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Electrodeposition of titanium diboride from fused salts

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Electrodeposition of TiB_2 has been performed in cryolite-based electrolytes at 960 °C and in KF-KCl melts at 800 °C. As electroactive species either boron oxide and titanium oxide or potassium tetrafluoroborate and potassium hexafluorotitanate were used. Preparation of coatings from cryolite-based electrolytes containing K_2TiF_6 and KBF_4 was not successful. Coatings prepared from cryolite-based electrolytes containing B_2O_3 and TiO_2 were not coherent. Owing to the relatively high temperature both types of electrolytes undergo thermal decomposition. Electrolysis in potassium fluoride–chloride electrolytes containing KBF_4 and K_2TiF_6 provides coherent coatings with good adhesion to the substrate.

1. Introduction

In aluminium reduction cells carbon is used both as anode material and cathode cell lining. Although having several advantages, carbon has also many shortcomings. When used as cathode, for example, it is not wetted by liquid aluminium, it is penetrated by molten electrolyte, it reacts with aluminium with the formation of aluminium carbide (Al_4C_3), etc. These problems have stimulated extensive investigations into the possibility of replacing it by other materials better suited to meet the severe conditions of an aluminium cell.

Based on reviews by Billehaung and Øye [1] and by Grjotheim *et al.* [2], the qualities sought in an alternative cathode material were recently discussed by Matiašovský *et al.* [3]. From an analysis of the published data it follows that from the great variety of materials tested, titanium diboride comes closest to meet the strict requirements to an 'ideal' cathode lining material. TiB_2 exhibits a high melting point and hardness, high electronic conductivity, it is wetted by molten aluminium and it is resistant towards chemical attack by both aluminium and cryolite-alumina melts.

The different methods used to prepare titanium diboride have been reviewed by Samsonov *et al.* [4]. At present, it is mainly produced as a powder by thermochemical reduction of boron and titanium oxides followed by hot pressing and sintering to process the final product. An interesting and less costly alternative appears to be to coat suitable substrate materials with titanium diboride or TiB_2-based composites. The various coating techniques (hot pressing of TiB_2 powder or composite onto a substrate, plasma spraying of TiB_2, chemical vapour deposition based on the reduction of titanium and boron chlorides by hydrogen in the gas phase, etc.) have been discussed in [5, 6]. However, these coatings have not been subjected to long-term performance tests under the conditions of aluminium electrolysis. Also, the substrates need to match the thermal expansion coefficient of TiB_2 in order to minimize crack formation. Among the various materials tested, molybdenum metal, titanium and tungsten carbides and graphite, were found to be best suited to meet this fundamental requirement.

Another promising alternative is high-temperature electrochemical synthesis of titanium diboride in molten salts. The electrolytes employed can essentially be divided into two groups according to the type of electroactive components:

(a) Molten systems containing oxygen-containing compounds of titanium and boron, e.g. $Me_2B_4O_7$, $MeBO_2$, B_2O_3, TiO_2, Me_2TiO_3 (where Me denotes alkali metal) [7–16]. To improve the physico-chemical properties of the electrolyte alkali metal halides [8, 9, 11, 15, 16], alkali earth metal oxides [7] or cryolite [10] are added to the melt. In some cases titanium oxide was replaced by natural minerals such as ilmenite [9] or rutile [10].

(b) Systems containing alkali metal fluoroborates and alkali metal fluorotitanates [14–17]. The electroactive components are dissolved in a supporting electrolyte which generally consists of a mixture of alkali metal halides.

Depending on the electrolyte used the working temperature covers a wide range from 540 to 1100 °C. The higher temperatures are generally applied with viscous electrolytes, or with electrolytes having high temperatures of primary crystallization, mainly cryolite or purely oxide-based melts [10].

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A graphite container is generally used in laboratory preparation of TiB_2 and, at the same time, it often serves as the anode. Anodes of titanium metal [12, 13, 16], mixtures of titanium and boron [16] and pressed TiB_2 [12, 13] are applied in electrolysis in non-oxide electrolytes.

