

ELECTROCHEMISTRY OF SILICON IN CHLORO-FLUORIDE AND CARBONATE MELTS

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Abstract

The electrochemical behavior of K_2SiF_6 in chloro-fluoride melts and that of SiO_2 in carbonate melts has been studied. Silicon, titanium silicides, boron silicide and ternary compounds Ti-Si-B have been deposited from chloro-fluoride melts. Only SiC was deposited from carbonate-silica melts under carbon dioxide atmosphere (that is, excessive pressure of CO_2).

Keywords: silicon, titanium silicides, silicon carbide, electrodeposition, molten salts

1. Introduction

The electrochemical deposition of silicon and its compounds from molten salts is an important direction of metallurgy (for example, co-deposition of aluminum and silicon in Hall-Heroult cell for the deposition of silumin). The reduction of K_2SiF_6 proceeds in one step in ref. [1] and in two steps, coupled with an antidisproportionation reaction in Ref.[2]. Refractory compounds of silicon have important properties. Titanium silicides exhibit notable metallic properties: thermal shock resistance, oxidation resistance up to 1400 °C etc. However, the thermal conductivity of titanium silicides is low. Silicon carbide is a semiconductor with high hardness and oxidation resistance up to 1200 °C. The production of silicon and its compounds is possible by electrodeposition from molten salts at 700-750 °C.

In this work, the electrochemical behavior of silicon in chloro-fluoride and carbonate melts, and the possibility of electrosynthesis of silicon compounds (*Ti-Si*, *Si-B*, *SiC*) have been studied.

2. Experimental

The electrochemical behavior of silicon in the melts mentioned above has been studied by cyclic voltametry. Electrochemical experiments were conducted in a hermetically steel cell in *NaCl-KCl* (with melting point of 660 °C)-*K₂SiF₆* (*K₂TiF₆*, *KBF₄*) melts under argon atmosphere at 700 °C, and in *Na₂CO₃-K₂CO₃* (with melting point of 710 °C), *Na₂CO₃-Li₂CO₃* (with melting point of 517 °C) silica-containing melts under carbon dioxide pressure at 650-800 °C. Glassy carbon was used as a crucible, which also served as the counter electrode. A glassy carbon rod or *Pt* wire was used as the working and reference electrode. After the electrolysis the cathodic product was analyzed by X-ray and SEM.

3. Results

Two cathodic (I, II) and two anodic peaks (I', II') (Fig. 1) appear in the voltamograms of *NaCl-KCl-K₂SiF₆* melt at scan rates of 0.01-1 V/s, while at a scan rate of 0.001 V/s only one cathodic peak (Fig. 2) appears. The peak current and peak potential are a function of the scan rate.

The disappearance of one of the peaks at 0.001 V/s and high current efficiency (95 %) of silicon electrodeposition in this melt point to a disproportionation reaction. On the basis of investigation of the electrochemical behavior of silicon in the chloro-fluoride melt, the following conclusions can be drawn. The electrodeposition process of silicon proceeds in two steps; the product of the first step undergoes a disproportionation reaction:

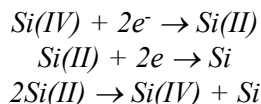


Fig.3 shows the morphology of the deposited silicon coating on a nickel cathode.

In the system *NaCl-KCl-K₂SiF₆-K₂TiF₆* new electrochemical processes were observed. They correspond to the electrosynthesis of titanium silicides. The stoichiometry of silicides was found to correlate with the mole ratio of *Ti* to *Si* in the melt. Powders of *TiSi₂*, *TiSi*, *Ti₅Si₄*, *Ti₅Si₃* and a coherent coating of *Ti₅Si₃* were deposited [3]. In the system *NaCl-KCl-K₂SiF₆-KBF₄* new electrochemical processes were observed, and they were attributed to the electrosynthesis of boron silicide. A new ternary compound *Ti₅Si₃B₃* was deposited in the system *NaCl-KCl-K₂TiF₆-K₂SiF₆-KBF₄* [4].

