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Electrochemical Synthesis of Chromium Silicides from Molten Salts

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Abstract: Electrochemical synthesis of chromium silicides from NaCl-KCl-K_2SiF_6-CrF_3 system has been investigated by cyclic voltammetry and DC (direct current) electrolysis at 850 °C. The process of Cr and Si joint electroreduction in chloride-fluoride melt proceeds in one stage in a kinetic mode. The cathode product was analyzed using XRD (X-ray diffraction) method. XRD data have confirmed that Cr_3Si is the dominant phase. SEM (scanning electron microscopy) results have shown that Cr_3Si powder samples consist of 50-150 μm particles and that tungsten silicide was formed at the surface of tungsten cathode after chrome-free system electrolysis.

Key words: Chromium, silicide, fluoride, molten salt, electrochemical synthesis.

1. Introduction

Transition metals silicides demonstrate exceptional properties at elevated temperatures, namely high electrical conductivity, temperature stability, strength and corrosion resistance [1]. Particularly, $CrSi_2$ is a promising thermoelectric material used for energy conversion at high temperature [2] or as anode material for Li-ion batteries [3]. Chromium silicides are among the most advanced high-temperature structural materials of the next generation [4].

Electrochemical synthesis, a promising technique, combines extraction and purification into a one step process [5] and leads to obtain high purity chromium silicides. Initially, electrochemical synthesis of chromium silicides was implemented in molten KCl-Na_3AlF_6-K_2CrO_4-SiO_2 mixture. Cr_2O_3, $CrSi_2$ and Cr_3Si silicide phases, together with the aluminum compounds, were obtained [6]. To optimize the production of chromium silicides, molten KCl-KF-K_2SiF_6-K_2CrO_4 system was used [7]. Cr_2O_3, Cr_3Si and $CrSi_2$ phases, together with the mix of these phases, were found. However, when choosing the CrO_4^{2-} and SiF_6^{2-} concentrations, it should be taken into account that the Cr_2O_3 salt "bulb" was formed in the first stage of electrolysis, which began to siliconize as the chromium was worked out in melt.

The aim of the present study is to choose the electrolyte composition and to optimize the electrolysis conditions. An important part of this work is to develop a method for electrochemical synthesis of high purity chromium silicides in molten salts.

2. Experiments

The electrochemical synthesis has been performed in the molten NaCl-KCl-K_2SiF_6-CrF_3 system at 850 °C using cyclic voltammetry and electrolysis methods. Investigations were carried out in an atmosphere of purified argon (99.99%). The processes of chromium-ion and silicon-ion joint electroreduction were studied using PI-50-1 potentiostat and the Pt indicator electrode. Platinum wire was used as a

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reference electrode for volt-ampere measurements. GC (glassy carbon)-2000 crucible was used, also serving as an auxiliary electrode.

Electrolysis experiments were implemented during 1-2 h at 850 °C under argon atmosphere. Graphite crucible was used as melt container and anode. Tungsten rod served as cathode. Cathodic products were investigated by X-ray analysis and SEM (scanning electron microscopy) methods.

3. Results and Discussion

According to literature data [8, 9], chromium(III) deposits from molten chloride-fluoride system in two stages:

$$\mathrm{Cr(III)} + e \rightarrow \mathrm{Cr(II)} \quad (1)$$

$$\mathrm{Cr(II)} + 2e \rightarrow \mathrm{Cr} \quad (2)$$

In the same system, silicon was found to deposit in two steps [10], as well:

$$\mathrm{Si(IV)} + 2e \rightarrow \mathrm{Si(II)} \quad (3)$$

$$\mathrm{Si(II)} + 2e \rightarrow \mathrm{Si} \quad (4)$$

Volt-ampere plots contain waves of Cr and Si complexes reduction at potentials of -0.7 V to -0.9 V (Red_1) and -1.6 V to -1.9 V (Red_2), respectively (Fig. 1).

As voltammetric measurements show, electrochemical synthesis of chromium silicides can be performed under the conditions of kinetic control only, with the more electropositive component (Cr) deposited first, and the second component (Si) deposited subsequently on its surface. Diffusion limitations result in formation of silicides of different compositions, up to the higher silicide $CrSi_2$ [6, 11].

