# Electrochemical deposition of $TiB_2$ in high temperature molten salts

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## Abstract

The electrochemical deposition of $TiB_2$ out of a $NaCl–KCl–NaF–KBF_4–K_2TiF_6$ electrolyte at 600 °C was tested on steel and molybdenum substrates using various current programs. The characterisation of the deposited layers has been carried out by X-ray diffraction methods, scanning electron microscopy and microhardness measurements. The pulse sequences and the current densities used influence in a significant way the homogeneity of the layers deposited, the crystal size, the texture and other physical properties like electrical and thermal conductivity. The microhardness range was up to 2900 HV, smooth and dense layers were prepared at a pulse frequency of 100 Hz.
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## 1. Introduction

Metals such as aluminium, magnesium, titanium, molybdenum and compounds of these metals, e.g. borides, cannot be deposited electrochemically out of aqueous solutions. Layers of these metals and compounds prepared by chemical (CVD) or physical vapour deposition (PVD) techniques show superior properties on various substrates. The preparation of thick layers with excellent quality within a short time scale can be done by electrodeposition processes out of molten salt systems at temperatures >600 °C.

The electrodeposition process shows many advantages compared to CVD or PVD deposition methods. Irregularly shaped specimens can be covered easily with a homogeneous and coherent layer and the deposition time is much shorter compared to these well established vacuum based techniques. Furthermore, electrochemical methods are more cost effective.

Titanium diboride ($TiB_2$) is a well known ceramic material with high hardness, high melting point, very good chemical stability even at high temperatures and excellent wear resistance

[1,2]. Current use of this material, however, is inhibited by economic factors; particularly the costs of densifying a material with a high melting point. Moreover, due to its low value of fracture toughness (4.9–8 $MPa\,m^{1/2}$) [1,2], massive $TiB_2$ parts are not suitable for applications exposed to fatigue or complex stress situations.

Thin layers of $TiB_2$ have a wide range of potential industrial applications due to the wear and corrosion resistance properties that $TiB_2$ can provide to a cheap and/or though substrate. The electrodeposition of $TiB_2$ layers has two main advantages compared with vacuum based deposition methods: the growing rate of the layer is 200 times higher (up to 10 μm/min) and the inconveniences of covering complex shaped products are dramatically reduced.

Among all the electrolytes reported in the literature [3–8], our work was focused on NaCl–KCl–NaF melt due to the high quality of the layers synthesised out of it and the high solubility of the melt in water, which makes easier the washing of the sample after deposition. It is also important for industrial applications that the NaCl–KCl–NaF melt is much less aggressive to the electrochemical cell materials than an all-fluoride electrolyte.

## 2. Experimental

The supporting electrolyte was prepared using KCl, NaCl and NaF in a concentration ratio of 43.3:43.3:13.4 mol%. The mixture was dried at 280 °C under

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Tel.: +43 2622 22266 13; fax: +43 2622 22266 50.
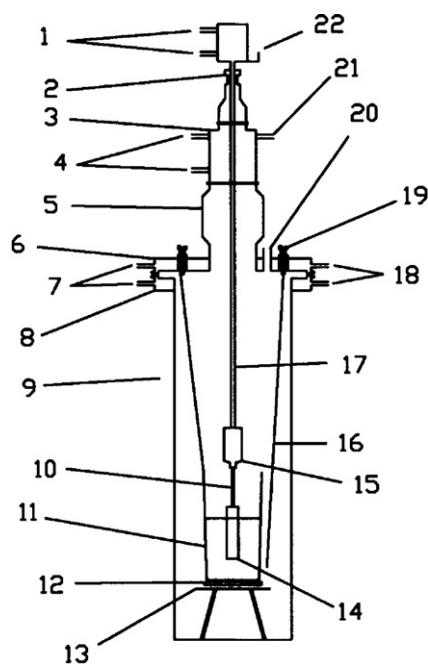    E-mail address: gerhard.nauer@echem.at (G.E. Nauer).

