Electrochemical Synthesis of Titanium Silicides from Molten Salts

S. V. Devyatkin, O. I. Boiko, N. N. Uskova, and G. Kaptay[a]

Institute of General and Inorganic Chemistry, Palladin avenue 32/34, 03680 Kiev 142, Ukraine
[a] Department of Physical-Chemistry, University of Miskolc, Miskolc 3515, Egyetemvaros, Hungary

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

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Electrochemical synthesis of titanium silicides from chloro-fluoride melts has been investigated by thermodynamic calculation, voltammetry and electrolysis. The electrochemical synthesis of four titanium silicides ($TiSi_2$, TiSi, Ti_5Si_4, Ti_5Si_3) was to be a one-step process, the stoichiometry of the deposited silicides being correlated with the concentration of Si and Ti ions in the melt.

Key words: Titanium silicides; Electrochemical Synthesis; Molten Salts.

1. Introduction

Titanium silicides are metal-like refractory compounds (MLRC) which exhibit notable metallic properties: Resistance below 20 μΩ cm, low thermal conductivity, thermal shock resistance, oxidation resistance up to 1400°C, etc. [1]. These characteristics open the possibility of their application in metallurgy, chemical industry and electronics. The formation of coatings and powders of MLRC is possible by electrochemical synthesis from molten salts. The electrochemical synthesis of titanium silicides was studied by thermodynamic calculations, cyclic voltammetry and electrolysis.

The Equilibrium Electrochemical Synthesis Diagram (EESD) was calculated and constructed for the Ti-Si binary system [2]. The thermodynamic properties of TiSi, $TiSi_2$, and Ti_5Si_3 were taken from [3], while those of Ti_5Si_4 and Ti_3Si were estimated by us.

2. Experimental

Voltammetric experiments on NaCl-KCl-K_2SiF_6-K_2TiF_6 were performed in a steel cell under argon atmosphere using different ratios x of titanium to silicon ions in the melt. Glassy carbon was used as a crucible, which also served as counter electrode. Cylindrical glassy carbon with a tungsten wire (S = 0.5 - 0.7 cm^2) was used as working electrode. A cylindrical glassy carbon electrode served as reference electrode.

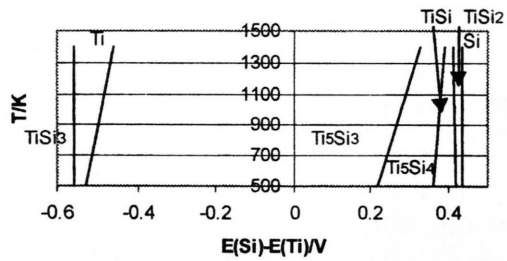

Fig. 1. Equilibrium Electrochemical Synthesis Diagram of the Ti-Si system.

Electrolysis experiments were performed at 973 K under argon atmosphere. The glassy carbon crucible served as melt container and as an anode. Tungsten and nickel were used as cathode materials. Cathodic products were analyzed by X-ray and SEM.

3. Results

From the ternary NaCl-KCl-K_2SiF_6 system silicon was found to deposit in two steps:

$$Si(IV) + 2e = Si(II), \quad Si(II) + 2e = Si.$$

In the other ternary system NaCl-KCl-K_2TiF_6 titanium was found to deposit in two steps, as well:

$$Ti(IV) + e = Ti(III), \quad Ti(III) + 3e = Ti.$$

These results agree with literature data [4, 5].

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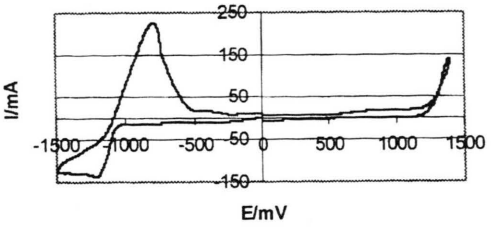

Fig. 2. Cyclic voltammogram of the system KCl - NaCl - K_2TiF_6 (6.6×10^{-5} mol/cm^3) - K_2SiF_6 (7.5×10^{-5} mol/cm^3) at 973 K, v = 0.5 V/s.

