Optimization of TiB$_2$ coatings electrodeposited
from halide melts

José Ricardo Assunção Godinho

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Jury
President: Maria Matilde Soares Duarte Marques
Supervisor: Alda Maria Pereira Simões
Specialist: Maria João Pedroso Carmesim

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Abstract

The electrodeposition of TiB$_2$ coatings was investigated under different conditions. The electrolyte used was FLINAK (LiF - NaF – KF) over the range of temperatures 580°C - 650°C, and the active substances used were K$_2$TiF$_6$ and KBF$_4$. The addition of TaCl$_5$ has been shown to improve the quality of the coating. The electrochemical technique used was periodically interrupted current (PIC), with different pulse shapes. Substrates of molybdenum, stainless steel and tungsten carbide with different geometries and areas were used.

Smooth, dense and adherent coatings were obtained for different conditions. The influence of temperature, electrolyte composition, current density, frequency of the pulses, substrate and impurities, was analysed and related to the quality of the coating.

Some of the coating properties were studied, such as adherence, texture (preferential orientation <001> or <001> + <110> in thicker coatings), roughness (Ra = 0.3µm - 2µm) and wetting in molten glass, microhardness (VH$_{0.5}$=2650-3200), crystalline structure, internal stress (-2GPa to -3GPa), composition of the layers, and corrosion stability in aluminum melts.

The deposition process on molybdenum cylinders with areas up to 53cm$^2$ was optimized. The coatings produced have the properties required to be used in the aluminum industry as a corrosion protection.

Keywords: titanium diboride, electrodeposition, FLINAK, molten salts, coatings.
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Chapter 1. Background

1.1 Introduction

Boron forms a wide range of compounds with transition metals\textsuperscript{[1]}. For example, TiB\textsubscript{2} presents some outstanding properties\textsuperscript{[2-5]} (see annex I), such as high hardness, high melting point, low electrical resistivity, good thermal conductivity, good thermal shock resistivity, and chemical resistance to molten metals and fluorides.

There are possible applications for each and every interesting property of TiB\textsubscript{2}\textsuperscript{[2,3,6-8]}. For its satisfactory resistance to neutron irradiation, TiB\textsubscript{2}-Ti cermets have been used for nuclear engineering. Its high hardness and wear resistance led to its use as a component in cermets for metal cutting and rock drilling, as well as wear-resistant coatings. The high temperature strength, refractiveness, and resistance to scaling in TiB\textsubscript{2} made it an interesting candidate in the composition of heat-resistant alloys, for example TiB\textsubscript{2}-CrB\textsubscript{2}. Its resistance to the action of molten metals combined with the linear dependence of electrical resistance on temperature makes the use of TiB\textsubscript{2} in electrodes feasible for high-temperature thermocouples, which can be used to measure the temperature of molten metals and alloys.

Some research groups have made progress in the electrodeposition process\textsuperscript{[9-12]}. However, all the available scientific information does not allow the implementation of the process on an industrial scale.

1.2 Esurf 1

Esurf 1 is a R&D project dealing with the electrodeposition of metal borides coatings from non-aqueous media. The electrolytes used are molten salts and ionic liquids. The project is financed by the industrial partners and the Austrian government through the Kplus program.

The primary goal of the project is to optimize the deposition parameters for the production of refractory coatings according to the special requirements of the companies involved. This includes the improvement of electrolyte composition in order to lower the working temperature and increase the conductivity, and the production of homogenous and smooth coatings on samples with non-trivial geometries.

The companies which contribute to the project are interested mainly in molybdenum substrates, for tools to be employed with molten metals, and on stainless steel and tungsten carbide substrates, for use as high temperature cutting tools.

The project started in 2000, and much work has been done, most of it on the optimization process using chloride fluoride melts\textsuperscript{[13-15]}. However, this electrolyte was abandoned due to the
high temperatures required, and all subsequent efforts concentrated on the use of FLINAK electrolyte (47%KF, 44%LiF, 9%NaF).

1.3 Theory

1.3.i Synthesis

There are different methods through which TiB₂ can be obtained:\cite{16}:

- Direct synthesis from the elements
- Synthesis from solution in melts
- Thermal reduction of metal oxides by metals
- Reduction of oxides and other compounds by nonmetals and their derivatives
- Gas-phase synthesis
- Magnetron sputtering
- Electrolysis from molten salts

Electrolysis from molten salts is one of the most promising techniques for the synthesis of refractory compounds. The advantages of this method are the rather simple initial compounds, the production of powders or coatings (while most of the other methods produce only powders), the unsophisticated equipment, the use of a relatively low temperature (below 800°C), and the possibility of regulating the morphology and composition of the product (with a lower concentration of impurities and pores in the coatings) through the appropriate tuning of the electrochemical parameters.

1.3.ii State of the art

The first steps on electrochemical synthesis of TiB₂ was published in 1929\cite{17,18}, reporting deposits of TiB₂ powder, from oxide melts at 950°C-1000°C, on graphite and Inconel substrates and using constant current. Over the next few decades different oxide melts were tried\cite{19,20} and in 1969, the first deposition of smooth and adherent coatings had been achieved on Inconel substrates at 900°C from a basic electrolyte of NaBO₂ and LiBO₂, with additions of Na₂TiO₃, Li₂TiO₃, and TiO₂\cite{21}.

After the 1970’s, there was a change concerning the electrolytes. It was found that deposition from halide-only melts improved the deposit properties and reduced the oxygen content in the form of TiO₂\cite{20,22}. Consequently the layer had a lower porosity and higher hardness. Another advantage of halide melts over oxide-containing melts is that their melting point is lower, which allows a decrease of the working temperature. The halides used for the electrosynthesis of TiB₂
are fluorides, chlorides, or mixtures of the two. The advantages of the chlorides as electrolytes are their lower costs compared to the fluorides, they are less corrosive towards the cell materials and substrates, and are more soluble in water, making them easier to analyze and remove from the product. The fluorides, on the other hand, usually give better yield and higher quality of the deposits, at lower temperatures.

There was a mounting interest during the 1980’s and the 1990’s in TiB₂ coatings for the aluminum electrolytic process, for its potential use as an inert cathode material. Therefore, Makyta and his group researched TiB₂ synthesis, in fluoride and fluoride-chloride melts, with K₂TiF₆ and KBF₄ as Ti and B donors, at temperatures above 750°C[23,24]. They were the first to study the mechanism of the cathodic reactions in LiF-KF-K₂TiF₆-KBF₄ and NaCl-KCl- K₂TiF₆- KBF₄ melts.

From the 90’s onwards some practical aspects of the deposition of different borides (e.g. TiB₂, ZrB₂, HfB₂) were clarified, along with basic electrochemical techniques and thermodynamic calculations for the synthesis of different borides[25,26,27,28]. In 1999 the first research using pulsed plating techniques was reported, with TiB₂ deposited from molten FLINAK, at 600°C[9,29]. The coatings obtained on graphite rods were optimized by both pulsed interrupted (PIC), and pulsed reversed (PRC) methods, as a function of the coating thickness. Recently, Jun Li and Bing Li studied some characteristics of electrodeposited TiB₂ layers[10,30].

1.3.iii Electrolyte

Molten salts form a liquid phase which can be considered as derived from either a gas or a solid, as it has some properties in common with both states[31]. For example, some short range order is preserved, similar to that found in the solid phase. On the other hand, above the critical point the transition between the liquid phase and the gaseous phase is continuous.

The properties of molten salts are not fully explained, and therefore their behavior is difficult to predict. Eyring et al. developed the theory of significant structures for molecular liquids[32], which was later applied to the interpretation of the structure of molten salts and salt mixtures[33,34].

The theory of significant structures states that each ion, in the solid phase, is symmetrically surrounded by a number of ions, the coordination sphere or nearest neighbors, which influence the central ion. This central ion has harmonic vibrations around its equilibrium position in the lattice. When the salt system is heated and expands upon melting, according to X-ray spectra, the long range ordering is destroyed.
The liquid consists of “significant structures” described by molecules with “solid-like” translational motions and other molecules which move in empty spaces with “gas-like” degrees of freedom. The properties of the liquid are then calculated from the weighted product of partition functions for the solid-like ions and the gas-like ions. This general approach can not only be used for molten salts but also for common molecular liquids.

A molecule can be solid-like at one moment and gas-like the next. This can be understood in terms of the possibilities available to any given molecule: either vibrate around an equilibrium position, or suddenly hop into a hole in the nearby space, gaining more degrees of freedom and thus approaching gaseous behavior.

This theory was corroborated\textsuperscript{[33]} for molten alkali halides with measurements of several properties (melting and boiling points, volume change upon melting, entropy change upon melting, and vaporization). However, there are some weak points to refer: there are no objective criteria for deciding whether a particle behaves in a solid-like or gas-like way at any given time, as this dichotomy is rather artificial, and the gas-like particles moving through holes are not as free as an ideal gas - a false assumption made by the theory. The measured change in volume upon melting of some molten salt systems was about 20%. This increase in volume was shown by X-ray diffraction analysis not to be associated with a corresponding increase in the distance between nearest neighbors. The theory of significant structures assumes that the volume increase at melting is due to two types of defects: holes and dislocations. These defects do not modify the distance between the nearest neighbors, but reduce the average coordination number, in agreement with experimental observations.

Another thermodynamic model\textsuperscript{[35]}, proposed by Temkin, takes into account the fact that the interaction forces in molten salts are very strong, and that the nearest neighbors of cations are anions, and conversely. Therefore the distribution of cations and anions in space is not random. The model, developed for ideal mixtures of molten salts, proposed the existence of two interlocking sub-lattices, one of anions and the other of cations. Deviations from ideal behavior can be calculated for all thermodynamic and transport functions of molten salts.

When it comes to establishing a molten salt process for industrial applications, the use of high temperatures is considered a disadvantage, since extra energy is required to keep the system in a liquid state. There are also problems associated with stricter safety protocols, equipment corrosion and melt decomposition.

There are as well other disadvantages, such as the hydrolysis of hygroscopic salts used in the electrolyte. Purification is often a prolonged process which requires considerable peripheral handling facilities.
Any molten salt solvent to be used in an industrial electrolytic process should have the following attributes:

- low vapor pressure
- high electrical conductivity
- low viscosity
- large decomposition voltage
- as non-corrosive as possible
- non-polluting
- inexpensive.

The first step towards achieving the goal of deposition at a lower temperature is the selection of suitable salt systems, focusing on the liquidus melting point. It is necessary to perform the deposition at, at least, 50°C above the liquidus melting point to ensure low viscosity, facilitating proper mass transport to the electrode, higher conductivity of the electrolyte, and greater solution homogeneity.

From the chemical standpoint, there are also some restrictions to consider, such as limitations on cations, which must have a deposition potential more negative than titanium and boron species. Also the anions should stabilize the active components, $\text{Ti}^{III}$ and $\text{B}^{III}$, by complexing them adequately, to achieve good solubility. The stability of the complexes formed is important, because it will significantly influence the deposition process.

Some of the investigated electrolytes present favourable properties (see annex II). However, the electrolyte should allow a working temperature which is low enough to prevent softening of the steel (below 650°C). The FLINAK electrolyte has proven\(^{[9,29]}\) to be efficient at these temperatures, presenting a low viscosity, high electrical conductivity, and efficient stabilization of the active substances. However, the highly corrosive environment causes some technical problems (see section 2.1).

