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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

# Chemical and Electrochemical Behavior of Carbonate Melts Containing Silicon Oxide

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**Abstract**—The optimal conditions of electrochemical synthesis of silicon carbide in carbonate melts containing silicon oxide were determined on the basis of thermodynamic calculations and data of cyclic voltammetry.

Carbonate melts have found wide use as electrolytes for fuel cells [1] and for treatment of castings. The behavior of molten carbonates has been studied extensively. At the same time, use of carbonates as supporting molten electrolytes in electrolysis aimed to obtain solid deposits is poorly studied. In [2, 3], the possibility of carbon deposition at the cathode in these media was examined.

Alkali metal carbonates react rather well with a number of metals [4] and dissolve oxides of refractory metals and *p* elements (B, Al, Si, Ge, etc.) [5]. The range of potentials in which carbonate melts do not decompose is 1.6-V-wide, but cathodic depolarization of electrochemical synthesis is possible because of the low energy of formation of silicon and titanium carbides [6] ($\Delta G_f^0$ = –65 kJ mol$^{-1}$ for SiC and $\Delta G_f^0$ = –173 kJ mol$^{-1}$ for TiC at 1000 K). Synthesis of carbides in molten carbonates may occur in the given range of potentials. Therefore, it may be considered promising to use carbonate melts to synthesize carbides. Commonly, a binary $K_2CO_3$–$Li_2CO_3$ (mp 492°C) or ternary eutectic $K_2CO_3$–$Na_2CO_3$–$Li_2CO_3$ (mp 397°C) are used [7]. However, lithium carbonate is poorly soluble in water [8], and, therefore, a binary eutectic $K_2CO_3$–$Na_2CO_3$ (mp 720°C) was chosen as object of study [7].

Potassium and sodium carbonates are well soluble in water, which makes unnecessary use of acid for washing of the cathode product. In [9], silicon carbide was obtained from an $SiO_2$ (20%)–$Li_2CO_3$ melt at 1050°C. However, the synthesis mechanism was not studied. Electrolysis was performed at elevated temperature because of the high concentration of the higher-melting component, silicon oxide. Silicon carbide is widely used in the industry, since its exhibits high hardness, refractoriness, oxidation resistance, and semiconducting properties.

The aim of this study was to analyze the ?interaction of molten alkali metal carbonates with silicon oxide and the electrochemical behavior of this system, and to choose the optimal conditions of electrochemical synthesis of silicon carbide.

To prognosticate processes occurring in the systems, the Gibbs energy, $\Delta G^0$, were calculated for a number of chemical reactions possible in molten carbonates at 750°C. The results obtained are presented in the table. It can be seen that silicon oxide is infinitely soluble in molten carbonates because of exchange reactions (4)–(6). The solubility of carbon dioxide in molten carbonates at 750°C is $10^{-4}$ mol cm$^{-3}$ (~0.22 wt %) [10]. Carbon dioxide dissolves in molten carbonates without chemical reaction, and, consequently, its solubility is directly proportional to pressure, i.e., is described by the Raoult law. Having positive Gibbs energies, molten carbonates of potassium, sodium, and lithium are not susceptible to decomposition [reactions (2) and (3)]. Introduction of silicon oxide into a melt leads in all cases to formation of free carbon dioxide. Consequently, to stabilize carbonate melts containing silicon oxide, it is necessary to create an excess pressure of carbon dioxide. Redox reactions (7)–(22) have positive Gibbs energies and do not occur under the given conditions. Thus, it may be suggested on the basis of thermodynamic calculations that electrochemical synthesis of silicon carbide from carbonate melts containing silicon oxide is possible.

## EXPERIMENTAL

Voltammetric measurements were carried out in two hermetically sealed quartz cells under elevated

