# Electrochemical Synthesis of Binary and Ternary Refractory Compounds in the System Ti-Si-B from Chloride-Fluoride Melts

Sergei V. Devyatkin

Institute of General and Inorganic Chemistry, Palladin avenue 32/34, Kiev 252142, Ukraine

Reprint requests to Dr. S.V. D.; Fax: 38-044-4443070; E-mail: devyatkin@ionc.kar.net

Z. Naturforsch. **62a,** 524 – 528 (2007); received March 15, 2007

*Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.*

Electrochemical synthesis of binary and ternary compounds in the system Ti-Si-B from chloride-fluoride melts has been investigated by voltammetry and electrolysis. Electrochemical syntheses of titanium diboride, four titanium silicides ($TiSi_2$, TiSi, $Ti_5Si_4$, $Ti_5Si_3$), silicon tetraboride and a new ternary compound, $Ti_5Si_3B_3$, have been found to be one-step processes. The stoichiometry of the deposited compounds has been found to correlate with the bulk concentration of Ti, Si and B ions in the melt.

*Key words:* Refractory Compounds; Electrochemical Synthesis; Molten Salts.

## 1. Introduction

Semiconducting and metal-like refractory compounds can be produced by electrochemical synthesis from molten salts in different forms (coating, dendrites or powder). The problem becomes simpler when the electrochemical potentials of the refractory compound components in the melt are close together. In this case, the most electropositive process in a particular system is the electrochemical synthesis of refractory compounds. One-step electrochemical synthesis allows deposition in a wide range of current densities of adherent coatings or powders of refractory compounds of stable stoichiometry. The system Ti-Si-B is of particular interest in terms of electrochemical synthesis since the titanium, silicon and boron potentials in the melt are close together. Binary phase diagrams of titanium, silicon and boron have been well investigated [1]. Ternary phase diagrams of Ti-Si-B have not been established.

Titanium diboride is a metal-like refractory compound which exhibits appreciable metallic properties: high thermal and electrical conductivity, oxidation resistance and high hardness [2]. Titanium silicides are metal-like refractory compounds which exhibit notable mix properties: low thermal conductivity, high electrical conductivity, thermal shock resistance, oxidation resistance and low hardness [2]. Silicon borides are semiconducting refractory compounds with diamond-like properties: low thermal conductivity, thermal shock resistance, oxidation resistance and high hardness [2].

Kaptay and Kuznetsov have reviewed the published papers on electrochemical synthesis of titanium diboride in molten salt [3]. Powders of titanium silicides and coatings of $Ti_5Si_3$ were deposited by electrochemical synthesis from a chloride-fluoride melt [4]. Silicon tetraboride was deposited from a fluoride melt [5].

## 2. Experimental

The electrochemical synthesis has been investigated in the system NaCl-KCl-$K_2TiF_6$-$K_2SiF_6$-$KBF_4$ (all salts of chemical purity) at 973 K using cyclic voltammetry and electrolysis experiments in a steel cell (INCOLOY 800HT). Experiments were carried out in an atmosphere of purified argon (99.996%). Glassy carbon (GC-2000) was used for the crucible, which also served as the counter-electrode. A cylindrical glassy carbon electrode with a surface area of $S = 0.5 – 0.7$ cm$^2$ was used as working electrode.

Electrolysis experiments were performed at 973 K under argon atmosphere. The glassy carbon crucible served as melt container and as anode. Stainless steel and nickel (99.99%) were used as cathode materials. Cathodic products were analyzed by X-ray spectroscopy, Auger electron spectroscopy, SEM-EPMA

(scanning electron microscopy with electron probe micro analysis) and SEM-EDS (scanning electron microscopy with energy dispersive spectrometry).

## 3. Results and Discussion

The electrochemical behaviour of titanium, boron and silicon ions in melts was investigated by cyclic voltammetry in previous papers [4, 6, 7].

