



# Electrochemical Titanium Diboride (TiB<sub>2</sub>) Synthesis from Fluoride Melts

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## Abstract

Titanium diboride (TiB<sub>2</sub>) is an intermetallic compound which has high melting point and high electrical and thermal conductivity like many other metal borides. That materials have higher resistance to corrosion and thermal shock compared to the others, also their oxidation properties are good at higher temperatures and they are resistant to molten phases. With respect to these properties, metal borides have several applications from aluminum production technology to laboratory materials, armor producing and several applications that demands high chemical stability, high hardness and resist to wear.

TiB<sub>2</sub> is investigated due to the special chemical and physical properties. Electrochemical production of TiB<sub>2</sub> depends to find suitable supporting electrolytes that has wide range electrochemical window, good physicochemical properties and allow producing pure compounds like fluoride or chloride systems. Electrochemical behavior of boron and titanium is really important to understand the mechanism of formation and also for other metal boride compounds.

Electrochemical synthesis of TiB<sub>2</sub> gives an opportunity to control the process parameters and material properties regularly. Obtaining of very pure compounds is possible and production of the TiB<sub>2</sub> as bulk, powder or thin layer can be controlled with the process parameters.

In this article, electrochemical synthesis of the TiB<sub>2</sub> and behavior of Boron were investigated to better understanding about the electrochemical deposition of TiB<sub>2</sub> like intermetallic compounds on molybdenum substrates. Molten fluorides mixture FLiNaK used as supporting electrolyte and KBF<sub>4</sub> and K<sub>2</sub>TiF<sub>6</sub> were used as Boron (B) and Titanium (Ti) source respectively. Cyclic voltammetry and potentiometric measurements were used as main investigation way for the determination.



# 1 Introduction

There are some production alternatives for  $TiB_2$  generally production method is chosen according to starting materials, expectations from the final product, product type etc. Electrochemical synthesis of that compound has an advantage of the sensitive controls of the processes. In the light of that advantage electrochemical synthesis methods are very special for the production of nano-macro powders or thin layer production on the complex shape products [1, 2].

## 1.1 Electrochemical Synthesis of Metal Borides at High Temperatures

Electrolysis in general term is chemical changes accompanying faradaic reactions at electrodes in contact with electrolytes. A current in which electrons cross the interface from the electrode to a species in solution is a cathodic current., while electron flow from a solution species into the electrode is an anodic current [3].

On the production of  $TiB_2$  via molten salt electrolysis, molten halides can be used as electrolyte. Usage of binary or ternary mixtures of fluorides, chlorides, oxides or combined halide/oxide mixed as electrolyte is possible [4, 5].

Generally synthesis of some metals, alloys or compounds, refining of the products and coating on a substrate can be achieved by molten salt electrolysis [4]. Metal borides were the first synthesized products in advanced ceramics by molten salt electrolysis. Later on, researchers found out that carbides and silicides can also be synthesized with molten salt electrolysis [5, 6]. Synthesis of metal borides by molten salt electrolysis has important advantages with respect to other processes. These are achievement of both coatings and powder materials by changing process parameters, variation of the type of metal boride compound by controlling process parameters and low costs of first investment compared with other production processes.

Physical and chemical properties of metal borides, produced electrochemically at high temperatures, are related with the production parameters. Composition of molten electrolytes (fluoride and chloride ionic molten phases), and process temperature are the most critical parameters which determines the form of the reaction and the end product. Chemical composition of the synthesized compound changes with current density, in addition to the parameters listed above. Electrolyte systems, end products and form of the products are shown in Table 1 for some of the metal borides [6].



Table 1. Electrochemical production parameters of some metal borides [6]

Electrolyte	Working temperatures, [°C]	Product	Form of the cathodic metal borides
Na <sub>3</sub> AlF <sub>6</sub> , TiO <sub>2</sub> , B <sub>2</sub> O <sub>3</sub> , NaCl	970	TiB <sub>2</sub>	Coating or powder
LiF, NaF, KF, K <sub>2</sub> TiF <sub>6</sub> , KBF <sub>4</sub>	600-700	TiB <sub>2</sub>	Coating or powder
LiF, NaF, KF, K <sub>2</sub> ZrF <sub>6</sub> , KBF <sub>4</sub> , B <sub>2</sub> O <sub>3</sub>	750	ZrB <sub>2</sub>	Coating
NaCl, KCl, -(NaF), K <sub>2</sub> ZrB <sub>6</sub> , KBF <sub>4</sub>	700-850	ZrB <sub>2</sub>	Powder

As shown in Table 1, many parameters, beginning with the composition of the electrolyte, effect the production of metal borides.

