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Cathodic deposition of refractory intermetallic compounds from FLINAK melts
Part II: Preparative cathodic deposition of TiB_2 and ZrB_2 and coatings thereof

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At 700° C the production of TiB_2 was performed by cathodic deposition of this refractory intermetallic compound on carbon cathodes from FLINAK melts containing Ti(IV) and B(III) in concentration ratios ranging from 1 : 3 to 1 : 2 and total concentrations from 2 to 10 mol % at current densities from 0.2 to 3 A cm^{-2}. Current efficiencies were always lower than 100% but the purity of the deposited TiB_2 was in almost all cases better than 98%. Generating augmented mass transfer by the anode effect, which develops at high current densities, improved cathodic current efficiencies and enhanced the purity of the coarse deposit. Current efficiencies decreased with decreasing temperature. Smooth and dense coatings on carbon substrate were only obtained if the thickness of the coating was kept below a critical value of 0.5 mm. It was impossible to produce dense, well adhering coatings on copper rod electrodes since, due to the mismatch of the thermal expansion coefficients of copper and TiB_2 the coatings detached from the substrate on cooling. To produce pure ZrB_2 material or ZrB_2-coatings necessitates low current densities ($i < 0.04$ A cm^{-2}). From the impure cathodically deposited mixtures of dendritic ZrB_2, which were obtained at higher current densities, solidified electrolyte and lower valent zirconium compounds could not be separated.

1. Introduction

Titanium diboride is mainly used for hard coatings of tools, to protect armoured vehicles and recently it has found an increasing interest in the aluminium industry. Ransley [1] proposed the use of TiB_2 cathodes for aluminium electrowinning in order to improve the current and energy efficiency of this process. Numerous patents had been filed concerning the use and preparation of TiB_2-covered carbon cathodes or massive TiB_2 electrodes, electrode studs and related equipment for aluminium smelters. Before 1980 the patent situation had been reviewed by Billehaug and Øye [2] and interest has been sustained throughout the last decade.

Plasma assisted chemical vapour deposition [3, 4] and normal chemical vapour deposition [5], sputtering [6], electrical spark alloying [7], but most often sintering (reactive or pressure enhanced) was used to prepare TiB_2 electrodes or coatings. Since all these techniques yield impure coatings which are not stable enough, being rapidly destroyed by erosion [8], it is worthwhile investigating whether cathodic deposition of TiB_2 from melts is possible and yields more pure and more stable coatings. Preparative production of TiB_2 by cathodic deposition or direct cathodic coating of carbon cathodes with TiB_2 has still to be reported.

Polyakova and associates [9] and Lepinay and coworkers [10] have investigated voltametrically cathodic Ti-deposition and Makita, Matiasovsky and Taranenko [11] have shown that in the presence of hexafluorotitanate (TiF_6^{2-}) and tetrafluoroborate (BF_4^-) anions titanium diboride can be formed by cathodic deposition. In a preceding paper [12] the thermodynamics and electrode kinetics of this reaction and of cathodic ZrB_2-deposition had been investigated. The present paper deals with the preparative aspects of these reactions aiming at producing pure TiB_2 and TiB_2 coatings by cathodic deposition of TiB_2 from FLINAK melts. Additionally ZrB_2 was investigated.

2. Experimental details

The experimental setup for preparative cathodic deposition was essentially the same as for electrode kinetic investigations [12]. The preparative deposition was performed galvanostatically omitting any additional potential monitoring as a reliable, stable and easily maintainable reference electrode is not yet available in FLINAK melts. As in the previous investigation a carbon crucible (6 cm diam., 8 cm high) served as a counter electrode and carbon rods machined from Acheson graphite EK 78 (Ringsdorf) or copper rods

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were used as working electrodes. The electrodes were polished and thoroughly rinsed with methanol and dried at 120° C before being introduced into the cell. All chemicals were of pA-grade and stored in a glove box before being transferred into the cell. The salts (FLINAK contains 46.5 mol % LiF, 11.5 mol % NaF and 42 mol % KF) which constituted the FLINAK melts were initially thoroughly dried at 200° C for 24 h before being transferred into the glove box where they were mixed and introduced to the carbon crucible under an argon blanket. After completion of a deposition experiment, the cathode was withdrawn from the melt and after cooling was rinsed with tap water for several hours. Finally the specimens were rinsed with distilled water, in order to remove the last traces of melt, and dried. Current yields were determined gravimetrically. The composition of the deposited TiB_2 and ZrB_2 materials was determined by quantitative analysis of Ti and Zr by AAS.

