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Electrochemical synthesis of coatings in the system Ti–Si–B from molten salts

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Abstract

Powder and coatings of metal-like refractory compounds (MLRC) can be produced by electrochemical synthesis from molten salts. The stoichiometry of the deposited MLRC was found to correlate with the molar ratio of MLRC component ions in the melts. 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. The electrochemical synthesis has been investigated in the system NaCl–KCl–NaF–K_2TiF_6–K_2SiF_6–KBF_4 at 700°C. The opportunity of deposition of new ternary compound in the system Ti–Si–B is shown by the electrochemical synthesis from molten salts.

Keywords: Ti–Si–B; Molten salts; Electrochemical synthesis

1. Introduction

Binary phase diagrams between titanium, silicon and boron have been well investigated [1]. Ternary phase diagrams Ti–Si–B are not established. Thermodynamic properties of boron silicides containing 5 wt% TiB_2 were studied in Ref. [2]. It was discovered that the heat capacity and enthalpy decreased, which was attributed to the formation of a ternary Ti–Si–B compound. Powders and coatings of titanium diboride were deposited from chloro-fluoride [3] and cryolite melts [4]. Powder of titanium silicides ($TiSi_2$, TiSi, Ti_5Si_4, Ti_5Si_3) and coating of Ti_5Si_3 were deposited by electrochemical synthesis from molten salts [5]. Silicon tetraboride was deposited from fluoride melt [6]. Possibility of electrochemical synthesis of ternary compound Ti–Si–B by cyclic voltammetry were investigated in work [7].

2. Experimental

The electrochemical synthesis has been investigated in the system NaCl–KCl–NaF–K_2TiF_6(Ti)–K_2SiF_6–KBF_4 (all salts chemical purity) at 700°C using cyclic voltammetry and electrolysis experiments in hermetical steel cell (INCOLOY 800HT). Experiments were carried out in an atmosphere of purified argon (99.996%). Glassy carbon (GC-2000) was used as 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 the 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, Auger electron spectroscopy and SEM.

3. Results and discussion

Voltammetry experiments were performed in NaCl–KCl melts containing K_2TiF_6, K_2SiF_6, or KBF_4 at 973 K. In the voltammograms for NaCl–KCl–K_2TiF_6–K_2SiF_6–KBF_4 system, after the wave of a single-electron reduction of titanium, a new wave arises. One wave occurs only at a Ti:Si:B ions mole ratio of about 5:3:3 in melts. The new electrochemical process is not among the earlier known processes of electrochemical synthesis of

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binary compounds in the Ti–Si–B system or single Ti, Si, or B deposition.

Cyclic voltammetry showed new electrochemical processes to be different from the deposition of titanium, silicon or boron.

Electrolysis experiments were performed in the system NaCl–KCl–KF–K_2TiF_6–K_2SiF_6–KBF_4 with metallic Ti. Ti were added to system for formation Ti(III) ions in melts:

$$K_2TiF_6 + Ti + 4KF \rightarrow 2K_3TiF_6. \tag{1}$$

In the system NaCl–KCl–KF–K_2TiF_6–K_2SiF_6–KBF were only one electrochemical process corresponds to the electrochemical synthesis Ti–Si–B, there are no losses on a current on discharge:

$$Ti^{4+} + e \rightarrow Ti^{3+}. \tag{2}$$

Coatings of Ti–Si–B compound were deposited on nickel and stainless-steel cathode at current density 0.05–0.07 A/cm^2.

Fig. 1 shows morphology of surface of coating deposited to nickel cathode, coating have layered type of structures [8].

Fig. 2 shows morphology of surface of coating deposited to stainless steel, coating have columnar type of structures [8].

Fig. 3 shows cross-section of coating deposited to nickel cathode. Coating have mixed structure types layered change columnar and columnar change layered. In the case of nickel sample electrolysis is interrupted in moment formation of layered structure and in the case of stainless-steel sample electrolysis is interrupted in moment formation of columnar structure.