In preparation of TiB_2 powders by molten salt electrolysis graphite or steel rods are often used as the cathode material. In the case of preparation of coherent coatings steel, nickel, copper, tungsten and molybdenum were used as a supporting material [13–17]. Among the metals mentioned molybdenum has a specific position, because the value of the thermal expansion coefficient of molybdenum ($5.75 \times 10^{-6}\,K^{-1}$ [18]) is relatively close to that of TiB_2 ($4.5 \times 10^{-6}\,K^{-1}$ [4]). This small difference in thermal expansion gives good adhesion of the coatings to the substrate material even when cooling the sample from working to room temperature. Cathodic current densities have been varied from 0.01 to $6\,A\,cm^{-2}$ depending on the character of the product.

The objective of the present work was to prepare TiB_2 coatings from cryolite-based electrolytes containing either oxide compounds of boron and titanium (B_2O_3, $Na_2B_4O_7$, TiO_2) or oxygen-free species (KBF_4, K_2TiF_6) as electroactive constituents of the bath. Thermodynamic analysis of the electrolyte systems was used to explain the results. Comparison of these results with results obtained in electrodeposition of TiB_2 coatings from chloride-fluoride electrolytes containing KBF_4 and K_2TiF_6 was also made.

2. Experimental details

The TiB_2 electrodeposition experiments were carried out in a container made of heat resistant steel. It was protected by a graphite lining and closed by an airtight water-cooled lid. A graphite crucible (inner diameter 80 mm, height 90 mm) served both as cell container and as anode. Graphite rods with a diameter of 4 mm or molybdenum sheets were used as cathode. The temperature of electrolysis was held at 960 °C in cryolite-based melts and at 800 °C in KF–KCl–K_2TiF_6–KBF_4 melts; current densities varied from 0.25 to $1.5\,A\,cm^{-2}$.

Commercially available chemicals ('pro analysis' and 'pure' grade) were used to prepare the elctrolyte. Before use the components of the electrolyte were dried in vacuum at 200 °C for 24 h. The mixture was then melted and used in the electrolysis. In the TiB_2 electrodeposition experiments, a stabilized power supply and a linear recorder were employed. The TiB_2 deposits were identified by X-ray diffraction analysis and the microstructure was evaluated by means of a Jeol JSM-35 scanning electron microscope.

3. Results and discussion

3.1. *Cryolite electrolytes containing K_2TiF_6 and KBF_4*

As it was already known that all-fluoride electrolytes are more suitable for the preparation of TiB_2 coatings [3], the first series of experiments were carried out in electrolytes where cryolite served as the supporting electrolyte, to which potassium hexafluorotitanate (K_2TiF_6) and potassium tetrafluoroborate (KBF_4) were added as the electroactive components.

A molybdenum cathode was employed in most of the experiments as it showed a better performance as a substrate material as compared to graphite. The effect of composition was studied by varying the concentrations of K_2TiF_6 and KBF_4 in the electrolyte from 2 to 8 mol % and from 10 to 20 mol %, respectively. Electrolysis was carried out at a cathodic current density (CCD) of 0.25 to $1\,A\,cm^{-2}$ at 960 °C for 30 min. Only TiB_2 powder was identified on the cathode in the first stage of electrolysis in the whole concentration range for both the electrochemically active components.

From these melts intensive evaporation was observed, indicating that the electrolyte undergoes the thermal decomposition. It is well established [2, 19] that molten cryolite partially dissociates forming AlF_4^- ions

$$Na_3AlF_6 \longleftrightarrow 2NaF + NaAlF_4 \qquad (1)$$

All the thermodynamic calculations in this work are based on data published in [20, 21]. The Gibbs energy of the exchange reaction

$$NaF(l) + KBF_4(l) \longleftrightarrow NaBF_4(l) + KF(l) \qquad (2)$$

$$\Delta_r G^o = 7.8\,kJ\,mol^{-1}, \quad T = 1233\,K$$

is slightly positive, indicating that both potassium tetrafluoroborate and sodium tetrafluoroborate are present in the electrolyte and can undergo thermal decomposition according to the reactions:

$$NaBF_4(l) = NaF(l) + BF_3(g) \qquad (3)$$

$$\Delta_r G^o = -15.0\,kJ\,mol^{-1}, \quad T = 1233\,K$$

$$KBF_4(l) = KF(l) + BF_3(g) \qquad (4)$$

$$\Delta_r G^o = -7.2\,kJ\,mol^{-1}, \quad T = 1233\,K$$

The values of the standard Gibbs energy for both reactions are negative at the working temperature, which shifts the equilibria to the right hand side. Evaporation of boron trifluoride from the electrolyte supports the decomposition of the electrolyte as well.