1.3.iv Deposition techniques

The way that current flows in the system, causing the reduction on the cathode, strongly affects the mechanism of the reaction, and thus the properties of the coating.

The easiest technique is direct current (DC), by which the current is constantly supplied to the system, with the same density. The current can also be supplied not constantly but instead, in a given waveform – pulse plating (PP). Frequently direct current is interrupted by time “off” pulses – pulse interrupted current (PIC) – by which the voltage varies through the duration of the pulse.
A combination of cathodic and anodic pulses may be used, superimposed with a direct current, interrupted by time “off” pulses – pulse reverse current (PRC)[36].

Some previous studies[9,10,29] compare the deposition of TiB₂, by DC and PP, focusing on the tailoring of the deposit properties, namely, porosity, hardness, adhesion and roughness. The manner in which the deposit properties are affected by pulse plating is specific to each electrochemical system.

The advantages of PP compared to DC plating are:

- the larger number of parameters available to optimize give to the PP technique flexibility, allowing more variability regarding possible results
- PP produces dense, finer-grained deposits
- smoother deposits
- very crystalline layers are regularly obtained
- dendritic growth is less frequent
- the use of anodic pulses allows the preferential dissolution of the deposit from those areas that tend to overplate during the cathodic cycle (i.e., corners and edges), leading to a more homogeneous thickness distribution
- the current efficiency is, in most cases, better than in DC plating
- the required electrolysis times are shorter

The disadvantage of PP is the long and complex optimization process due to the large number of potential variables.

1.3.ν Parameters influence

Pulse plating technique have several parameters which can be manipulated in order to change the characteristics of the deposits, by affecting the reaction mechanism [36,37,38].

For the crystallization process to occur the active ions, BF₄⁻ and TiF₆⁻³, must be transported - by diffusion, convection, and coulombic migration - from the bulk of the electrolyte to the cathode surface. Once on the cathode surface the ions are reduced forming the metallic species Ti⁰ and B⁰. Due to highly favorable thermodynamics these species react easily to form TiB₂. This process occurs by two competing reactions: the formation of new nucleation sites and the growth of existing crystals.
Nucleation decreases the average distance between neighboring growing sites, reducing the surface diffusion distances and decreasing the maximum magnitude of the ad-atom concentration profile. A balance between this process and the competitive growth of existing crystals is then established, such that crystallization overpotential is kept as low as possible.

Once reduced, the atoms move along the surface until they find a suitable site, where they can incorporate into the crystal lattice. This movement is characterized by their surface diffusion rate, which is difficult to relate with the electrochemical parameters because it depends on the adsorption-desorption behavior of the different components in the electrolyte. For high surface diffusion rates, the population of reduced atoms at the surface is low and therefore the crystallization overpotential is low. In this case the growth of existing crystals is enhanced. Conversely, when the surface diffusion rate of the ad-atoms is low, their concentration at the surface is high, and therefore the crystallization overpotential is high. In this case new nucleation sites are preferentially created, which leads to a finer grained structure.

Immediately next to the cathode surface there is a pulsating layer, i.e., a layer in which the concentration decreases when the pulse is applied and relaxes back once it is over.

If the pulse is applied for a short time, as is generally the case, this first diffusion layer does not have time to extend very far into the solution, thus it does not reach the region where convection takes over mass transport. Therefore, from the bulk of the solution the ions must be transported by diffusion to the pulsating diffusion layer. This creates a concentration gradient in the bulk, which leads to a second layer. Ions also move through this outer diffusion layer during the off-time, and this transport is responsible for the relaxation of the pulsating diffusion layer. The outer diffusion layer is essentially stationary, therefore the magnitude of the slope of the concentration profile is much smaller in the stationary layer compared to the pulsating layer.

As a general rule, when the layer next to the cathode surface is strongly depleted of the active species, very rough deposits or powders are obtained. This prohibits the use of a current density close to the limiting current density in DC plating.

Well below the limiting current density, the current distribution is mainly governed by the geometry of the system, the conductivity of the electrolyte, and the overpotential due to the low rate of charge exchange at the electrode-solution interface. If the change of the overpotential with the current density is large enough, it equals the current distribution and there is no tendency towards the growth of the initial roughness.

When the current density approaches the limiting current density, the rate of the cathodic reaction is controlled by mass transport of the ions towards the cathode. Eventually, due to this mechanism, the initial roughness gets highly amplified, leading to the production of dendrites or powders.
In pulse plating, the pulsating diffusion layer can be made much smaller by using very short pulses, which results in peaks too large to be asperities, included in the diffusion layer. Now peaks and recesses are equally accessible to the ions, and the roughness does not get amplified, making higher peak current densities available while avoiding the undesirable production of dendrites or powders. This is valid as long as the outer diffusion layer does not suffer a strong depletion of active species.

The off-time is a very active period in which recrystallization processes, selective dissolution and new nuclei formation occur. Recrystallization is driven by the most stable thermodynamic state: larger crystal formation is therefore favored, especially with a larger $t_{\text{off}}$. However, if other species are blocking the growth zones, then the system generates new nuclei at each new pulse, while in the off-time some re-dissolution of the deposit takes place. The total observed effect is increased grain refinement.

In the case of $t_{\text{on}}$, it is difficult to generalize for every system, but it is usual to find crystal enlargement when $t_{\text{on}}$ increases, especially if approaching the limit of DC plating: $t_{\text{on}}$ large, $t_{\text{off}}$ very short.

When a pulse is applied, there is a drastic change in the current density from zero to a certain $j_p$ value, and then back to zero (i.e., as in PIC). This causes a subsequent abrupt change in the double layer state. Part of the current at the beginning of the pulse will be invested into charging the double layer – non-faradaic current – and the rest – faradaic current – will be used for the reaction on the electrode surface.

In DC electrolysis, the non-faradaic current is zero, meaning that all the charge is used in electron transfer processes. In PP electrolysis, the faradaic current that is lost for non-faradaic processes – double layer charging – at the beginning of the pulse is recovered, if there are no side reactions involved, at the end of it, resulting in a 100% efficiency for the deposition.

1.3. Mechanism

Makyta et al. studied the behavior of titanium and boron by adding K$_2$TiF$_6$ and KBF$_4$ to a LiF-KF eutectic mixture$^{[39,40]}$, obtaining the following results.
Fig. 1-1 shows the voltammogram of the pure supporting electrolyte, at 750°C, with a scan rate of 1V.s⁻¹. It can be seen that there are no important impurities present, although there are some features in the spectrum not discussed by the authors, e.g. a redox couple with peaks at approximately –0.38 V in the anodic direction and –0.55 V in the cathodic direction.

Fig. 1-2 shows three different voltammetric curves, performed in melts of different compositions. Curve 1 is the LiF-KF equimolar eutectic mixture electrolyte plus K₂TiF₆ (0.3 mol%). Curve 2 is the LiF-KF basic supporting electrolyte with addition of KBF₄ (0.5 mol%). Curve 3 is the melt
that contains both active species, for the synthesis of TiB₂: LiF-KF, K₂TiF₆ 0.3 mol%, KBF₄ 0.6 mol%. These three curves were measured at a scan rate of 1 V.s⁻¹ and at a temperature of 750°C, with a platinum wire working electrode (Area: approximately 0.2 cm²).

Curve 1 shows the reduction of Ti⁴⁺ to metallic titanium. The mechanism for this reduction is:

\[
\text{Ti(IV)} \rightarrow \text{Ti(III)} \rightarrow \text{Ti(0)}
\]

where the first reduction step, Ti⁴⁺ → Ti³⁺, occurs at approximately −1.80 V, and the second step, Ti³⁺ → Ti⁰, at roughly −2.55 V (all the potential values are referred in this case to the dissolution potential of platinum). Comparing with Fig. 1-1 the last reduction process occurring at −3.0 V is the deposition of the alkali metal.

Curve 2 shows a single maximum at nearly −2.55 V, which can be assigned to the 3-electron reduction:

\[
\text{BF}_4^- + 3 \text{ e}^- \rightarrow \text{B} + 4 \text{ F}^-
\]

The position of this maximum is independent of the concentration of the electrochemically active species and the scan rate.

Curve 3 shows a maximum at approximately −2.6V, slightly more negative than for the reduction peaks for titanium and boron. It corresponds to the electrosynthesis of TiB₂. The shoulder at approximately −2.55V corresponds to the boron reduction peak, since the ratio Ti:B is not exactly stoichiometric (boron is in excess).

In order to determine which type of electrode process each reaction corresponds to, the dependence of peak current on the scan rate was studied. In a reversible deposition of an insoluble substance based on a simple charge transfer electrode process – the rate of which is controlled by the diffusion of the electrochemically active species, the dependence of the peak current on scan rate can be described by the relation:

\[
Ip = 1.056 \times 10^6 \times D_0^{1/2} A C_{0,b}^{1/2} \nu^{1/2}
\]

Eq.1

\(D_0\): diffusion coefficient \((\text{m}^2.\text{s}^{-1})\),

\(A\): area of the electrode \((\text{m}^2)\),

\(C_{0,b}\): concentration of the active species in the bulk of the electrolyte \((\text{mol m}^{-3})\),

\(\nu\): scan rate used for polarizing the working electrode \((\text{V.s}^{-1})\),
From equation 1 the linear dependence of the peak height on the square root of the scan rate is evident, which can be used as a criterion for the determination of the type of electrode reaction. This relationship is plotted in:

Fig. 1-3: Dependence of the peak current, $I_p$, on the square root of the scan rate, $\sqrt{\nu}$, in the system electrolyte $+$ KBF$_4$. Full lines: experimental; Dashed lines: theoretical; 1- [KBF$_4$]=42 mol.m$^{-3}$; 2- [KBF$_4$]=67 mol.m$^{-3}$; 3- [KBF$_4$]=136 mol.m$^{-3}$; 4- [KBF$_4$]=217 mol.m$^{-3}$.

The best fit for the equation is observed only at low scan rates ($\nu < 1$ V.s$^{-1}$), as the deviation between the experimental dependence and the calculated linear relationship is larger at increasing scan rates.

Makyta and his group explained this behavior by proposing a gradual shift in the character of the electrode process from reversible to partially irreversible.

Based on an analysis of curves 1 to 3 as well as additional electrochemical analysis, Makyta et al. proposed the following reaction steps for the electrochemical synthesis of TiB$_2$ in the system LiF-KF-K$_2$TiF$_6$-KBF$_4$:

$$\text{TiF}_6^{2-} + e^- \rightarrow \text{TiF}_6^{3-} \quad E = -1.7 \text{ V} \quad 3$$

$$\text{TiF}_6^{3-} + 2 \text{BF}_4^- + 9 e^- \rightarrow \text{TiB}_2 + 14 \text{F}^- \quad E = -2.4 \text{ V} \quad 4$$

The steps involved in reaction 4 are not yet clear.

Given the complexity of studying electrode processes in molten salts, it is no surprise that agreement on interpretation issues is seldom found in the literature, and the interpretations are
more often guesses instead of facts. There are two different hypotheses concerning the mechanism of the ion-adatom step.

The thermodynamic model, proposed by Taranenko et al.\cite{41}, states that intermetalldes, can be deposited at a joint potential due to the formation of heteronuclear complexes in the molten system, thus allowing the components in the substance to be co-deposited with the right stoichiometry.