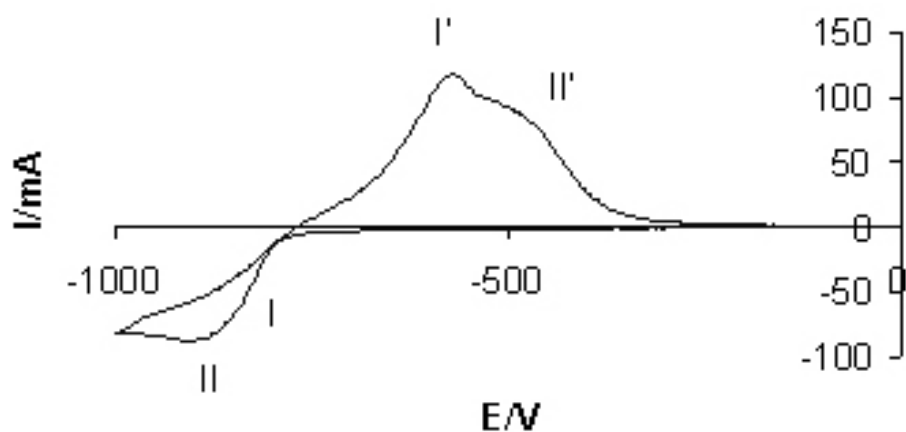


Fig. 1. Cyclic voltammogram of NaCl-KCl-K₂SiF₆(5.5 x 10⁻⁵ mol/cm³) melt. 700 °C, v=0.5 V/s

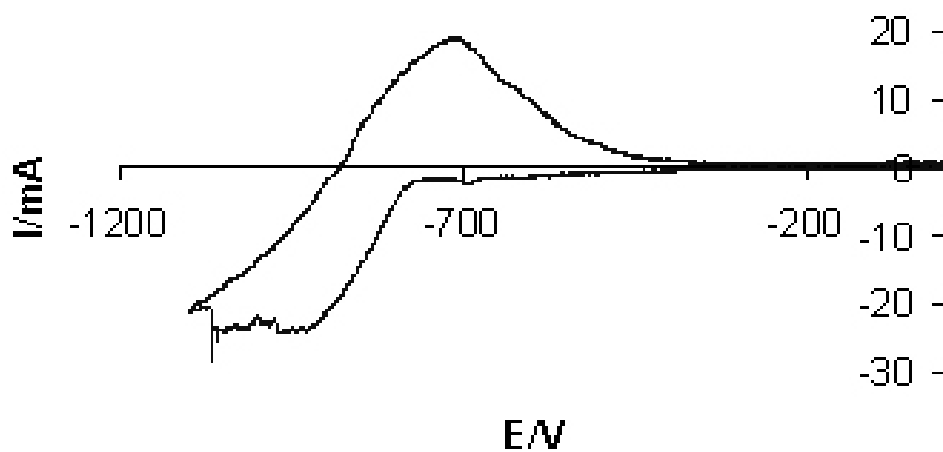


Fig. 2. Cyclic voltammogram of NaCl-KCl-K₂SiF₆(5.5 x 10⁻⁵ mol/cm³) melt. 700 °C, v=0.001 V/s

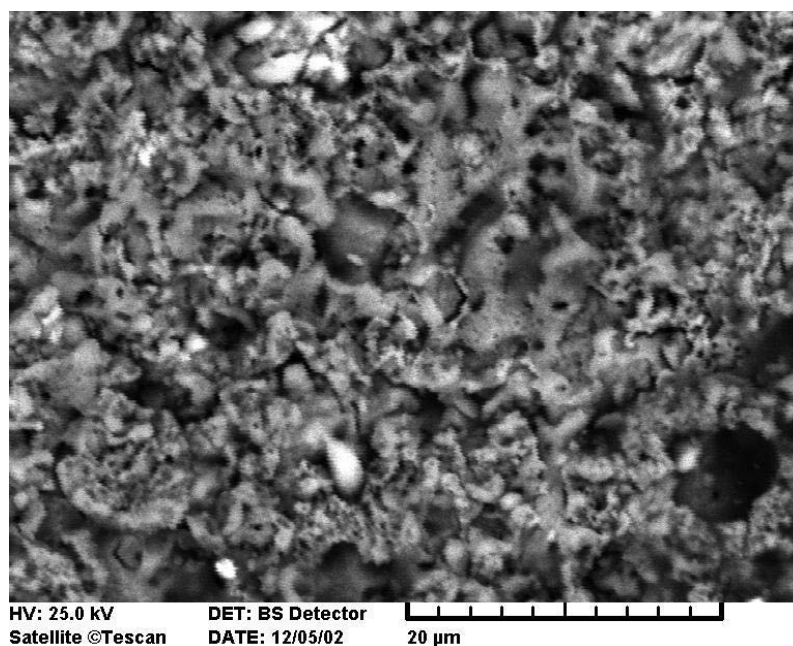


Fig. 3. Surface morphology of silicon coating deposited on nickel

The decomposition potential of silica is more negative than the decomposition potential of carbonates. In this case silicon cannot be deposited from carbonate-silica melts. The electrosynthesis of silicon carbide is possible from carbonate-silica melts under carbon dioxide pressure (Table 1). In Ref. [5] we show the possibility of electrochemical synthesis of silicon carbide from carbonate-silica melts in carbon dioxide atmosphere.