In this work, FLiNaK ( LiF, NaF, KF) type supporting electrolyte was used due to the some electrochemical advantages even it is highly corrosive. Although there are several works on this system, it is still one of the most important electrolytes for the production of metals and compounds from molten salts.

## 2 Experimental

Electrochemical synthesis of metal and compounds on molten salts require high sensitivity against to humidity, air, oxygen and water that can destroy or change targeted aims. Especially on the electrochemical measurements effect of those impurities play a huge role about the changing of the reactions and reaction mechanisms. Because of that, all preparation steps, experiments and pre-experiments process have to be carried out under protective atmosphere. The preparation and storage of chemicals and all other operations were done inside of the over-pressurized glove box.

Ternary mixture of LiF, NaF and KF act as a one of the supporting electrolyte on the synthesis of TiB<sub>2</sub> because fluoride electrolytes are good media for the carrying of targeting ions like Ti and B and also it is not as chemically active as molten chlorides. On the other hand one of the biggest disadvantages of the electrolyte is being extremely corrosive. Because of that correct material selection and design for experiments are important.

A two part, water cooled stainless steel (Thermax/SS310) chamber designed and built for electrochemical research at high temperatures that can be seen on Figure 1.

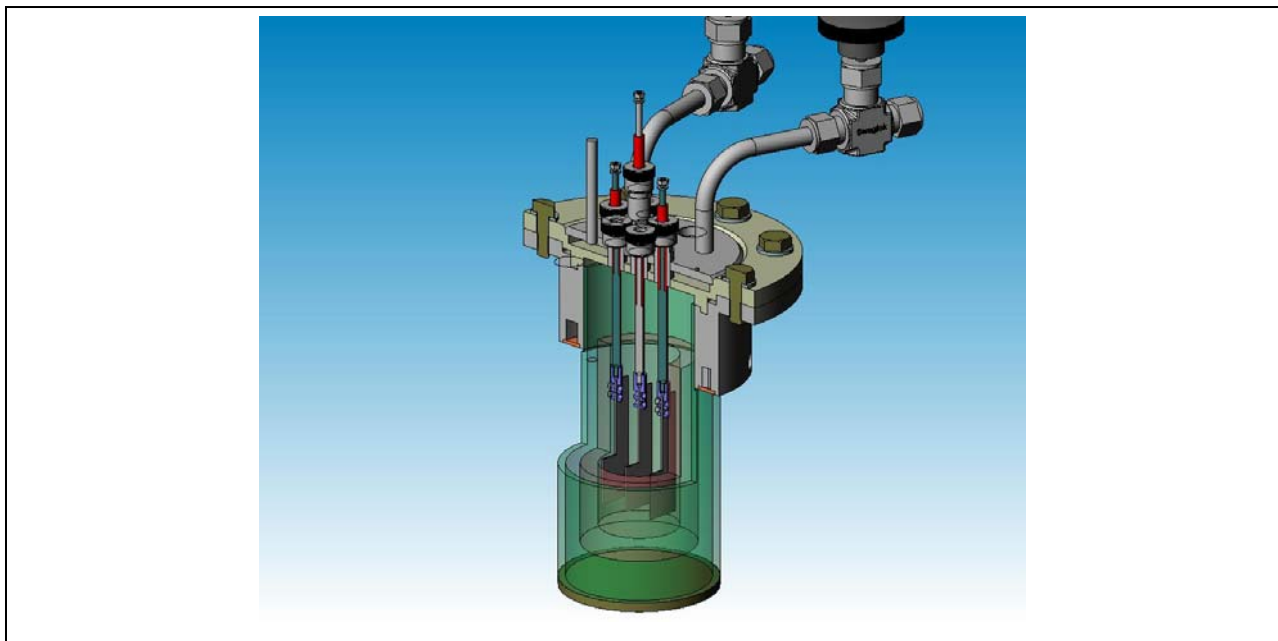


Figure 1: A cross view of Air Tight closed stainless steel chamber that used for electrochemical investigations