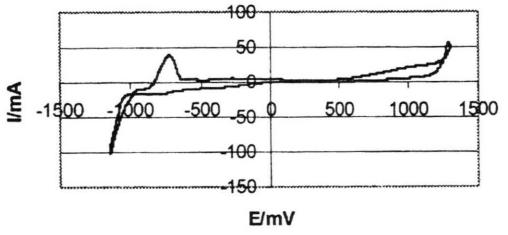

Fig. 3. Cyclic voltammogram in the system KCl - NaCl - K_2TiF_6 (9.9×10^{-5} mol/cm^3) - K_2SiF_6 (7.5×10^{-5} mol/cm^3) at 973 K, v = 0.5 V/s.

In the quaternary system NaCl-KCl-K_2SiF_6-K_2TiF_6 a new process, being more electropositive than the deposition of titanium and silicon has been observed. This process corresponds to the deposition of titanium silicides. In the case of the mole ratios x = 1:2 and x = 1:1 of Ti to Si ions in the melt, a reversible charge transfer with formation of an insoluble product was observed (Fig. 2). With x = 5:4 and x = 5:3 an irreversible charge transfer with formation of an insoluble product was found (Fig. 3). With x = 3:1 and above, electrodeposition of titanium was found.

Coatings of Ti_5Si_3 were deposited on nickel cathodes from the system NaCl-KCl-K_2SiF_6-K_2TiF_6 at 973 K (Fig. 4). Powders of titanium silicides were deposited on nickel cathodes from the system NaCl-KCl-K_2SiF_6-K_2TiF_6-SiO_2-TiO_2 at 973 K (Table 1). The stoichiometry of the deposited silicides was found to correlate with the concentration ratio of Ti to Si ions in the melts.

Table 1. Results of electrolysis experiments in the system KCl-KF-K_2SiF_6-K_2TiF_6-TiO_2-SiO_2 at (973±20) K.

Ti:Si mole ratio in melt	j_k A/cm^2	U V	Current efficiency, %	Powder composition
1:2	0.3	2.0	70 - 75	$TiSi_2$ (Ti_5Si_3)
	0.4 - 2.0	2.2 - 3.4	78 - 81	$TiSi_2$
1:1	0.4 - 2.0	2.5 - 3.5	77 - 79	TiSi
5:4	0.3	2.4	72 - 73	Ti_5Si_4($TiSi_2$)
	0.4 - 2.0	2.6 - 3.3	77-79	Ti_5Si_4
5:3	0.3	2.4	71 - 72	Ti_5Si_3($TiSi_2$)
	0.4 - 2.0	2.6 - 3.7	74 - 76	Ti_5Si_3

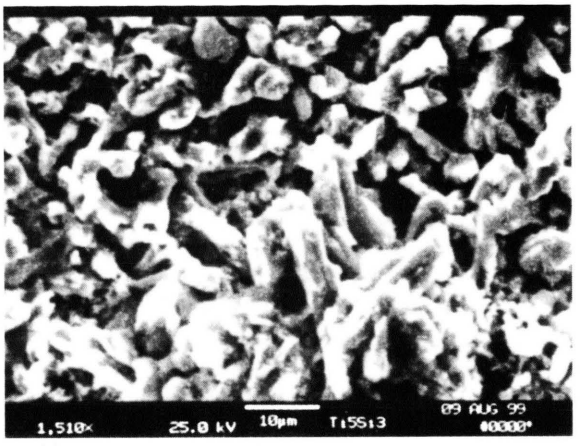

Fig. 4. Morphology of Ti_5Si_3 coating deposited onto nickel.

4. Conclusion

Thermodynamic calculations, voltammetry and electrolysis showed the possibility of one step electrochemical synthesis of four titanium silicides ($TiSi_2$, TiSi, Ti_5Si_4, and Ti_5Si_3). The stoichiometry of the deposited silicides was found to correlate with the mole ratios of Ti to Si in the melt.

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