Moreover, the content of tetrafluoroborates in the electrolyte is strongly decreased by the reaction between cryolite and KBF_4 under the formation of potassium hexafluoroaluminate, sodium fluoride and boron trifluoride. The decomposition reaction can also be written in the form

$$Na_3AlF_6(l) + 3KBF_4(l) = K_3AlF_6(s) + 3NaF(l) + 3BF_3(g) \qquad (5)$$

$$\Delta_r G^o = -43.8\,kJ\,mol^{-1}, \quad T = 1233\,K$$

The value of $\Delta_r G^o$ of this reaction indicates that the equilibrium is shifted in favour of the formation of BF_3.

This thermodynamic analysis shows that electrolytes composed of molten cryolite and potassium

Table 1. Compositions of the cryolite-based electrolytes containing oxide compounds of boron and titanium (mol %)

Electrolyte	Na_3AlF_6	TiO_2	B_2O_3	$Na_2B_4O_7$	*NaCl*
1	88	2	10		
2	78	2	20		
3	87	3	10		
4	77	3	20		
5	86	4		10	
6	82	8		10	
7	66	4		10	20

tetrafluoroborate are subject to thermal decomposition. Boron trifluoride is evaporated from the melt, lowering the content of the tetrafluoroborate anion which is the source of boron in the electrodeposition of TiB_2. The decomposition of the electrolyte proceeds relatively fast, so after melting and a short period of electrolysis the electrolyte does not contain enough boron for deposition of TiB_2.

It might be suggested, that the titanium-containing components undergo decomposition according to similar reactions. The lack of thermodynamic data for the titanium compounds does not allow similar thermodynamic analysis.

3.2. *Cryolite electrolytes containing B_2O_3 and TiO_2*

To suppress the decomposition of the electrolyte, oxide compounds of both boron and titanium were used as electroactive components. In some cases aluminium trifluoride was added to the melt in order to decrease the temperature of primary crystallization which makes possible electrolysis below the decomposition temperature of KBF_4 and $NaBF_4$. The results of these experiments are discussed in the following.

The compositions of electrolytes containing oxide-compounds of boron and titanium are listed in Table 1. As electroactive components B_2O_3 and TiO_2 were added to molten cryolite (electrolytes 1–4). In some experiments boron oxide was replaced by $Na_2B_4O_7$ (electrolytes 5–7) to improve the physicochemical properties of the electrolyte and to decrease the decomposition rate by adding sodium oxide to the melt.

The effect of the electrolyte composition on the deposition of titanium diboride was studied at the concentrations of 10 and 20 mol % B_2O_3 and from 2 to 8 mol % TiO_2 at a temperature of 970 °C. As in the previous case, the cathodic current density was varied from 0.25 to 1 A cm^{-2}. Contrary to the all-fluoride electrolytes, electrodeposition of titanium diboride was observed in the whole concentration range tested. Titanium diboride was electrodeposited mostly in the form of powder. X-ray diffraction analysis showed that it consisted of relatively pure TiB_2.

Poor quality coatings of TiB_2 were prepared at CCD's varying from 0.25 to approximately 0.55 A cm^{-2}. Figure 1 shows a micrograph of a cross-section of a molybdenum cathode coated at CCD 0.4 A cm^{-2} for approximately 20 min. The coating was nonhomogeneous and not coherent with a thickness of about 7 μm. The nonuniformity of the coatings did not allow us to determine the coating thickness against time and CCD. At CCD higher than approximately 0.5 A cm^{-2} only titanium diboride powder was electrodeposited on the cathode.