Deposition of such heteronuclear complexes takes place in one step, with the immediate formation of the intermetallide on the cathode at a single potential value, resulting in the follow mechanism.

\[
[\text{BF}_4^-\text{TiF}_6^{3-}\text{BF}_4^-] + 9 \text{e}^- \rightarrow \text{TiB}_2 + 14\text{F}^- 
\]

The authors claim that the assumption of the structure of the heteronuclear complex is supported by the preferential deposition of TiB\textsubscript{2} in the synthesis, the appearance of the superfluous component, Ti or B, in the cathodic deposit at molar ratios \([\text{Ti}] : [\text{B}] \neq 1:2\), and by the increased stability of MBF\textsubscript{4} in the melt.

Nonetheless, evidence that these complexes exist in the electrolyte has yet to be proven.

The second model, proposed by Kaptay\cite{42} does not assume any specific complex structure for the active species in solution. It is instead based on adatom-adatom interaction at the surface.

It is known from basic electrode kinetics that the cathodic process for the deposition of a given element, i.e., boron or titanium, takes place at a certain rate even at potentials more positive than the equilibrium potential. At this more positive potential value, however, the rate of the anodic process is higher, which leads to a redissolution via oxidation of all reduced adatoms appearing at the cathode surface. If instead two different adatoms appear and contact, the energetic environment may be favorable for them to stay on the surface, in the form of a compound. Thus, the deposition of the compound can occur at a more positive potential value than the potentials for the reduction of any of its components.

Kaptay concludes that as the electrode processes in molten salts have very high exchange current density values, this consecutive mechanism is feasible.

Both mechanisms fail to explain some experimental evidences, and do not allow us to predict favourable experimental parameters.
Also none of the proposed mechanisms consider the hexagonal structure of titanium diboride\textsuperscript{[43]}. According to this structure boron atoms are bonded not only to the metal but also to other boron atoms, as shown in Fig. 1-4 (see crystalline parameters in annex 1). Conductivity studies\textsuperscript{[44]} conclude that boron atoms are also bonded in different plans, like graphite.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1-4}
\caption{TiB\textsubscript{2} structure.}
\end{figure}
Chapter 2. Experimental

2.1 Equipment

The layers were characterized with an environmental scanning electron microscope (Philips XL-30 ESEM) equipped with an energy-dispersive X-ray spectrometer (EDX), a X-ray diffractometer (Philips XR MPD), an optical microscope (Olympus GX51) equipped with a microhardness tester (Anton Paar MHT-10), a profilometer (Mahr S2), a raman spectrometer (Horiba Lab Raman Aramis).

The samples used have different geometries which are shown in Fig. 2-1 along with their respective surface areas. Sample 1 is a tungsten carbide alloy with cobalt as a binder (WC). Sample 2 is constituted of a stainless steel alloy (St) specially designed for high temperature applications\(^1\). Samples 3 and 4 are composed of molybdenum (Mo).

1 – 13 cm\(^2\) (tungsten carbide)

2 – 17 cm\(^2\) (stainless steel)

3 – 17 cm\(^2\) (molybdenum)

4 – 52 cm\(^2\) (molybdenum)

Fig. 2-1: Geometry of the samples and correspondent areas and composition.

The high temperature cell (see Fig. 2-2 and annex III) currently used is the result of long a process of optimization. Due to the high temperatures, and vacuum maintained within the cell, the extreme corrosive environment and strict safety protocols, the materials and equipment used are not trivial.

The cell is comprised of two main parts, the oven and the evacuation chamber. The oven heating system consists of electric heating coils attached to a stainless steel chamber, which is covered with a thermal isolator. The bottom is lined with stones which isolate the crucible and prevent the dispersion of current out of the system. The crucible holder sits directly on the

\(^1\) The composition is a secret of Swarovski Co.
stones and fits the glassy carbon crucible which contains the melt. The crucible has cylindrical shape and a total volume of 3L. The current is passed through a stainless steel rod connected to a graphite block attached to the crucible holder. The thermocouple and the rod outlets are isolated from the cell wall with pieces of Teflon. The evacuation chamber is separated from the oven by a water cooling section, and a sliding pressurized door. Two CaF₂ windows, one on the top and the other in the middle, allow the operator to see the melt and the sample. The sample holder, made of stainless steel, is connected to a water cooling system, and is attached to the top of the evacuation chamber by a sealing ring system, which allows it to be lifted. It is also connected to an engine, which can be used to rotate the sample. The air outlet is connected to a carbon filter, which is connected to the pump. All the parts of the cell are sealed by vacuum systems, with high temperature resistance.

Fig. 2-2: Cell scheme. Water flow in green.

This cell is only experimental, and some operational problems were detected and can be solved.
• For the use on an industrial scale, the dimensions can be optimized according to the size of the sample, reducing the cost of the process.

• The sample holder is frequently corroded after some experiments, a problem which can be solved by changing from stainless steel to nickel.

• The isolation stones should be substituted with a permanent isolation system.

• The water cooling system should cover all parts of the extraction chamber.

• The carbon filter should be replaced with a system more efficient in retaining fluorides.

2.2 Techniques

2.2.i Electrolyte and temperature

The electrolyte used is an eutectic mixture of KF – NaF – LiF, with a total solid volume in the range of 500ml to 650ml. Due to the large quantity of chemicals used in each experiment, lower-purity chemicals are used. However, if costs were not an issue higher purity chemicals would be preferred.

The melting point of the electrolyte is 454ºC. However, to assure low viscosity, high conductivity and homogeneity, the experiments were performed in the range of temperatures between 580ºC and 650ºC, with an error of ±5ºC.

The electrolyte used had the composition shown in Tab. 2-1:

<table>
<thead>
<tr>
<th>Substance</th>
<th>KF</th>
<th>NaF</th>
<th>LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (mol%)</td>
<td>47.3</td>
<td>8.7</td>
<td>44</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

Tab. 2-1: Electrolyte composition.

In addition to the electrolyte two ratios of active substances were used, one including tantalum and another without (Tab. 2-2):

<table>
<thead>
<tr>
<th>Substance</th>
<th>KBF₄</th>
<th>K₂TiF₆</th>
<th>TaCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Ta</td>
<td>5.8</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>With Ta</td>
<td>5.8</td>
<td>1.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Purity (%)</td>
<td>&gt;97</td>
<td>&gt;98</td>
<td>99.8</td>
</tr>
</tbody>
</table>

Tab. 2-2: Active substances ratio.
2.2.ii  Drying of the chemicals

The fluoride salts used are hygroscopic, especially KF. In order to remove the undesirable water, several procedures were tried. The following procedure has shown to give reproducible results:

- Drying of the electrolyte in a vacuum oven between 100-200ºC for at least 24h.
- Drying of the active substances in a vacuum oven between 100-105ºC for at least 24h.
- Pre-melt the electrolyte at 500ºC (50ºC over the boiling point).

2.2.iii  Samples pre-treatment

The molybdenum and tungsten carbide samples were pre-treated in the supplier company. The methods used were, degreasing in a solution 30% NaOH, etching in a solution 10% HNO₃, and sand blasting with Al₂O₃ 300 mesh at 2.5bar.

The procedure which gave better results when using stainless steel substrates was:

- Degreasing in an ultra sonic bath using ethylacetate for 10min,
- Degreasing in an ultra sonic bath using a solution NaOH(10%) for 5min,
- Etching in an ultra sonic bath using a solution H₂SO₄ (10%) for 1 min,
- Sandblast under 8-9bar pressure.

2.2.iv  Oven operation

Before every sequence of experiments the melt is electrochemically cleaned using a current density of -0.2A.cm⁻², for 30-60min, to eliminate the impurities contained in the commercial salts and others associated with the crucible and the handling of the salts.

Every time the oven is opened, the upper section is evacuated and filled with Argon three times, to avoid contamination of the room with fluorides and to cool the sample avoiding substrate oxidation.

For safety reasons the operators should wear gloves and a mask.

After insertion of the sample the upper part is closed, and then evacuated and filled with Argon three times to avoid the contamination of the melt with oxygen or water.

Before every deposition the sample is left in the melt for thermal equilibration, under cathodic protection.
- Mo: 10min. -0.1 mA.cm$^{-2}$
- St: 3-5min. -0.2 mA.cm$^{-2}$
- WC: 3-5min. -0.1 mA.cm$^{-2}$

In a daily experience eight samples can be coated with reproducible results.

### 2.2.\nu Parameters

CD, PIC and PRC techniques were tested in the optimization process. However, better results were obtained when PIC was used. Fig. 2-3 shows the three different pulse shapes used. The main optimization process was done using pulse shape 2.

![Figure 2-3: Difference in the pulse shapes used (current intensity vs duration of the pulse).](image-url)
2.2.vi Sample cleaning

It is important to remove the salts from the sample before the analysis. The following steps assure a cleaned surface.

- Boiling distilled water (1h)
- 0,5% HCl solution (4h)
- Rinsed with acetone

2.2.vii Cross section preparation

For a good analysis of the cross section the surface must be polished after cutting, which can damage the coating. To avoid that, the samples are covered with nickel, electrodeposited in a Watt bath\textsuperscript{2}, for 30min. using a current density of -70mA/cm\textsuperscript{2}, at 50ºC. The samples are then covered with a hot pressed resin. It is important that this resin is conductive and presents low porosity, for the SEM analysis. After that the sample is cut and then polished with Si-C grinding papers.

2.2.viii Sample analysis

- X-ray - Detection of TiB\textsubscript{2} peaks, preferential orientation, crystallite size, internal stress, cell volume;
- SEM - roughness, homogeneity, quantification of the elements present in the coating, crystal size (see annex VIII);
- Cross section - analysis of the interlayer substrate-coating, thickness, homogeneity;
- Roughness analysis - average surface roughness measurement, crystal size;
- Vickers micro-hardness - in cross section and surface;
- GDOES - composition of the coating and substrate in depth (see annex VIII);
- Raman - identification of surface compounds, detection of impurities;
- Corrosion tests - stability in aluminum melts.

\textsuperscript{2}NiSO\textsubscript{4} (1M), NiCl\textsubscript{2} (0.21M), H\textsubscript{3} BO\textsubscript{3} (0.51M)
Chapter 3. Results and discussion

3.1 Introduction

All work previously performed on the electrodeposition of TiB₂ coatings does not allow the utilization of this technique on an industrial scale. No previous studies have made a global comparison between the different parameters which affect the quality of TiB₂ coatings. This global approach is important in order to make the process useful for industrial purposes.

Due to the objective of this project (optimization of the electrochemical process in order to obtain coatings with defined properties), some of the parameters were not exhaustively studied. Therefore, some of the results presented in this chapter were obtained parallel to the main goal.

3.2 Temperature and electrolyte

The first problem in the optimization process is determining the composition of the system to be used. The composition of the eutectic mixture used as the electrolyte, FLINAK, is well known. According to our studies the best relative quantities of the active substances was found to be a K₂TiF₆:KBF₄ molar ratio of 5.8:1.