Table 1. Results of thermodynamic calculations ($T=750^{\circ}\text{C}$)

Reaction	$\Delta G^{\circ}_{\text{R}}$, kJ	ΔE° , V
$\text{CO}_2 = \text{C} + \text{O}_2$	395.868	-1.026
$\text{SiO}_2 + \text{CO}_2 = \text{SiC} + 2\text{O}_2$	1055.266	-1.367
$\text{Na}_2\text{CO}_3 = 2\text{Na} + \text{C} + 3/2\text{O}_2$	844.991	-1.459
$\text{SiO}_2 = \text{Si} + \text{O}_2$	723.953	-1.876

Cyclic voltametry experiments were performed in the system $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-SiO}_2$ (4 wt. %) at 750 °C under a carbon dioxide pressure of 1, 5 and 10 atm. Figure 4 shows typical cyclic voltamogram of this melt under pressure of carbon dioxide of 5 atm. The first cathodic peak corresponds to the deposition of carbon, while the second cathodic and anodic peaks correspond to the electrochemical synthesis of silicon carbide and its oxidation.

The minimal temperature needed for the electrochemical synthesis of SiC is $700\text{ }^{\circ}C$. The voltammograms of $Na_2CO_3-Li_2CO_3-SiO_2$ melt below $700\text{ }^{\circ}C$ do not reveal electro-synthesis peaks. The solubility of carbon dioxide in molten carbonates depends on the temperature, and at $650\text{ }^{\circ}C$ carbon dioxide is practically insoluble in the melt. Electrolysis experiments were performed in the system $Na_2CO_3-Li_2CO_3-SiO_2$ (4 wt.%) at $750\text{ }^{\circ}C$ under pressure of carbon dioxide of 1 atm. The deposited SiC layer on stainless steel has a grain structure.

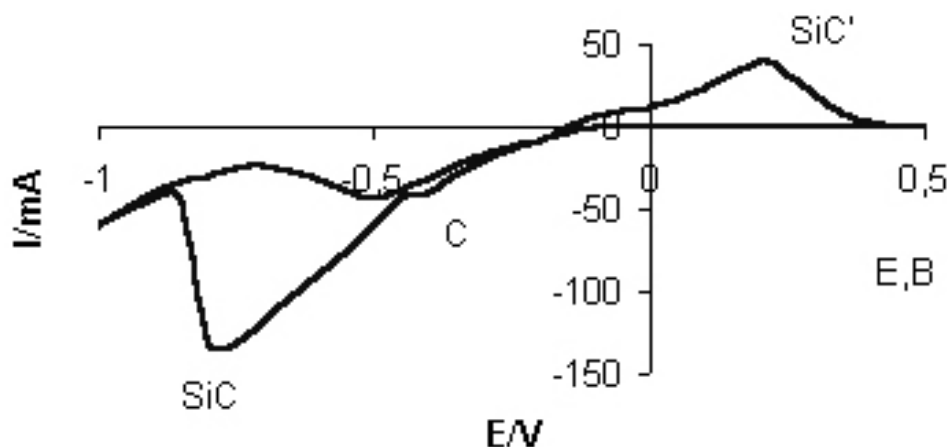


Fig. 4. Cyclic voltammogram of $Na_2CO_3-K_2CO_3-SiO_2$ ($2 \times 10^{-3} \text{ mol/cm}^3$) melt. $750\text{ }^{\circ}C$, $P_{CO_2}=5 \text{ atm.}$, $\nu=0.001 \text{ V/s}$, $A_{Pt}=0.6 \text{ cm}^2$

4. Conclusions

Powders and coatings of silicon and its compounds (silicides) can be deposited from chloro-fluoride melts. Silicon cannot be deposited from carbonate melts, only silicon carbide is deposited from carbonate-silica melts under carbon dioxide pressure.

References

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