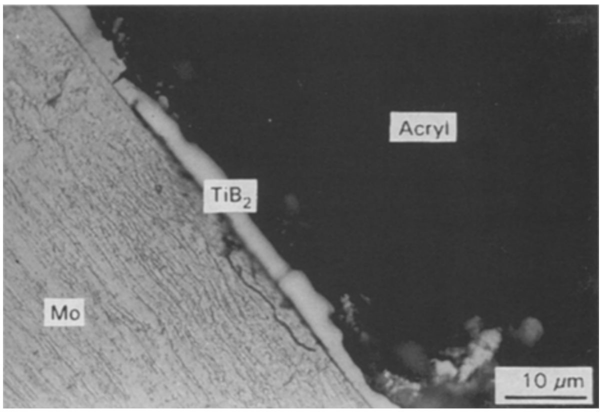

Fig. 1. Cross-section of a TiB_2-coated molybdenum cathode. Electrolyte: 78 mol % Na_3AlF_6 + 20 mol % B_2O_3 + 2 mol % TiO_2. Temperature 970 °C, cathode current density 0.4 A cm^{-2}, time of electrolysis 20 min.

As mentioned above, oxide-fluoride electrolytes are suitable for preparation of powders [16] which corresponds with the results obtained in cryolite-based B_2O_3 and TiO_2 containing melts. The formation of coatings at the beginning of electrolysis after the mixture had melted can be explained by the chemical reactions taking place during dissolution of boron oxide and titanium oxide in the cryolite under the formation of small amounts of BF_4^- and TiF_6^{2-} anions in the melt.

As already mentioned in Section 3.1 the dissociation of cryolite according to Equation 1 provides a certain amount of free sodium fluoride and sodium tetrafluoroaluminate in the melt. These three constituents (including molten Na_3AlF_6) can react with B_2O_3 and TiO_2 which are added to the mixture as a source of boron and titanium. It was shown by cryoscopic measurements [22] that the dissolution of boron oxide in molten systems containing alkali metal fluorides is accompanied by chemical reactions with the formation of alkali metal borates and fluoroborates or boron trifluoride. In the case of sodium fluoride, the following reactions can proceed:

$$3NaF(l) + 2B_2O_3(l) = 3NaBO_2(l) + BF_3(g) \quad (6)$$

$$\Delta_r G^o = -14.5\,\mathrm{kJ\,mol^{-1}}, \quad T = 1243\,\mathrm{K}$$

$$3NaF(l) + 7B_2O_3(l) = 3Na_2B_4O_7(l) + 2BF_3(g) \quad (7)$$

$$\Delta_r G^o = -92.2\,\mathrm{kJ\,mol^{-1}}, \quad T = 1243\,\mathrm{K}$$

Both Reactions 6 and 7 have negative values of $\Delta_r G^o$ at the working temperature. The formation of volatile boron trifluoride shifts Reactions 6 and 7 in favour of the formation of sodium borates. It can be suggested that boron trifluoride, which is short-lived in the melt, influences positively the electrodeposition of TiB_2 coatings. The electrodeposition of TiB_2 coatings takes place until BF_3 has escaped from the melt.

The situation becomes more complicated if we consider possible reactions of sodium tetrafluoroaluminate with boron-containing species under the formation of aluminium oxide and boron trifluoride:

$$2NaAlF_4(l) + B_2O_3(l) = 2NaF(l) + Al_2O_3(s) + 2BF_3(g) \qquad (8)$$

$$\Delta_r G^o = -84.7\,kJ\,mol^{-1}, \quad T = 1243\,K$$

$$14NaAlF_4(l) + 3Na_2B_4O_7(l) = 7Al_2O_3(s) + 20NaF(l) + 12BF_3(g) \qquad (9)$$

$$\Delta_r G^o = -167.4\,kJ\,mol^{-1}, \quad T = 1243\,K$$

$$4NaAlF_4(l) + 3NaBO_2(l) = 2Al_2O_3(s) + 7NaF(l) + 3BF_3(g) \qquad (10)$$

$$\Delta_r G^o = -99.4\,kJ\,mol^{-1}, \quad T = 1243\,K$$

The standard Gibbs energies of the above reactions have strongly negative values, which indicates a strong tendency to form gaseous BF_3. Moreover, one of the products of these reactions is aluminium oxide, which can precipitate from electrolytes saturated with Al_2O_3.

Concerning the results obtained for the cryolite electrolyte containing B_2O_3 and TiO_2 it can be concluded that this molten system undergoes decomposition with the formation of gaseous BF_3. The continuous decrease in the boron content in the electrolyte causes the disruption of the TiB_2 deposition.