3. Cathodic deposition of TiB_2 and ZrB_2 on copper and carbon substrates

The cathodic deposition of the refractory intermetallic compounds was investigated with two objectives:

(a) Preparation of TiB_2 and ZrB_2 as raw material of particularly high purity, being deposited in thick ($d > 1$ mm), not necessarily smooth, deposits on carbon substrates.

(b) Preparation of dense and possibly smooth coatings on carbon substrates with the aim of preparing TiB_2 and/or ZrB_2-coated cathodes for cathodic aluminium deposition.

Table 1. Data for selected examples of preparative TiB_2 deposition experiments. Electrolyte: FLINAK; 600 to 700° C; anode: carbon crucible; cathode: carbon plates of 19 cm^2 and carbon rods; stirring by free thermal convection

Run number	*121*	*143*	*144*	*145*†	*147**
Temperature (° C)	700	700	700	700	600
Depolarizer concentration (mol %)					
KBF_4	4	9	10	10	3
K_2TiF_6	2	4	4	4	1
c.d. ($A\,cm^{-2}$)	300	200	700	2000	300
Duration of experiment (h)	16	28	26	4	40
Gravimetric current effic. (%)	21	13	21	47	8
Cell voltage (V)‡	1.8	1.7	1.9	10./.15	1.45
Contamination (%)§	0.9	0.6	3	0.9	5 to 6
Physical strength of the deposit	very hard	very hard	loose	loose	almost powderous
Density# ($g\,cm^{-3}$)	–	4, 15	–	4.18	–
Mean length of crystals (mm)	3–6	4–15	5–20	3–10	almost powder
Mean bredth of crystals (mm)	3–5	2–5	2–5	3–7	
Appearance dendritic	no	no	yes	yes	–

* By bubbling argon through the melt mass transport was enhanced though in a poorly defined way.

† At 2 $A\,cm^{-2}$ at the anode there develops an anode effect with heating and strong stirring of the electrolyte.

‡ High cell voltage of run No. 145 indicates the anode effect. Very effectively enhanced mass transfer results in enhanced current efficiencies.

§ Contamination is based on analytical Ti-determination.

\# Density is determined by pycnometry. The theoretical density of TiB_2 is 4.15 $g\,cm^{-3}$.

3.1. *Preparation of thick layers of coarse crystals of TiB_2 on carbon substrates*

At 700° C TiB_2 was deposited under galvanostatic conditions on the surface of carbon rod cathodes (2.5 cm^2 exposed surface) and carbon plates (19 cm^2 surface) which were immersed in FLINAK melts containing KBF_4 and K_2TiF_6. Deposition lasted from 4 to 40 h. The concentrations of KBF_4 and K_2TiF_6 ranged from 2 to 10 and 2 to 4 mol %, respectively, and the concentration ratio $c(B)/c(Ti)$ ranged from 2 to 3. Applied current densities ranged from 0.3 to 2 $A\,cm^{-2}$.

Table 1 shows data for five experiments which were selected from a total of more than twenty. The data of Table 1 demonstrate that cathodic TiB_2 deposition may generate relatively coarse crystals. Enhancing the current density beyond the mass transfer limits (No. 144, 147) yields, as expected, powders which are composed of insufficiently pure material. If the current density is kept low (Nos 121 and 143) a dense agglomerate of relatively large crystals of high purity is generated. The strong anode effect which develops at the highest current densities (No. 145) and which stirs the electrolyte very efficiently results in a sizeable increase of current efficiency without deterioration of the deposit quality*.

Most of these experiments were conducted without forced convection but free thermal convection is relatively strong, as is usually found with most high temperature molten salt experiments for which the Raleigh number is usually quite high. Common to all these experiments is:

(i) All deposits contain mainly TiB_2 – very often in coarse crystals which strongly adhere to the carbon support.

(ii) The deposits are almost pure but contain some impurities – mostly occluded salt – ranging from as low as 0.1 wt % to some 6 wt %.

(iii) The current efficiency of cathodic TiB_2-deposition is always sizeably lower than 100% and is particularly low, if forced convection is applied by bubbling argon gas through the electrolyte, whereas enhancement of mass transfer generated by the anode effect improves the current efficiency.

(iv) The quality of the deposits expressed by the size of well developed crystals, purity of the material and adherence to the support is influenced by many parameters which interact in a complex way and cannot yet be defined in terms of optimal operating parameters of the electrolysis.

* X-ray diffractograms of the material exhibit the expected hexagonal structure with $a = 303 \pm 1$ pm and $c = 323 \pm 1$ pm. Literature data reported are: $a = 302.9$; 303.0 and 302.3 pm and $b = 323.3$; 322.7 and 322.6 pm, respectively [13, 14 and 15].