On the water cooled lid there are Swagelok assisted (6mm, Ultratorr) six connections through the cell that were used for all electrolysis and measurement operations. Also there are two more connections for gas in and outlet that also assisted with Swagelok gas valves. At the bottom side of the lid there is a high temperature resisted rubber o-ring. The holes on the lid were used as;

- Cathode holder and current collector
- Anode holder, current collector
- Temperature measurement
- Reference electrode
- Current collector through crucible (if necessary)

To prevent the shortcuts, all current collectors/holders isolated with boron nitride (BN) tubes that also useful protection equipment for Swagelok o-rings. All isolation and protection parts were made with BN that is easy to handling and shaping also chemically inert against to molten halides / oxides.

Additionally, two 10 mm Swagelok gas valves used to create a protective atmosphere inside the cell. High purity argon gas used as protective shield against oxygen and humidity. Inside pressure of the cell was kept (just a few mB) over atmospheric pressure that helps to protect inside of the cell also does not play effect on the reactions. Bottom part of the chamber is again water cooled on the top region and it has 200 mm dia. and 200 mm height. 150 mm of the chamber stays inside of furnace heating zone and top part cooled for easy handling of the cell.



A glassy carbon crucible used as electrolyte vessel. Molybdenum sheets (10x10x1 mm) / wires (0.5 mm Dia.) and graphite rods (6 mm Dia.) were used as cathode and anode respectively. A pure Pt Wire (0.5 mm Dia.) served as Quasi-Reference Electrode (QRE) since there are no any stable reference electrodes for molten fluoride media. Preparation of electrodes was made according to previous works. Several scientists have tried to obtain an universal reference electrode but because of the extremely high corrosive character of the melt it is not possible especially temperature over 550 °C [7, 8].

Cyclic voltammetry analysis was applied as main electrochemical analytical technique since it is possible to get a lot electrochemical and chemical information from the desired electrolyte system. IVIUM brand potentiostat (IVIUMSTAT) (10V-10A) and company software used for electrochemical analysis.

A well known ternary eutectic of LiF:NaF:KF at 454 °C was used as supporting electrolyte which has  $X_{\text{LiF}}=0.46.5$ ,  $X_{\text{NaF}}=11$  and  $X_{\text{KF}}=42.5$ . Supporting electrolyte was prepared in following amounts; LiF=1.020 mol, NaF=0.23 mol, KF=0.92 mol that gives a constant height in crucible and allows to make an assumption about surface area calculations. As Ti source K<sub>2</sub>TiF<sub>6</sub> and as boron source KBF<sub>4</sub> were used. All chemicals were analytical grade and high purity Argonne gas used as protective gas both in glove box and chamber during the experiments.

Experiments were conducted to understand the electrochemical limits of the FLiNaK and boron behavior on a molybdenum wire. After that a new series of experiments were carried out on to molybdenum sheets to see current-potential changes during the electrolysis. The molar ratio of the active species were 2% of FLiNaK and 1:4, Ti:B molar ratio were kept.

### 3 Results and Discussion

Electrochemical investigations were conducted on certain electrolyte (FLiNaK) and certain temperature. Temperature was set to 700 °C to keep boron in the electrolyte as BF<sub>4</sub><sup>-</sup>. On the higher temperatures BF<sub>3</sub> (gas) formation and loss of boron is possible and also this gas is poisonous. So it is important to keep boron inside of electrolyte. Figure 2 shows theoretical calculations about the electrolyte. After 600°C, KBF<sub>4</sub> starts to dissolve inside of the electrolyte and immediately after 800°C BF<sub>3</sub> formation can be observed.

