Chemical and Electrochemical Behavior of Titanium Diboride in Cryolite-Alumina Melt and in Molten Aluminum

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Titanium diboride is the most perspective material for protection of the cathode lining of aluminum electrolysis cells. One of the possible methods for obtaining a titanium diboride coating is an electrochemical synthesis from cryolite melt containing oxides of titanium and boron. In the present paper the behavior of oxides of titanium and boron in cryolite melt is considered. Coherent coating of titanium diboride has been deposited from the molten system $Na_3AlF_6–Al_4B_2O_9–CaTiO_3$. © 2000 Academic Press

Key Words: TiB$_2$; cryolite-alumina bath; electrochemical synthesis.

INTRODUCTION

In the past century aluminum has been produced practically in the same manner all over the world, in the so-called Hall–Heroult aluminum electrolysis cells. Liquid metallic aluminum in those cells is deposited in an electrochemical way on carbon cathode blocks from alumina (Al_2O_3) dissolved in molten cryolite melt at about 950°C (1). The weakest part of the aluminum electrolysis cell is its cathode block, limiting the service life of the cell and "producing" a large amount of waste cathode materials contaminated by cyanides. One of the possible ways to increase the lifetime of the cells and to decrease the problems connected with waste cathodes is to produce protective coatings on the carbon cathodes. It was shown decades ago that the most perspective cathode protective layer is titanium diboride (TiB$_2$) (2,3). However, till now there has been no technique allowing the production of nonporous protective TiB$_2$ cathode layers on carbon cathodes in aluminum electrolysis cells, due to the major difference in the linear expansion coefficients of carbon and titanium diboride, leading to inevitable cracks when the carbon block with the TiB$_2$ layer is heated from room temperature to the working temperature of 950°C.

In the present work a new technique is developed making it possible to produce the protective TiB$_2$ coating on carbon blocks right in the cell at 950°C, from the cryolite – alumina melt. The technique is called "electrochemical synthesis." The principle of the electrochemical synthesis technique is the *in situ* formation of the titanium diboride phase during electrolysis at the surface of the cathode material when ions of titanium and boron are dissolved in the cryolite melt.

EXPERIMENTAL

The electrochemical behavior of cryolite–alumina melts with different additions (Al_2O_3, B_2O_3, $Al_4B_2O_9$, TiO_2, $MgTiO_3$, $CaTiO_3$) was studied by linear voltametry at 1300 K in air. A Pt crucible was used as the counter electrode, and Pt wires were used as working and reference electrodes. Electrolysis experiments in laboratory scale were performed at 1300 K in air. X-ray and SEM techniques were applied to analyze the cathodic products.

RESULTS OF EXPERIMENTS AND DISCUSSION
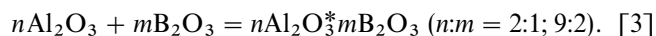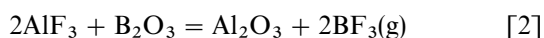
The $Na_3AlF_6–Al_2O_3–B_2O_3$ System

The density and surface tension of liquid boron oxide have values lower than those of components of the cryolite-alumina melt. Therefore boron oxide will obviously be a surface-active component in this system, and will be adsorbed onto its surface layer.

TABLE 1
Density and Surface Tension of Components of the Melt at 1000°C

| Melt	ρ (Mg m^{-3})	γ (mN m^{-1})
B_2O_3(l)	1.518	83
Al_2O_3(l)	3.03	1000
Na_3AlF_6(l)	2.095	136

Boron oxide will interact with the components of the cryolite-alumina melt according to the reactions

$$NaF + mB_2O_3 = NaF*mB_2O_3 \ (m = 1, \text{ or } 2) \quad [1]$$

$$2AlF_3 + B_2O_3 = Al_2O_3 + 2BF_3(g) \quad [2]$$

$$nAl_2O_3 + mB_2O_3 = nAl_2O_3^*mB_2O_3 \ (n{:}m = 2{:}1; 9{:}2). \quad [3]$$

The process of interaction was studied by derivatography and infrared spectroscopy (4). High losses of boron from the melt have been observed, obviously due to the formation of gaseous boron fluoride (see reaction [2]). Stabilization of boron oxide in the cryolite melt has been achieved by introducing B_2O_3 into the melt in the form of a complex oxide $Al_4B_2O_9$. Boron is deposited from a cryolite-alumina melt in a three-electron irreversible charge transfer process.