Whenever crystal quality and purity of the TiB_2 deposit are poor and the current efficiencies are poorly reproducible, the main reason is to be seen in the chemical reactions of cathodically formed Ti(III) cations (*cf.* [10]). The formation of Ti(II)-fluoride by disproportionation of Ti(III) which had been described and investigated by Polyakova and coworkers [9] must be taken into account. Ti(II)-fluoride has a low solubility in FLINAK-melts and would be deposited together with TiB_2 to an extent, which depends mainly on current densities, Ti(III) and B(III) concentrations and mass transfer conditions.

3.2. *Preparation of thin and dense TiB_2 and ZrB_2 coatings on carbon supports*

Stationary cylindrical carbon rod anodes (external diam. 10 mm) were cathodically coated by TiB_2 or ZrB_2, respectively, in mixed fluoride/chloride (40 mol % KF, 47 mol % KCl) melts and in FLINAK melts containing either titanium in the four valent or three valent state or zirconium in the four valent state, respectively. Boron is added as KBF_4. The rods were immersed to a depth of 2 cm so that the surface area exposed to the melt amounted to 7 cm^2. The rod served as the cathode and again the carbon crucible containing the melt served as the anode. The deposition was performed on carbon rod cathodes under free thermal convection and current densities of 0.3 A cm^{-2} and the deposition ended after 1 to 4.5 h time corresponding to a hypothetical deposit of 1.2×10^{-3} to 5.3×10^{-3} mol of MeB_2 per cm^2 giving a hypothetical thickness of the coating of approximately 0.02 to 0.08 cm assuming 100% current yield.

The current efficiencies decrease with increasing temperature for TiB_2 from 80% at 600° C to 40% at 800° C and are relatively temperature-independent and close to 80% for ZrB_2-coatings.

TiB_2-coatings are smooth as long as their thickness does not exceed 0.05 cm but become progressively rougher the more TiB_2 is deposited. Figure 1 shows a carbon rod cathode covered with a coating of only 0.3 mm thickness. Magnification of the shiny surface reveals that it is composed of hexagonal TiB_2 crystallites with a mean diameter of approximately 10 μm (Fig. 2). Originally these coatings are completely dense as demonstrated by Fig. 3 which shows a broken coating with a dense packing of TiB_2-needles. The crystals adhere strongly to the carbon support. TiB_2-deposits of the quality of that shown in Fig. 1 are also of highest purity, containing at the most some 100 wt p.p.m. of impurities.

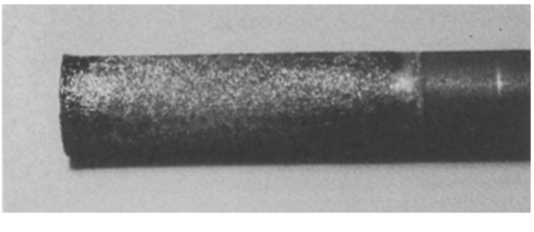

Fig. 1. Carbon rod anode coated with 0.3 mm thick layer of TiB_2.

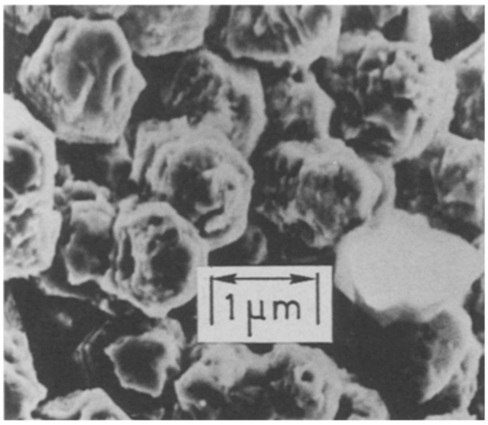

Fig. 2. Scanning electron micrograph of the surface of TiB_2-coating shown in Fig. 1.

Due to the thermal expansion coefficient of the coating (6×10^{-6} K^{-1}) and the carbon substrate (3.8×10^{-6} K^{-1}) the coating shrinks more than the substrate upon cooling and irregular, very narrow, cracks are formed. Nevertheless these coatings adhere very strongly to the carbon support. In contrast such coatings formed on copper rod cathodes detach from this substrate on cooling because the mismatch is reversed and enhanced as the thermal expansion coefficient of copper is higher than that of carbon and titanium diboride.

It was, however, impossible under any experimental condition to obtain comparably smooth deposits of ZrB_2, which, even if the deposited amount of refractory metal was very low, electrocrystallized in the form of very coarse crystals. Table 2 shows the data for ZrB_2-deposition. Deposition at low current densities (0.04 A cm^{-2}) generates very coarse but nevertheless strongly adhering and dense material of high purity (No. 4 and 5). But at higher current densities the deposition becomes spongy, or fluffy, contaminated with frozen melt and detaches from the surface.