MoCl₅, CoCl₂ and TaCl₅ were tested as additives to the FLINAK melt. The presence of Ta(V) in the molar proportion 1(Ta):17(Ti):85(B) in the melt, results in a substantial improvement of the coating properties, decreasing the tendency for holes to form when low current density was used, and decreasing the formation of dendrites when high current density was used. The X-ray diffractograms do not identify tantalum species, but the peaks correspondents to TiB₂ are shifted. However, the presence of this element is visible in the EDX, which show some places of higher concentration (white spots in Fig. 3-1), where spherolitic growth is observed.

Fig. 3-1: Uneven distribution of Ta in the coating. High concentration visible as white spots.
The effect of tantalum is not fully understood but it is proposed that the similar covalent radius and electronegativity, when compared with titanium, causes an additional stabilization of the coating’s crystalline structure. Some special properties of coatings with tantalum will be discussed further on this chapter.

According to reference [49], it is possible that a continuous series of solid solutions between TaB$_2$ and TiB$_2$ exists.

Neither molybdenum nor cobalt had positive effects, the coatings obtained were uneven.

Once the composition of the system is optimised the next step was to find the lowest operating temperature which still produces good coatings. Varying the temperature of deposition strongly affects the deposition, by changing thermodynamic and kinetic parameters. As the temperature is decreased, the viscosity of the melt increases, and thus decreases the diffusion rate of the active substances, having obvious consequences for the double layer (previously discussed 1.3.v). Also the thermodynamic properties of the reactions are affected but with less predictable consequences, especially in the crystallization mechanism already discussed (1.3.vi). However, the Gibbs energy of formation for TiB$_2$ becomes more negative as the temperature is lowered (within the working range) [7], favouring the reaction. At the interface substrate - coating, the temperature effect is unclear, and is difficult to generalise for different substrates.

The lower deposition temperature limit was 580ºC. At this temperature the coating presented some adherence and homogeneity problems. However, it was possible to obtain homogeneous coatings at 600ºC, though the smoothest were obtained at 650ºC over a molybdenum substrate.

### 3.3 Deposition optimization

From the techniques used, PIC produced the best results and was more intensively studied. Different parameters were tested and divided in different ranges of values (Tab. 3-1, Tab. 3-2 and Tab. 3-3) to facilitate the comparison.

| Tab. 3-1: Range of parameters studied, on Mo and St substrates, and melt without Ta. |
|-----------------|------------------|----------------|-----------------|-----------------|-------------------|
| $j_1$ (A.cm$^{-2}$) | $j_2$ (A.cm$^{-2}$) | $j_3$ (A.cm$^{-2}$) | $\nu$ (Hz) | Temp (ºC) | $T_{tot}$ (s) |
| 0,7-0,9 | 1,77-2,2 | 0 | 36 | 580-650 | 600 |

All steel samples show bad adhesion, being the deposits formed powder (Fig. 3-2). At these current densities the deposition of metallic titanium also occurs. Better results were obtained when using molybdenum substrate, however the coatings are frequently uneven and very rough.
A comparison of deposits on molybdenum at different temperatures can be seen in Fig. 3-3. In both samples the coating has holes below the powder deposited on the surface. At lower temperatures the coating has more cracks and is more uneven.

As discussed in 1.3.ν nucleation is favored when high current densities are used. Also, is easier the depletion of active ions in the diffusion layer, leading to uneven coatings.

It is possible to conclude that this range of current density values is too high for the formation of homogeneous and compact coatings.

| Tab. 3-2: Range of parameters studied, St substrate, and melt without Ta. |
|-----------------|-----------------|-----------------|-----------|-----------|-----------|-----------|
| $j_1$ (A.cm⁻²) | $j_2$ (A.cm⁻²) | $j_3$ (A.cm⁻²) | $\nu$ (Hz) | Temp (ºC) | $T_{tot}$ (s) |
| 0,45-0,75       | 0,72-1,37       | 0              | 56        | 580-625   | 200-600    |

Under this range of conditions, the coatings presented similar properties. Below 600ºC the coating became rougher and less adherent. At the higher current densities larger dendrites were observed. Fig. 3-4 shows one of the best results, which obtained a coating with 6μm
thickness and a Vickers microhardness of 3200 (surface) and 2700 (cross section). However, the surface is too rough.

![SEM image of a sample obtained, on Mo substrate, with the following parameters: j₁=-0.5 A.cm⁻², j₂=-1.2 A.cm⁻², T=605°C; tₜot=200s.](image)

**Fig. 3-4:** SEM image of a sample obtained, on Mo substrate, with the following parameters: $j_1=-0.5\,\text{A.cm}^{-2}$; $j_2=-1.2\,\text{A.cm}^{-2}$; $T=605^\circ\text{C}$; $t_{\text{tot}}=200\,\text{s}$.

The lower working temperature was settled to 600°C. In order to reduce the roughness, lower current densities must be used. The total time of deposition must be increased to obtain thicker coatings.

<table>
<thead>
<tr>
<th>$j_1$ (A.cm⁻²)</th>
<th>$j_2$ (A.cm⁻²)</th>
<th>$j_3$ (A.cm⁻²)</th>
<th>$v$ (Hz)</th>
<th>Temp (°C)</th>
<th>$T_{\text{tot}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07-0.7</td>
<td>0.07-0.7</td>
<td>0</td>
<td>43-56</td>
<td>650</td>
<td>600-1200</td>
</tr>
</tbody>
</table>

All molybdenum substrates were coated with a layer of 5-20μm. The smoothest coatings were obtained when lower current densities were applied (Fig. 3-5). At high current densities uneven coatings were obtained as can be seen in Fig. 3-6.

Under this range of parameters the results were highly reproducible. However, the coatings are more susceptible to impurities, when present.
The smoothest coatings (Ra=0.8 μm), on molybdenum samples, were obtained when using the pulse shape 3, in which the two pulses were separated by a rest period (Fig. 3-7). The X-ray analyses show a shift in the usual TiB$_2$ peaks, which suggests a different synthesis mechanism and structural organisation.

These results are difficult to explain with the information available on the electrosynthesis mechanism.

**Fig. 3-5:** SEM image of a sample obtained, on Mo substrate, with the following parameters: $j_1$=-0.07 A.cm$^{-2}$; $j_2$=-0.13 A.cm$^{-2}$; $\nu$=56Hz; $t_{tot}$=1200s.

**Fig. 3-6:** SEM image of a sample obtained, on Mo substrate, with the following parameters: $j_1$=-0.3 A.cm$^{-2}$; $j_2$=-0.7 A.cm$^{-2}$; $\nu$=43Hz; $t_{tot}$=1200s.
This range of parameters produce coatings, on molybdenum samples with geometry 4, with the properties required for the industry.

The optimization process is not finished for stainless steel or tungsten carbide substrates. However, the best coatings were obtained with these ranges of parameters. Nevertheless they do not satisfy the required quality.

The adherence and homogeneity of coatings on steel substrates (discussed in section 3.4.ii) still need to be improved. The optimization process is more difficult because stainless steel substrate is more susceptible to current density variations than molybdenum. In Fig. 3-8 a promising result can be seen, though the coating is uneven, with pores and cracks.
When using tungsten carbide samples, with geometry 1, the coatings present some cracks at
the edges (discussed in section 3.4.iii), as can be seen in Fig. 3-9. The edges are the most
critical part of the sample because they are exposed to brazing and wear.

![SEM image of a coating obtained, on WC substrate, with the following parameters: \( j_1 = -0.3 \text{A.cm}^{-2} \); \( j_2 = -0.14 \text{A.cm}^{-2} \); \( \nu = 58 \text{Hz} \); \( t_{\text{tot}} = 1200 \text{s} \).](image1)

**Fig. 3-9:** SEM image of a coating obtained, on WC substrate, with the following parameters: \( j_1 = -0.3 \text{A.cm}^{-2} \); \( j_2 = -0.14 \text{A.cm}^{-2} \); \( \nu = 58 \text{Hz} \); \( t_{\text{tot}} = 1200 \text{s} \).

### 3.4 Substrate

#### 3.4.i Reactivity in the melt

Several times it was found that after the deposition the sample weight was lower than before the
deposition. Traces of iron, molybdenum and chromium compounds were occasionally found on
the surface or within the coatings (Fig. 3-10).

![SEM picture of some molybdenum particles over the coating, as white particles.](image2)

**Fig. 3-10:** SEM picture of some molybdenum particles over the coating, as white particles.
The logical explanation for these observations is the dissolution of the substrate during the pre-heating of the sample. However, this was not expected due to the cathodic protection applied during this time. In order to understand what is happening during this time some tests were performed with molybdenum substrate.

First, the influence of the current density\(^3\) in the dissolution was studied. It was expected that an increase on current density decrease the oxidation of the molybdenum surface, and thus decreasing the molybdenum dissolution in the melt.

A linear correlation was found (Fig. 3-11), but contrary to what was expected, the increase in current density led to an increase in dissolution.

![Fig. 3-11: Linear correlation between current density and weight lost per area. The samples were placed in the melt for 10min.](image)

The second study relates the weight lost per surface area with the exposure time of the substrate in the melt. A linear relation was also found, which allows the extrapolation of the dissolution rate directly from the slope of the graphic in Fig. 3-12.

---

\(^3\) Cathodic current
The dissolution of molybdenum in the electrolyte (without active substances) was also tested. The result was a decrease in the dissolution rate, the magnitude was about three times lower then the rate determined with active substances (Tab. 3-4).

<table>
<thead>
<tr>
<th>Melt</th>
<th>Dissolution rate (mg.cm(^{-2}).min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLINAK</td>
<td>0.019</td>
</tr>
<tr>
<td>FLINAK + active substances</td>
<td>0.058</td>
</tr>
</tbody>
</table>

When the test was performed in a melt containing active substances, the sample surface was covered with a black powder (after the test). This powder was removed from the surface of the sample using an ultrasound bath. Both the sample surface and powder were analyzed by Raman spectroscopy, X-ray and EDX quantification (see annex IV). The powder was a mixture of the melt salts together with a compound also detected on the sample surface which has not yet been identified.

The EDX show the presence of carbon, oxygen, molybdenum and boron in the proportions given in Tab. 3-5.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>44</td>
</tr>
<tr>
<td>C</td>
<td>8</td>
</tr>
<tr>
<td>O</td>
<td>4</td>
</tr>
<tr>
<td>Mo</td>
<td>44</td>
</tr>
</tbody>
</table>
The carbon detected by EDX and GDOES was identified by Raman as amorphous graphite. It was not possible to attribute the three peaks between 380 cm\(^{-1}\) and 460 cm\(^{-1}\) to any compound. No peaks corresponding to molybdenum oxides were found, nor were the peaks corresponding to Mo\(_2\)B and MoB. The peaks might be associated with other molybdenum borides like Mo\(_2\)B\(_5\) or MoB\(_2\), but no literature was found to support this theory. Also, the straight shape of the peaks suggests a well defined structure.

The x-ray diffractogram corresponding to the surface of the sample after experiments identifies the peaks corresponding to molybdenum and an extra single peak. This correspond to the most intense peak of MoB\(_2\) or one of the peaks of TiO\(_2\). However, the other peaks corresponding to these compounds were not detected (see annex V).

The GDOES only detects small amounts of boron (less that 1\%), within the uppermost micron of the substrate surface. This suggests that the Mo – B compounds are only formed on the surface, as the diffusion of boron into the substrate was not detected by this method. For this reason the low value of boron detected is not reliable.