The Na_3AlF_6–TiO_2 System

TiO$_2$ dissolved in the melt interacts with reducing phases in the cell, such as the carbon cathode. Before the surface can be protected by the titanium diboride coating (some CO_2 can also form in addition to CO), the following chemical reactions take place on the carbon surface obviously right upon melting:

$$2TiO_2 + C = Ti_2O_3 + CO \quad [4]$$

$$Ti_2O_3 + C = 2TiO + CO \quad [5]$$

$$TiO_2 + C = TiO + CO. \quad [6]$$
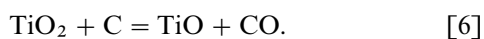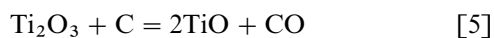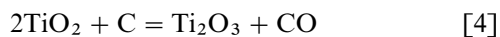
As a result of the above reactions the cathode surface will be passivated by TiO, being insoluble in the cryolite melt. In order to prevent this undesired event, Ti(IV) oxide was added to cryolite in the form of a $MgTiO_3$ or $CaTiO_3$ complex.

On the basis of the voltammetry experiments the following deposition mechanism of Ti can be deduced:

Electrochemical deposition of TiO$_2$ from cryolite–alumina melts takes place in two steps. The first step is the one-electron charge transfer, according to reaction

$$Ti^{4+} + e \leftrightarrow Ti^{3+}. \quad [7]$$
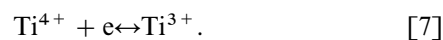
The second step corresponds to the three-electron transfer with formation of metallic titanium:

$$Ti^{3+} + 3e \rightarrow Ti^0. \quad [8]$$

The deposition of titanium is followed by an irreversible chemical reaction:

$$Ti + 3TiO_2 \rightarrow 2Ti_2O_3. \quad [9]$$
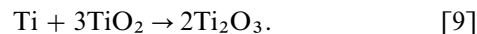
The Na_3AlF_6–$Al_4B_2O_9$–TiO_2 System

In the system Na_3AlF_6–$Al_4B_2O_9$–TiO_2 after process [7], a new process, more electropositive than the deposition of pure titanium or boron, has been observed. This new electrochemical process corresponds to the nine-electron irreversible charge transfer with the formation of an insoluble product:

$$Ti^{3+} + 2B^{3+} + 9e \rightarrow TiB_2. \quad [10]$$
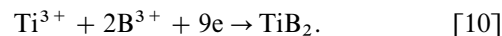
The Na_3AlF_6–$Al_4B_2O_9$–$MgTiO_3$ System

Electrochemical deposition of metallic titanium from the Na_3AlF_6–Al_2O_3–$MgTiO_3$ melt takes place in a one-step irreversible four-electron process, followed by an irreversible chemical reaction:

$$Ti^{4+} + 4e \rightarrow Ti^0 \quad [11]$$

$$Ti + 3MgTiO_3 \rightarrow 2Ti_2O_3 + 3MgO. \quad [12]$$
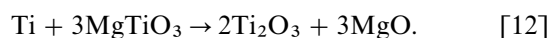
However, in the system Na_3AlF_6–$Al_4B_2O_9$–$MgTiO_3$ two electrochemical processes have been observed. The first process corresponds to the deposition of titanium and the second to the deposition of boron on titanium with the formation of titanium diboride:

$$Ti + 2B^{3+} + 6e \rightarrow TiB_2. \quad [13]$$

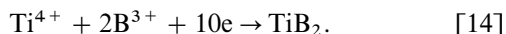#### The Na_3AlF_6–$Al_4B_2O_9$–$CaTiO_3$ System

Starting from the Na_3AlF_6–Al_2O_3–$CaTiO_3$ melt, electrochemical deposition of titanium takes place in a one-step irreversible four-electron process, reaction [11]. Hence, stabilization of titanium oxide in the cryolite melt has been achieved by introducing TiO_2 into the melt in the form of a complex oxide $CaTiO_3$. In the system Na_3AlF_6–$Al_4B_2O_9$–$CaTiO_3$ a new process, appearing at a potential
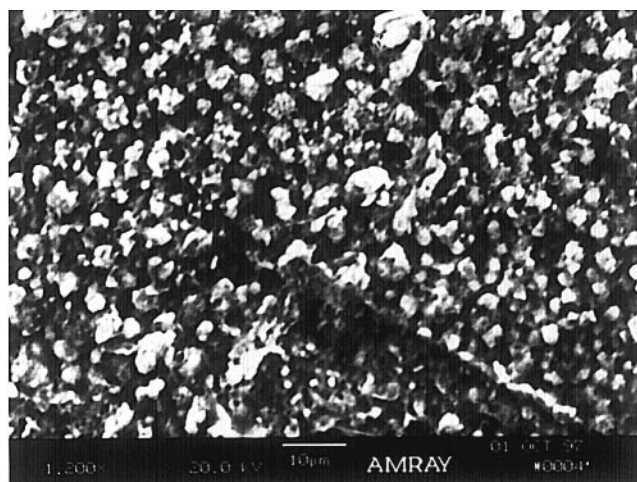
FIG. 1. SEM micrograph: TiB$_2$ surface deposited from molten Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–CaTiO$_3$ system at 1300 K.