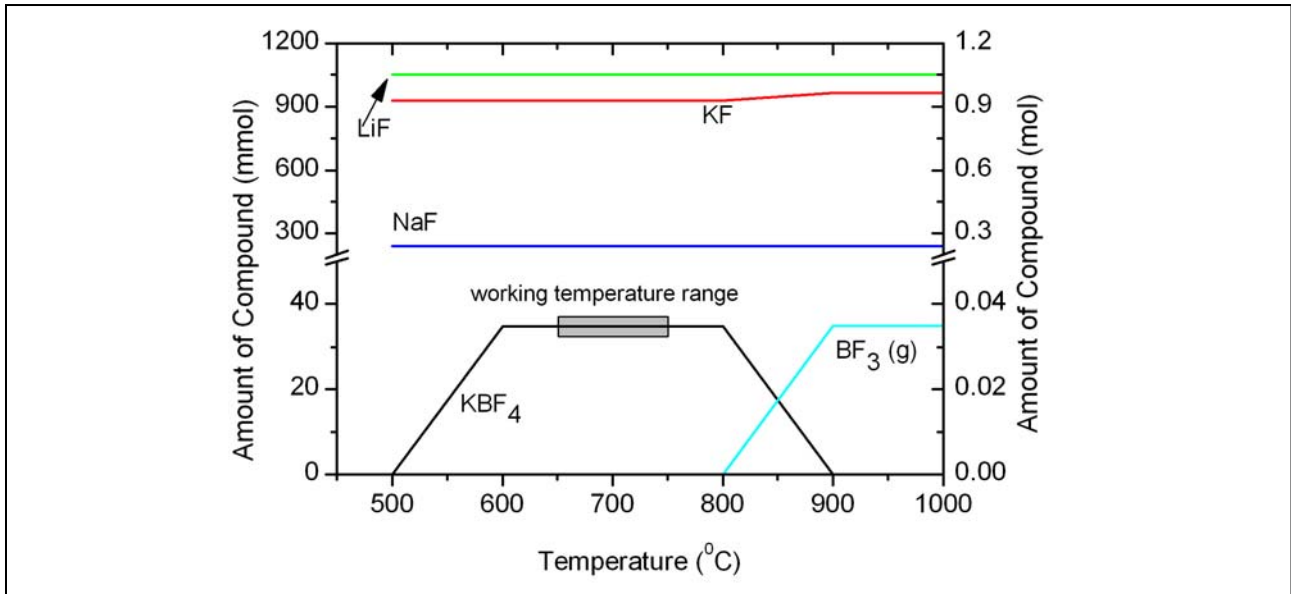


Figure 2: Theoretical calculation with FactSage© about Dissolution of  $\text{KBF}_4$  on the molten FLiNaK and  $\text{BF}_3$  gas evolution.  $\text{LiF}=1.020$  mol,  $\text{NaF}=0.23$  mol,  $\text{KF}=0.92$  mol,  $\text{KBF}_4=0.034$  mol

### 3.1 Determination of Electrochemical Window of FLiNaK Electrolyte

On the production of  $\text{TiB}_2$  molten FLiNaK electrolyte investigated to find an electrochemical window for the active species like Boron and Titanium. At Figure 3 cyclic voltammograms of the FLiNaK can be seen at two different potential limits.

Cyclic voltammetry experiments shows that up to  $-0,6$  V vs. Pt QRE current level is nearly zero and up to  $-1.2$  V there is no any completed reaction for FLiNaK electrolyte. Above that potential, potassium and sodium reduce on to molybdenum surface.