An increase in the current density can cause a higher rate of formation of molybdenum borides on the surface. The higher rate of dissolution when boron species are present in the melt, and the higher solubility at higher potentials suggest a higher solubility of these borides.

The mechanisms which lead to the oxidation of molybdenum, even under cathodic protection, are not understood. However, the presence of metallic boron on the surface, when no current is applied, suggests electron transference at the surface leading to the oxidation of molybdenum. This phenomenon should be studied in more detail by cyclic voltammetry.

If the deposition process starts at the moment when the sample is inserted into the melt, the result is frequently uneven coatings. This observation was explained by thermal shock which minimizes the adherence of the first layers. This study suggests that the reactions between the melt and the sample change the surface having a positive effect on the adherence of the coating.

3.4.ii Adherence

The relationship between the parameters and the quality of the coating differs depending on the substrate composition. This can be explained by the different compounds formed at the interface coating – substrate. The first interfacial layer has a direct influence on the rest of the coating.

The following compounds can be formed at the interface, depending on the substrates.
Molybdenum substrate: MoB, MoB₂, Mo₂B₅, Mo₃B₂, MoB₄

Stainless steel substrate: FeTi, Fe₂Ti, Fe₃B, Fe₂B

Tungsten carbide substrate: WB₄, W₂B₅, WB₂, WB, CB₄, TiC, TiC₄

For the substrates considered, molybdenum had the highest affinity with boron, forming different species\(^{[46,47]}\) \(\text{Mo}_n\text{B}_m\), being the most favourable \(\text{Mo}_2\text{B}_5\), resulting in the best coating adherence. However, the surface should still be appropriately pre-treated, in order to provide a good rate of boron diffusion. The best results were obtained with sandblasted samples.

The compounds in the Fe-Ti-B system are form less readily. In the system Ti-B-W-C some complexes are stable at high temperatures, and their formation is favoured. However, it is difficult for these complexes to diffuse through the very stable WC structure.

Steel and tungsten carbide substrates show adherence problems at low temperatures. This can be explained by different studies\(^{[48,49]}\) which show that diffusion of boron in different hard metals is only significant over 700ºC. On the other hand the diffusion of boron within molybdenum occurs easily\(^{[46]}\), as can be seen in the cross section analysis in Tab. 3-6. Boron has been detected in the substrate at depths of up to 60µm into the substrate.

### Tab. 3-6: Relation Ti:B:Mo, obtained by EDX quantification at the interface coating-substrate.

<table>
<thead>
<tr>
<th>Coating close to substrate</th>
<th>B/Ti = 2.19; Mo &lt; 1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate close to coating</td>
<td>B/Mo = 1.5; no Ti</td>
</tr>
</tbody>
</table>

The GDOES depth quantification (Fig. 3-13), gives evidence of the presence of higher boron concentration within the interlayer. In the first 4µm (line 1) from the top only the coating was detected, with a Ti:B ratio of 1:1.86. Over the next 5-6µm (line 2) the titanium percentage decreases, while the molybdenum percentage proportionally increase. However, the percentage of boron remains the same, indicating the presence of a molybdenum boride interlayer. Approximately 14% of the boron is associated with about 8% of molybdenum, suggesting the presence of an average ratio of \(\text{Mo}_0.\text{B}_{1.75}\). The proportion between molybdenum, boron and titanium is approximately the same, across line 3 – %Ti = %Mo – and line 4 - %Mo = %B – for different samples. At approximately 14µm the proportion of Ti:Mo:B is 1:1:2.6 (line 3). At approximately 19µm the proportion of Ti:Mo:B is 1:2.7:2.7 (line 4).

The diffusion process is explained by the small atomic radius of boron, which can penetrate the structure of molybdenum. However, boron has a low inter granular solubility which causes a low

\(^{4}\) Also other constituents of stainless steel, like Cr or V form stable borides.
degree of penetration. The bound formation in the lattice spaces causes a decrease in the interfacial free energy. This should increase the affinity for initial TiB₂ layers, improving the adherence and homogeneity of the coating, and the reproducibility of the technique. There is no known crystalline structure with the three atoms Mo – B – Ti.

An analysis of the GDOES depth quantification of a TiB₂ coating on a stainless steel substrate indicates a proportional decrease in the percentage of boron and titanium (Fig. 3-14). This indicates that no boron is diffusing into the substrate, thus the adherence is lower than in the molybdenum samples.

Some iron was also detected in the coating, which may be due to diffusion into the coating. The high percentage of boron can be attributed to the compounds missing from the steel, which are also detected by the analysis but eliminated from the graphic for simplification.
When comparing the thermal expansion coefficients (Tab. 3-7) of the different substrates, stainless steel is shown to have the highest value. As the sample cools the substrate compresses 2-3 times more that the coating, which can cause low adherence and cracks.

**Tab. 3-7:** Comparison of thermal expansion coefficient$^{[500]}$ of the different substrates with TiB$_2$.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Thermal expansion coefficient ($\mu$m $\times 10^6$/m$^0$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB$_2$</td>
<td>4.6</td>
</tr>
<tr>
<td>Mo</td>
<td>5-6</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>11-16</td>
</tr>
<tr>
<td>Tungsten carbide cermet</td>
<td>4-7</td>
</tr>
</tbody>
</table>

In previous results we can see that under the same conditions, the homogeneity of the coating is different for stainless steel and molybdenum substrates. The difference in the thermal expansion coefficient can only explain some of the cracks, but not the difference in homogeneity. This suggests that there is an optimal current sequence for different substrates, and this initial layer will strongly influence the rest of the deposition.

Due to the thermodynamic differences in the formation of the interlayer complexes and the predominant concentration of boron or titanium, the conditions of the interlayer electrodeposition should be different for different substrates, and also from the rest of the deposition process.
After a few nanometers of the interlayer have been formed, the surface characteristics become independent of the substrate. There is no longer any reason for the conditions to be tailored to the individual substrate. So, both parameters can be independently optimized.

3.4.iii Geometry

The geometry of the substrate is also relevant to the optimization of deposition parameters. It was verified that for samples with sharp edges, the coating differs from coatings on flat surfaces. When lower current densities were applied the coating at the edge was thicker. Conversely, when higher current densities were applied, the edge of the sample was not covered, despite the rest of the coating exhibiting good quality.

A computational model shows that in samples with geometry 1, the maximum of current density is concentrated at the edges of the sample. This is in agreement with the mentioned experimental data. When low current densities are applied the layer is thicker at the edges (Fig. 3-15). The increased thickness at the edges causes an increase in the internal stress and a decrease in the hardness of the coating. It was verified that this effect is more intense for lower edge angles (Fig. 3-16).

![Fig. 3-15: Effect of current density concentration in the edge, on samples with geometry 1.](image-url)
It is known that at high local current densities the deposition becomes powdery and easily removable. According to this model, if higher currents are employed, the coating at the corners will be thinner, reducing the undesirable increase in the internal stresses (Fig. 3-17 and Fig. 3-18).

**Fig. 3-16:** Experimental results of the variation of the coating thickness at different distances from the corners, at three different angles.
Some promising results were obtained with tungsten carbide samples, as can be seen in Fig. 3-19. It can also be seen that the method of electrodeposition influences the edge profile. This difference can be explained by the preferential redissolution of less stable crystals, formed at the edge due to the higher current densities, when using PRC method.

**Fig. 3-17:** Deviation from the model for high local current densities.

**Fig. 3-18:** Effect of powdery due to high current densities.
Cylindrical geometry presents the biggest surface area (53cm\(^2\)) ever covered homogeneously with TiB\(_2\). The thickness is typically 1.5 times higher at the rounded tip. The difference in thickness can be explained by the form of the crucible, which causes a concentration of the current at the bottom surface, which in the case of cylinders is the rounded tip. Over the remainder of the cylinder area the thickness is approximately constant. However, no difference in roughness or microhardness was observed, compared with the rest of the surface.

The absence of corners in the sample geometry facilitates the optimization process of covering the sample with uniform coatings.

### 3.5 Texture

The preferential orientation of the crystals was measured by x-ray. The measured X-ray diffraction patterns of the TiB\(_2\) layers studied were indexed on the basis of hexagonal TiB\(_2\) lattice parameters\(^{[51]}\) \(a = 0.303\) nm, \(c = 0.322\) nm, space group P6\(/mmm\) No. 191, Pearson code hP3. Titanium atoms occupy the 1a positions at fractional coordinates 0,0,0; boron atoms occupy the 2d positions at fractional coordinates 1/3, 2/3, 1/2 as given in reference.
The intensities of the reflections in some of the experimental diffraction patterns show a deviation from those calculated from crystal structure data (see annex VI).

The coatings show variations of the crystallographic textures according to the current density applied. In Fig. 3-20 the pole figures are shown for two samples coated by PRC at 620°C, over 25min, with different current densities, A) \( j = -96\text{mA} \cdot \text{cm}^{-2} \), B) \( j = -134\text{mA} \cdot \text{cm}^{-2} \). At lower current densities there is only a \(<001>\) texture component indicated by the peak in the center of the pole figure. The peak in the center of the pole figure only appears for sample A, plated under higher current density, indicating additional \(<110>\) orientation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(001) Pole Figure</th>
<th>(101) Pole Figure</th>
<th>(110) Pole Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>B</td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
</tbody>
</table>

**Fig. 3-20:** Pole figures of the samples coated by PRC at two different current densities.

It was found that a change in substrate does not affect the preferential orientation of the crystals. Also no texture was found in layers thinner that 10\(\mu\text{m}\). Therefore the texture only starts to develop as the coating grows. This was also verified in deposits synthesized by sputtering\[^{52}\].

### 3.6 Impurities

The quality and homogeneity of the coating is highly affected by the presence of impurities in the melt or at the surface of the substrate. Some of these impurities are difficult to avoid when working with large areas on an industrial scale. Common impurities are, iron from corrosion products in the cell wall (FeF\(_2\)), silicium from the greased parts (silicon), calcium from CaF\(_2\) as an impurity in the salts, and oxygen from residual water within the system and hygroscopic salts. As can be seen in Fig. 3-21, holes appear in areas of higher iron and nickel concentration.
The presence of O, Si or Ca is commonly associated with dendritic growth and non-homogeneous coatings.

**Inside the hole**  
Fe=5%, Si=1%

**Inside the holes**  
Ni=7%

**Dendrites**  
Ca=0.7%, Fe=0.5%

**Dendritic coating**  
O=15%, Si=5%

**Fig. 3-21:** SEM images showing different effects of impurities in the quality of the coating.
The impurity levels remain low in the middle of the coating, and rise near the exposed TiB₂ surface.

For high current densities, the relation B/Ti is <1.5, leading to uneven layers and the formation of dendrites.

The highest levels of impurities are observed in dendritic coatings, as expected.

### 3.7 Melt decomposition

The active elements, Ti, B and Ta, are stabilized in the melt because of the complexes formed with fluorine anion[^44]. However, at working temperatures some species are volatile, being lost from the cell during evacuation. The main compound lost is BF₃, but TiF₃ and TaF₅ are also lost. This decomposition does not allow the reuse of the electrolyte after some experiments, by the addition of more active substances. It is also not possible to make a rigorous study relating the effect of the melt composition on the coating quality.

Several analytical methods were tried to determine the content of active substances in the melt. However, their insolubility in water and fluorine interference cause the analysis to fail.