In the ternary system NaCl-KCl-$K_2TiF_6$ titanium was found to be deposited in two steps:

$$\mathrm{Ti(IV)} + \mathrm{e} = \mathrm{Ti(III)}, \quad \mathrm{Ti(III)} + 3\mathrm{e} = \mathrm{Ti},$$

in the ternary system NaCl-KCl-$K_2SiF_6$ silicon was found to be deposited in two steps:

$$\mathrm{Si(IV)} + 2\mathrm{e} = \mathrm{Si(II)}, \quad \mathrm{Si(II)} + 2\mathrm{e} = \mathrm{Si},$$

and in the ternary system NaCl-KCl-$KBF_4$ boron was found to be deposited in one step:

$$\mathrm{B(III)} + 3\mathrm{e} = \mathrm{B}.$$

These results agree with literature data [8 – 10]. Diffusion coefficients for $[SiF_6]^{2-}$, $[TiF_6]^{3-}$ and $[BF_4]^-$ at 973 K were $(3 \pm 0.2) \cdot 10^{-5}$ cm$^2$/s [6].

In the quaternary system NaCl-KCl-$K_2TiF_6$-$K_2SiF_6$ the observed electrochemical processes corresponded to charge exchange of titanium silicides [4]. Thermodynamic calculations showed the possibility of depositing four titanium silicides ($TiSi_2$, TiSi, $Ti_5Si_4$, and $Ti_5Si_3$) by one-step electrochemical synthesis [4, 7].

In the quaternary system NaCl-KCl-$K_2SiF_6$-$KBF_4$ a process which was more electropositive than the deposition of boron and silicon was observed. This process corresponded to the charge exchange of silicon tetraboride. This result correlated with thermodynamic calculations [7].

In the other quaternary system NaCl-KCl-$K_2TiF_6$-$KBF_4$ a new process, being more electropositive than the deposition of boron and titanium, was observed. Thermodynamic calculations showed the possibility of one-step electrochemical synthesis of titanium diboride [3, 7]. This process corresponded to the recharge of titanium diboride. In the case of the molar ratio $x = 1:2$ of Ti to B ions in the melts, only one wave in the cathodic range of the voltammogram was observed (Fig. 1). In the case of the molar ratio $x = 1:1$ of Ti to B ions in the melts, only two waves in the cathodic range of the voltammogram were observed

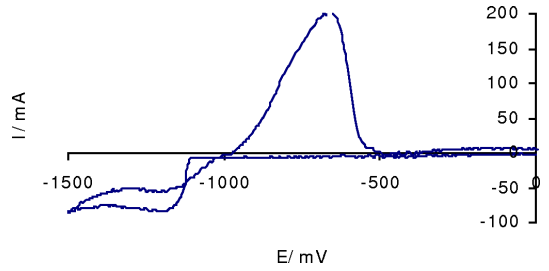


Fig. 1. Cyclic voltammogram of the system NaCl - KCl - $K_2TiF_6$ ($5 \cdot 10^{-5}$ mol/cm$^3$) - $KBF_4$ ($1 \cdot 10^{-4}$ mol/cm$^3$) at 973 K, $v = 0.5$ V/s.

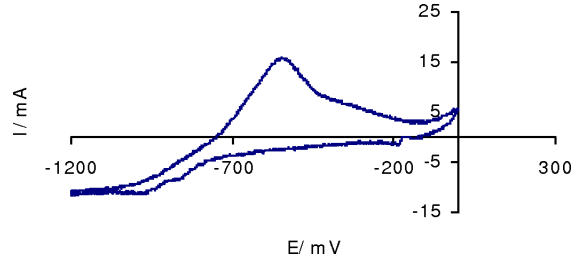


Fig. 2. Cyclic voltammogram of the system NaCl - KCl - $K_2TiF_6$ ($5 \cdot 10^{-5}$ mol/cm$^3$) - $KBF_4$ ($5 \cdot 10^{-5}$ mol/cm$^3$) at 973 K, $v = 0.1$ V/s.