Cross section were analyzed for atomic concentration of elements. Fig. 4 shows the results of energy dispersive X-ray microanalysis made by Philips XL30 ESEM-FEG. Atomic ratio of Ti and Si approximately 5:3. Atomic ratio of B for this SEM was lover.

Fig. 5 shows result of Microanalysis made by CAMECA SX50, boron atomic ratio higher, then titanium and silicon (Ti:Si = 5:3).

The coatings of Ti–Si–B compounds obtained on stainless steel were examined by Auger electron spectroscopy. In addition to peaks of substrates (Fe, Cr, Ni), peaks of Ti, Si, and B were recorded. X-ray diffraction pattern deposited coatings were not interpreted, because the database contains no Ti–Si–B ternary compounds.

Hardness of deposited Ti–Si–B coating was higher then quartz (> 1500 kg/mm^2).

In our opinion stoichiometry of Ti–Si–B compounds was 5:3:3 on the base of voltammetry experiments, stoichiometry of deposited compound correlate with the mole ration of Ti, Si and B ions in the melts.

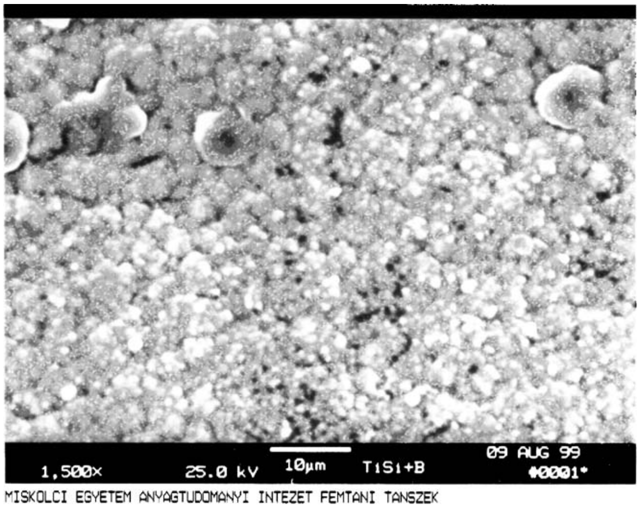

Fig. 1. SEM micrograph: Ti–Si–B surface deposited onto nickel.

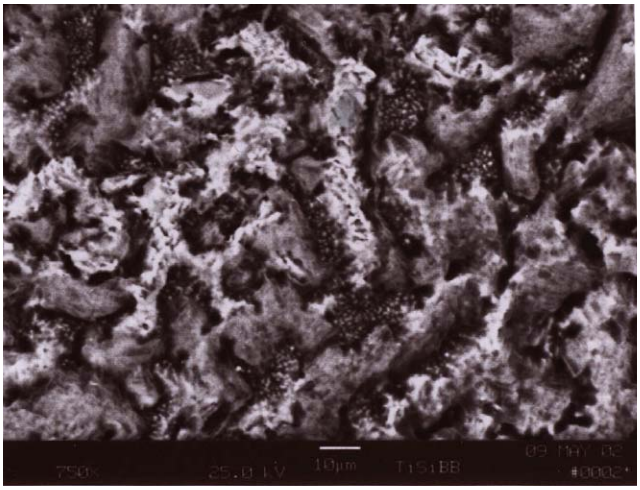

Fig. 2. SEM micrograph: Ti–Si–B surface deposited onto stainless steel.

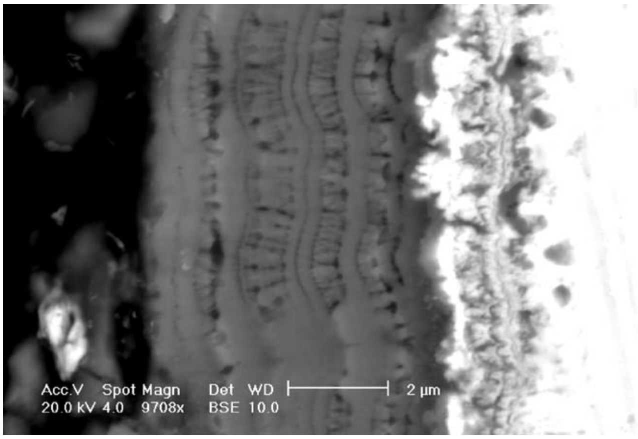

Fig. 3. SEM micrograph: cross-section of deposited Ti–Si–B onto nickel.