Fig. 2 shows deposits obtained after experiments on W cathode after salt removal. The deposits were adherent and their roughness was relatively high.

The potentiostatic electrolysis at the potential of observed (Red_2) wave leads to the formation of chromium silicides. It was confirmed by X-ray patterns of obtained product (Fig. 3).

Thermodynamic calculations for the Cr interaction with Si on the cathode based on the data [12] and aimed on the estimation of possibility of production of different silicides (Cr_3Si, Cr_5Si_3, CrSi, $CrSi_2$) (Table 1) were carried out for the 800-900 °C conditions. Formation of the Cr_3Si and Cr_5Si_3 silicides was found to be the most thermodynamically efficient process.

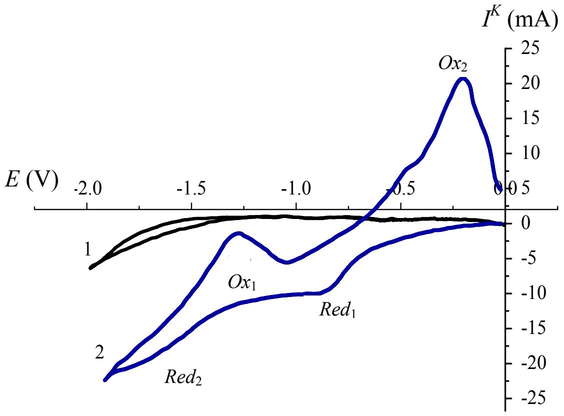

Fig. 1 Cyclic voltammograms of the $NaCl\text{-}KCl_{eq.}\text{-}CrF_3\text{-}K_2SiF_6$ system at 850 °C; cathode—Pt, υ = 0.1 $V \cdot s^{-1}$: 1—$NaCl\text{-}KCl_{eq.}$, 2—$NaCl\text{-}KCl_{eq.}\text{-}CrF_3$ (1×10^{-5} $mol \cdot cm^{-3}$)-K_2SiF_6 (2×10^{-5} $mol \cdot cm^{-3}$).

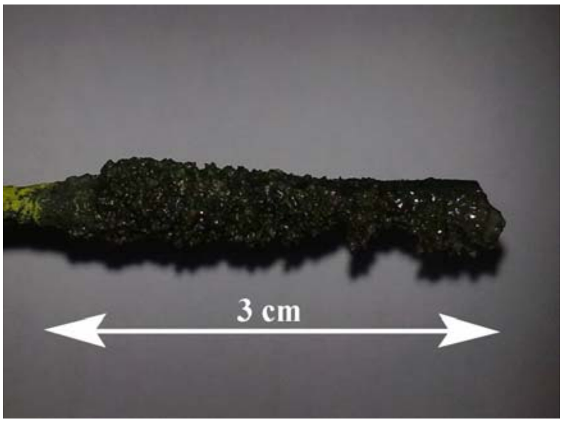

Fig. 2 W-cathode photograph after electrolysis in molten $NaCl\text{-}KCl\text{-}CrF_3\text{-}K_2SiF_6$: i = 0.27 $A \cdot cm^{-2}$ at 850 °C.

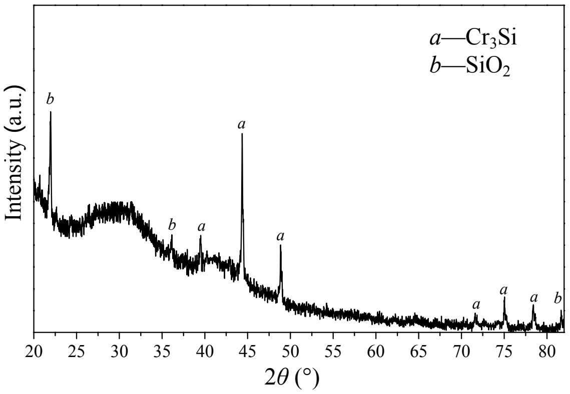

Fig. 3 XRD (X-ray diffraction) pattern of the cathodic product electrolyzed for 1 h.

Table 1 The Cr + Si → Cr_xSi_y reaction ΔG value ($ccal \cdot mol^{-1}$).

