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Current problems of the electrochemistry of titanium and boron. Synthesis of titanium diboride and titanium intermetallic compounds in ionic melts

V I Shapoval, I V Zarutskii, V V Malyshev, N N Uskova

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Abstract. The current state of research into the titanium and boron electrochemistry and high-temperature electrochemical synthesis of titanium diboride and titanium intermetallic compounds with the iron triad metals is analysed. The prospects for the development of these studies are discussed. Primary attention is paid to the electrochemical properties and stability of halide systems containing titanium in various oxidation states together with boron. The bibliography includes 81 references.

I. Introduction

Studies on the electrochemical properties of titanium and boron and the processes of joint electroreduction of two or more components from ionic melts present interest for both theoretical and practical purposes. On the one hand, the results of these studies help one to understand characteristic features of multielectron processes and to follow the development of high-temperature electrochemical synthesis; on the other hand, they underlie the development of new technologies for the production of nontraditional materials with unique properties.[1–3] Despite the numerous publications devoted to the electrochemistry of titanium and boron as well as titanium diboride, data on the forms of their existence, the mechanisms of joint and separate electroreduction in ionic melts (especially chloride and fluoride melts) are quite scarce and contradictory. These processes serve as the basis for the technology of the electrochemical production of titanium, boron, titanium diboride and titanium intermetallic compounds; therefore, studies in this field are topical for the development of modern high-temperature electrochemistry.

II. Electrochemical behaviour of titanium

Electrolysis of titanium melts is a promising method for the production of metallic titanium and the synthesis of high-melting compounds (carbides, borides, silicides, intermetallic compounds) based on it. However, the complex pattern of the behaviour of titanium-containing melts accounts for the stringent requirements in the process engineering and selection of the salt systems. Thus it is necessary to study systematically and comprehensively the electrochemical and chemical properties of titanium in various oxidation states in molten electrolytes.

1. Electrolysis of titanium-containing melts

Titanium metal is mainly produced either by electrolysis of the melts of titanium oxygen compounds, fluorides or chlorides or by electrolytic refinement of crude titanium and its compounds.

Electrolysis of oxygen compounds of titanium has several advantages over electrolysis of other compounds, first of all, ready availability and low cost of the raw materials, namely, titanium dioxide and alkali metal titanates. These advantages also include simplicity of the equipment and the environmental safety of the process. Numerous publications have been devoted to the electrolysis of TiO_2 in melts of alkali metal chlorides or fluorides or potassium (sodium) hexafluorotitanate. The low solubility of titanium dioxide in various melts (0.02% – 0.07%) precludes its use for the production of titanium. In addition, during electrolysis of the $NaCl-K_2TiF_6$ melt containing titanium dioxide, the dioxide is reduced at the cathode to Ti_2O_3. This is accompanied by the formation of a non-decomposing precipitate near the cathode. Electrolytic preparation of pure titanium in this system is impossible because of the formation of titanium monoxide at the cathode.

Study of a similar system based on calcium chloride showed that in this case, titanium metal is formed in a secondary process, namely, reduction of TiO_2 at the cathode by calcium produced in electrochemical processes. Normal operation of the electrolytic cell requires a low concentration of TiO_2 in the electrolyte, its continuous feed to the cell and replacement of the electrolyte after it has been saturated with CaO. Electrolysis of TiO_2 dissolved in molten alkali metal borates or phosphates has been considered.[4,5] The researchers point to the necessity of additional purification of the resulting metal from oxygen.

Thus, the use of oxygen compounds for the electrolytic preparation of titanium and the synthesis of its derivatives is hardly promising, because lower titanium oxides, which contaminate the product, are formed at the cathode.

Calculations and experimental results show that electrolysis in molten salts of oxygen-containing acids, alkalis, oxides or many other melts does not ensure the preparation of pure titanium. The range of molten media is mainly limited to metal halides. However, these compounds, too, are not all suitable for electrolysis. Indeed, metals of Group IV and of subsequent Groups of the

V I Shapoval, I V Zarutskii, V V Malyshev, N N Uskova V I Vernadskii Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, prosp. Palladina 32/34, 252680 Kiev, Ukraine. Fax (38-044) 444 30 70. Tel. (38-044) 444 01 11 (V I Shapoval). E-mail: postmaster@ionc.kiev.ua

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Periodic Table are usually much more electropositive than titanium; hence, halides of these metals are, most often, thermally unstable or possess low electrical conductivity. Alkali and alkaline earth metal chlorides and fluorides are best suited for this purpose.

Numerous studies have been devoted to the development of a method for the production of titanium by electrolysis of fluoride melts. Potassium and sodium fluorotitanates are recognised as the most promising titanium raw materials.[5–9] It is not expedient to subject pure hexafluorotitanate to electrolysis. During electrolysis, it is reduced to K_2TiF_5 and, after that, the electrodes become passivated.

The system subjected to electrolysis is usually K_2TiF_6 dissolved in molten salts. An electrolyte consisting of potassium, lithium and sodium fluorides has been proposed as the medium for the electrolytic production of titanium.[6] However, a process carried out in a purely fluoride melt can result in passivation of the anode by a gas film (anodic effect). In addition, since this melt is highly corrosive, the equipment soon goes out of service. Therefore, a mixture of alkali metal chlorides and potassium fluorotitanate has been proposed as the electrolyte for the electrolysis of titanium fluoride derivatives.[5–9] When titanium metal reacts with a chloride–fluoride melt, a black crust insoluble in a mixture of alkali metal chlorides and fluorides is formed gradually on its surface. The existence of a fluoride complex of divalent titanium, $M_2[TiF_4]$, has been reported.[8] Insoluble compounds formed at the cathode contaminate the cathodic product, which casts doubt on the expediency of using chloride–fluoride–fluorotitanate melts for producing pure titanium.

Preparation of titanium from titanium chlorides presents substantial interest. Titanium, having a variable valence, forms several chlorides, namely, $TiCl_4$, $TiCl_3$ and $TiCl_2$. The most readily available compound is $TiCl_4$; the production and purification of this compound on an industrial scale is now a routine practice. In the electrolysis of alkali or alkaline earth metal chlorides, $TiCl_4$ is either supplied onto the electrolyte surface or bubbled through the electrolyte, either neat or with a flow of an inert gas (see, for example, Refs 10, 11). Titanium tetrachloride is poorly soluble in molten alkali metal chlorides (the solubility is up to 2% at 1073 K); therefore, this technology does not provide high output. If the current density at the cathode is high, the alkali metal will be evolved together with titanium. It has been proposed to make use of this phenomenon, *i.e.* to carry out electrolysis at current densities sufficient for the evolution of the alkali metal. In this case, titanium tetrachloride is partially reduced by the reducing metal.

The solubility of titanium chlorides in which the metal oxidation number is less than four is substantially higher than the solubility of titanium tetrachloride. This fact has been taken into account in the development of a method for the preparation of titanium by electrolysis of its lower chlorides dissolved in chloride melts.[10] Salts used in this process should be relatively pure as regards oxygen and elements that are more electropositive than titanium. Lower titanium chlorides can easily be prepared from titanium tetrachloride; they are readily soluble in molten salts and fairly stable at temperatures of electrolysis. These compounds possess high electrical conductivities and relatively low volatilities; however, they are chemically reactive. Under conditions of electrolysis, lower titanium chlorides react with almost any standard refractory lining material; evidently, the rate of such a reaction would depend substantially on the presence of oxygen in the cell.

A method has been proposed[10] for continuous production of titanium by electrolysis of $TiCl_3$ and $TiCl_2$, which are formed in a separate reactor upon the reaction of titanium tetrachloride with hydrogen. To simplify this method, the synthesis of lower titanium chlorides and electrolysis can be carried out in one vessel. In this case, electrolysis occurs in two stages, namely, reduction of $TiCl_4$ to $TiCl_2$ and $TiCl_3$ at an auxiliary cathode and reduction of lower titanium chlorides to the metal on the main cathode.[11]

It has been considered until recently that the cathodic process is a secondary reaction, consisting in the reduction of titanium by the alkali metal, which was evolved at the cathode. However, recent studies demonstrated that, under certain conditions, direct electrochemical discharge of the titanium ions occurs at the cathode. For this discharge to be possible, it is required, first of all, that the concentration of titanium ions in low oxidation states in the near-cathode layer be sufficiently high.

Electrolysis of titanium chlorides is carried out under the atmosphere of an inert gas (argon, helium). For rough purification of the electrolyte from moisture and occluded gases, the electrolytic cell is usually evacuated at 400–650 °C to a residual pressure of 10–20 mm Hg. Preliminary electrolysis at an auxiliary cathode with a voltage on the cell terminals equal to 1.8–2.0 V is also employed for this purpose. Other methods for the purification of the electrolyte also exist. To remove moisture, dry hydrogen hydrochloride is passed through the melt for a short period of time. Oxygen can be removed by passing tetrachloromethane through the melt. The cathode materials used in these processes are mainly tungsten, molybdenum, silver, steel or nickel. The best adhesion of the titanium deposits has been noted for silver cathodes; however, this metal is expensive. Liquid cathodes made of zinc or lead can hardly find wide application because they form intermetallic compounds with titanium, which are difficult to destroy.