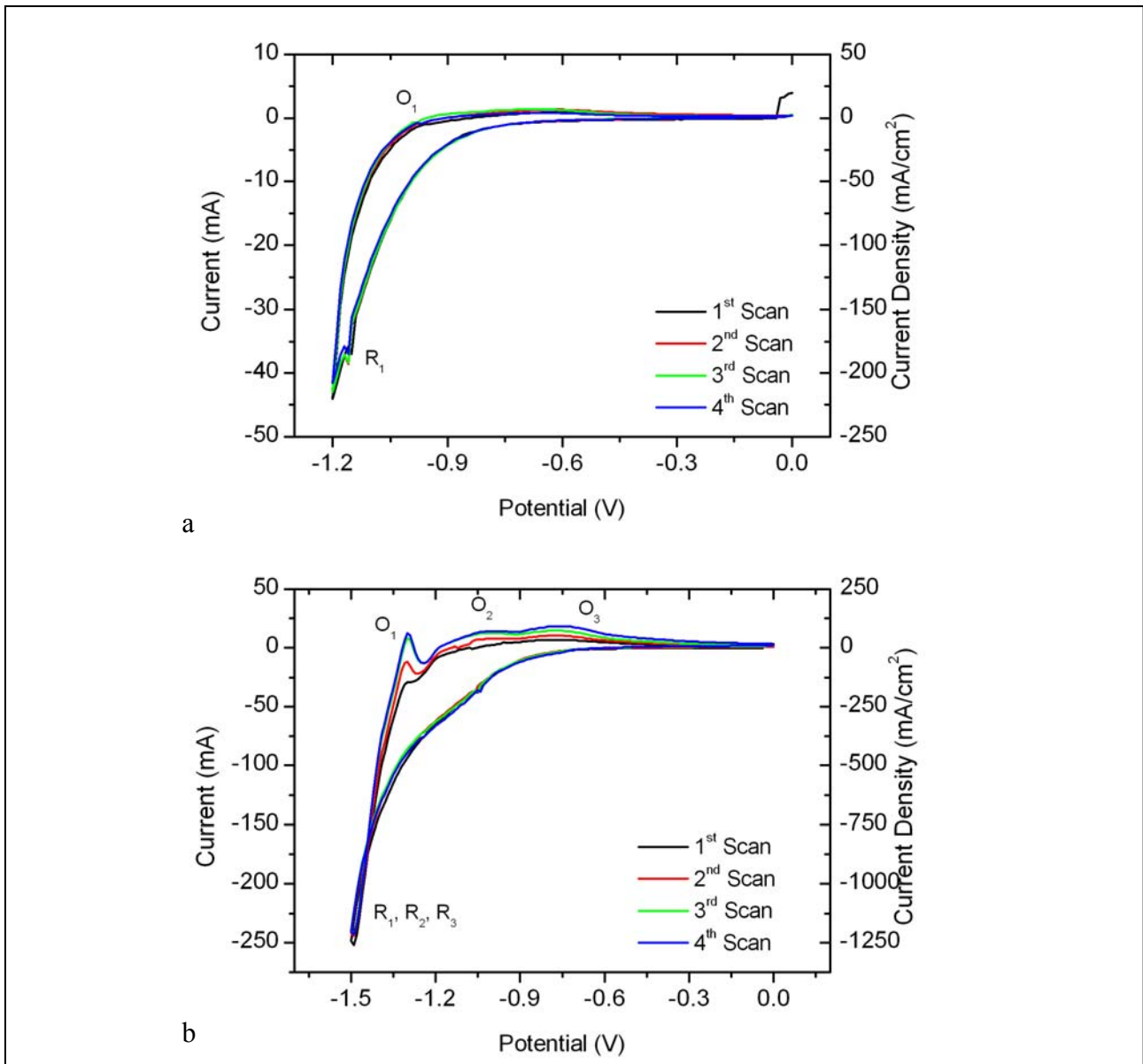


Figure 3: Cyclic Voltammogram of FLiNaK melt at 700°C on different cathodic potential ranges. Scan rate :0.3 mV/s, Mo-WE, Graphite -CE, Pt QRE. a: -1.2 V, b:-1.5 V

Firstly, system was scanned up to -1.2 V vs. Pt QRE (Figure 2.a) and a small reduction peak( $R_1$ ) was observed on the -1.1V and also oxidation peak of that also could be seen( $O_1$ ) that is probably an impurity in the electrolyte. On the fluoride systems first decomposition expect with  $K/K^+$ .

After -1.2 V electrolyte starts to decompose. When system shifted up to -1.5 V vs. Pt QRE (Figure 2.b) reduction and oxidation of active species like potassium and sodium can be observed. Because of the high scan rate all reduction peaks are on the same peak but the oxidation of the species can be seen separately at different potential ranges.  $O_1$ ,  $O_2$  and  $O_3$  show the oxidation of cathodic products to ionic species like  $K^+$ ,  $Na^+$  and  $Li^+$  respectively. Potential values against Platinum Quasi Reference Electrode (QRE) have to remain under -1.2 V level to obtain pure  $TiB_2$  compound.