(Fig. 2). The first peak corresponded to titanium diboride electrochemical synthesis and the second peak to deposition of titanium after titanium diboride with formation of titanium boride.

The electrochemical synthesis of hafnium diboride from a chloride-fluoride melt is possible in one step, and the diffusion coefficients of $[HfF_6]^{2-}$ $[(1.36 \pm 0.05) \cdot 10^{-5}$ cm$^2$/s] and $[BF_4]^-$ $[(3.2 \pm 0.05) \cdot 10^{-5}$ cm$^2$/s] at 973 K differed by a factor of three [6]. In the quaternary system NaCl - KCl - $K_2HfF_6$ ($5 \cdot 10^{-5}$ mol/cm$^3$) - $KBF_4$ ($1 \cdot 10^{-4}$ mol/cm$^3$), the ratio of Hf and B ions in the melts correlated with the stoichiometry of hafnium diboride. The cyclic voltammogram reflected three processes: charge exchanges of hafnium diboride, boron and hafnium [6].

Coatings of $Ti_5Si_3$ [4], $SiB_4$ [5] and $TiB_2$ [6] were deposited on nickel, molybdenum or stainless steel cathodes from chloride-fluoride melts at 973 K. The influence of the current density on the morphology of the titanium diboride coating is shown in Figs. 3 and 4.

For the electrochemical synthesis of binary refractory compounds, the following thermodynamic, kinetic and stoichiometry criteria were obtained. Only one electrochemical process on a melt background is observed in the cyclic voltammogram in the cases of:

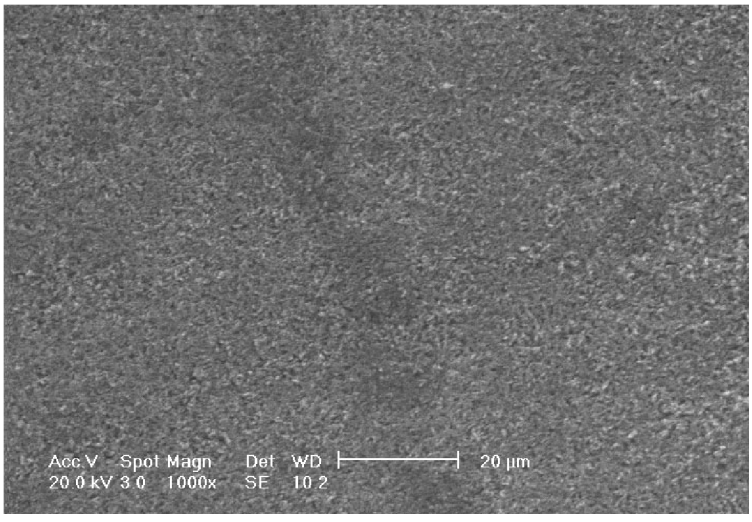


Fig. 3. Surface morphology of $TiB_2$ coating deposited from the system NaCl-KCl-$K_2TiF_6$-$KBF_4$ at 973 K, $i = 40$ mA/cm$^2$.

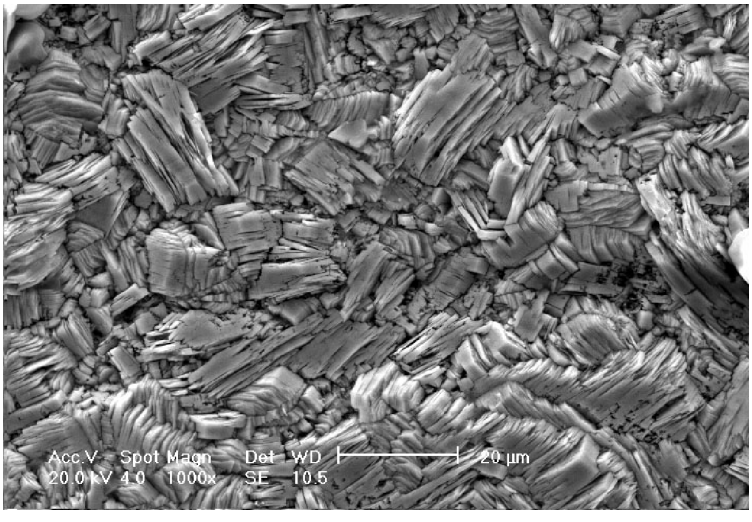


Fig. 4. Surface morphology of $TiB_2$ coating deposited from the system NaCl-KCl-$K_2TiF_6$-$KBF_4$ at 973 K, $i = 80$ mA/cm$^2$.

