HIGH-TEMPERATURE ELECTROCHEMICAL SYNTHESIS
OF COATINGS OF CARBIDES, BORIDES, AND SILICIDES
OF METALS OF THE IV–VI B GROUPS FROM IONIC MELTS (REVIEW)

A. I. Hab

We present historical information and the state of the art of the high-temperature electrochemical synthesis of refractory compounds of metals of the IV–VI B groups from ionic melts.

The interest in new efficient methods for the production of coatings of metal-like refractory compounds (MRC), i.e., carbides, borides, and silicides of metals of the IV–VI groups, is dictated by the requirements of present-day technology. Comparative analysis of existing methods for the synthesis of MRC shows that the method of high-temperature electrochemical synthesis (HES) in ionic melts is promising but has been studied quite insufficiently.

The HES of MRC is based on many-electron processes of the electrowinning of metals and nonmetals from ionic melts. It is customary to think that compounds with a melting point higher than that of iron (1808 K) are refractory. Two-component compounds of transition metals with boron, carbon, silicon, nitrogen, and oxygen which melt at temperatures higher than 1773–1873 K represent examples of refractory compounds. Sulfides, selenides, phosphides, etc. also belong to such compounds. The main methods for the synthesis of MRC are classified in monographs and reviews [1–4] fairly completely.

The method of HES was first applied by Andrieux [5, 6] for borides. Afterwards, he and other researchers extended it to carbides [5, 6, 8] and silicides and, somewhat later, developed this method in more detail for the synthesis of borides [7–9], carbides [8, 9], and silicides [10–12]. Nitrides have not yet been obtained by this method, but their synthesis is possible in principle on both the cathode and anode. Oxides are deposited by passivating the surface of the metal. For example, titanium and niobium oxides are produced in the melts of carbonates and nitrates of alkali metals [4, 13].

In industry, this method has not been applied widely up till now. This is connected with difficulties in controlling the many-electron electroreduction of components of synthesis and with the properties of high-temperature electrolytes. The main parameters of the electrolysis of melts and solutions in melts are process temperature 1023 to 1473 K, air atmosphere in most cases, and duration up to 2 h. As compared with other methods, HES has several advantages:

— the technological scheme of the production of MRC is simplified significantly (there is no need for intermediate stages of preparation of powders of the refractory metal and nonmetal);

— the process is realized at the atomic level and, hence, at lower temperatures;

— the initial components for synthesis can be chosen from less critical and expensive compounds of refractory metals and nonmetals;

“Kyiv Polytechnic Institute” National Technical University, Kyiv; “Ukraine” Open International University of Human Development, Kyiv.

— one can control the process of synthesis and the form of deposits, which makes it possible to obtain the final product in the form of both powders with regulated degree of dispersion (they need not be milled) and coatings.

However, this method has the following shortcomings: it is necessary to purify the cathodic products, and it is difficult to obtain compounds of strictly determined composition. One can overcome these shortcomings by applying continuous electrolysis, selecting fusible and cheap solvents and initial components for synthesis, and studying the structure and properties of electrolytes and electrolysis in detail.

Historical Information on the Method of HES in Ionic Melts

**Synthesis of Borides of Refractory Metals.** Before Schlain and his colleagues [14–17], borides of alkaline- and rare-earth as well as refractory metals of the IV–VI groups were synthesized by the method of HES in the form of disperse powders. To obtain coatings of titanium boride, these researchers investigated the oxide melts of borates of alkali and alkaline-earth metals to which titanium oxide was added. Titanium or sintered TiB₂ was used as an anode. The anode made of TiB₂ stabilized the bath. The rate of application of the coatings was 2 to 220 µm/h (Table 1).

A method for the production of coatings of vanadium, niobium, and tantalum borides is described in patents [18, 19]. Here, it is proposed to use an oxide melt based on borates, graphite, or heat-resistant steel as a material of the bath, and its case or an electrode made of graphite, heat-resistant steel, or an alloy containing vanadium, niobium, or tantalum as an anode. Another patent [20] proposes to produce TiB₂ coatings by the electrolysis of molten salts with the introduction of BF₄⁻ ions by dissolving gaseous BF₃ with the use of a soluble anode made of boron. It is necessary that the bath composition contain fluoride of an alkali metal. In [21], a method is patented for the application of TiB₂ coatings onto different articles by the electrolysis of LiF–KF–K₂TiF₆–KBF₄ melt.

In [22], one can find a description of the electrosynthesis of tantalum boride from chloride-fluoride KCl–K₂TaF₇–KBF₄ melt and attempts to clarify the mechanism of this process. By varying the electrolyte composition, anode current, and voltage on the bath, a mixture of tantalum mono- and diboride or one of these borides was obtained.

A method for the formation of coatings of zirconium diboride from a fluoride-oxide melt is described in patent [23]. Instead of K₂ZrF₆, ZrF₄ can serve as a source of zirconium. Zirconium diboride was also obtained from a fluoride-oxide melt containing only zirconium and boron [24]. In this case, one can control the process by the B₂O₃ concentration in the melt, and, under high current densities, metallic zirconium is deposited together with diboride.

Australian scientists synthesized ZrB₂ [25, 26] from fluoride-oxide melts. Here, KF or Na₃AlF₆ melts served as the solvent, ZrF₄ or ZrO₂ was the source of zirconium, and B₂O₃ was the source of boron. These researchers succeeded in lowering the synthesis temperature to 873 K in a melt based on potassium fluoride.

**Synthesis of Carbides of Refractory Metals**

A coating of carbides of refractory metals was first synthesized in [27, 28]. Here, a method was developed for the electrolytic synthesis of tantalum and niobium monocarbides from NaF–KF–Na₂B₄O₇–Na₂CO₃–Ta₂O₅ (Nb₂O₅) melt at 1023 K. In addition, a narrow range of the formation of stable carbide was found, and the influence of melt composition and the parameters of deposition on the deposit composition and its morphology was discussed (Table 1).