3.3. *Reasons for lowered current efficiencies of TiB_2 deposition*

The reduction of Ti(IV) to Ti(III) ions, which are not completely consumed by TiB_2-deposition because TiB_2 is deposited with lower than mass transfer limited current densities, generates an electrochemical short circuit, since Ti(III) and Ti(II) leaving the cathode are reoxidized at the anode to Ti(IV). This causes

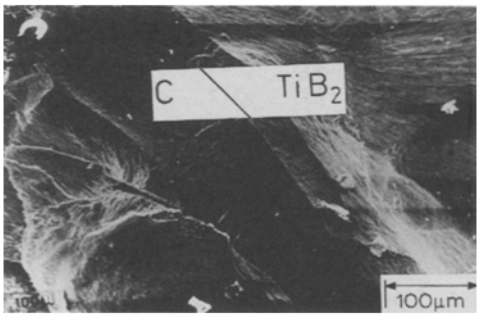

Fig. 3. Appearance of broken, dense TiB_2-coating deposited on carbon.

Table 2. Data for cathodic ZrB_2 deposition from FLINAK melts on carbon rod cathodes. x and y are the concentrations of K_2ZrF_6 and KBF_4, respectively, in mol %

Experiment	*x/y*	*T* (°*C*)	*i* ($A\,cm^{-2}$)	*Current yield* (%)	*Cell voltage*	*Deposit quality**
1	2/5	700	0.5	50	20	2
2	2/5	680	0.2	-	10	2
3	2/5	800	0.95	73	3 to 5	2
4	2/5	800	0.04	87	2 to 3	1
5	4/20	800	0.04	66	2 to 3	1

* Quality of the deposit:
1 = Coarse and budlike crystallites on very thin ($h < 1$ mm), smooth coating. The material is dense and very pure (impurities less than 1.000 p.p.m.)
2 = Fluffy or spongy, loose deposit contaminated with residual melt. The material detaches easily from the cathode after prolonged leaching of the melt with water. It is composed of dendrites with diameters of less than 10 μm.

remarkable reductions in current efficiency. Since for zirconium similar redox and disproportionation reactions are of minor importance (*cf.* [12]) the high current efficiencies for zirconium diboride deposition are not unexpected.

3.4. *The anode effect of TiB_2 deposits induced convective stirring and deposit quality*

In the course of the deposition experiments, in which Ti(IV) was added as K_2TiF_6, only a limited part of the Ti(III) which is generated cathodically from Ti(IV) is reduced to Ti metal and incorporated into the deposit as the applied current density is lower than the diffusion limited value. Therefore the Ti(III)-concentration increases slowly in the melt eventually reaching a limiting steady state value. As soon as mass transport controlled current density of Ti(III)-oxidation at the anode becomes lower than the applied current density, chloride is evolved at the anode from fluoride/chloride melts or fluorine and fluoro-carbon compounds, respectively, are evolved anodically in fluoride melts generating a strong "anode effect' with sparking and overheating which is well known from Al_2O_3-depleted cryolite melts in aluminium smelters. Chlorine evolution in melts containing chloride, and, even more, the anode effect which generates anodic overpotentials of more than 10 V, generate strong convection and enhanced mass transfer at the cathode.

Mass transfer in experiments with high Ti(III) contents, where anodic gas evolution does not occur, because anodically Ti(III) is oxidized to Ti(IV), is relatively weak and only due to thermal free convection. Thermal free convection generates much poorer mass transfer in the melt and on the cathode than gas evolution. Under this condition much poorer quality cathodic deposits are observed. As is typical for metal deposition with applied current density approaching mass transfer limited current density, a highly dendritic TiB_2 deposit is obtained. Such deposits are contaminated by an excess of boron and of lower valent titanium compounds stemming mainly from the melt which is occluded or adheres to the very finely distributed deposit.