During electrolysis of titanium chlorides, chlorine formed at the anode oxidises lower titanium chlorides present in the anode chamber to give $TiCl_4$, which is distilled off together with chlorine. In addition, electrolytic oxidation of $TiCl_2$ and $TiCl_3$ at the anode, leading to the same consequences, is possible. Meanwhile, titanium tetrachloride entering the cathode chamber would react with titanium metal, which would result in the loss of the pure metal. Therefore, the cathode and anode chambers should be separated by a diaphragm. The problem of selection of the diaphragm materials has not been solved yet, due to the high chemical reactivity of lower titanium chlorides; research along this line is now in progress. For instance, it has been proposed to manufacture the diaphragm from alumina (these diaphragms are not virtually metallised under certain conditions) or graphite (in this case, half-sintered metal is formed at the cathode at 1305 °C).[4,5] It should also be noted that working with titanium chloride requires a high voltage at the electrolytic cell terminals (usually 9–12 V); therefore, power expenditure per unit product is high.

Whereas the expediency of one or another method for electrolytic production of titanium is still debated and electrolysis has not been adopted on an industrial scale, the efficiency of electrolytic refining of titanium is beyond doubt. The soluble anode can be manufactured from any material possessing electronic conduction, capable of reacting with the electrolyte and insoluble in it. Titanium forms lots of systems and compounds with such properties.

Powders with various chemical and grain-size compositions are currently produced from titanium by electrolysis with a soluble anode in the melts of alkali and/or alkaline earth metal chlorides. Electrolytic refinement of titanium is carried out using various electrolytes, namely, NaCl, NaCl–KCl, NaCl–$SrCl_2$, NaCl–$BaCl_2$, KCl–LiCl and KCl–NaCl–$MgCl_2$. Electrolytes based on sodium chloride, an equimolar mixture of sodium and potassium chlorides and the NaCl–KCl–$MgCl_2$ ternary system are the most widespread. The electrolytic refinement of titanium consists in the anodic dissolution of the metal to be refined and cathodic deposition of the pure metal. Electrochemical investigations show that in the temperature range 750–850°C, which is the best for the refinement, titanium passes from the anode to the melt as Ti^{2+}. An increase in the temperature or in the anode current density increases the yield of the Ti^{3+} ions. Upon anodic dissolution, titanium passes into the melt mostly in an ionic form, the average oxidation state being 2.02–2.13.

The total content of impurities, which are to be eliminated during titanium refinement (oxygen, nitrogen, hydrogen, carbon, iron) is normally relatively low, 1 mass % – 2 mass %. In the studies dealing with the electrochemical refinement of titanium, special role belongs to the purification from oxygen. When the process is carried out under precisely pure conditions, the only way by which oxygen can pass from the anode to the cathode is the formation of the titanyl ion TiO^{2+}. Thermodynamic calculations indicate that the probability of formation of this ion is fairly low even at high concentrations of oxygen in the anode material. A significant role in the production of a high-quality powder at the cathode is played by the ratio of the titanium concentration in the electrolyte to the current density at the cathode. The best powders are obtained if this ratio ranges from 2 to 3. The anode current density during electric refinement should be 4 – 8 times lower than the cathode current density. In this case, divalent titanium disproportionates in the electrolyte (especially in the near-anode layer), resulting in the formation of highly dispersed metallic titanium in the bulk of the melt. The use of the refining tank for the synthesis of titanium borides is not expedient, due to the formation of an uncontrollable amount of dispersed titanium, which disrupts the stoichiometry of the product.

Various opinions concerning the role of fluoride ions have been expressed in studies dealing with the electrolytic refinement of titanium in mixed chloride – fluoride electrolytes (see, for example, Ref. 12). Some researchers believe that the addition of fluorides has a negative effect on the electrolysis characteristics (the anode material disintegrates, the current yield decreases). Conversely, some other investigators believe that fluoride additives are favourable for the performance characteristics of the process. It should be noted that anodic dissolution of titanium in a mixed chloride and fluoride electrolyte affords poorly soluble compounds of divalent titanium, which contaminate the cathodic product.

The foregoing demonstrates that halide melts are the most suitable systems for the high-temperature electrochemical synthesis of titanium compounds and production of the pure metal. However, when using chloride melts, one should create conditions for increasing the solubility of $TiCl_4$ and suppressing disproportionation, and when mixed chloride – fluoride electrolytes are used, the formation of poorly soluble divalent titanium fluoride should be prevented and the electroreduction of titanium complex ions should be performed in one stage.

2. State of titanium in halide melts

a. Thermodynamics of titanium-containing halide systems

Titanium halides react with titanium metal in molten alkali metal halides. The following heterogeneous equilibrium is established with time:

$$2\,TiCl_3 + Ti \rightleftharpoons 3\,TiCl_2\,. \tag{1}$$

As a rule, one oxidation state of titanium predominates in the melt; the ratio of various oxidation states depends on the temperature and the nature of the salt acting as the solvent. Heterogeneous equilibrium (1) can be characterised by several parameters such as equilibrium constant, apparent standard potentials $E^*(Ti^{2+}/Ti)$, $E^*(Ti^{3+}/Ti)$ and the formal redox potential $E^*(Ti^{3+}/Ti^{2+})$.[13,14] The equilibrium potential of the titanium electrode (E) would be simultaneously the potential of the $Ti/TiCl_2$, $Ti/TiCl_3$ and $TiCl_2/TiCl_3$ systems. The apparent standard potentials and the formal redox potential are related (in accordance with the Luter rule) by the equation [13]

$$3E^*(Ti^{3+}/Ti) = E^*(Ti^{3+}/Ti^{2+}) + 2\,E^*(Ti^{2+}/Ti)\,. \tag{2}$$

The task of finding these values reduces to the determination of the number of ionic forms of titanium in the potential measurement.

The equilibrium potentials of titanium in an equimolar mixture of potassium and sodium chlorides in the temperature range 973 – 1148 K have been reported.[14] The temperature variations of $E^*(Ti^{2+}/Ti)$ and $E^*(Ti^{3+}/Ti)$ are described by the following empirical equations:

$$E^*(Ti^{2+}/Ti) = -2.38 + 4.8\times10^{-4}\,T, \tag{3}$$

$$E^*(Ti^{3+}/Ti) = -2.16 + 3.2\times10^{-4}\,T. \tag{4}$$

The equilibrium potentials of titanium measured at 843 K *vs.* chlorine reference electrode amount to $E^*(Ti^{2+}/Ti) = -1.97$ V and $E^*(Ti^{3+}/Ti) = -1.90$ V.

In order to identify the full picture of equilibrium between metallic titanium and a chloride melt containing minor amounts of Ti^{4+}, in addition to Ti^{2+} and Ti^{3+}, the $E^*(Ti^{4+}/Ti^{3+})$ redox potential, and, hence, the standard $E^*(Ti^{4+}/Ti)$ potential should be determined. The temperature variation of this potential in the KCl – NaCl melt is described by the equation

$$E^*(Ti^{4+}/Ti) = -1.91 + 3.84\times10^{-4}\,T. \tag{5}$$

Various values for the arbitrary formal redox potential $E^*(Ti^{3+}/Ti^{2+})$ in a molten equimolar mixture of sodium and potassium chlorides, determined experimentally by potentiometric titration, have been reported in the literature: -1.807 ($T = 973$ K), -1.762 ($T = 943$ K), -1.726 V ($T = 984$ – 1130 K). The $E^*(Ti^{3+}/Ti^{2+})$ value calculated in accordance with the Luter rule from Eqn (2) using the known experimental $E^*(Ti^{3+}/Ti)$ and $E^*(Ti^{2+}/Ti)$ values is described by the equation

$$E^*(Ti^{3+}/Ti^{2+}) = -1.710 - 0.17\times10^{-4}\,T. \tag{6}$$

It can be seen that the theoretical value of the potential $E^*(Ti^{3+}/Ti^{2+})$ depends slightly on the temperature and at 1000 K it is equal to -1.727 V *vs.* chlorine reference electrode.

The known standard potentials for the Ti^{3+}/Ti and Ti^{4+}/Ti systems were used to calculate the Ti^{4+}/Ti^{3+} redox potential and to elucidate its temperature dependence

$$E^*(Ti^{4+}/Ti^{3+}) = (-1.473 + 5.86\times10^{-4}\,T) \pm 0.007\,. \tag{7}$$

The variation of the equilibrium potential of titanium as a function of the concentration of titanium ions in the melt have shown that in alkali metal chloride melts, titanium is equilibrated with the Ti^{2+} and Ti^{3+} ions. Knowing the standard electrode potentials of the Ti^{2+}/Ti and Ti^{3+}/Ti systems, it can be written [15]

$$\log K = \log\frac{[Ti^{2+}]^3}{[Ti^{3+}]^2} = \frac{6\times10^4}{1.984T}\,[E^*(Ti^{3+}/Ti) - E^*(Ti^{2+}/Ti)] \tag{8}$$