### 3.2 Boron Behaviour in FLiNaK Melt

After boron addition to system (.69 mol/l) a new set of cyclic voltammetry measurements were conducted.

Cyclic voltammetry analysis (Figure 4) shows that also on the molybdenum surfaces  $B^{3+}$  has a single step 3 electron transfer reduction. On the reverse peak there is a nucleation crossover that indicated boron starts to crystallize on the molybdenum surface. Shifting of peaks can be explained due to change in the scan rates.

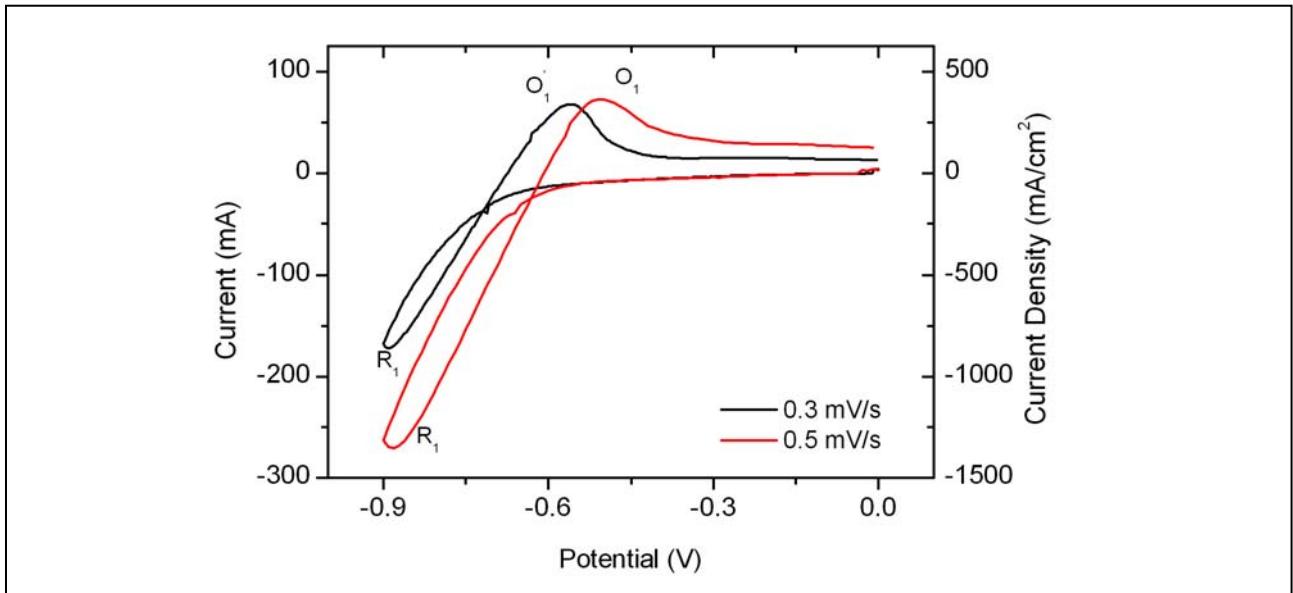


Figure 4: Cyclic voltammogram of Flinak + 0.69 m/l KBF<sub>4</sub> at 700°C on different scan rates. Mo-WE, Graphite -CE, Pt QRE.

According to equation 1, a single step 3 electron reduction of boron (III) ions in to Boron is possible and also this is a reversible reaction.



FLiNaK melts allows to use KBF<sub>4</sub> on the electrochemical metal boride production.

### 3.3 Electrochemical Production of TiB<sub>2</sub>

Investigations were conducted to understand the TiB<sub>2</sub> formation on different current densities. (Fig 5)

Boron and titanium were added to electrolyte together to produce TiB<sub>2</sub>. Expectation was reduction of Titanium and boron on the molybdenum surface to achieve a TiB<sub>2</sub> layer.

According to Figure 3 it is obvious that after potentials of -1.2 V vs Pt QRE electrolytes starts to decompose and secondary reactions can occur. Because of that cathodic potential level has to be below that -1.2 V vs. Pt QRE.