• one-step electrochemical synthesis of refractory compounds;

• the diffusion coefficients of refractory compound ions in the melt being close together;

• the stoichiometry of the refractory compound correlating with the molar ratios of this compound's ions in the melt.

Ternary phase diagrams of Ti-Si-B have not been established. The stoichiometry of ternary compounds in the system Ti-Si-B was investigated by cyclic voltammetry.

In the quintary system NaCl-KCl-$K_2TiF_6$-$K_2SiF_6$-$KBF_4$ a new process was observed. Process I corresponded to Ti(IV)/Ti(III) electron transfer. A small peak (II) corresponded to carbide formation; this peak depended on the scan rate and the quality of the glassy carbon surface [11]. A new process III was observed at more electropositive potential values than the deposition of titanium, silicon, boron or their binary compounds. In the case of the molar ratio $x = 5:3:3$ of Ti, Si and B ions in the melt, the voltammogram reflects only one electrochemical synthesis process (Fig. 5). In other cases, at the molar ratio $x = 6:2:1$ of Ti, Si, B ions in the melt (Fig. 6), the cyclic voltammograms show more electrochemical processes (III and IV).

The cross-section of the adherent coating of the ternary refractory compounds of the system Ti-Si-B

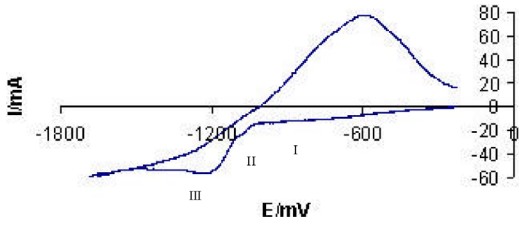


Fig. 5. Cyclic voltammogram of the system NaCl - KCl - $K_2TiF_6$ ($1 \cdot 10^{-4}$ mol/cm$^3$) - $K_2SiF_6$ ($6.2 \cdot 10^{-5}$ mol/cm$^3$) - $KBF_4$ ($6.3 \cdot 10^{-5}$ mol/cm$^3$) at 973 K, $v = 0.1$ V/s.

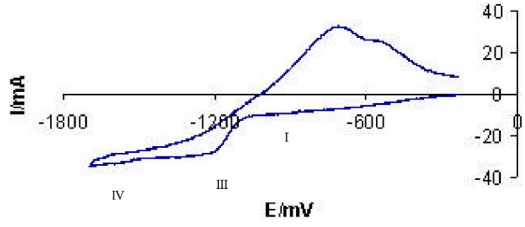


Fig. 6. Cyclic voltammogram of the system NaCl - KCl - $K_2TiF_6$ ($1.24 \cdot 10^{-4}$ mol/cm$^3$) - $K_2SiF_6$ ($4.1 \cdot 10^{-5}$ mol/cm$^3$) – $KBF_4$ ($2.3 \cdot 10^{-5}$ mol/cm$^3$) at 973 K, $v = 0.5$ V/s.