Thus the equilibrium constants for the reaction

$$2\,Ti^{3+} + Ti \rightleftharpoons 3\,Ti^{2+}. \tag{9}$$

can be calculated. For lithium chloride,

$$\log K = -4.234 + \frac{6351}{T}\,, \tag{10}$$

for potassium chloride,

$$\log K = -6.956 + \frac{8165}{T}\,, \tag{11}$$

for cesium chloride,

$$\log K = -6.956 + \frac{7440}{T}\,, \tag{12}$$

and for the KCl – NaCl melt,

$$\log K = -5.038 + \frac{6774}{T}\,. \tag{13}$$

As the temperature increases, the equilibrium constant decreases, which points to disproportionation of Ti^{2+}. If the temperature remains constant, the equilibrium constant decreases with an increase in the radius (r) of the alkali metal cation of the molten salt, *i.e.* the equilibrium shifts towards disproportionation of Ti^{2+}. This dependence has the form

$$\log K = \frac{8468}{T} - \frac{1512}{Tr} - 9.073 - \frac{3.175}{r}\,. \tag{14}$$

A substantial number of studies have been devoted to the process of disproportionation (see, for example, Refs 16–18). The oxidation states of titanium can be described by four disproportionation reactions

$$2\,Ti^{3+} + Ti \rightleftharpoons 3\,Ti^{2+}, \quad (15)$$

$$2\,Ti^{3+} \rightleftharpoons Ti^{2+} + Ti^{4+}, \quad (16)$$

$$4\,Ti^{3+} \rightleftharpoons Ti + 3\,Ti^{4+}, \quad (17)$$

$$2\,Ti^{2+} \rightleftharpoons Ti + Ti^{4+}. \quad (18)$$

These reactions occur simultaneously and are heterogeneous. The outcome depends on the experimental conditions, namely, temperature, composition of the atmosphere, surface area, and so on. It has also been noted that Ti^{3+} rapidly disproportionates in the lithium chloride melt. When lithium chloride is replaced by cesium chloride, the stability of Ti^{3+} increases. In halide melts, titanium metal reacts with the components of the melt. When the radius of the alkali metal cation in the melt is greater than the radius of potassium, Ti^{2+} ions appear; they disproportionate to give highly dispersed titanium metal; therefore, a high concentration of Ti^{2+} cannot be attained. In the case where the LiCl melt is used, the solution becomes rich in Ti^{2+}.

The main reaction which proceeds at a substantial rate in molten potassium chloride is

$$2\,TiCl_3\,(liq) + Ti(solid) \rightleftharpoons 3\,TiCl_2\,(liq). \quad (19)$$

Thus, vast experimental data have been accumulated and a number of important practical conclusions have been drawn concerning the thermodynamics of titanium-containing chloride melts, namely, the equilibrium and standard potentials of titanium in various oxidation states were determined; the equilibrium constants for chemical reactions in the melts were calculated; and disproportionation of titanium ions in low oxidation states was detected. However, in some cases, the thermodynamic functions are rough. For example, the measurement of the equilibrium potentials of the Ti^{4+}/Ti, Ti^{3+}/Ti and Ti^{2+}/Ti systems does not appear quite correct because actually, the near-electrode layer would contain titanium ions in various oxidation states formed in chemical reactions. In addition, thermodynamic characteristics do not provide exhaustive information on the mechanism of electroreduction of titanium, which needs to be known for performing successful electrolysis of titanium-containing melts. Therefore, in addition to the thermodynamic characteristics, the mechanism of the electroreduction of titanium has also been studied.

b. Mechanism of the electroreduction of titanium

It is not always possible to interpret unambiguously experimental data characterising the mechanism and kinetics of electroreduction and electrooxidation of titanium complexes. The complexity of interpretation of these data is due to the fact that side processes, not related directly to electrode reactions, proceed in the melt. In some studies, it is suggested that titanium metal is evolved in the reaction of titanium-containing complex ions with an alkali metal, resulting from reduction at the cathode. In other studies, it is suggested that two processes of titanium deposition occur simultaneously; titanium is formed in the primary electrochemical process at the cathode

$$Ti^{2+} + 2e \longrightarrow Ti^0$$

and in a secondary chemical process, thermal reduction by sodium in the bulk of the electrolyte. Some researchers believe that in the case of chloride melts, an alkali metal reduces Ti^{2+} ions (see, for example, Refs 19, 20) and in the chloride–fluoride melts, the species being reduced is Ti^{3+}. Titanium in higher oxidation states is preliminarily reduced to lower oxidation states by either electrochemical or chemical reactions. However, voltammograms characterising the cathodic evolution of titanium display a wave corresponding to the discharge of titanium complexes.[18] In several studies (see, for example, Ref. 21), the mechanism of direct reduction of $TiCl_3$ to the metal without the intermediate formation of Ti^{2+} has been assumed. A study of the electroreduction of $TiCl_3$ in the LiCl, CsCl and KCl–LiCl systems at 973 K by linear sweep voltammetry demonstrated that the reduction of Ti^{3+} in all three electrolytes involves the stage of recharge to Ti^{2+}

$$Ti^{3+} + e \rightleftharpoons Ti^{2+}, \quad (20)$$

$$Ti^{2+} + 2e \rightleftharpoons Ti^0. \quad (21)$$

The stepwise character of the process was pointed out in several other publications.[18,22–26]

Electroreduction of titanium tetrachloride in the $BaCl_2-CaCl_2-NaCl$,[22] LiCl–KCl, KCl–LiCl–NaCl[23] and $BaCl_2-KCl-LiCl$[24] melts occurs as three consecutive stages:

$$Ti^{4+} + e \longrightarrow Ti^{3+}, \quad (22)$$

$$Ti^{3+} + e \longrightarrow Ti^{2+}, \quad (23)$$

$$Ti^{2+} + 2e \longrightarrow Ti^0. \quad (24)$$

The voltammograms for the electroreduction of Ti^{2+} in the $KCl-NaCl-TiCl_3-NaF$–Ti(solid) melt exhibit one clear-cut wave at potentials of $-(2.53-2.6)$ V *vs.* chlorine reference electrode, which corresponds to the electroreduction of titanium.[20]

The diffusion coefficients for titanium in chloride melts have been calculated;[21,26,27] in KCl–NaCl at 973 K, they are equal to 3.72×10^{-5} and 1.94×10^{-5} $cm^2\,s^{-1}$ for Ti^{3+} and Ti^{4+}, respectively. The diffusion coefficient for divalent titanium in the LiCl–KCl melt at 773 K amounts to $(1.54 \pm 0.17) \times 10^{-5}$ $cm^2\,s^{-1}$ (see Ref. 28).

Thus, certain progress in the study of chloride and chloride–fluoride titanium-containing melts has been achieved by now; however, the overall picture of the electrochemical and chemical behaviour of titanium in various oxidation states does not appear clear and unambiguous. There is no consensus of opinion on the mechanism of the cathodic process. Several aspects of the stability of systems containing titanium in various oxidation states are poorly documented, namely, which of the lower titanium chlorides is more stable and what is the limiting concentration up to which this stability is retained; what are the concentration limits for the stability of other titanium-containing species; what are the ratios of Ti^{2+} to Ti^{3+} in the melt at which the system remains stable, *i.e.* no disproportionation reactions occur, and what are the ways of suppressing these reactions. Answers to these questions present considerable interest from the practical viewpoint, because they would make it possible to create conditions for long continuous operation of an electrolysis cell and to estimate the influence of unstable titanium compounds on the technological parameters of the production of titanium and of the electrochemical synthesis of titanium compounds.

III. Electrochemical behaviour of boron

The electrochemical method permits preparation of high-purity boron in large quantities. In the first studies, carried out 70 years ago, elementary boron was produced by the electrolysis of borides. The product contained not more than 60%–70% of the target material, 20%–30% of oxygen and 5%–6% of the metal that served as the cathode material. When magnesium boride was used, elementary boron was formed at the cathode together with low-stability magnesium borides; the latter can be partially removed by treatment of the cathodic product with an acid.

Currently, oxygen-containing compounds of boron and boron halides are mainly used for the electrolytic production of boron. Numerous studies have been devoted to the electrolysis of oxygen compounds of boron. In all systems boron oxide serves as the source of boron.[29] When oxygen-containing melts are used, the process does not give high-purity boron because the product is contaminated by substantial amounts of oxygen. This is the major drawback of this method.

The use of purely fluoride electrolytes is limited because fluoride melts are corrosive and toxic.[30] The use of mixed chloride–fluoride electrolytes presents considerable interest; in this case, high-purity boron free from oxygen impurities can be obtained at relatively low temperatures, the corrosiveness of the melts being relatively low.[30–36]

Several studies have been devoted to the mechanism of electroreduction of boron.[37–46] The cathodic processes occurring during the electrodeposition of boron from a purely fluoride ($LiF-KF-KBF_4$) and fluoride–oxide ($LiF-KF-B_2O_3$) electrolytes have been studied.[36,37] It was shown that in a purely fluoride melt, boron is reduced directly from the tetrafluoroborate complex anion in one step involving three electrons. In the $LiF-KF-B_2O_3$ system, boron oxide reacts with fluorine present in the electrolyte to give the $[BF_4]^-$ anion and oxyfluoride complexes, mainly those with a molar ratio of oxygen to boron equal to 1.66. The ratio of the concentrations of $[BF_4]^-$ and the oxyfluoride complexes is 0.1. The potentials of deposition of boron from these two electrochemically active species differ by 0.47 V, and the diffusion coefficient for $[BF_4]^-$ calculated from experimental data is 4.4×10^{-9} m^2 s^{-1} at 973 K.

