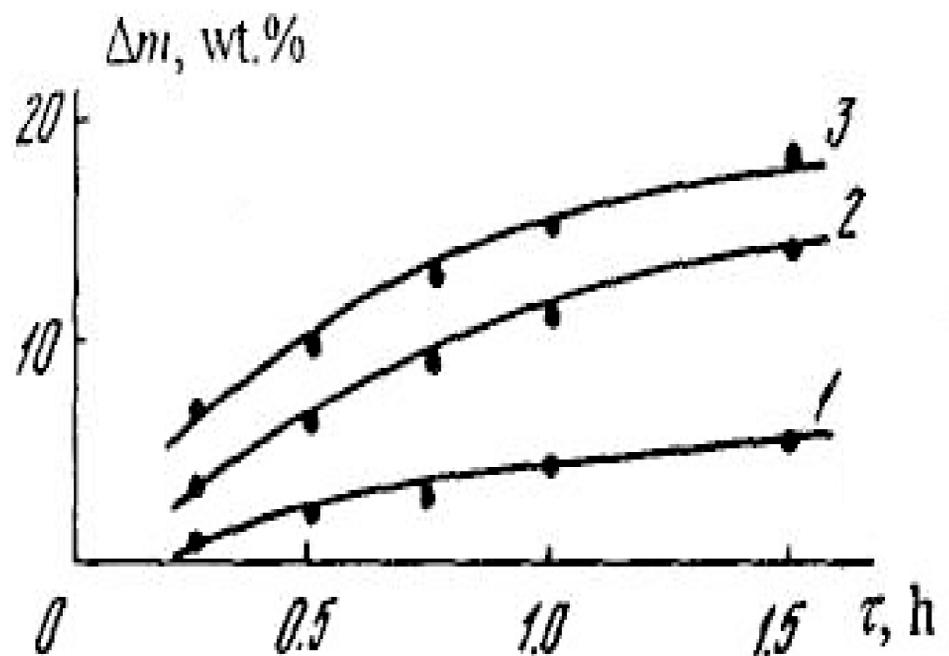
The oxidation of boron carbide to metaborate or boron oxide was found to be the energetically most preferable processes. The compounds involving carbon or a Group VI element are expected to reduce to give the element in the free state or its intermediate-valence oxide. At 900-1200 K, boron carbide should actively interact almost with all the considered compounds. The redox processes occur at the semi-conductor-melt interface in the presence of "mild" oxidizers with establishment of the electrochemical equilibrium and space separation of charges. In contact with "strong" oxidizers, B_4C undergoes noticeable corrosion.

The electroreduction of oxyanions MoO_4^{2-} (WO_4^{2-}) was studied in the NaCl-KCl melt containing Ca^{2+} cations, at the platinum-pin, platinum-gauze, and boron carbide electrodes (Fig. 1). Comparison of the limiting currents at the empty and filled platinum containers allowed us to estimate the surface area of B_4C grains working as the cathode. From the difference in currents at the empty and filled gauze-container electrodes, the partial currents due to reduction of MoO_4^{2-} at the B_4C grain surface were calculated.

Fig. 1. Cyclic voltammograms at the platinum-pin (1), platinum-gauze (2), and boron carbide (3 - 0.025 g B_4C , 4 - 0.05 g B_4C) electrodes in the NaCl-KCl melt containing 5×10^{-5} mol/cm³ Na_2MoO_4 and 2×10^{-4} mol/cm³ $CaCl_2$. $T = 1023$ K, reference electrode - Pb/O^{2-} , $F = 0.1$ V/s.

Chemical deposition of molybdenum, tungsten, and their carbides were performed onto B_4C grains from the halide-oxide, NaCl-KCl- Na_2MoO_4 - $CaCl_2$, and oxide melts Na_2WO_4 - MO_3 , Na_2WO_4 - MO_3 - Li_2CO_3 at different temperatures, cathodic current densities and duration of the process. The chemical deposition of molybdenum and tungsten was carried out from the melts NaCl-KCl-3 mol.% Na_2MoO_4 -5 mol.% $CaCl_2$ and Na_2WO_4 -5 mol.% MO_3 . The electrochemical deposition of molybdenum carbide was conducted in the melt Na_2WO_4 -5 mol.% MoO_3 -10 mol.% Li_2CO_3 at the current density of 10 to 200 A/m² and the temperature of 1073 to 1173 K (powder deposits are formed at < 1073 K). The degree of metallization of B_4C grains was found to depend on the cathodic current density and duration of the electrochemical or chemical deposition (Fig. 2). The boron carbide grains (dispersity 315/250) coated with molybdenum carbide have the breaking load coefficient of 1.6-2.3 and capillarity increased by 3.1 to 3.6 times.

Fig. 2. The gain in weight of B_4C grains in the melt Na_2WO_4 -5 mol.% MoO_3 -10 mol.% Li_2CO_3 after the currentless (1) and galvanic (2,3) treatment: 2 - $i_c = 7.5$ A/m²; 3 - $i_c = 10$ A/m².



Conclusions

The results presented above allow the concept explaining the generation of electrochemical potential due to redox processes at the interface to be extended to boron carbide. The phenomenon can be used to apply plating or chemical coatings to semiconductive boron carbide materials.

References

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2. A. N. Porada and M. I. Gasik, *Electrothermics of Inorganic Materials* [in Russian], Moscow, Metallurgiya, 1990