Gibbs energies, $\Delta G^0$, of reactions (1)–(22) at 750°C

| Reaction | $\Delta G^0$, kJ | Reaction | $\Delta G^0$, kJ |
|---|---|---|---|
| $Li_2CO_3 = Li_2O + CO_2$ (1) | 88.892 | $K_2CO_3 = K_2O + C + O_2$ (12) | 629.839 (–1.632) |
| $Na_2CO_3 = Na_2O + CO_2$ (2) | 187.731 | $CO_2 = CO + 1/2O_2$ (13) | 193.326 (–1.002) |
| $K_2CO_3 = K_2O + CO_2$ (3) | 233.970 | $CO = C + 1/2O_2$ (14) | 202.542 (–1.050) |
| $Li_2CO_3 + SiO_2 = Li_2SiO_3 + CO_2$ (4) | –88.478 | $CO_2 = C + O_2$ (15) | 395.868 (–1.026) |
| $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$ (5) | –46.478 | $SiO_2 = Si + O_2$ (16) | 723.953 (–1.878) |
| $K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2$ (6) | –39.428 | $SiO_2 + CO_2 = SiC + 2O_2$ (17) | 1055.266 (–1.367) |
| $Li_2CO_3 = 2Li + C + 3/2O_2$ (7) | 919.656 (–1.588)* | $Li_2CO_3 + SiO_2 = Li_2O + SiC + 2O_2$ (18) | 1144.158 (–1.482) |
| $Na_2CO_3 = 2Na + C + 3/2O_2$ (8) | 844.991 (–1.459) | $Na_2CO_3 + SiO_2 = Na_2O + SiC + 2O_2$ (19) | 1242.996 (–1.482) |
| $K_2CO_3 = 2K + C + 3/2O_2$ (9) | 850.496 (–1.469) | $K_2CO_3 + SiO_2 = K_2O + SiC + 2O_2$ (20) | 1289.236 (–1.670) |
| $Li_2CO_3 = Li_2O + C + O_2$ (10) | 484.761 (–1.256) | $CO_2 + Na_2SiO_3 = Na_2O + SiC + 2O_2$ (21) | 896.616 (–1.162) |
| $Na_2CO_3 = Na_2O + C + O_2$ (11) | 583.599 (–1.512) | $CO_2 + K_2SiO_3 = K_2O + SiC + 2O_2$ (22) | 942.856 (–1.222) |

* The electromotive force V in a circuit in which a given current-forming reaction proceeds is given in parentheses.

pressure of carbon dioxide at 750°C. In one case, a platinum crucible served as a container for the melt and an auxiliary electrode, with platinum wire ($S$ = 0.2 cm$^2$) as working electrode and oxygen–platinum reference electrode in air. In the other, glassy carbon crucible with working electrode ($S$ = 0.8 cm$^2$) and reference electrode made of glassy carbon rods were used. Prior to experiments, reagents of chemically pure grade were recrystallized and silicon oxide was dried at 300°C. As cathode materials in electrolysis were used platinum and stainless steel. After electrolysis, cathode deposits were analyzed by X-ray diffraction analysis, Auger spectroscopy, and electron microscopy.

The rise in current observed in the anodic range of potentials in voltammetric curves obtained on a glassy carbon electrode in carbonate melts containing no $SiO_2$ is due to oxygen evolution, and the rise in the cathodic region, to deposition of carbon and alkali metal (Fig. 1a). The range of potentials in which there are no redox reactions is 0.5 V narrower in the case of glassy carbon electrodes, compared with that for platinum electrodes. This is due to the formation of carbon oxides on glassy carbon subjected to anodic polarization. In titration of the melt with silicon oxide to a concentration of $5 \times 10^{-4}$ mol cm$^{-3}$, which corresponds to the limiting solubility of carbon dioxide, the rise in current observed in the cathodic range of potentials in the voltammetric curves obtained on a platinum electrode is due to discharge of carbon dioxide dissolved in the melt to elemental carbon (Fig. 1b). A peak of anodic current, associated with oxidation of carbon, is observed in the reverse run. No anodic current peak is observed on the glassy carbon electrode.

Stable platinum monocarbide exists only in the gas phase [11]. Thermodynamic characteristics of platinum carbide cannot be found in the literature, and, therefore, it is impossible to assess the possibility of formation of a compound of platinum and carbon at 1023 K. With increasing silicon oxide concentration in the melt, a new peak of anodic current appears in voltammetric curves (Fig. 1c) on both platinum and glassy carbon electrodes. The potential at which this current peak is observed is independent of silicon ox-

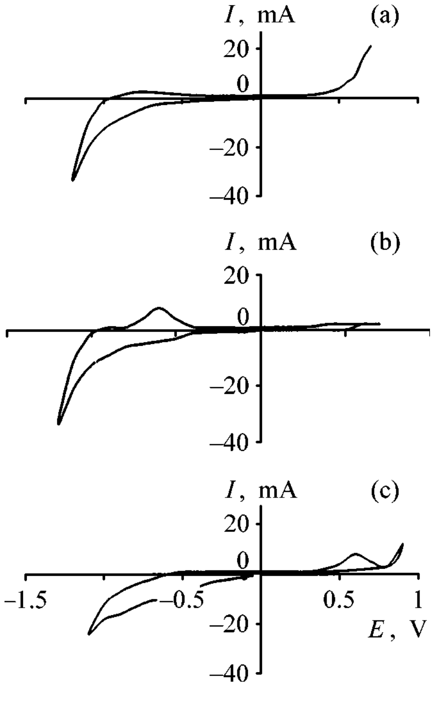

**Fig. 1.** Cyclic voltammetric curves obtained in (a) carbonate melt and (b, c) in carbonate melt containing $SiO_2$. Temperature 750°C, potential sweep rate 0.1 V s$^{-1}$. ($I$) Current and ($E$) potential. Electrode: (a, c) glassy carbon and (b) platinum. $SiO_2$ concentration (mol cm$^{-3}$): (b) $1 \times 10^{-5}$ and (c) $9 \times 10^{-5}$.