In a study of the electrochemical properties of boron in chloride and chloride–fluoride melts, the solubility of BCl_3 in the CsCl melt was found to be 1.74×10^{-1} mol.% at 973 K; thermodynamic functions of BCl_3 in CsCl were calculated, the equilibrium potentials of boron were determined and equations for them were reported.[32] The equilibrium potentials of boron shift to the negative region in chloride–fluoride electrolytes, indicating that the reactivity of boron ions in fluoride complexes is lower than that in chloride complexes.[31,32,34] The calculation of the average number of fluoride ions (three or four) in the complex ions by the procedure proposed by Ivanovsky *et al.*[31] attests indirectly that in the temperature range studied, most of the boron ions in the chloride–fluoride melts occur in the $[BF_4]^-$ and $[BF_3Cl]^-$ groups. Based on the results of voltammetric studies, Chemezov[32] arrived at the conclusion that electroreduction of boron in a chloride–fluoride electrolyte occurs by a one-stage mechanism; conversely, Tsiklauri *et al.*[41] have discovered a recharge stage, $B^{3+} \longrightarrow B^+$, followed by the discharge of B^+ at the cathode to give elementary boron.

For low current densities, charge transfer is the rate-determining step in the electrodeposition of boron, whereas for high current densities, the rate of the process is limited by the diffusion of boron from the bulk of the melt towards the surface. This is typical of both chloride and chloride–fluoride melts. A somewhat different opinion on the kinetics of electroreduction of boron is held by the authors of another study,[39] who claim that the rate of this process is limited by mass transfer over a broad range of polarisation rates and that the proper electrochemical stage is irreversible.

Examination of the switching-on curves (potential–time) for various polarisation current densities demonstrated[32] that neither a homogeneous chemical reaction (*e.g.*, dissociation of the $[BF_4]^-$ or $[BCl_4]^-$ complexes), nor chemisorption of electrically active species on the electrode surface retards the reduction of boron in the melts studied. The $\log D - I/T$ plots (D is the diffusion coefficient of boron calculated from the Sand equation using the results of chronopotentiometric measurements, I is the current density and T is the temperature) in the temperature range 932–1123 K are straight lines; the calculation of the activation energy gives 35.5 ± 2.3 kJ mol^{-1} (see Refs. 31, 32). However, in another study,[41] it has been stated that electrochemically active species (mainly molecular boron fluoride) are produced in a chloride–fluoride melt upon dissociation of boron complexes coupled with homogeneous exchange reactions between the initial complexes and the electrolyte.

Study of the solubility and the kinetics of electroreduction of BF_3 in the $KCl-NaCl$ melt at 973 K in the range of BF_3 pressures of $(1.01-5.05) \times 10^5$ Pa showed the presence of two sorts of electrochemically active species.[44] This accounts for the two waves displayed on the voltammograms; the heights of the waves increase proportionally to the pressure. In the opinion of the researcher cited, the first wave corresponds to a two-electron transition involving BF_3; at the potential of the second wave, the product formed in the first stage is reduced, the mixed chloride–fluoride complex $[BCl_xF_3]^{x-}$ being involved in the cathodic process.

Thus, despite the large number of publications dealing with the electrochemical properties of boron, no clear views on the mechanism and kinetics of its electroreduction from halide electrolytes have been developed so far.

IV. Methods for the synthesis of titanium diboride. High-temperature electrochemical synthesis

The principal methods used to synthesise high-melting compounds have been classified[23] into the following groups: (1) direct synthesis from elements, (2) synthesis from solutions in melts, (3) thermal reduction of metal oxides by metals, (4) reduction of oxides and other compounds by nonmetals and their derivatives, (5) gas-phase synthesis, and (6) electrolysis of salt melts. This classification is also applicable to the methods used to prepare titanium diboride.

Direct synthesis from elements is based on the reaction of a metal (titanium) with a nonmetal (boron), which can be carried out (at various physical states of the elements) by fusing, sintering or hot pressing. In accordance with this, some researchers suggest conducting this synthesis by keeping samples of pure titanium for 5 h in amorphous boron at a temperature of 1273 K and a residual pressure of 0.133 Pa; according to other researchers, mixtures of titanium and boron powders should be heated by an electric discharge.[47] The advantages of this method include the possibility of preparing large amounts of the product, the possibility of hot moulding the product in order to manufacture the required articles, simplicity of the equipment and the relatively short time needed for the synthesis. The facts that it is difficult to prepare borides with a precise composition and that the temperature of the process is too high are drawbacks of the direct synthesis.

The synthesis from solutions in melts involves a chemical reaction between transition metal atoms and nonmetal atoms (or molecules of a nonmetal compound) occurring in molten salts or metals. An example is provided by the synthesis of titanium borides in an iron melt at temperatures of 1673–2273 K. This route can afford both pure, doped and complex (mixed) compounds. In addition, it ensures the recovery of metal serving as the solvent and is relatively simple. The drawbacks of this method include low yields and high cost of the product, caused by the large amounts of salts and metallic solvents consumed, the possible contamination of the product by the solvent, the necessity of vigorous stirring of solutions in melts in order to obtain homogeneous compounds and high temperatures of the process.

The thermal reduction of oxides consists in the reduction of titanium and boron oxides by a reducing metal (in the presence of oxygen-evolving compounds) to give borides at temperatures of 2273–3273 K over periods of 2–3 min. This is the simplest method among those listed above. However, it is not in general use because of the low quality and inhomogeneous composition of the products obtained in this way and also because it is difficult to isolate the product from the slag.

The fourth method is based on the reduction of oxides and other compounds by nonmetals and their compounds. For instance TiB_2 can be prepared by the reaction of BCl_3 with highly dispersed titanium at 873–1373 K. The advantages of this method include the possibility of preparing large quantities of the product and the fact that oxides and other readily available compounds of titanium and boron are suitable for the synthesis. The main drawback of this method is that the products of the synthesis are contaminated by metal and nonmetal oxides.

Gas-phase synthesis includes decomposition of chemical compounds followed by reactions of the fragments (both ions or

radicals and the atoms or molecules produced upon their reduction) occurring in the gas (vapour) phase to give high-melting compounds. A method for the synthesis of titanium diboride by the reduction of a vapour–gas mixture consisting of $TiCl_3$ and BCl_3 by hydrogen at temperatures of 1273–3773 K and pressures of 1–3 atm has been described.[47] The major advantage of this method is the possibility of preparing single crystals and coatings on various materials. The inhomogeneity of the phase composition and the relatively low yields of the products as well as complexity of the equipment and the processes involved are drawbacks of this technique.

High-temperature electrochemical synthesis from molten salts can be regarded as being one of the most promising methods for the preparation of high-melting compounds. The advantages of this method are relative simplicity of the equipment, the ready accessibility of the initial compounds, the possibility of preparing simple or complex composite coatings of high-melting compounds, the relatively low temperature of the process, and the possibility of controlling the morphology and the composition of the cathodic deposit by varying the electrolysis parameters. The theoretical grounds of this method have been described in detail,[48] and examples of its practical implementation can be found in reviews.[49,50]

Depending on the nature of the electrolyte used, two variants of electrochemical synthesis of titanium diboride can be distinguished, namely, syntheses from oxygen-containing systems and from halide systems.[51] The former variant commonly employs systems based on alkali and alkaline earth metal borates, which differ in the manner of saturation of the melt by the synthesis components. Boron can be introduced in the melt as B_2O_3, and titanium can be added as TiO_2; the concentration of titanium in the electrolyte can be maintained by anodic dissolution of titanium metal.[51] However, though seemingly advantageous, the synthesis based on oxygen-containing systems suffers from serious drawbacks. Specifically, the reaction temperatures are too high (> 1023 K), and a pure product (free from oxygen) cannot be prepared in this way.

The second variant can be implemented using either purely fluoride electrolytes, for example F/Li, Na, K, LiF–KF, Li, Rb, Cs/F and cryolite and mixed chloride–fluoride electrolytes. The sources of titanium and boron in this case are either titanium and boron fluorides or soluble anodes made of boron, titanium and boron carbides or titanium diboride. The use of mixed chloride–fluoride electrolytes with the lowest possible content of fluorine is the most interesting. This decreases the corrosion activity and the cost of the melt; in the case where a soluble anode is used, the formation of fluorocarbons can be avoided and the stage of hydrotreating of the cathodic deposits can be simplified.

The mechanism of the cathodic process in the electrochemical synthesis of titanium diboride in the LiF–KF melt has been studied.[52,53] Potassium hexafluorotitanate and tetrafluoroborate were used as the sources of titanium and boron. It was found that reduction of Ti^{4+} in the $LiF-KF-K_2TiF_6-KBF_4$ system occurs in two steps

$$Ti^{4+} \longrightarrow Ti^{3+} \longrightarrow Ti\,.$$

This is followed by the reduction of boron complexes to elementary boron, which then reacts with the reduced titanium to yield titanium diboride. This is accompanied by electrode depolarisation, which is due, in the opinion of the researchers, to the great negative value of the Gibbs energy for the formation of TiB_2.

Thus, analysis of the studies devoted to the methods of electrochemical synthesis of titanium diboride shows that mainly applied studies can be found in the literature. The information available from the literature is inadequate to interpret the mechanism of the synthesis; therefore, this process needs to be studied more comprehensively.

V. Electrochemical properties and stability of halide systems containing titanium in various oxidation states and boron

1. Study of electrochemical properties and stability of titanium-containing systems

Experiments on the stability of halide systems containing titanium in various oxidation states and boron and on the electrochemical synthesis of TiB_2 and titanium intermetallic compounds have been performed under an argon atmosphere, inert with respect to the melts under study.