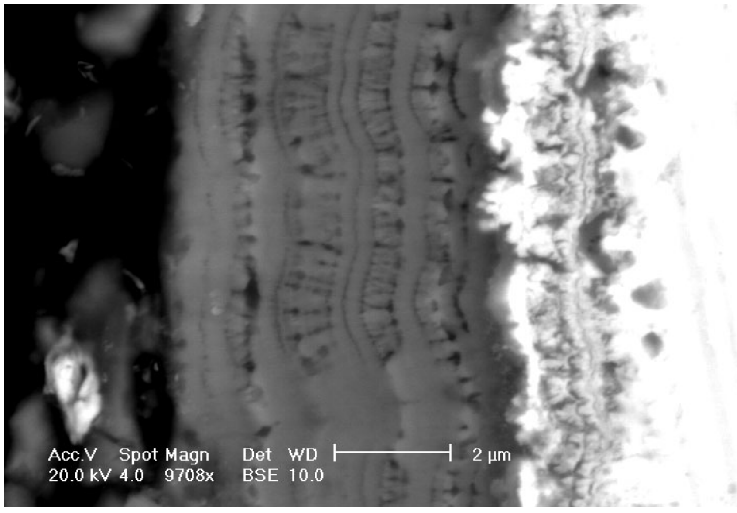


Fig. 7. SEM micrograph: cross-section of $Ti_5Si_3B_3$ coating deposited onto nickel.

is shown in Figure 7. Deposited coatings have mixed structure types, layered structure changes to a columnar one. The Auger spectrum of coatings deposited from the quintary system NaCl-KCl-$K_2TiF_6$-$K_2SiF_6$-$KBF_4$ showed peaks of titanium, silicon and boron [7]. SEM-EPMA showed an atomic ratio of titanium to silicon of 5 : 3 [12]. SEM-EDS showed an atomic ratio of titanium to silicon of 5 : 3 and boron [12]. On the basis of SEM analyses and voltammetry experiments it may be assumed that the stoichiometry of the deposited compound is $Ti_5Si_3B_3$.

## 4. Conclusion

Voltammetry and electrolysis experiments showed the possibility of one-step electrochemical synthesis of four titanium silicides ($TiSi_2$, TiSi, $Ti_5Si_4$, and $Ti_5Si_3$), titanium diboride and silicon tetraboride. The possibility of electrochemical synthesis of ternary refractory compounds in the system Ti-Si-B was shown by voltammetry experiments. Adherent coatings of $TiB_2$, $Ti_5Si_3$, $SiB_4$ and ternary refractory compounds in the system Ti-Si-B were deposited by electrochemical synthesis from a chloride-fluoride melt.

[1] H. Baker, Alloy Phase Diagrams, ASM International, Materials Park 1992.
[2] G. V. Samsonov and I. M. Vinitskii, Refractory Compounds, Metallurgia, Moscow 1976.
[3] G. Kaptay and S. A. Kuznetsov, Plasmas Ions **2**, 45 (1999).
[4] S. V. Devyatkin, O. I. Boiko, N. N. Uskova, and G. Kaptay, Z. Naturforsch. **56a**, 739 (2001).
[5] S. Aleonard, Bull. Soc. Chim. France **1**, 34 (1960).
[6] S. V. Devyatkin, G. Kaptay, V. I. Shapoval, I. V. Zarutskii, V. P. Lugovoi, and S. A. Kuznetsov, in: Refractory Metals in Molten Salts (Eds. D. H. Kerridge and

E. G. Polyakov), Kluwer Academic Publishers, Dordrecht 1998, p. 73.
[7] S. V. Devyatkin, Russ. J. Electrochem. **38**, 421 (2002).
[8] A. Girginov, T. Z. Tzvetkoff, and M. Bojinov, J. Appl. Electrochem. **25**, 993 (1995).
[9] J. De Lepinay, J. Bouteillon, S. Traore, D. Renaud, and M. J. Barbier, J. Appl. Electrochem. **17**, 294 (1987).
[10] L. P. Polyakova, G. A. Bukatova, E. G. Polyakov, E. Christiensen, J. H. von Barner, and N. J. Bjerrum, J. Electrochem. Soc. **143**, 3178 (1996).
[11] L. P. Polyakova, J. H. van Barner, and N. J. Bjerrum, J. Electrochem. Soc. **143**, 3178 (1996).
[12] S. V. Devyatkin, J. Solid State Chem. **177**, 407 (2004).