Thermodynamic analysis of the reactions between molten cryolite and titanium oxide with formation of TiF_4, Na_2TiO_3 and Al_2O_3 gives positive values for the standard Gibbs energies and will not be presented here. It is suggested that TiO_2 is dissolved in the form of complex species containing both boron and titanium atoms [15, 16]. However, due to the very low contents of these species in the melt, they do not play an important role in the thermodynamic analysis.

3.3. *Cryolite electrolytes containing B_2O_3 and TiO_2 with AlF_3 and KF additives*

Excess AlF_3 was added in order to decrease the activity of sodium fluoride and to lower the temperature of primary crystallization of the melt. Small additions of potassium fluoride were made to stabilize boron trifluoride (formed by the reaction of boron oxide with fluorides) as a potassium tetrafluoroborate. The composition of the melts with AlF_3 and KF additions are listed in Table 2.

The cryolite ratio (NaF/AlF_3 molar ratio) of electrolyte 8 is about 1.6, and it exhibits a relatively low temperature of primary crystallization (visually determined value around 860 °C) and high vapour pressure. Probably, due to the high activity of aluminium containing species in this melt, electrodeposition of titanium diboride did not take place. A white crystalline deposit, most probably Al_2O_3, was observed on the cathode after the electrolysis ($j = 0.5\,A\,cm^{-2}$) at different temperatures (880, 900 and 950 °C).

The standard Gibbs energy of the reaction between boron-containing species and aluminium fluoride present in the melt with the formation of aluminium oxide and boron trifluoride is very negative, for example,

$$B_2O_3(l) + 2AlF_3(g) = Al_2O_3(s) + 2BF_3(g) \qquad (11)$$

$$\Delta_r G^o = -178.8\,kJ\,mol^{-1}, \quad T = 1243\,K$$

This confirms the experimental observation on the formation of a crystalline precipitate during electrolysis.

To decrease the activity of aluminium containing species and increase the stability of KBF_4 the content of potassium fluoride in the melt was increased. The cryolite ratio of both electrolytes 9 and 10 expressed as $(NaF + KF)/AlF_3$ was 2.3. The temperature of primary crystallization of these electrolytes (determined visually) is over 900 °C and the experiments were carried out at 950 °C. In electrolyte 10 sodium carbonate was added in an amount equivalent to that of TiO_2. B_2O_3 was replaced with $Na_2B_4O_7$ in order to lower the vapour pressure, because electrolyte 9 was strongly fuming.

Electrolysis in electrolyte 9 yielded a coarse-grained TiB_2 deposit in the first stage of the experiment when using low current densities (0.3–$0.5\,A\,cm^{-2}$). The coatings had poor adherence to the substrate, regardless of whether molybdenum or graphite was used as a cathode. Electrolysis for longer times and higher current densities yielded pure titanium diboride powder. Also the electrolysis with electrolyte 10 yielded only TiB_2 powder.

The main purpose of the addition of KF to the electrolyte was to suppress the decomposition reactions by stabilizing the BF_4^- anion. On the other hand this addition increased the temperature of primary crystallization of the electrolyte over the decomposition temperature of KBF_4 (900 °C [21]). On the basis of the experimental results and the thermodynamic analysis it can be concluded that melts containing potassium fluoride are not suitable for electrochemical synthesis of TiB_2 at temperatures over 900 °C because of the decomposition of the electrolyte. Moreover, only powders were prepared in the electrolysis.

Table 2. Composition of the cryolite-based electrolytes containing oxide compounds of boron and titanium with AlF_3 and KF additions (mol %)

Electrolytes	*Na_3AlF_6*	*AlF_3*	*KF*	*TiO_2*	*B_2O_3*	*$Na_2B_4O_7$*	*Na_2CO_3*
8	41	36	5	2	16		
9	41	20	20	2	16		
10	43	22	22	2		9	2

Table 3. Composition of the chloride-fluoride electrolytes containing K_2TiF_6 *and* KBF_4 *(mol %)*