The voltammograms characterising the electroreduction of Ti^{3+} at polarisation rates of > 0.5 V s^{-1} (Fig. 1) exhibit two persistent waves with clear-cut peak currents. The waves are due to the recharge and discharge of titanium ions

$$[TiCl_6]^{3-} + e \longrightarrow [TiCl_4]^{2-} + 2\,Cl^-, \quad (25)$$

$$[TiCl_4]^{2-} + 2e \longrightarrow Ti + 4\,Cl^-. \quad (26)$$

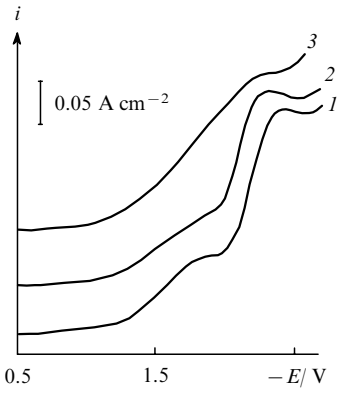


Figure 1. Voltammograms for the electroreduction of Ti^{3+} ions in the $KCl-NaCl-TiCl_3$ melt.
$T = 1000$ K, $[TiCl_3] = 8.3 \times 10^{-5}$ mol cm^{-3}, chlorine reference electrode; polarisation rate /V s^{-1}: (*1*) 1.0; (*2*) 0.1; (*3*) 0.05.

To confirm the assumption that the potentials of the second wave correspond to the reduction of titanium complexes to the metal, potentiostatic electrolysis was carried out at these potentials. X-Ray diffraction identification of the electrolysis products showed the presence of titanium metal on the cathode.

When the potential sweep rate is < 0.1 V s^{-1}, the peak current of process (25) becomes feebly defined and at polarisation rates of < 0.05 V s^{-1}, the waves of processes (25) and (26) coalesce. As a consequence, the overall process appears as occurring in one stage (see Fig. 1, curve *3*). In all probability, this is the reason for the disputes concerning the number of stages in the reduction of Ti^{3+} (see Refs 47, 51), because most of the studies have been carried out at polarisation rates close to the steady-state values (not higher than 10 mV s^{-1}).

Analysis of voltammograms of the type presented in Fig. 2 showed that at high polarisation rates, processes (25) and (26) are not complicated by any additional reactions and, in the range of $TiCl_3$ concentrations studied (up to 10 mass %), they completely obey the Faraday law. This is confirmed by the fact that the peak currents follow a linear dependence on the concentration of $TiCl_3$.

The dependence of the peak potential on the polarisation rate and the magnitude of the transport coefficient αn, equal to 0.45, imply that at high polarisation rates, the charge transfer step in the recharge process (25) is retarded. The diffusion coefficient is equal to $(3.5 \pm 0.3) \times 10^{-5}$ cm^2 s^{-1}.

The abnormal increase in the $i_p/V^{1/2}$ ratio at $V < 0.5$ V s^{-1} (see Fig. 2) is evidently due to the fact that the recharge is complicated by a catalytic reaction, *i.e.* electroreduction is accompanied by regeneration of electrochemically active species.

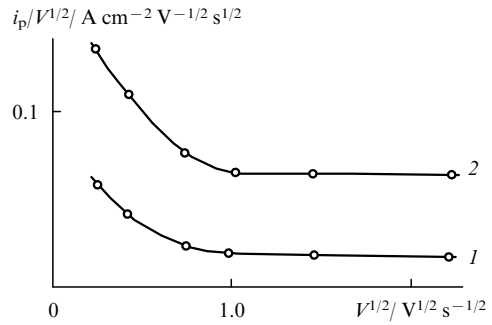


Figure 2. Variation of $i_p/V^{1/2}$ *vs.* $V^{1/2}$ (i_p is the peak current, V is the polarisation rate) for processes (25) (*1*) and (26) (*2*) in the KCl – NaCl – $TiCl_3$ melt.
$T = 1000$ K, $[TiCl_3] = 5.5 \times 10^{-5}$ mol cm^{-3}.

This might be disproportionation of the divalent titanium formed. For a redox process not accompanied by catalytic reactions, the ratio of the peak currents of the waves obtained in the forward (cathodic) and reverse (anodic) recording of voltammograms should be equal to unity. If this ratio is greater than unity, the product of electroreduction enters into a subsequent chemical reaction; when this is disproportionation, it increases the current and changes correspondingly the $i_p/V^{1/2}$ value. Study of cyclic voltammograms for process (25) has confirmed [54] that disproportionation of divalent titanium occurs in the near-electrode layer

$$3\,[TiCl_4]^{2-} = 2\,[TiCl_6]^{3-} + Ti\,. \qquad (27)$$

The minimum lifetime of the divalent titanium species is 0.08 – 0.8 s for the $TiCl_3$ concentration ranging from 5×10^{-4} to 5×10^{-5} mol cm^{-3}; the rate constant for disproportionation is $(2.2 \pm 0.2) \times 10^4$ cm^2 mol s^{-1}.

Methods for controlling the course of electroreduction by varying the acid – base properties of the medium have been considered [53–57] in relation to oxygen-containing complex ions. According to the idea of these studies, the electrochemical activity of oxygen-containing anions is due to the mechanism of formation of electrochemically active species peculiar to molten salts, namely, the acid – base interactions in the melt. The formation and interactions of electrochemically active species in the near-electrode layer occur at a limited rate because these processes require rearrangement of the structure of reacting species. Thus, by changing the acid – base properties of the medium, one can influence the mechanism and the rate of the process in a specified manner.

Elimination of disproportionation reactions by changing the mechanism of the process can be attained in two ways, namely, by addition of either cations possessing greater polarising ability than potassium and sodium or anions having stronger basic properties than the chloride anion. In the former case, the acidity of the melt diminishes, while in the latter case, the basic properties of the electrolyte are enhanced (for instance, when sodium fluoride is introduced).

The mechanism of the cathodic process in the electroreduction of titanium trichloride in chloride melts with different cationic compositions has been studied.[58] It was found that reduction of titanium in the cesium chloride melt occurs *via* recharge stage (25), whereas in an eutectic LiCl – KCl melt, when the temperature diminishes to 673 K, trivalent titanium is reduced to the metal in one stage

$$Ti^{3+} + 3e \longrightarrow Ti\,.$$

However, the LiCl – KCl system cannot be used for the synthesis of titanium diboride because the minimum temperature for the onset of the electrochemical synthesis markedly exceeds 673 K and amounts to 843 K.

It has been found [59] that fluoride ions added to the melt replace the chlorine in the titanium complex species and, as a consequence, the electroreduction process switches to a one-stage mechanism.

In order to elucidate the potential for the synthesis of titanium diboride from chloride and fluoride electrolytes, it is significant to study the influence of fluoride ions, in particular, the $[Ti^{3+}]:[F^-]$ molar ratio, on the mechanism of titanium electrodeposition and the type of titanium species in the melt. It is also necessary to determine the optimum electrolyte composition,[60] which would preclude both disproportionation reactions and the formation of lower titanium fluorides, insoluble in the melt.

As shown above, electroreduction of trivalent titanium in the chloride melt includes the recharge to the divalent state. Upon introduction into the chloride melt of fluoride ions in the ratio $[Ti^{3+}]:[F^-] > 1:2$, the peak current of the recharge wave decreases proportionally to the content of fluoride ions in the electrolyte. In addition, as the current of the recharge wave decreases, the peak current of the $Ti^{2+} \longrightarrow Ti$ discharge wave proportionally increases. When the molar ratio $[Ti^{3+}]:[F^-] = 1:2$ is attained, the recharge wave is no longer displayed on the voltammogram and the discharge of the complex ions of titanium becomes a one-stage process (Fig. 3). The switching to a different mechanism is accompanied by the simultaneous shift of the wave potentials towards more negative values. Experimental results imply that the change in the anionic composition of the melt upon the introduction of fluoride ions results in the formation of mixed chloride- and fluoride-containing complexes. The replacement of chlorine in the $[TiCl_6]^{3-}$ complex (this is the species in which $TiCl_3$ occurs in the KCl – NaCl melt) by the smaller fluoride ion makes this complex stronger and changes the mechanism of its reduction. The fact that the mechanism changes at $[Ti^{3+}]:[F^-] = 1:2$ suggests that the composition of the resulting titanium complex is $[TiF_2Cl_4]^{3-}$.

Titanium chloride – fluoride complexes occur in equilibrium with components of the melt; generally, the equilibrium is described by the equation

$$[TiF_xCl_y]^{3-} \rightleftharpoons [TiF_x]^{3-y} + y\,Cl^-. \qquad (28)$$

Electroreduction involves dissociated species $[TiF_x]^{3-y}$, the concentration of which is lower than the total concentration of titanium in the electrolyte.

The dependence of the potential of the reduction wave peak on the polarisation rate in the broad range of potential sweep rates and also the value $\alpha n = 1.0 \pm 0.05$, found from the Matsuda – Ayabe equation, imply that the charge transfer step is slow.