Fig. 1. Detailed sketch of the electrochemical cell: (1) rod cooling water inlet/outlet, (2) O-ring sealing, (3) prechamber, (4) prechamber cooling water inlet/outlet, (5) valve, (6) stainless steel cooled lid, (7) lid cooling water inlet, (8) stainless steel cooled top of the cell, (9) steel cell, (10) stainless steel or molybdenum rod, (11) Sigradur® glassy carbon crucible, (12) electrical isolator, (13) crucible stage, (14) sample, (15) molybdenum sample holder, (16) thermocouple, (17) cooled rod, (18) lid cooling water outlets, (19) inlets (3×): thermocouple, crucible electrical contact, and reference electrode, (20) Ar-vacuum inlet/outlet, (21) cathode electrical contact, and (22) prechamber Ar/vacuum inlet/outlet.

vacuum during 48 h prior to use. $K_2TiF_6$, $KBF_4$, and metallic titanium were added as sources of boron and titanium. The concentration of $KBF_4$, $K_2TiF_6$ and $Ti^0$ was 1.42, 0.71 and 0.11 mol/l, respectively.

All the deposition experiments were done galvanostatically in a high temperature electrochemical cell (Fig. 1) at 600 °C using a glassy carbon crucible (electrolyte volume 170 ml) as anode.

For improving the quality of the layers pulse interrupted current (PIC) sequences (Plating Electronic Pe86-20-5-25 power supply) were applied.

The $TiB_2$ layers synthesised were characterised with a scanning electron microscope (Philips XL-30 ESEM) equipped with an energy-dispersive X-ray spectrometer (EDX), an X-ray diffractometer (Philips XR MPD) and an optical microscope (Olympus GX51) equipped with a microhardness tester (Anton Paar MHT-10). The Vickers hardness was determined on cross sections of the cathodes with the deposited layers on it. The efficiency of the bath was calculated measuring the gain weight of each sample and related to the charge flowing during the electrodeposition.

## 3. Results and discussion

The mechanism of $TiB_2$ cathodic deposition used in the calculations was proposed by Devyatkin and Kaptay [9] as follows:

$$Ti^{3+} + 2B^{3+} + 9e^- \rightarrow TiB_2 \qquad (1)$$

According to this reaction, $TiB_2$ is produced from the electrochemical reduction reaction of $Ti^{3+}$ and $B^{3+}$. Metallic titanium added to the melt is consumed in the production of the $Ti^{3+}$ [10] according to reaction (2):

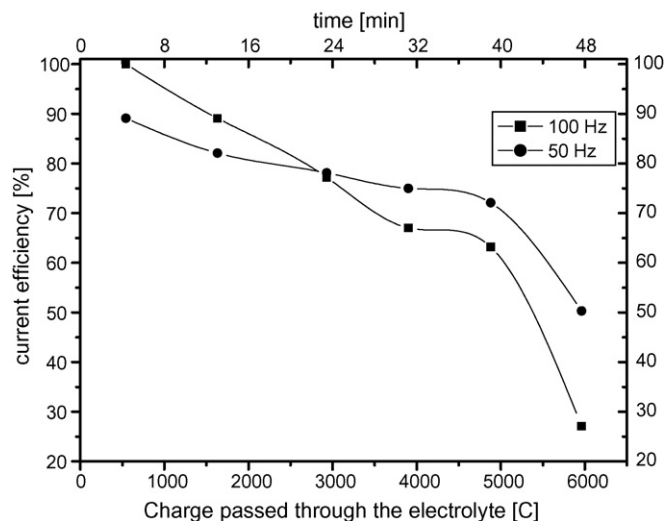$$Ti^0 + 3Ti^{4+} \rightarrow 4Ti^{3+} \qquad (2)$$



Fig. 2. Influence of the amount of charge passed through the melt and time of the current flow on the current efficiency of the deposition process for deposition frequencies of 50 and 100 Hz.

In the first deposition experiment a coulomb efficiency of approximately 100% was achieved, after passing the first 1500 Coulombs (C) trough the electrolyte the efficiency decreases slightly.

This behaviour was observed in all the deposition experiments using this electrolyte and steel and molybdenum substrates. After passing up to 5000 C through the electrolyte, the efficiency of the bath is dramatically reduced. This charge corresponds to a consumption of approximately 7% of the initial concentration of boron and titanium. Within this charge range, homogeneous and dense layers of $TiB_2$ with a crystallinity of <1 µm and a microhardness in the range of 2000–3000 HV were achieved. Fig. 2 shows a plot current efficiency versus charge passed through the electrolyte for two groups of samples plated with square wave pulses with equal cathodic and off times at 100 and 50 Hz. After each experiment the inner surface of the stainless steel cell was covered with a white, very hygroscopic powder. Samples of this white powder analyzed by X-ray diffraction showed the presence of $FeF_2$. The iron fluoride must be formed in the walls of the cell following the reaction:

$$2HF + Fe \rightarrow H_2 + FeF_2 \qquad (3)$$

where the HF is formed with the residual water that the system may contain (<30 ppm).