To determine the evaporation rate of BF₃, an extraction system was tested. The system consisted of a heated melt with the same composition as the ones used in the experiments, under a continuous flow of argon. The argon flow is cooled by a water condensation system, which retains the fluoride salts. Finally the flow is bubbled into a CaCl₂ solution. The pH and conductivity of this solution were controlled during the experiment. The recovery solution was analyzed by a colorimetric method[^53] which quantified the boric acid formed according to reaction 6.

The follow reaction should take place in the recovery solution[^54]:

\[
2\text{BF}_3(g) + 3\text{CaCl}_2(aq) + 6\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{BO}_3(aq) + 6\text{HCl}(aq) + 3\text{CaF}_2(s)
\]

Consequently the pH of the solution decreased substantially. The conductivity of the solution remained stable which indicated low contamination of fluoride salts. As expected, a precipitate was formed, and was identified as CaF₂ by X-Ray analysis.

The rate of evaporation could not be calculated. However, there are evidences of substantial BF₃ evaporation, and instability of the FLINAK melt at 650°C. This opposes some literature based in thermodynamic calculations which claims that evaporation only occurs over 900°C.
After 6 hours and 40 minutes of experiment, about 60% of the boron in the melt was evaporated. Due to this instability the conditions of electrodeposition are affected during a daily experiment.

Leaving the oven under vacuum over night should remove all the boron from the melt. The next day more KBF$_4$ can be added, regenerating the melt without the cost of complete substitution.

After daily experiments the cell wall is covered with a violet substance, which indicates the presence of Ti(III) salts.

Infrared spectroscopy is currently being studied as a precise method to quantify the active substances in the melt, though this study is not yet finished.

### 3.8 Physical properties

#### 3.8.i Roughness and contact angle

The roughness is highly related to the different physical properties of the coating which determine the applicability of the sample for industrial proposes.

A higher roughness of the coating is associated with increased wetting behavior of the surface. This is important in the case of tools in contact with molten metals, as in the aluminum industry, or molten glass. Adhesion to molding dies and forming tools are critical problems which limit the quality of glass products and the performance of molding dies and forming tools$^{[55]}$.

Contact angle, $\theta$, is a quantitative measure of the wetting behavior of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where liquid, gas and solid intersect. The higher the contact angle, the lower the wetting. This is in fact desired when it comes to tools which will work on molten glass, in order to achieve a low interaction between the tool and the media.

The wetting behavior of glass on two titanium diboride samples, S9 (Fig. 3-22) and S0 (Fig. 3-23) with different roughness – Ra=1250nm and Ra=335nm respectively – was studied and compared with the wetting behavior of the steel substrate. These studies were performed at Swarovski & Co.
The results for the dependence of the contact angle on temperature are shown in Fig. 3-24. It can be seen that there is more wetting on TiB$_2$, compared to uncoated steel, and thus its performance is better. Also, sample S9, due primarily to its higher roughness and grain size, is more wetted by molten glass than sample S0, which has a lower roughness and finer grain structure. Physical factors which lead to mechanical interlocking and a larger interfacial area contribute to the strength of the interaction between the liquid and the solid surface, thus increasing the wetting\(^{[56]}\).

The transition from non-wetting (\(\theta>90^\circ\)) to wetting (\(\theta<90^\circ\)) behavior occurs at around 705°C for steel, 725°C for sample S9, and 750°C for sample S0. Clearly, sample S0 exhibits a 25°C extension in the operational temperature range over sample S9.

**Fig. 3-22:** AFM image of the TiB$_2$ coating deposit on sample S9.

**Fig. 3-23:** AFM image of the TiB$_2$ coating deposit on sample S0.
The roughness is also related with the wear behavior of the coating. The rougher the samples are, the more wear they suffer.

3.8.ii Microhardness

The technique and device used to measure the Vickers microhardness of the coating are only precise when the layer thickness is over 20µm. However, the thicknesses of the electrodeposited coatings are usually less than 15µm, which make accurate measurement of the cross section difficult. A microhardness measurement over the surface of the coating is possible for layers thicker than 10µm. However, superficial roughness causes errors in the measurement. It is not possible to polish the surface due to the low thickness of the layers. Indentations in the surface of rough samples result in inaccurately low hardness values (negative error). The decreased interaction area between the probe tip and the surface result in lower resistivity. Low coating thickness can result in the interaction of the probe tip with the substrate, which has a lower microhardness, also resulting in negative error.

---

5 Warmarbeitsstahl – Steel for working at high temperatures.
Measurements on the thicker coatings resulted in a range of Vickers microhardness values from 2650 to 3200.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Vickers microhardness</th>
<th>Vickers microhardness of the coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>280</td>
<td>2650 – 3200</td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>1660</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>257</td>
<td></td>
</tr>
</tbody>
</table>

The error associated with the measurement does not allow any comparison between these values and other properties or the deposition conditions. However, when compared to the microhardness of the substrate (Tab. 3-8) there is a substantial improvement in the microhardness. This is especially important for the tungsten carbide and stainless steel samples, as they are used as cutting tools. This increase in microhardness represents a high degree of wear protection for the sample.

3.8.iii Internal stress

The internal stress value is related to coating stability. The formation of cracks is more favourable in a highly stressed coating (Fig. 3-25). The presence of cracks decreases the wear resistance and might facilitate the penetration of corrosive agents into the substrate, thus decreasing the chemical protection resistance.

![Fig. 3-25: SEM picture of a cracked coating on Mo substrate.](image)

The residual stress in TiB₂ coatings on stainless steel substrates were determined by x-ray using a Young’s modulus of 5.4 x10¹¹ Pa and 0.110 as Poisson’s coefficient. The resulting
values of stress are in the -2GPa to -3GPa range. The negative values of the stresses indicate a compressive type of stress in the coatings.

These values are undoubtedly very high, but they are comparable to reported values. For example, Yoshizawa et al.\cite{57} reported a value of -2.2 GPa for TiB\textsubscript{2} coatings by magnetron sputtering on graphite (lowest stress value), and -19.6 GPa for TiB\textsubscript{2} coatings deposited by the same technique on copper (highest stress value). Perry et al.\cite{58} found -1GPa to be the minimum value for the residual stress in TiB\textsubscript{2} coatings. Berger et al.\cite{59} performed an evaluation of TiB\textsubscript{2} coatings in sliding contact against aluminum. They concluded that TiB\textsubscript{2} coatings, synthesized by magnetron sputtering had relatively low compressive residual stress (-0.5GPa). In addition the TiB\textsubscript{2} coating synthesized was more resistant to detachment and chemical wear compared to highly stressed (-6.1 GPa) TiB\textsubscript{2}. TiN and TiC coatings on steels also have high compressive stresses: -2.5 to -3.5 GPa\cite{60}.

These few literature references confirm that the stresses determined for the coatings electrodeposited from FLINAK melts are within normal ranges for titanium diboride coatings deposited by other methods. Also, other refractory ceramic coatings with similar characteristics, such as TiN and TiC, present similar values.

### 3.9 Chemical properties

#### 3.9.i Crystallite size and cell volume

The shapes of the peaks in x-ray diffractograms provide valuable information about crystalline structure. Particularly, the width of the peak is a measure of the thermal oscillations amplitude of the atoms at their regular lattice sites. The crystallite size can be extracted from the peak shape. In Tab. 3-9 the ranges of crystallite sizes obtained for several coatings are compared, with and without tantalum, and at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Composition</th>
<th>Crystallite size range (nm)</th>
<th>Crystallite size average (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>Ti – B</td>
<td>15 – 112</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Ti – B – Ta</td>
<td>8 – 53</td>
<td>31</td>
</tr>
<tr>
<td>600</td>
<td>Ti – B</td>
<td>9 – 32</td>
<td>26</td>
</tr>
</tbody>
</table>

It can be seen that the presence of tantalum is related to lower crystallite sizes. This suggests that tantalum acts as a growth inhibitor in the TiB\textsubscript{2} crystallite. This inhibition can be related to the improvement in the smoothness of the coating when tantalum is present.
A comparison of crystallite sizes at different temperatures shows a decrease in size at lower temperatures. This can be explained by a decrease in the surface diffusion coefficients of the reduced atoms, resulting in an increased probability of new crystallite formation as opposed to the growing of pre-existing crystallites.

No relation was found between the crystallite size and the others deposition parameters.

An increase in the ideal cell volume \( (25.683\,\text{Å}^3) \), when tantalum was present, which allows an estimation of the tantalum concentration. The maximum value found was \( 26.273\,\text{Å}^3 \) which corresponds to 60 at\% tantalum. This value obviously does not correspond to the average concentration of tantalum within the coating but only in some spots where is concentrated (also identified by the EDX).

When tantalum is not present a slight decrease in the cell volume was consistently obtained. The values were in the range from \( 25.627\,\text{Å}^3 \) up to \( 25.680\,\text{Å}^3 \). No relation to the deposition parameters or the quality of the coating was found.

### 3.9.ii Composition of the layer

It was found by EDX quantification of the coating cross section of molybdenum samples (Tab. 3-10) that the composition is not constant along the layer depth. These values are in agreement with the values obtained by the GDOES.

<table>
<thead>
<tr>
<th>Tab. 3-10: EDX quantification of the coating, without Ta, at different parts of the layer.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating surface</td>
</tr>
<tr>
<td>Middle of the coating</td>
</tr>
<tr>
<td>Coating close to substrate</td>
</tr>
</tbody>
</table>

The coating close to the substrate is rich in boron due to the compounds formed in the interlayer. Possibly this enrichment starts before the electrodeposition, when the sample is heated inside the melt (as discussed in section 3.4.i).

The content of boron decrease after 2-3µm from the substrate, reaching a minimum (B/Ti = 1.4) in the middle of the coating (about 5-7µm from the substrate). The amount of boron after 10µm thickness is about B/Ti = 1.8.

The distribution of tantalum is also uneven along the coating. In Fig. 3-26 can be seen alternated white and grey stripes. The SEM identifies with darker colors lighter elements. In this case the difference in colors distinguishes layers rich in titanium from layers rich in tantalum. Being tantalum heavier than titanium, the white stripes corresponds to the layers rich in tantalum. The layers are continuous and heterogeneously distributed. The higher concentration
of layers rich in tantalum is situated close to the surface and near the substrate darker zones are observed.

![SEM picture of a TiB₂/Ta layer on a WC substrate.](image)

Fig. 3-26: SEM picture of a TiB₂/Ta layer on a WC substrate.

The EDX quantification of the zones marked in red confirmed the uneven distribution of elements in the coating (Tab. 3-11).

<table>
<thead>
<tr>
<th>Zone</th>
<th>Elements ratio (Ta : Ti : B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 2 : 16.6</td>
</tr>
<tr>
<td>2</td>
<td>1 : 7 : 32</td>
</tr>
<tr>
<td>3</td>
<td>1 : 10.6 : 44</td>
</tr>
</tbody>
</table>

Tab. 3-11: EDX quantification of the zones marked in Fig. 3-26.

A higher proportion of boron was detected in coatings with tantalum (compare Tab. 3-10 with Tab. 3-12). The content of boron is higher in the zones rich in tantalum (Tab. 3-12).