The diffusion coefficient calculated from the Delahay equation using peak currents corresponding to the total concentration

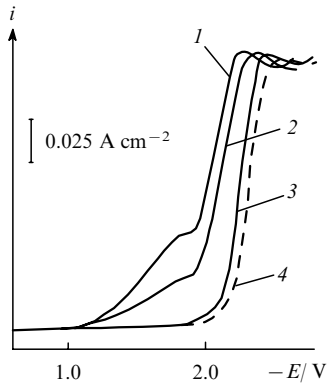


Figure 3. Voltammograms for the electroreduction of titanium ions in the KCl – NaCl – NaF – $TiCl_3$ melt at a $[Ti^{3+}]:[F^-]$ molar ratio, equal to 1 : 0 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), < 1 : 2 (*4*).
$T = 1000$ K, polarisation rate 1.0 V s^{-1}, $[Ti^{3+}] = 1.55 \times 10^{-4}$ mol cm^{-3}, chlorine electrode as the reference electrode.

of titanium in the melt is equal to $(3.0 \pm 0.4) \times 10^{-5}$ cm^2 s-1. The underestimated value of the diffusion coefficient, $(0.7 \pm 0.4) \times 10^{-5}$ cm^2 s^{-1}, found using the currents corresponding to high polarisation rates confirms the assumption that the concentration of elecrochemically active species under these conditions does not coincide with the total titanium concentration in the melt.

The number of ligands attached to the initial $[TiF_2Cl_4]^{3-}$ species during titration of the melt by fluoride ions, determined on the basis of the slope of the straight line plotted in the 'shift in the wave peak – depolariser concentration' coordinates ($\Delta E - \ln c_{F^-}$) (Fig. 4) is equal to two. With allowance for the composition of the initial species, the composition of the titanium complex in the bulk of a melt containing an excess of fluoride ions should be $[TiF_4Cl_2]^{3-}$. Then the formation and discharge of electrochemically active titanium complexes can be described by the following scheme:

$$[TiCl_6]^{3-} + 2F^- \rightleftharpoons [TiF_2Cl_4]^{3-} + 2Cl^-, \quad (29)$$

$$[TiF_2Cl_4]^{3-} + 2F^- \rightleftharpoons [TiF_4Cl_2]^{3-} + 2Cl^-, \quad (30)$$

$$[TiF_2Cl_4]^{3-} \rightleftharpoons TiF_2^+ + 4Cl^-, \quad (31)$$

$$TiF_2^+ + 3e \rightleftharpoons Ti + 2F^-. \quad (32)$$

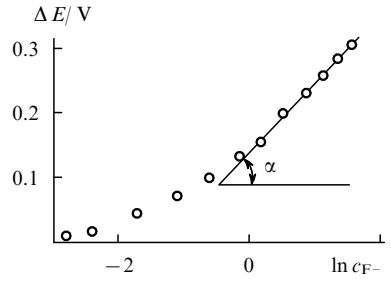


Figure 4. Calculation of the coordination number of titanium in the complexes occurring in the KCl – NaCl – NaF – $TiCl_3$ melt.

Thus, the electroreduction of trivalent titanium in the near-electrode layer of a chloride melt involves disproportionation of divalent titanium. In a chloride melt, the $Ti^{3+} \rightleftharpoons Ti^{2+}$ recharge is a catalysed process and the charge transfer step is retarded over a broad range of polarisation rates. Stabilisation of the KCl – NaCl – $TiCl_3$ system can be attained by changing the acid – base properties of the melt by introducing fluoride ions into the chloride electrolyte, which results in the formation of mixed chloride and fluoride complexes such as $[TiF_2Cl_4]^{3-}$. The reduction of these complexes at the molar ratio $[Ti^{3+}] : [F^-] < 1 : 2$ occurs in one stage involving the transfer of three electrons.

2. Study of electrochemical properties and stability of boron-containing systems

In order to arrange a high-temperature electrochemical synthesis of titanium diboride, it is necessary that the potentials of the evolution of products used in the synthesis be close. Therefore, investigations into the electrochemical properties and stability of boron-containing chloride – fluoride melts are topical. Analysis of the published data indicates that, despite the fact that numerous studies have been devoted to electroreduction of boron complexes, there are still no clear views on the electroreduction mechanism or the composition of the boron-containing species existing in chloride – fluoride melts.

The voltammograms of the electroreduction of boron exhibit one wave in the potential range from −2.35 to −2.7 V with a clear-cut peak current (Fig. 5). Further polarisation results in an increase in the current, caused by the discharge of alkali metal ions. The potentiostatic electrolysis at the potential corresponding to the reduction wave affords elementary boron. The dependence of the peak potential of the wave of electroreduction of boron

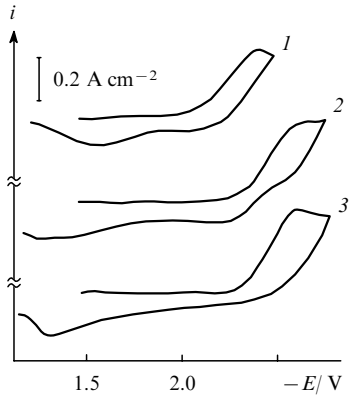


Figure 5. Cyclic voltammograms for the $B^{3+} \longrightarrow B$ process occurring in the KCl – NaCl – NaF – $NaBF_4$ melt (*vs.* chlorine reference electrode). $[B^{3+}] : [F^-]$: (*1*) 1 : 0, (*2*) 1 : 7, (*3*) 1 : 14.

complexes on the polarisation rate, the substantial difference between the wave peak potentials found in the forward and reverse recording of voltammograms, and the values $\alpha n = 0.96 - 1.08$ for the three-electron process calculated from the Matsuda – Ayabe equation lead to the following conclusion. In the range of polarisation rates from 0.1 to 20.0 V s^{-1}, the discharge of boron complexes is irreversible, *i.e.* it is controlled by the rate of charge transfer.[61]

The $[BF_4]^-$ ions added to a chloride melt enter into an exchange reaction with chloride anions to give mixed chloride – fluoride complexes

$$[BF_4]^- + xCl^- \rightleftharpoons [BF_{4-x}Cl_x]^- + xF^-. \quad (33)$$

The unstable boron complexes undergo thermal dissociation, which can be generally represented by the following scheme:

$$[BF_{4-x}Cl_x]^- \rightleftharpoons [BF_{4-x}]^{x-1} + xCl^-. \quad (34)$$

Electroreduction involves species resulting from dissociation of the initial complexes; the concentration of these species in the melt bulk is small compared to the total concentration of boron ions in the electrolyte. Thus, the melt contains simultaneously two sorts of species, namely, the initial $[BF_{4-x}Cl_x]^-$ complexes and electrochemically active species $[BF_{4-x}]^{x-1}$. Upon the discharge of boron complexes, the near-electrode layer becomes depleted in the $[BF_{4-x}Cl_x]^-$ complexes, which displaces the equilibrium towards the formation of electrochemically active species. Analysis of the $i_p/V^{1/2} - V^{1/2}$ dependence shows [62] that a decrease in the potential sweep rate diminishes the influence of dissociation on the electroreduction of boron complexes. The influence of $i_p/V^{1/2}$ on $V^{1/2}$ can be extrapolated to the $i_p/V^{1/2}$ axis if the peak current of the wave corresponds to the total concentration of boron in the melt. The linear type of dependence of the peak currents on the boron concentration in the melt implies that the preceding chemical reaction exerts no retarding influence under these conditions. The diffusion coefficient calculated from the Delahay equation using the peak current values corresponding to the total concentration of boron in the melt is equal to $(3.3 \pm 0.4) \times 10^{-5}$ cm^2 s^{-1}.

Thermal dissociation of alkali metal fluoroborates added to a chloride melt yields volatile boron fluorides, poorly soluble in the melt and passing into the gas phase. This results in a lower concentration of electrochemically active species and, hence, in a lower rate of boron electroreduction.[63] The non-controllable change in the concentration of one component hampers the selection of operating conditions suitable for the electrochemical synthesis of titanium diboride. Therefore, it is necessary to find a method for stabilisation of the chloride melt containing an alkali metal fluoroborate. It has been shown [61, 62] that the introduction of NaF into the KCl – NaCl – $NaBF_4$ melt induces a shift of the

peak potential of the wave corresponding to the discharge of mixed chloride–fluoride boron complexes, due to the replacement of chloride ions by fluoride ions. When $[B^{3+}]:[F^-] \geqslant 1:2$, the melt is stabilised upon the formation of mixed chloride–fluoride complexes of boron and the rate of the reduction of boron no longer varies with time. It is of interest to determine the composition of boron-containing complexes in the initial chloride melt and the complexes formed upon titration of the melt by fluoride ions.

The coordination number of boron in the chloride–fluoride complex was calculated using a procedure taking account of the dependence of the shift of the wave peak potential for the reduction of boron complexes on the concentration of the free ligand in the melt. The concentration of the free ligand was assumed, as the first approximation, to be equal to the total concentration of fluorine added to the melt. The coordination number determined from the slope of the straight line plotted in the $\Delta E - \ln c_{F^-}$ coordinates (Fig. 6) is equal to unity, *i.e.* during titration of the $KCl-NaCl-NaBF_4$ melt by fluoride ions, one fluoride ion adds to the initial species. Hence, the mixed chloride–fluoride complex of boron in the NaCl–KCl melt has the composition $[BF_3Cl]^-$ and the species occurring in the melt with excess fluoride ions is BF_4^-. The application of a correction for the concentration of the bound ligand, determined by the molar ratio $[B^{3+}]:[F^-] = 1:1$, did not alter the results.