Melts containing tetrafluoroborates of alkali metals are known to undergo thermal decomposition following the reaction (4):

$$KBF_4 \rightarrow KF + BF_3(g) \qquad (4)$$

The formation of $FeF_2$ and $BF_3$ discussed above leads to changes in the chemical composition of the melt and therefore decreases the efficiency the electrochemical reaction (1), due to the decrease of the $B^{3+}$ complex concentration in the melt.

In investigating the effect of current density, $TiB_2$ layers were deposited on molybdenum samples using a plating temperature of 650 °C. A current sequence with square pulses with equal
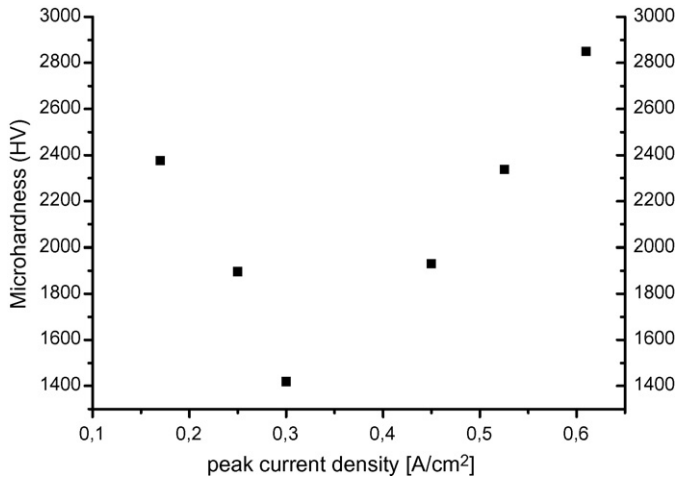
Fig. 3. Influence of the peak current density on the hardness of the deposited TiB$_2$ layers (measuring conditions: 200 p load for 10 s).

cathodic and off times at 50 Hz was used. The amount of charge flowing for each deposition was kept constant. The microhardness of the samples was measured, a plot of the values versus the peak current density (Fig. 3) shows a minimum at 0.3 A/cm$^2$.
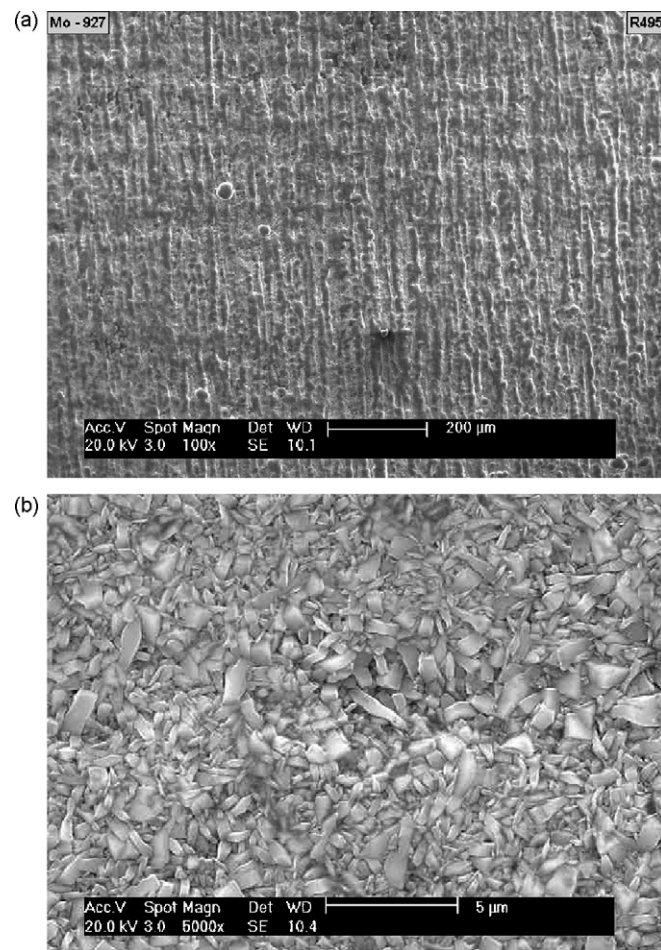