Electrolytes	*KCl*	*KF*	K_2TiF_6	KBF_4
11	5	78	2	15
12	5	77	3	15

3.4. *Potassium chloride-fluoride electrolytes containing* K_2TiF_6 *and* KBF_4

Two electrolytes with different concentrations of potassium hexafluorotitanate were used for the electrodeposition of TiB_2 coatings from chloride-fluoride melts (Table 3). The electrolysis was carried out at 800 °C at current densities in the range of 0.2–1.2 A cm^{-2}. Molybdenum and graphite were used as cathode substrates. The coatings formed were homogeneous with good adherence to the substrate. Coherent coatings were electrodeposited with CCDs ranging from 0.2 to 0.8 A cm^{-2} in electrolyte 11 and from 0.8 to 1.2 A cm^{-2} in electrolyte 12. At higher CCDs only dendrites and powders were electrodeposited.

Figure 2 shows a micrograph of a cross-section of a TiB_2 coating prepared on a molybdenum substrate in electrolyte 11 at a cathodic current density of 0.5 A cm^{-2}. The thickness of the layer is about 80 μm. In the figure traces of the diamond pin used for microhardness measurements are shown as well. The value of the microhardness determined by the Vickers method is about 48.10^3 N mm^{-2}. This high value of microhardness confirms that the coatings were compact. In Fig. 3 is shown a cross section of a TiB_2 coating prepared on a graphite substrate under the same experimental conditions. It can be seen from the figure

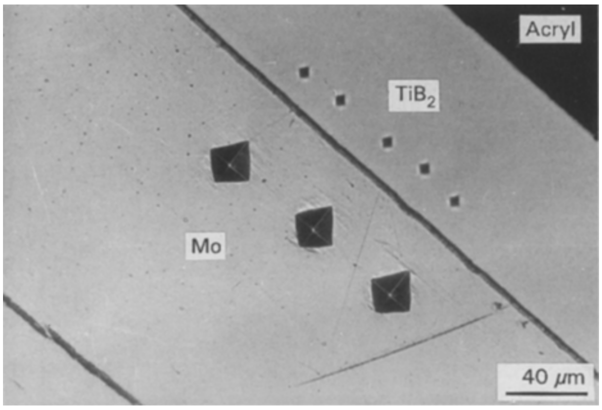

Fig. 2. Cross-section of a TiB_2-coated molybdenum cathode. Electrolyte: 78 mol % KF + 5 mol % KCl + 2 mol % K_2TiF_6 + 15 mol % KBF_4. Temperature 800° C, cathode current density 0.5 A cm^{-2}, time of electrolysis 30 min.

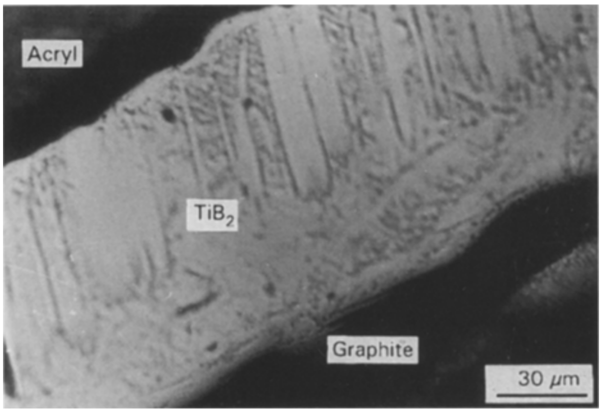

Fig. 3. Cross-section of a TiB_2-coated graphite cathode. For conditions see Fig. 2.