4. Cathodic aluminium deposition on titanium diboride coated carbon cathodes

In the framework of an investigation of the wear and dissolution rate of TiB_2-cathodes for aluminium deposition, sintered titanium diboride cathodes and carbon cathodes with a coarse 0.7 to 1 mm thick TiB_2-coating, have been compared [8]. Whereas sintered titanium diboride electrodes are dissolved and eroded at rates of 0.16 cm year^{-1}, the erosion of electrodeposited titanium diboride cannot be detected. The titanium content of aluminium which is continuously anodically dissolved and cathodically redeposited at a current density of 1 A cm^{-2} on titanium diboride-coated carbon cathodes in a 500 h experiment is below the detection limit. From this it may be concluded that the wear rate of such electrodeposited titanium diboride coatings is definitely less than 0.016 cm year^{-1}. The different behaviour of sintered and cathodically deposited TiB_2 was shown to be due to the higher purity of the cathodically generated diboride. Figure 4a and b show

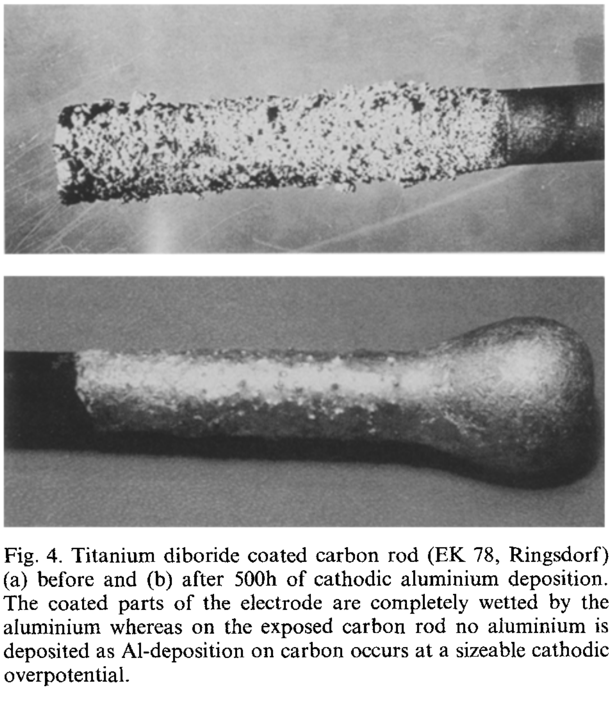

Fig. 4. Titanium diboride coated carbon rod (EK 78, Ringsdorf) (a) before and (b) after 500h of cathodic aluminium deposition. The coated parts of the electrode are completely wetted by the aluminium whereas on the exposed carbon rod no aluminium is deposited as Al-deposition on carbon occurs at a sizeable cathodic overpotential.

such a TiB_2-coated carbon electrode before and after cathodic aluminium deposition. It can clearly be seen in Fig. 4b, that contrary to the carbon substrate, the lower part of the cathode, which is coated by titanium diboride is completely covered by aluminium because it is wetted by the deposited liquid metal. No aluminium is deposited on the carbon. The reason is that Al deposition on carbon proceeds with an overpotential of more than 100 mV but is not hindered on molten aluminium. From these findings it may be of interest to use such coatings in aluminium electrowinning [16].

5. Conclusion

It has been shown that cathodic deposition of TiB_2 from FLINAK-melts containing Ti(IV) or Ti(III) and B(III) of several mol % in stoichiometric or higher than stoichiometric B/Ti ratio may yield thick and coarse, but very pure, coatings of TiB_2 on carbon electrodes. This procedure may therefore serve for producing TiB_2 of high purity. Well adhering, dense and smooth TiB_2-coatings can be obtained if the thickness of the coating is kept below 0.5 mm. Such coatings, however, are expected to detach from metallic substrates, as this is experienced with copper rods. Therefore it seems questionable whether cathodic TiB_2 deposition can be applied to modify and harden metallic surfaces. The experience gathered by Inman and coworkers [17], that pulse plating of chromium from melts assures the formation of closed layers is of some help. But the mismatch of expansion coefficients of layer and substrate cannot be compensated by interlayers, because TiB_2 has too high an elasticity modulus and is too brittle so that such coatings can never be expected to withstand thermal cycling without crack formation. Such cracks are of no harm for the TiB_2-coated Al-deposition graphite cathodes. The reported experience with TiB_2-coatings on carbon substrate render it feasible and promising to produce TiB_2-coated cathodes for Al-winning cells. *In situ* formation of the coating by TiB_2-deposition from cryolite melts containing B(III) and Ti(III) fluoride is possible in principle, as TiB_2-deposition occurs at a potential which is more anodic than aluminium deposition by more than 400 mV.

It would also be desirable to use ZrB_2-coatings as, due to the higher Gibbs energy of formation, ZrB_2 is expected to be even more stable than TiB_2. It was not possible to obtain ZrB_2-layers of comparable purity and quality under any mass transfer condition not even on rotating electrodes; but the reason for this is not clear. It certainly is not a difference in deposition kinetics as it has been shown that the exchange current densities of TiB_2 and ZrB_2 are of the same order of magnitude, though i_0 (TiB_2) is smaller than i_0 (ZrB_2) by a factor of two [12].

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