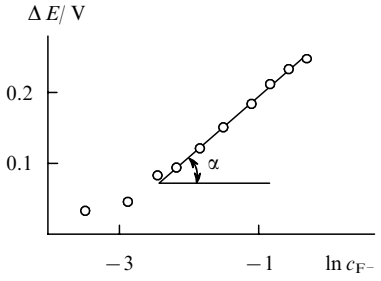


Figure 6. Calculation of the coordination number of boron in the complexes occurring in the $KCl-NaCl-NaF-NaBF_4$ melt.

Based on the foregoing, it can be concluded that the formation of mixed chloride–fluoride complexes of boron can be described by the following equations.

In the absence of excess fluoride ions in the melt

$$BF_4^- + Cl^- \rightleftharpoons [BF_3Cl]^- + F^-, \quad (35)$$

$$[BF_3Cl]^- \rightleftharpoons BF_3 + Cl^-; \quad (36)$$

and in the presence of excess fluoride ions in the melt

$$BF_4^- \rightleftharpoons BF_3 + F^-. \quad (37)$$

VI. Electrochemical synthesis of titanium diboride and titanium intermetallic compounds in a chloride–fluoride melt

1. Joint electroreduction of titanium and boron in the chloride–fluoride melt and electrodeposition of titanium diboride powders

It has been shown[64] that the addition to the $KCl-NaCl-NaF-KBF_4$ melt of titanium trichloride in a concentration close to half that of potassium tetrafluoroborate results in a sharp increase in the current at potentials 0.25 V more positive than the potential of reduction of titanium complexes. This brings about a wave characterised by a steeper slope than the waves for the discharge of the titanium and boron complex ions. This wave is displayed on voltammograms over broad ranges of polarisation rates and $TiCl_3$ and MBF_4 concentrations (Fig. 7). If the ratio $[Ti^{3+}]:[B^{3+}] = 1:2$ does not hold, then electroreduction

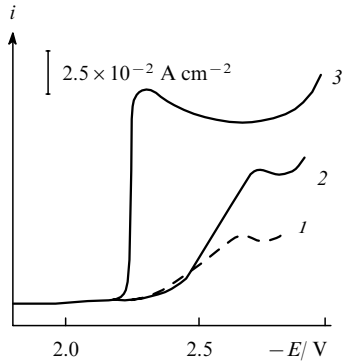


Figure 7. Voltammograms for various processes ($T = 1000$ K, polarisation rate 1.0 V s^{-1}, chlorine reference electrode); (*1*) electroreduction of titanium from the NaCl–KCl–NaF melt containing 4.5×10^{-5} mol cm^{-3} of $TiCl_3$; (*2*) electroreduction of boron from the NaCl–KCl–NaF melt containing 8×10^{-5} mol cm^{-3} of $NaBF_4$; (*3*) electrochemical synthesis of titanium diboride from the NaCl–KCl–NaF–$TiCl_3$–$NaBF_4$ melt ($[Ti] + [B] = 1.2 \times 10^{-4}$ mol cm^{-3}).

of TiB_2 is followed (before the discharge of the alkali metal) by the discharge of the excess (with respect to this ratio) of a component (titanium or boron). When this ratio is lower than 1:2, this wave is exhibited at less negative potentials than in the case where the ratio is greater than 1:2. The cyclic voltammograms (reverse recording) for $[Ti^{3+}]:[B^{3+}] = 1:2$ were found to contain one peak, while those for $[Ti^{3+}]:[B^{3+}] \neq 1:2$ exhibit at least two peaks. Identification of the products of potentiostatic electrolysis demonstrated that the electrolysis product obtained at the potential of the first cathodic wave is titanium diboride, while that deposited at the second cathodic wave potential is titanium diboride together with the component (either titanium or boron) in excess with respect to the ratio $[Ti^{3+}]:[B^{3+}] = 1:2$.

The formation of titanium diboride is accompanied by evolution of a substantial amount of energy; therefore, its synthesis proceeds at more positive potentials than the separate reduction of either component of the synthesis. Depolarisation is equal to 0.15–0.3 V (with respect to the initial components), depending on the electrolyte composition. Comparison of the dependences of $i_p/V^{1/2}$ on $V^{1/2}$ for the joint and individual electroreduction of titanium and boron shows that at high polarisation rates, the peak current of the synthesis wave is much lower than the sum of the partial currents corresponding to the discharge of the titanium and boron complexes. This fact implies that the process is retarded due to the preceding chemical reaction; the higher the polarisation rate, the more pronounced the retardation (Fig. 8). This is due to the fact that the titanium and boron complex ions present in the melt form mixed complexes such as $[B_2TiF_xCl_y]$.[65] The absence of a horizontal section on the $i_p/V^{1/2}$ *vs.* $V^{1/2}$ plot (as well as on the plots for the partial currents for titanium or boron), which would be due to the flow of electrochemically active species moving from the bulk melt, provides grounds for considering, according to the diagnostic electrochemical criteria, that the lifetime of the arising species is short with respect to the lifietime of species formed by titanium and boron in the corresponding systems. A decrease in the polarisation rate results in a lower contribution of the formation of joint complexes. Extrapolation of this dependence for the limiting current to the rate axis gives the current corresponding to the total concentration of titanium and boron in the melt.

The introduction of boron as BF_4^- into the chloride melt containing $[TiCl_6]^{3-}$ ions gives rise to exchange reaction (35). The fluoride ion thus liberated adds to the titanium complex

$$[TiCl_6]^{3-} + 2F^- \longrightarrow [TiF_2Cl_4]^{3-} + 2Cl^-.$$

When there is no excess fluoride ions in the melt, the composition of the joint complex is $[B_2TiF_8Cl_4]^{3-}$. The wave of

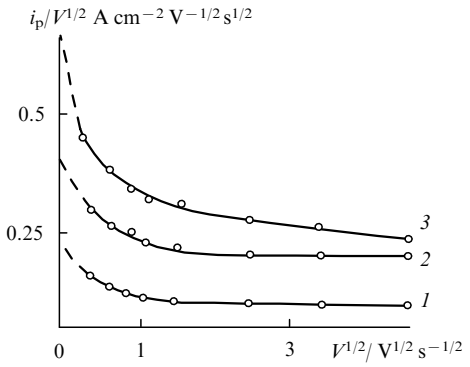


Figure 8. Variation of $i_p/V^{1/2}$ *vs.* $V^{1/2}$ for a number of processes; (*1*) electroreduction of titanium complexes, [Ti] = 6×10^{-5} mol cm^{-3}; (*2*) electroreduction of boron complexes, [B] = 1.2×10^{-4} mol cm^{-3}; (*3*) electrochemical synthesis of titanium diboride, [Ti] + [B] = 1.8×10^{-4} mol cm^{-3}, [Ti^{3+}] : [B^{3+}] = 1 : 2.

the joint electroreduction (synthesis) is extended along the potential axis; the peak width reaches 0.5 V and the potential difference between the peaks of the waves displayed during the forward and reverse recording of voltammograms is 1.0 V. The introduction of fluoride ions into the melt decreases the width of the wave and shifts the wave to the negative region; the difference between the potentials of the peaks of the cathodic and anodic waves decreases simultaneously. For the molar ratio ([Ti^{3+}] + [B^{3+}]) : [F$-$] $\geqslant$ 1 : 15, the wave width and the difference between the peak potentials barely change.

The shift of the peak potentials of the synthesis wave towards negative values is due to the formation of stronger complexes upon the attachment of the fluoride ions in the melt to the initial complex species

$$[B_2TiF_8Cl_4]^{3-} + n\,F^- \longrightarrow [B_2TiF_{8+n}Cl_{4-n}]^{3-} + n\,Cl^-. \qquad (38)$$

The fact that the peak and half-peak potentials of the synthesis waves do not depend on the polarisation rate as well as the S-shape of the voltammograms imply a reversible step of charge transfer at polarisation rates of < 2.0 V s^{-1}. The number of electrons involved in the elementary electrochemical step, calculated using the Matsuda – Ayabe equation, is equal to 9. This means that the discharge of the arising joint complexes at a polarisation rate of < 2.0 V s^{-1} involves simultaneous transfer of nine electrons without kinetic limitations. Study of the electrochemical behaviour of a titanium diboride electrode in a chloride – fluoride melt showed that there is no equilibrium between the electrode and the melt and that the electrochemical step proper is reversible. During dissolution of titanium diboride, limitations appear associated with the chemical interaction at the electrode – melt interface.

As noted above, the charge transfer steps in the separate discharge of titanium and boron complexes are retarded and the electrochemical stage of the synthesis of titanium diboride is reversible. This confirms the assumption that the complexes react chemically in the bulk of the melt to give electrochemically active species, the discharge of which is reversible.

The calculation of the coordination number for a mixed titanium and boron complexes shows that during titration of the melt with fluoride ions, four fluoride ions are attached to the initial species, $[TiB_2F_8Cl_4]^{3-}$, to give $[TiB_2F_{12}]^{3-}$.

It has been established relying on chronovoltammetric measurements [72, 73] that, for the discharge of joint titanium and boron complexes to persist, the molar ratio ([Ti^{3+}] + [B^{3+}]) : [F^-] = 1 : 4 (for [Ti^{3+}] : [B^{3+}] = 1 : 2) should be maintained in the melt.