Fig. 4. Scanning electron microscopic picture of an electrochemically deposited TiB$_2$ layer; magnification: (a) 100× and (b) 5000× (600 °C and deposition time: 15 min).
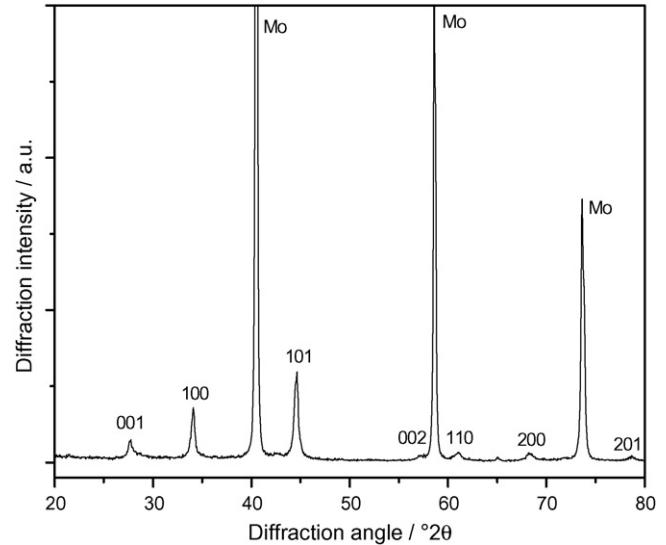


Fig. 5. X-ray diffractogram of TiB$_2$ layer deposited on molybdenum substrate. Molybdenum peaks are denoted by "Mo", the numbers refer to the crystallographic indices of the TiB$_2$ phase as given in ICDD-JCPDS database entry 35-0741.

The rise of hardness after the minimum can be a consequence of the grain refinement when plating at higher current densities. The hardness of the layers deposited at current densities below 0.3 A/cm$^2$ might be due to the change in the morphology of the TiB$_2$ layers.

Metallic titanium was added to the melt in order to produce the Ti$^{3+}$ needed for reaction (1). Nevertheless, Shapoval and Zarutskii [11] mentioned that the addition of Ti$^0$ produces other titanium oxidation states (reactions (5) and (6)) in addition to (2):

$$Ti^{4+} + Ti^0 \rightarrow 2Ti^{2+} \tag{5}$$

$$2Ti^{3+} + Ti^0 \rightarrow 3Ti^{2+} \tag{6}$$
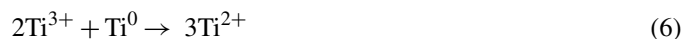
The presence of titanium(II) ions in the melt complicates the determination of the actual concentration of Ti$^{3+}$. A concentration of Ti$^{3+}$ in the range of the stoichiometric ratio (Eq. (1)) is of great importance for establishing a good quality of the TiB$_2$ layers and for a sufficient process stability in an industrial application.

The macroscopic appearance of the samples produced using various pulse sequences is very homogeneous. Fig. 4 shows a scanning electron microscopic picture of a TiB$_2$ layer produced. The TiB$_2$ layer obtained presents a fine grain structure, ranging from 0.5 to 3 μm crystal size. EDX-spectra of the sample just show the peaks corresponding to titanium and boron.

X-ray diffraction analysis ($\theta/2\theta$ geometry) shows the presence of TiB$_2$ reflections and reflections attributed to the substrate molybdenum (Fig. 5). All layers exhibit a texture behaviour. A detailed discussion will be reported elsewhere [12].

## 4. Conclusions

The efficiency of the NaCl–KCl–NaF-KBF$_4$–K$_2$TiF$_6$ electrolyte decreases with the use of the bath due to the

decomposition of the electrolyte. The best frequency to obtain smooth and hard TiB$_2$ layers in this melt using square wave current pulses was 100 Hz.

Dense TiB$_2$ layers were obtained from the NaCl–KCl–NaF–KBF$_4$–K$_2$TiF$_6$ melt by means of specially developed pulse sequences.

## Acknowledgements

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