<table>
<thead>
<tr>
<th>Zone</th>
<th>Ratio metal : boron</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 5.5</td>
</tr>
<tr>
<td>2</td>
<td>1 : 4</td>
</tr>
<tr>
<td>3</td>
<td>1 : 3.5</td>
</tr>
</tbody>
</table>

Tab. 3-12: Relative proportion of Ti + Ta : B at the zones marked in Fig. 3-26.

The results from the GDOES depth analyses (Fig. 3-27) show a maximum of the proportion Ta/Ti at about 2µm from the substrate, which decrease with the grown in thickness. Is important to mention that the percentage of tantalum is 10x lower that the one correspondent in the graphic. The higher content of boron due to the presence of tantalum was also found.
The high content of boron when tantalum is present can be associated to the formation of TaBₙ fases with n>2.

The uneven distribution of elements is not yet completely understood. It can be explained by differences in the conductivity of layers with different compositions, which can lead to different crystalline organization.

3.9.iii Crystal size and shape

As previously discussed in section 1.3.v the deposition parameters influence in crystal growth.

It was verified that the crystal size and shape are strongly dependent on the thickness of the coating. In Fig. 3-28 two different microcrystalline structures are present in the same sample. The left region is thicker, presenting crystals in the form of needles orientated in the same direction. The region to the right is thinner, presenting small, undefined crystals. This is in
agreement with the texture detected by X-ray in thicker coatings, which has already been discussed in section 3.5.

![SEM picture of a TiB₂ coating presenting two different types of microcrystalline structure.](image)

**Fig. 3-28:** SEM picture of a TiB₂ coating presenting two different types of microcrystalline structure.

Due to the evolution of crystal shape and size with the thickness, it was not possible to relate this property to the deposition parameters. However, as exemplified in Fig. 3-29 a variation in the crystal size and shape was obtained by changing the current densities, producing coatings with approximately the same thickness, when the pulse shape 2 was applied.
The crystalline structure also changes for different pulse shapes. Finer grain sizes are usually obtained when pulse shape 3 is used. This can explain the smoother deposits obtained when this pulse shape is used, as mentioned in section 1.3.v.

The presence of tantalum is frequently associated with refinement of the crystalline structure. Smaller crystals are obtained when tantalum is present, if the coatings are deposited under the same parameters, as can be seen in Fig. 3-30.

**Fig. 3-29:** SEM pictures of TiB₂ microcrystalline structure, on Mo substrates. Sample 15- \(i_1=0.4\text{A.cm}^{-2}, i_2=-0.14\text{A.cm}^{-2}\); Sample 103- \(i_1=0.33\text{A.cm}^{-2}, i_2=-0.15\text{A.cm}^{-2}\); Sample 78- \(i_1=0.18\text{A.cm}^{-2}, i_2=-0.09\text{A.cm}^{-2}\).
In general, the microcrystalline structure can be related to the quality of the coating. Smaller crystals are present in the smoother and more homogeneous coatings. Finer crystals can be found on thinner layers, and have a tendency to grow in size for thicker coatings. These finer crystals, and thus the roughness, are frequently associated with the optical aspect of the coating, presenting a bright surface.

### 3.9.iv Raman analysis

In order to detect possible impurities in the coating and analyze the nature of the chemical bonding, the samples were studied by Raman spectroscopy.

Carbon can be an important impurity in the melt caused by the corrosion of the crucible. It is also known that when carbon is co-deposited within a layer the internal stress increases, and the microhardness decreases[^61].

Carbon was identified several times in EDX spectra. However, the corresponding peaks were not detected by Raman. For this reason the carbon was attributed to an external contamination on the surface and not as a result of the deposition process, and therefore not contained within the coating.

It was found that TiB₂ presents three characteristic vibration peaks at 266cm⁻¹, 409cm⁻¹ and 604cm⁻¹ (see annex VII). The relative intensities between the peaks and small shifts are associated with the nature of the chemical bonding in the crystal, differing between the graphite-like or diamond-like structures[^52]. This chemical property is obviously related to physical properties, such as microhardness or conductivity. However, due to the large peaks, the comparisons between different samples were not accurate and no relation with the deposition...
parameters has been found. The detection of bands instead of peaks indicates shifts in the bonding lengths and angles, explaining the high internal stress values.

3.9.5 Dynamic corrosion test in $\text{Al}_9\text{Si}_3\text{Cu}$

This test was performed in the Österreichischen Gießerei Institut. The samples to be analyzed were molybdenum cylinders, and the test consisted of partially immersing the TiB$_2$-coated samples in a $\text{Al}_9\text{Si}_3\text{Cu}$ melt at 700°C, while rotating them continuously, for different lengths of time (2.5 and 12.5 days). Before the test samples were warmed up by suspending them over the molten media for 15 minutes under argon atmosphere.

To evaluate the corrosion action of the melt, tests on both TiB$_2$-coated Mo samples, and naked Mo and TZM$^6$ substrates were performed. The analyses after the tests consisted of measuring the diameters of the cylinders after the procedure and compare it with the original values, thus estimating a wear rate of the material. Also SEM images of cross-sections performed both longitudinally and transversally, allow the verification the shape change.

Fig. 3-31 shows the cross sections of the studied samples after the test. The molybdenum and TZM substrates show an important reaction zone, as expected, although this is clearly more visible in the case of molybdenum. The TiB$_2$-coated samples show that the TiB$_2$ layers remain well-adhered to the molybdenum surface, preserving their integrity and not reacting with the melt, thus efficiently protecting the substrate.

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$^6$ alloy with a composition: 0.40-0.55wt% Ti, 0.06-0.12wt% Zr, 0.01-0.04wt% C and the rest Mo.
<table>
<thead>
<tr>
<th>Conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>coated molybdenum sample</td>
<td>coated molybdenum sample after 2.5 days.</td>
</tr>
<tr>
<td>after 2.5 days</td>
<td></td>
</tr>
<tr>
<td>coated molybdenum sample</td>
<td>coated molybdenum sample after 12.5 days</td>
</tr>
<tr>
<td>after 12.5 days</td>
<td></td>
</tr>
<tr>
<td>molybdenum sample, after</td>
<td>molybdenum sample, after 2.5 days</td>
</tr>
<tr>
<td>2.5 days</td>
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</tr>
<tr>
<td>molybdenum sample, after</td>
<td>molybdenum sample, after 7.5 days</td>
</tr>
<tr>
<td>7.5 days</td>
<td></td>
</tr>
<tr>
<td>TZM sample, after 2.5 days</td>
<td></td>
</tr>
</tbody>
</table>

*Fig. 3-31: Optical microscope pictures of the samples cross section after being tested during different times.*
3.9.6 Static corrosion test in AlSi7Mg

Two coated molybdenum cylinders were half submerged (flat tip into the melt) in AlSi7Mg melt at 750ºC, during 5h, under argon atmosphere. Two other cylinders, coated with tantalum, were half submerged (flat part into the melt) in AlSi7Mg melt at 720ºC, for 168h, without argon. After the test, the samples were studied by electron microscopy and elemental analysis by EDX, on the respective cross-sections.

Under the conditions the experiments were performed, molybdenum uncoated samples suffer severe corrosion, being destroyed after a few hours of exposition in the melt.

It was observed in both cases that the layers did not react with the AlSi7Mg melt. For example, figure 5a shows the cross section of one of the samples tested for 5h. The coating conserved the original structure and shows good adhesion to the substrate.

![Cross-section images](image.png)

**Fig. 3-32:** a) Optical microscope image of the cross section on sample MO-008-DC; b) SEM image of the cross section on an uncoated TZM sample. (From the bottom of the picture upwards: sample, reaction zone, aluminum melt).

This corrosion protection effect is better exemplified when comparing Fig. 3-32a with Fig. 3-32b. This last, shows a TZM sample which has been exposed to the same static test treatment. A thick reaction zone can be seen (>20μm) between the substrate and the AlSi7Mg melt. It is also visible the uneven surface due to the corrosion process.

The samples tested for 7 days in air show the conservation of the original shape. However, the green powder on the surface suggests the formation of molybdenum oxides. These results indicate a low degree of corrosion (Fig. 3-33).
Comparing the different sections of the cylinder, it is shown that the coating remains adherent to the substrate on the part in contact with the melt (Fig. 3-34c). At the sections exposed to air and at the interface, the coating disappears (Fig. 3-34a and Fig. 3-34b). The corrosion effect is more intense at the interface zone, probably because the higher temperatures are verified and oxygen is present. The products resulting from the coating oxidation are TiO\textsubscript{2} and B\textsubscript{2}O\textsubscript{3}. However, it was not possible to identify the presence of these compounds. The compound B\textsubscript{2}O\textsubscript{3} is volatile at working temperatures, being lost from the surface. But TiO\textsubscript{2} should be visible on the coating as a white powder.

**Fig. 3-33:** Optical aspect of the cylinder. a) Before test; b) after test; c) Longitudinal cut of the cylinder after the test.
The EDX analysis at the interface shows that in some parts the melt penetrated through the coating, corroding the substrate (Fig. 3-35). This effect might occur as a result of the presence of pores in the coating.

**Fig. 3-34:** Microscope pictures of transversal cuts of the cylinder; **a)** Air; **b)** Interface melt-air; **c)** Inside the melt.
Fig. 3-35: Analysis of the elements in the cross section.
Chapter 4. Conclusions

The process of the electrochemical synthesis of TiB$_2$ coatings in FLINAK electrolyte has been optimized using the PIC technique below 650°C. The best results were obtained using two pulses with different intensities separated by a rest time, at 650°C. It was also possible to obtain homogeneous coatings at 600°C, on a molybdenum substrate, although they were less smooth. Uneven coatings with low adherence were obtained at 580°C.

Adherent, homogeneous and dense coatings were deposited on molybdenum cylinders with areas up to 53cm$^2$. The range of current densities which produced the best results was between 0.07A.cm$^{-2}$ and 0.70A.cm$^{-2}$. The coatings are rougher and less homogeneous when deposited at higher current densities. The frequency of deposition which produces best coatings was between 40 Hz and 60Hz.

Corrosion tests showed an improvement in the chemical resistance of the coated samples, relative to the uncoated substrate.

The coatings show good stability against the AlSi7Mg alloy melt at 750°C for 5 hours, and at 720°C for 168 hours, in a static mode. However, the coating on the tip which was exposed to air was destroyed by oxidation after 168 hours, leading to substrate corrosion, though the shape of the sample was maintained. Molybdenum cylinders were destroyed under the same conditions after approximately 5 hours.

The dynamic test in Al9Si3Cu melt at 700°C showed that stability of the coating results in an efficient protection of the substrate. Molybdenum and TZM substrates, not covered with a TiB$_2$ protective coating, suffer corrosion through reaction with the aluminum melt. Molybdenum is the material suffering the most damage by corrosion in this melt.

Stainless steel samples with areas up to 17cm$^2$ were coated with TiB$_2$. However, the coatings showed adherence problems when high current densities were used, and homogeneity problems when low current densities were used. Thus, the properties required by the industry for utilization as wear protection, were not achieved.