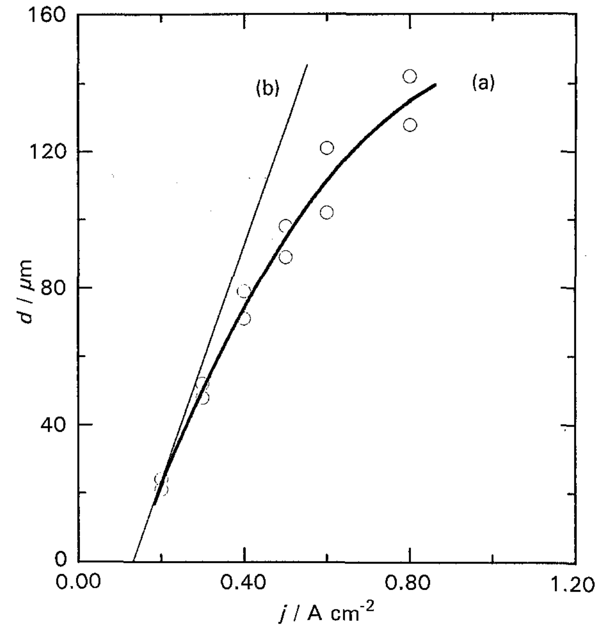

Fig. 4. Dependency of the thickness of the TiB_2 coatings (d) against cathodic current density (j). Temperature 800 °C, time of electrolysis 30 min. Electrolyte composition: 78 mol % KF + 5 mol % KCl + 2 mol % K_2TiF_6 + 15 mol % KBF_4. (a) Experimental; (b) theoretical.

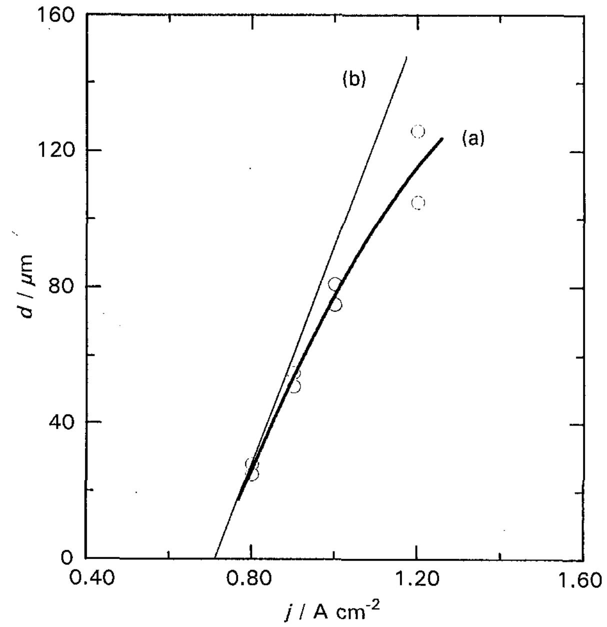

Fig. 5. Dependency of the thickness of the TiB_2 coatings (d) against cathodic current density (j). Temperature 800 °C, time of electrolysis 30 min. Electrolyte composition: 77 mol % KF + 5 mol % KCl + 3 mol % K_2TiF_6 + 15 mol % KBF_4. (a) Experimental, (b) theoretical.

that the layer consists of big columnar crystals growing perpendicular to the substrate.

The experimental and theoretical dependency of the thickness of the electrodeposited TiB_2 layer on the cathodic current density is shown in Fig. 4 (electrolyte 11) and in Fig. 5 (electrolyte 12). The theoretical dependency was calculated from Faraday's law for the reaction

$$2BF_4^- + TiF_6^{3-} + 9e^- = TiB_2 + 14F^- \qquad (12)$$

It can be seen from Figs 4 and 5 that the extrapolation of experimental dependencies to zero thickness of the TiB_2 layers intersects the CCD axis at two different values. This may indicate that a parallel electrode reaction, e.g. reduction of Ti(IV) to Ti(III), participates in the charge transfer. The proportion of CCD representing this reaction increases with increasing content of titanium compounds in the melt. These current densities were subtracted from the overall current densities in the calculation of the theoretical thickness of TiB_2 coatings.

The deviation of the experimental curves from the theoretical ones, which represent 100% current efficiency, is most probably caused by the formation of dendrites. These were formed on sharp edges of the cathode due to the irregular distribution of the current.

4. Conclusion

It can be concluded that cryolite melts containing KBF_4 and K_2TiF_6 as electroactive components are not suitable for preparation of titanium diboride in any form. These melts undergo rapid decomposition with the formation of BF_3 which evaporates from the melt.

Electrolytes consisting of boron oxide and titanium oxide dissolved in molten cryolite contain, after the dissolution of B_2O_3, sodium metaborate and tetraborate as a source of boron for the TiB_2 deposition. These compounds are most probably responsible for the deposition of titanium diboride in the form of powder.

Electrolysis in potassium fluoride-chloride electrolytes containing K_2TiF_6 and KBF_4 provides coherent coatings with good adhesion to the substrate.

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