A set of experiments were conducted on the same working conditions to understand the effect of current density. Temperature was 700 °C, duration 1h, 1:4= Ti:B Ratio.



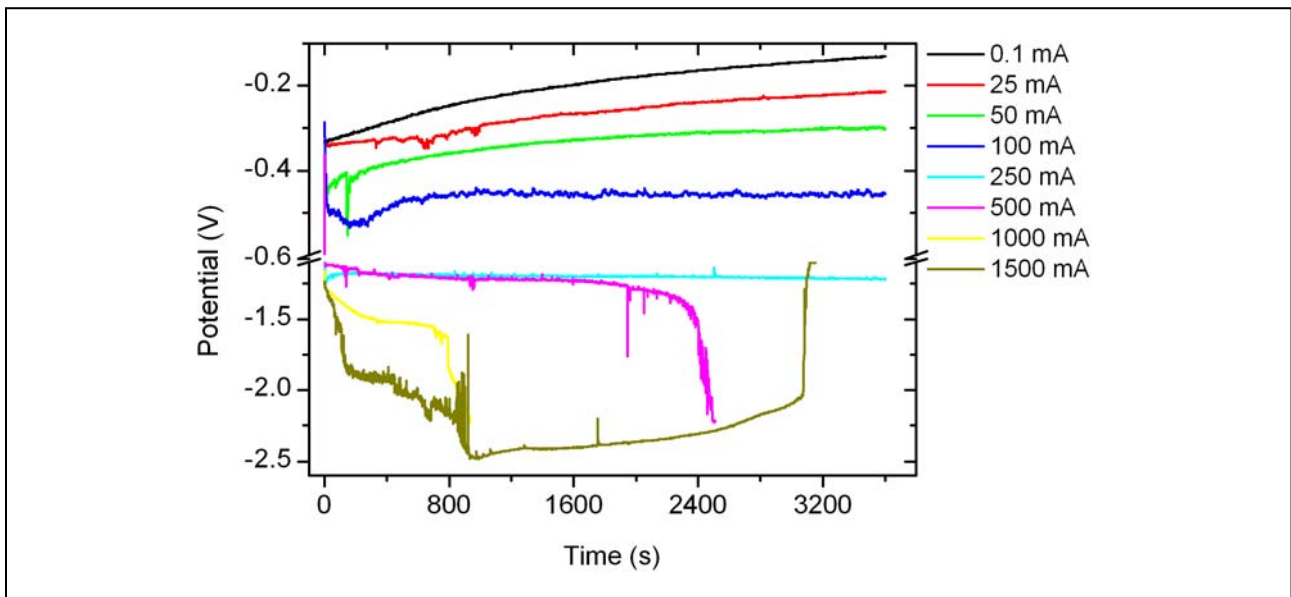
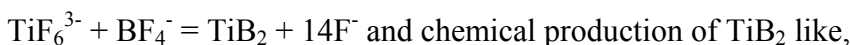


Figure 5: Cathodic potential on different current ranges. Electrolyte FLiNaK + 2% mol total active species (KBF<sub>4</sub>/K<sub>2</sub>TiF<sub>6</sub>). B:Ti=4:1. Mo-WE, Graphite-CE, Pt QRE.

On the lower current densities it is possible to produce relatively pure TiB<sub>2</sub>; however, 250 mA/cm<sup>2</sup> can be used as maximum limit for the production of the TiB<sub>2</sub>. The high current densities over than 250 mA/cm<sup>2</sup> cause side reactions that affects the purity of the cathodic product. And also supporting electrolyte destroys. At higher current densities that 250 mA/cm<sup>2</sup> TiB<sub>2</sub> formation can changed from thin layers to bulk and it is easy to detach from cathode surfaces.

Electrochemical production of the TiB<sub>2</sub> is a chemically assisted electrochemical reaction, Titanium and Boron goes to cathode and on the cathode surface TiB<sub>2</sub> production can occur according to previous works [8].

Total electrochemical reaction,



A XRD measurement results (Figure 6) of the experiment that conduct at 100 mA/cm<sup>2</sup> is given below. Together with TiB<sub>2</sub> also there are some additional peaks which are generally LiF and KF peaks because of the carrying of electrolyte with the cathode. A better washing process after electrochemical production will solve that problem.