Cr_xSi_y	Temperature (°C)	
	800	900
Cr_3Si	-24.74	-24.64
Cr_5Si_3	-55.3	-55.71
CrSi	-13.53	-13.64
$CrSi_2$	-17.47	-17.23

After electrolysis, obtained deposits were collected from the W-cathode surface and analyzed using XRD method. Fig. 3 shows the XRD pattern of cathodic products, which reveal that Cr_3Si phase with small content of SiO_2 has been produced during 1 h of electrolysis. We assume that further electrochemical reduction (during more than 1 h) can lead to the formation of silicides with higher Si content.

SEM image of cathodic products is shown in Fig. 4. It was found that particle size of Cr_3Si powder is 50-150 μm.

Fig. 5 shows the cathode cross section after the electrolysis. Change of color of W surface was observed after the experiment. SEM analysis indicated that the deeper colored area of W-cathode is composed of around 70% W and 30% Si.

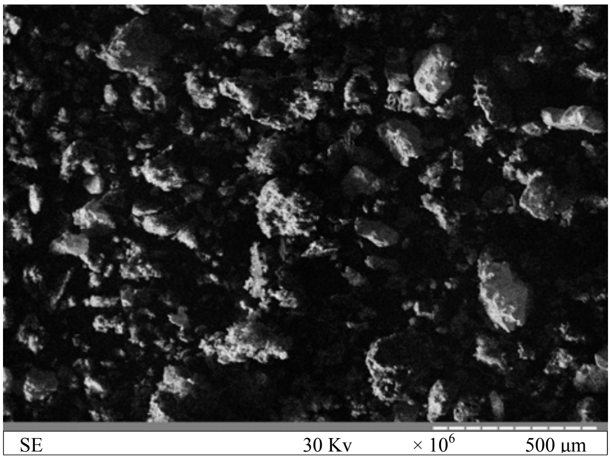

Fig. 4 SEM image of cathodic products obtained during 1 h.

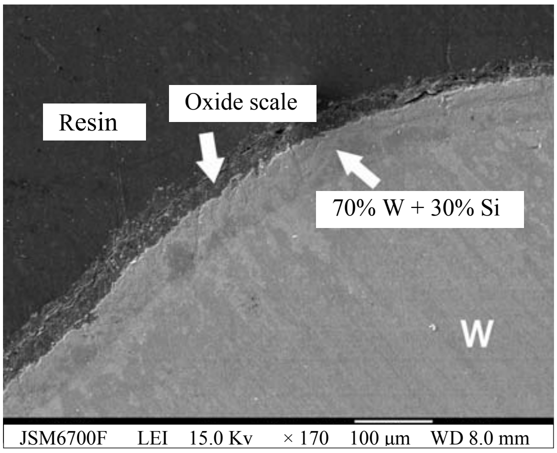

Fig. 5 SEM micrograph of the cathode cross section after electrolysis of molten $NaCl\text{-}KCl_{eq.}\text{-}CrF_3\text{-}K_2SiF_6$ system with i = 0.27 $A \cdot cm^{-2}$ at 850 °C during 1 h.

Current efficiency for the chromium silicide synthesis was calculated. The current efficiency is the ratio of the actual mass (m_a) of a substance liberated from an electrolyte by the passage of current to the theoretical mass (m_t) liberated according to Faraday's law [13] and expressed as:

$$\eta = \frac{m_a}{m_t} \tag{5}$$

where, η is the current efficiency. Theoretical and practical product weights were 9.1 g and 3.2 g, respectively. So, the current efficiency was 35% after 1 h electrolysis.

4. Conclusions

Cr_3Si was synthesized by joint electrochemical reduction of chromium and silicon complexes in molten $NaCl\text{-}KCl_{eq.}\text{-}CrF_3\text{-}K_2SiF_6$ system at 850 °C. The mechanism for the Cr_3Si formation is a one-step process. X-ray analysis data have confirmed that the dominant phase of the obtained product is Cr_3Si. The electrochemical synthesis of chromium silicides is influenced by the temperature and the process duration. The current efficiency was calculated to be 35%. It confirms that the electrochemical synthesis is an efficient and environmentally safe process to produce silicides from their compounds, and it is promising for industrial application.

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