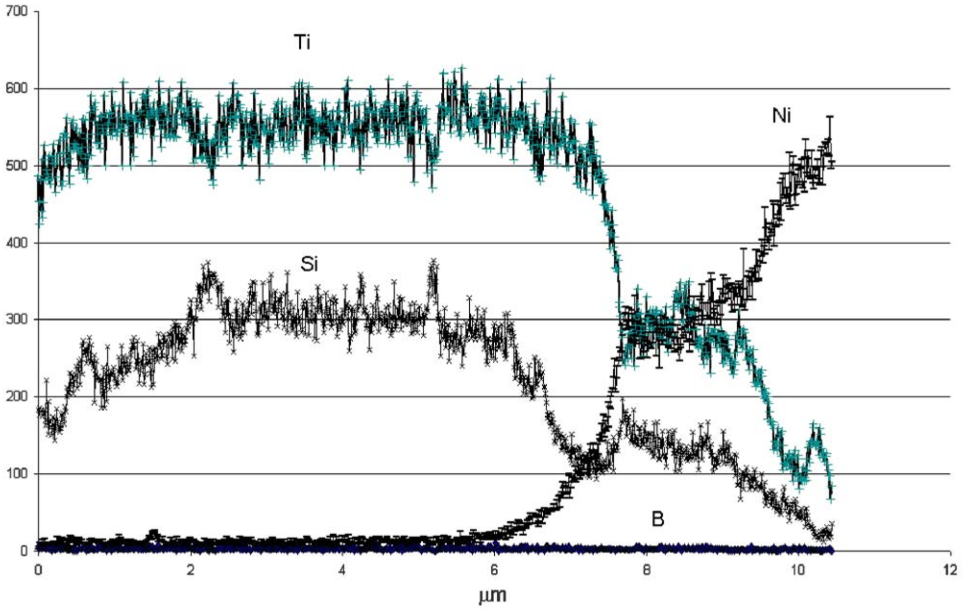

Fig. 4. Energy dispersive X-ray microanalysis. The acceleration voltage should have been 20 kV (Philips XL30 ESEM-FEG).

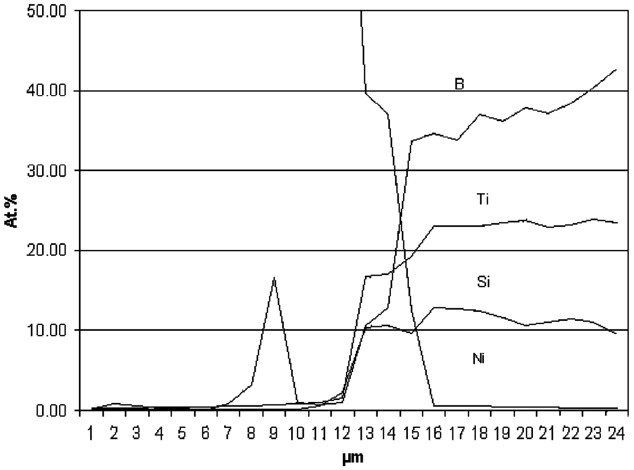

Fig. 5. Energy dispersive X-ray microanalysis. The acceleration voltage should have been 20 kV (CAMECA SX50).

4. Conclusion

Coating of deposited Ti–Si–B have mixed structure types layered change columnar and columnar change layered. Powder of deposited Ti–Si–B have globular form and size 70–100 µm. On the basis of voltammetry experiments it is possible, to assume that stoichiometry of the deposited composition $Ti_5Si_3B_3$. The studies of properties of the deposited new composition will be continued by a method X-ray analysis.

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