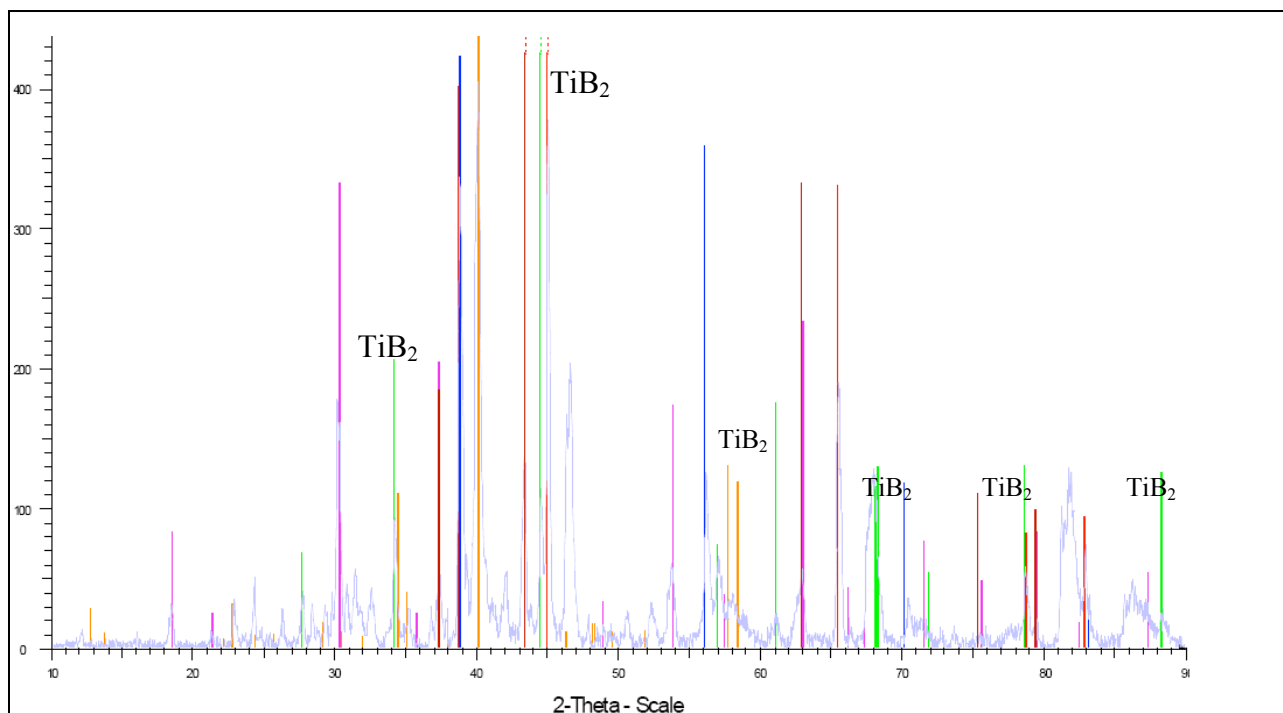


Figure 6: XRD pattern of cathode after experiment : Production parameters, Current density 100 mA/cm<sup>2</sup> , :4 Ti:B Ratio, 0.034 mol KBF<sub>4</sub>, 700 °C, 1 h

On the other hand, it is obvious that pretreatment of the cathodes after processes is really important otherwise surfaces contains residue of electrolyte which can affect the further operations or usage also causes some side reactions on the cathode surface.

## 4 Summary

Electrochemical synthesis of TiB<sub>2</sub> from FLiNaK melts with very low or zero oxygen levels is possible. FLiNaK has a good electrochemical window that allows working with Titanium and Boron ions as active species. Up to -1.2 V vs. Pt QRE it is possible to work with that electrolyte – electrode systems to produce the compound.

Current density can be risen up to 250 mA/cm<sub>2</sub> and after that product can change to bulk material and also some chemical changes can occur due to secondary electrochemical reactions which affect the purity and properties of the TiB<sub>2</sub>.

## 5 References

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