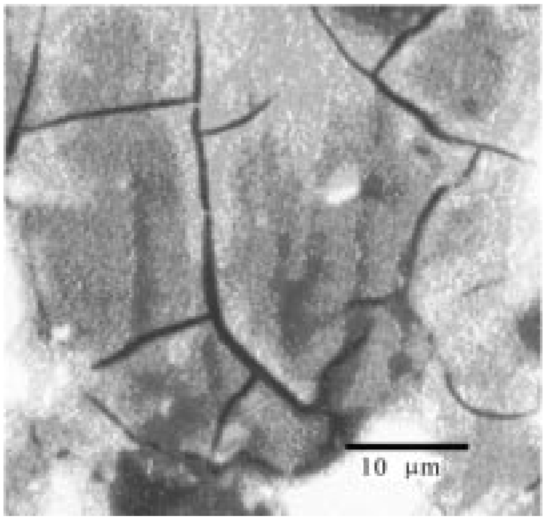

**Fig. 2.** Electron micrograph of the surface of a silicon carbide film obtained by electrolysis. Magnification 1500.

ide concentration and potential sweep rate at silicon oxide concentrations exceeding $5 \times 10^{-4}$ mol cm$^{-3}$. The cathodic process corresponding to the appearance of a new peak of anodic current in the reverse run proceeds at potentials corresponding to residual currents and merges with the background. To shift the potential corresponding to the cathodic process by 24 mV, the carbon dioxide pressure is to be raised to 10 atm.

The results of voltammetric studies suggest that electrochemical synthesis of silicon carbide occurs on glassy carbon and platinum electrodes in molten carbonates containing silicon oxide under elevated carbon dioxide pressure and cathodic polarization.

To confirm the results obtained, electrolytic experiments were performed. By electrolysis of an $Na_2CO_3$–$K_2CO_3$–$SiO_2$ (5%) melt at 750°C, $CO_2$ pressure of 1 atm, and current density not exceeding 0.2 A cm$^{-2}$, carbon coatings were produced on steel and platinum, with a glassy layer of 20% carbon and 80% platinum formed on the latter. Under certain electrolysis conditions, coatings of black α-SiC (with increased carbon content) were obtained on steel. Figure 2 illustrates the surface morphology of an SiC coating obtained on steel by means of electrolysis. The coating had block structure with a grain size of 10–20 μm. The carbide coating was dense, had high hardness, easily scratched glass, and possessed semiconducting properties.

## CONCLUSIONS

(1) Carbonate melts containing silicon oxide are unstable because of the occurrence of an exchange reaction to give carbon dioxide. This process can be stabilized by creating a carbon dioxide atmosphere with elevated pressure over the melt.

(2) The optimal conditions of electrochemical synthesis of silicon carbide in carbonate melts containing silicon oxide are found.

## REFERENCES

1. Cassir, M. and Belhomme, C., *Plasmas Ions*, 1999, vol. 2, no. 1, pp. 3–15.
2. Delimarskii, Yu.K., Grishchenko, V.F., Tumanova, N.Kh., and Shapoval, V.I., *Ukr. Khim. Zh.*, 1970, vol. 36, no. 2, pp. 136–140.
3. Ingram, M.D., Baron, B., and Janz, G.J., *Electrochim. Acta*, 1966, vol. 11, no. 11, pp. 1629–1639.
4. Manukhina, T.I., Sannikov, V.I., and Penyagina, O.P., *Vzaimodeistvie metallov i splavov s rasplavlennymi karbonatami shchelochnykh metallov* (Interaction of Metals and Alloys with Molten Alkali Metal Carbonates), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 1999.
5. Orel, V.P. and Dmitruk, B.F., *Issledovaniya v oblasti khimii rasplavov i tverdykh elektrolitov* (Investigations in Chemistry of Melts and Solid Electrolytes), Kiev: Naukova Dumka, 1985, pp. 71–88.
6. Barin, Ih., *Thermodynamic Data of Pure Substances*, Weinheim: VCH, 1993.
7. *Diagramma plavkosti solevykh sistem* (Fusion Diagram of Salt Systems), Posypaiko, V.P., Ed., Moscow: Metallurgiya, 1977, part 2.
8. Nekrasov, B.V., *Osnovy obshchei khimii* (Fundamentals of General Chemistry), Moscow: Khimiya, 1969, vol. 2.
9. Elwell, O., *Mater. Res. Bull.*, 1982, vol. 17, no. 6, pp. 697–706.
10. *Solubility Data Series: Gases in Molten Salts*, Tomkins, R. and Bansal, P., Eds., Oxford: Pergamon, 1991, vol. 45/46.
11. Fromm, E. and Gebhardt, E., *Gase und Kohlenstoff in Metallen*, Berlin: Springer, 1976.