Dense and hard coatings ($V_{H_{0.5}}$=2650-3200) were deposited on tungsten carbide samples with areas up to 13cm$^2$. Due to sample geometry, the coatings present homogeneity problems at the sharp edges. A computational model, based on experimental results, was developed to predict the impact of current density on the quality of the coating at the edges. It was shown that the current concentrates at the edge causing undesirably excessive growth of the coating. However, for high current densities the deposits become powdery and non-adherent. The ideal current density at which an optimal coating can be obtained has not yet been found.
The co-deposition of tantalum, in the relative molar ratio 1(Ta):17(Ti):78(B), improved the quality of the coating. The effect of tantalum on the crystalline structure is not yet completely understood, though it is known to increase the average cell volume. Due to the lower crystallite sizes produced when tantalum is present it is proposed that tantalum acts as an inhibitor to the crystallite growth. As a consequence, the crystals are smaller compared to crystals without tantalum. The global result is a denser and smoother coating.

Impurities such as oxygen, silicon, iron, nickel and carbon produce undesirable effects in the coating, such as holes or dendrites. Thus, salts purity, cell cleanliness, and appropriate sample pre-treatment are essential to obtain good coatings and reproducible results on an industrial scale.

The electrodeposition on molybdenum substrates was less susceptible to the variation of the experimental conditions, when compared to the electrodeposition on stainless steel or tungsten carbide samples, especially at lower temperatures. This was explained by the formation of molybdenum borides in the substrate - coating interlayer. This is supported by the detection of boron at depths of up to 60µm from the substrate surface. The concentration of boron on the surface can be up to 75at%. It was not possible to identify these compounds formed, possibly because they are concentrated in a very thin layer at the surface. This layer is formed when the sample is inserted in the melt under cathodic deposition, before the deposition sequence starts. The mechanism of boron reduction is not understood. However, it is suggested that occurs through charge transfer at the surface, by the formation of surface complexes, which leads to molybdenum oxidation and thus dissolution into the melt. The diffusion of boron into the substrate acts as a catalyst for the reduction of more boron atoms, explaining the increased in molybdenum dissolution when higher current densities were used as cathodic protection.

It was found that the composition of the layers and the crystals organization are not constant along the coating depth.

The layer close to the substrate is rich in boron, which is a consequence of the proximity to the substrate - coating interlayer. The higher boron content can lead to extra conductivity in the TiB₂ structure[45], resulting in more titanium deposition, producing a layer with lower conductivity. The effect of the next layer on the deposition is a progressive decrease in the rate of metal reduction. This effect is attenuated with the growth of the coating leading to an approximately ideal proportion of 66% of boron to 33% of titanium at a thickness of 15-20µm.

When tantalum is present the proportion of boron is higher, and increases with the coating growth. This implies an increasing conductivity, which causes the deposition of layers richer in tantalum. For this reason the concentration of boron and tantalum increases with the growth of the coating.
Near the substrate no preferential orientation of the crystals was found in the coating. However, in thicker coatings the orientation <001> starts to develop. When higher current densities are used the referential orientation <110> is also verified.

The values of residual stress measured in the TiB₂ electrodeposited layers are in the -2GPa to -3GPa range. The negative sign of the stresses found indicates a compressive type of stresses in the coatings. These values for residual stresses are high explaining the frequent cracks and blisters in the layers. However, the values are of similar magnitude to others reported in the literature for coatings produced by different methods.

The microhardness values obtained are in the range of 2650 to 3200 HV₀.₅, agreeing with the values reported in the literature[3]. They also represent a high increase in the microhardness compared to the substrate, which is important for the application of the coating as wear protection.

The roughness was related to the wetting behavior of the coating by molten glass. Rougher samples were wetted more due to higher physical interactions on the surface.

The general results of the performance tests described above are very satisfactory for the use of these layers as functional coatings.

The method of synthesis and the equipment used are reliable for industrial use, though they still need improvements.

The optimization of the production processes for TiB₂ coatings on stainless steel and tungsten carbide are not yet finished. The homogeneity at the sample edges still needs to be improved.
Bibliography


[22] H. Giess, German Patent N° 2214633, 1972


### Annexes

I. TiB$_2$ properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>3225°C</td>
</tr>
<tr>
<td>Rupture modulus</td>
<td>2.756 Pa</td>
</tr>
<tr>
<td>$\Delta H^\circ_{f, 298K}$</td>
<td>-218 kJ/mole</td>
</tr>
<tr>
<td>Superconductive</td>
<td>1.28 K</td>
</tr>
<tr>
<td>Energy of the crystal lattice</td>
<td>13640 kJ/mole</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Hexagonal $a = 3.03$ Å, $c = 3.22$ Å, radius ratio $= 0.66$</td>
</tr>
<tr>
<td>Cell volume</td>
<td>25.683 Å$^3$</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>26.1 – 27 W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Microhardness</td>
<td>2500 – 3350 Hv$_{0.5V}$</td>
</tr>
<tr>
<td>Tensile strength at 1000°C</td>
<td>2.669 Pa</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>5.4 x10$^{11}$ Pa</td>
</tr>
<tr>
<td>Spectral emissivity</td>
<td>0.26 at 725°C, 0.24 at 2125°C</td>
</tr>
<tr>
<td>$\Delta G^0_{br,1000K}$</td>
<td>-254 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>9μΩ cm</td>
</tr>
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II. Possible melts for electrodeposition of TiB₂

<table>
<thead>
<tr>
<th>Year – Author</th>
<th>Salt system</th>
<th>T (°C)</th>
<th>TiB₂ as:</th>
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<tbody>
<tr>
<td><strong>Oxide Melts</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1929 – Andrieux</td>
<td>B₂O₃·TiO₂·MgO·MgF₂</td>
<td>1000</td>
<td>powders or fine crystals</td>
</tr>
<tr>
<td></td>
<td>B₂O₃·TiO₂·CaO·CaF₂</td>
<td>990</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TiO₂·B₂O₃·Na₂O·NaF</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>1960 – Stern</td>
<td>TiC·B₂C·K₂TiF₆·KB₆F₄·NaCl</td>
<td>1000</td>
<td>powders</td>
</tr>
<tr>
<td>1961 – Nies</td>
<td>TiO₂·B₂O₃·KF·KCl</td>
<td>800</td>
<td>powders</td>
</tr>
<tr>
<td>1969 – Schlain</td>
<td>NaBO₂·LiBO₂·Na₂TiO₃·Li₂TiO₃·TiO₂</td>
<td>900</td>
<td>coatings</td>
</tr>
<tr>
<td>1972 – Ganesan</td>
<td>TiO₂·B₂O₃·NaCl·NaF</td>
<td>800</td>
<td>dendritic deposit</td>
</tr>
<tr>
<td>1975 – Gomes</td>
<td>Na₂B₄O₇·TiO₂·Na₂CO₃·Na₂AlF₆·NaCl</td>
<td>1050</td>
<td>dendrites / crystals</td>
</tr>
<tr>
<td><strong>Halide Melts</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1972 – Gies</td>
<td>KBF₄·TiF₃·KF·MeF</td>
<td>900</td>
<td>coatings</td>
</tr>
<tr>
<td>1973 – Kellner</td>
<td>K₂TiF₆·KB₆F₄·Na₂AlF₆</td>
<td>500-850</td>
<td>coatings</td>
</tr>
<tr>
<td>1988 – Makyta</td>
<td>TiO₂·B₂O₃·Na₂B₄O₇·NaCl·Na₂AlF₆</td>
<td>970</td>
<td>powders</td>
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<tr>
<td></td>
<td>K₂TiF₆·KB₆F₄·KF·KCl</td>
<td>800</td>
<td>coatings</td>
</tr>
<tr>
<td>1992 – Wendt</td>
<td>K₂TiF₆·KB₆F₄·LiF·NaF·KF</td>
<td>700</td>
<td>coatings</td>
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<tr>
<td>1993 – Shapoval</td>
<td>K₂TiF₆·KB₆F₄·NaCl·KCl·NaF</td>
<td>700</td>
<td>coatings</td>
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<tr>
<td>1996 – Yamamoto</td>
<td>NaF·NaBF₄·NaTiF₆</td>
<td>400</td>
<td>not specified</td>
</tr>
<tr>
<td>1999 – Pessine</td>
<td>K₂TiF₆·KB₆F₄·LiF·NaF·KF</td>
<td>600</td>
<td>coatings</td>
</tr>
</tbody>
</table>
III. High temperature cell
IV. Results of molybdenum dissolution experiments

EDX spectra of the sample surface after the test

X-ray diffractogram of the sample surface after the test
Raman spectra of the sample surface after the test
V. Comparison between the extra peak and TiO$_2$ and MoB$_2$
VI. Diffraction pattern of TiB$_2$ calculated from structural data\textsuperscript{[51]}

![Diffraction pattern of TiB$_2$](image1)

VII. TiB$_2$ Raman spectra of the coating

![TiB$_2$ Raman spectra](image2)
VIII. Theory of some techniques used

**ESEM**

The electron microscope can be understood in analogy to the light microscope. Reflected waves can resolve details of objects only when the details are larger than the wavelength of the reflected wave. Thus, in order to obtain very high resolutions electrons are used rather than light, since the wavelengths of electrons can be tuned according to the desired resolution (their wavelength varies inversely with the square root of their kinetic energy.

Basically, electrons from a heated filament, the electron gun, are accelerated to a higher energy. The electrons strike a thin target and are then focused by a magnetic lens. Another magnetic lens projects the electron beam onto a fluorescent screen to produce the image.

When X-ray analysis is combined with electron imaging techniques, the resulting tool is very powerful for the understanding of the composition and structure of materials. Analysis of X-rays emitted from a sample can be accomplished by an energy dispersive spectrometer discriminating X-ray energies.

**EDX**

Energy dispersive X-ray microanalysis (EDX) is an electron beam induced X-ray spectrochemical technique which allows the determination of the local chemical composition of a solid sample by means of an in-situ, non-destructive analysis on a microscopic scale.

As a result of the interactions between the impinging electrons and the target atoms, X-rays are emitted which have characteristic energies for different elements. The resulting X-ray spectra enable not only the identification but also the quantification of the chemical elements present in the specimen.

Some relevant characteristics of the SEM EDX technique are:

- range of chemical elements: all elements in the periodic system from boron onwards
- minimum detectable mass fraction: from 0.1 wt% to 1 wt%
- time of analysis below 1 minute for up to 16 elements by PC controlled data acquisition and on-line data reduction
- spatial resolution depends on the mean atomic number and density of the specimen and also on the primary beam energy; 0.2-10 micron in a SEM.
For a reliable analytical result, the sample preparation must satisfy certain requirements:

- the sample must be flat and smooth, specially for quantitative analysis
- EDX enables analysis of rough specimens, but the application is limited to qualitative and semi-quantitative determinations
- the sample must be electrically and thermally conductive.

**GDOES**

GDOES combines sputtering and atomic emission to provide an extremely rapid and sensitive technique for element depth profiling. The technique is capable of quantitative multielemental analyses for about 40 elements.

During analysis, a plasma is generated in the analysis chamber by the applied voltage between the anode and the cathode (the sample surface) in the presence of argon under low pressure. Ionized argon atoms cause sputtering on the sample surface. Sputtered atoms excited in the plasma rapidly de-excite by emitting photons with characteristic wavelengths.

**IX. Symbols and short names**

ESURF: Electrochemical Surface Treatment

ESURF 1: Wear Resistant Layers with Corrosion Stability at High Temperatures

PP: pulse plating

PIC: pulsed interrupted current

PRC: pulsed reversed current

EDX: emission dispersive X-ray

ESEM: environmental scanning electron microscope

GDOES: glow discharge optical emission spectroscopy