The results obtained were taken as the basis for practical implementation of the high-temperature electrochemical synthesis of titanium diboride. The influence of temperature, current density, and the concentrations of the synthesis components on the composition and properties of the product were studied. A crucial condition for this process is that the molar ratio [Ti^{3+}] : [B^{3+}] = 1 : 2 is maintained in the melt. In this case, a homogeneous phase of titanium diboride is deposited at the cathode over a broad range of current densities. If this condition is not fulfilled, titanium diboride is deposited at the cathode at relatively low current densities (up to 0.5 A cm^{-2}), while at higher current densities, it is deposited together with the component present in excess with respect to this ratio. The total concentration of titanium and boron in the electrolyte in the 0.6 mol.% – 30 mol.% range does not influence significantly the product composition or economical characteristics of the process. A decrease in the total concentration to < 0.6 mol.% is not expedient for technological reasons (frequent correction of the cell, low current density and low output), whereas an increase in the concentration to > 30 mol.% brings about a greater loss of boron due to the thermal dissociation of potassium tetrafluoroborate, enhanced corrosiveness of the melt, and difficulty in washing out the cathodic deposit.

The temperature threshold for the onset of the electrochemical synthesis of titanium diboride in the system studied is 873 – 893 K.[66] The optimum temperature range is 963 – 1123 K. An increase in the temperature above 1123 K is not expedient as it diminishes the thermal stability of the cell and deteriorates the conditions of the formation of the metal salt precipitate. In the temperature range of 963 – 1123 K, highly dispersed titanium diboride powders with a specific surface area of up to 10 m^2 g^{-1} are produced.

Dispersed powders of titanium diboride were obtained using the KCl – NaCl – NaF (30 mol.%) – $TiCl_3$ (5 mol.%) – KBF_4 (10 mol.%) system as the electrolyte, current densities of 0.5 to 1.6 A cm^{-2}, and a temperature of 1023 K. The degree of dispersion of the powders increased with an increase in the current density; when the current density was < 0.5 A cm^{-2}, dendrites were formed, while at a current density of > 1.6 A cm^{-2}, titanium diboride was deposited at the cathode together with an alkali metal.

2. Joint electroreduction of titanium, nickel, cobalt and iron and electrodeposition of titanium intermetallic compounds

In the electrolysis of melts containing simultaneously titanium and iron (nickel, cobalt) chloride, powdered intermetallic compounds (IMC) of titanium, TiFe, $TiFe_2$, Ti_2Ni, $TiNi_3$ and TiCo, are formed at the cathode.[67 – 69] The ways of controlling the processes of formation of IMC have been studied allowing for the mechanisms proposed for high-temperature electrochemical synthesis.

Electrochemical behaviour of titanium and iron chlorides occurring in the melt has been studied by linear chronovoltammetry with cyclic potential sweep according to the three-electrode scheme.[67] The dependence of the limiting current on the concentration was non-linear (unlike this dependence for simple reversible or irreversible processes). The fact that the height of the wave remains constant when the potential sweep rate increases above 0.5 V s^{-1} implies a retarding influence of the preceding chemical reaction. The illegibility of the peak wave also confirms that the chemical and electrochemical stages are coupled.[70] It was noted [67] that potential of the cathode current shifts to the negative region and that the difference between the peak and half-peak potentials of the cathode current increases with an increase in the potential sweep rate. In view of the foregoing, with the assumption of first-order chemical reactions, two stages of high-temperature electrochemical synthesis can be distinguished.

1. Chemical reaction to give the equilibrium

$$x\,[TiCl_6]^{3-} + y\,Fe^{2+} \rightleftharpoons [Ti_xFe_y]^{z+} + 6\,x\,Cl^-, \qquad (39)$$

where $z = 3\,x + 2\,y$, which shifts towards the formation of the heteronuclear complex $[Ti_xFe_y]^{z+}$; the heat of formation of the corresponding intermetallic compound increases.

2. Electrochemical reduction of the heteronuclear complex cation after the discharge potential has been attained

$$[Ti_xFe_y]^{z+} + ze = Ti_xFe_y. \quad (40)$$

Analysis of the diffusion coefficients shows that charge numbers of 3 and 4 are preferred for complex IMC (the particular number depends on the particular compound). Therefore, the intermetallic chloride complexes discharged at the cathode are $[TiFe_2]Cl_3$ and $[TiFe]Cl_3$.

A series of experiments dealing with the influence of the concentration of titanium on the peak potential of nickel discharge has been carried out. [68] Titanium is formally considered as a 'quasi-ligand', although, in accordance with the views of the coordination chemistry of melts,[71] it is incorporated in the nucleus of the heteronuclear complex $[Ti_xNi_y]^{n+}$. The variation of the difference between the potentials of nickel reduction $\Delta E_{p\,Ni}$ in the presence and in the absence of $TiCl_3$ as a function of the Napierian logarithm of the ratio of $TiCl_3$ and $NiCl_2$ concentrations has three linear sections characterised by different slopes and a horizontal section for a large excess of titanium (Fig. 9). The formal coordination numbers of nickel with respect to titanium (the number of titanium atoms per nickel atom in the complex), determined from the slopes of the linear sections, are 0.4, 0.95 and 1.78. They are close to theoretical values of 0.33, 1.0 and 2.0 respectively, which correspond to the heteronuclear complexes $[TiNi_3]^{n+}$, $[TiNi]^{n+}$, $[Ti_2Ni]^{n+}$. The assumed formation of these complexes has been confirmed [68] by X-ray diffraction analysis of the products of electrolysis at the potential of the intermediate wave of the synthesis; in addition to nickel, the powder contained intermetallic compounds $TiNi_3$, TiNi and Ti_2Ni.

The reaction of $NiCl_2$ and $TiCl_3$ can be represented in the following way. According to spectroscopic measurements, [72] Ni^{2+} and Ti^{3+} cations form octahedral complexes $[NiCl_6]^{4-}$ and $[TiCl_6]^{3-}$ with chloride anions. Evidently, when the titanium concentrations are low (5×10^{-5} mol cm^{-3}) and the ratio [Ti] : [Ni] = 1 : 1, only these nickel and titanium complexes exist. The fact that upon an increase in the titanium concentration, a wave for the discharge of the intermetallic compound $[Ti_xNi_y]^{n+}$ appears between the discharge waves for titanium and nickel implies [68] a reaction between the two species to give heteronuclear complexes according to the following equations

$$[TiCl_6]^{3-} + 3\,[NiCl_6]^{4-} \longrightarrow [TiCl_6]^{3-} \cdot [NiCl_6]_3^{4-}, \quad (41)$$

$$[TiCl_6]^{3-} + [NiCl_6]^{4-} \longrightarrow [TiCl_6]^{3-} \cdot [NiCl_6]^{4-}, \quad (42)$$

$$2\,[TiCl_6]^{3-} + [NiCl_6]^{4-} \longrightarrow [TiCl_6]_2^{3-} \cdot [NiCl_6]^{4-}. \quad (43)$$

When titanium is present in a 25-fold (or higher) excess with respect to nickel, the potential of nickel discharge does not shift to negative values. Apparently, this situation corresponds to that in systems with excess complex-forming ions. In these systems, the structures of complexes are distorted; they are destroyed or turn into chain structures or into structures of individual molten salts.[71]

A study of the electrochemical behaviour of titanium and cobalt present simultaneously in chloride melts [69] has been the generalising stage in the investigations into the possibility of producing intermetallic compounds of titanium with iron group elements by high-temperature electrochemical synthesis. The appearance of the synthesis wave and the character of its variation for Ti–Co and Ti–Ni systems are similar.[68] The negative slope ratios for the variation of the product of the limiting cathode current by the polarisation rate *vs.* the limiting cathode current of the synthesis wave makes it possible to propose a process of electrochemical reduction of the heteronuclear complex $[TiCo]^{n+}$. The electrolysis yields a black finely dispersed metallic powder, TiCo. The powder is based on aggregates of dendrites with an average size of 20 μm. The specific surface area of the powder is 30 m^2 g^{-1}.

The works that are worth mentioning among the most recent studies devoted to the electrochemistry of titanium and its alloys include investigation of the influence of the cationic and anionic compositions of the melts on the corrosion of titanium in alkali and alkaline earth metal halides,[73] deposition of silicon,[74] silver [75,76] and copper [77,78] protective coatings onto titanium articles and preparation of titanium and its alloys for deposition.[79] Electrochemical behaviour of titanium and boron and electrodeposition of titanium intermetallic compounds have been studied in detail. [80,81]

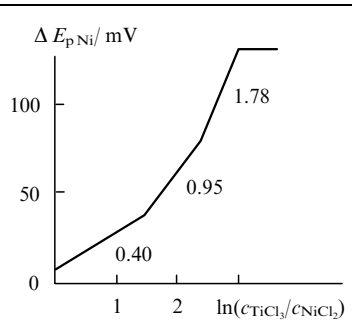


Figure 9. $\Delta E_{p\,Ni}$ *vs.* $\ln(c_{TiCl}/c_{NiCl})$ plot for the KCl–NaCl–$NiCl_2$–$TiCl_3$ melt; $T = 973$ K.
The numbers on the curve are explained in the text.

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