more electropositive than that of the deposition of titanium or boron, has been observed. The process corresponds to a 10-electron irreversible charge transfer with insoluble product:

$$Ti^{4+} + 2B^{3+} + 10e \rightarrow TiB_2. \qquad [14]$$

Electrolysis Experiments

Electrolysis experiments were conducted at 1300 K. Nickel, tungsten, graphite, and glassy carbon were used as cathode materials. Coatings have been obtained in the Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–TiO$_2$ and Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–CaTiO$_3$ systems on nickel and tungsten cathodes. In the Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–MgTiO$_3$ system only titanium oxides of lower oxidation state have been obtained. On graphite and glassy carbon cathodes coatings have been obtained only in the Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–CaTiO$_3$ system. Figure 1 shows the surface of the TiB$_2$ coating deposited from the molten Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$–CaTiO$_3$ system. The coating thickness of the deposited TiB$_2$ was 15–20 μm (deposited rate 50 μm/h).

Chemical Interaction of Titanium Diboride with Liquid Aluminum

Solubility of TiB$_2$ in molten aluminum at 1300 K is 6×10^{-3} wt.% (5). Equilibrium between liquid aluminum and solid titanium diboride is reached within 10 h of their contact in a laboratory cell (5). The solubility of aluminum in titanium diboride at 1300 K is so low that it could not be measured.

Wetting of Titanium Diboride by Liquid Aluminum

When titanium diboride is used in Hall–Heroult aluminum electrolysis cells as cathode coating, one of the essential requirements to the coating is that it should be perfectly wetted by liquid aluminum. To measure the contact angle of liquid aluminum the sessile drop technique was used. A sample of aluminum was placed on a solid substrate and heated under an argon atmosphere.

At first wetting of hot-pressed titanium diboride by liquid aluminum was studied. Right after melting the aluminum does not take the shape of a liquid droplet due to a rigid oxide layer on its surface. However, when at higher temperature the oxide layer disappears due to the formation of gaseous Al$_2$O compound between the liquid Al and solid Al$_2$O$_3$. Indeed, at 1000°C the sample took the shape of a liquid. After 4 min. of real Al/TiB$_2$ contact the contact angle became about 30^0, and liquid aluminum started to penetrate into the porous titanium diboride sample.

In addition contact angle measurements of liquid Al were performed on the surface of titanium diboride deposited on a nickel cathode from the cryolite melt. The measured contact angle was 0°, i.e., total wettability was achieved.

CONCLUSION

1. Titanium diboride coating has been deposited by electrochemical synthesis from a Na$_3$AlF$_6$–Al$_4$B$_2$O$_9$ (4 wt.%)–CaTiO$_3$(2 wt.%) molten system at current densities between 0.2 and 0.6 A/cm^2.

2. The titanium diboride deposit was perfectly wetted by liquid aluminum after its oxide layer had been removed.

REFERENCES

1. K. Grjotheim and B. J. Welch, "Aluminum Smelter Technology." Aluminum-Verlag, Düsseldorf, 1980.
2. K. Billehaug and H. A. Oye, *Aluminium (BRD)* **56,** 642–648 (1980).
3. Yu. V. Borisoglebskii, M. M. Vetyukov, M. I. Karimov, and G. Kaptay, *Izv. VUZov, Cvetnaya metallurgiya* **2,** 41–43 (1991). [In Russian]
4. S. V. Devyatkin, K. I. Arsenin, and G. Kaptay, *in* "Proc. of 10th Internatinal Symposium on Molten Salts" (R. T. Carlin, Sh. Deki, M. Matsunaga, D. S. Newman, J. R. Selman, and G. R. Stafford, Eds.), 96–7, pp. 312–319. The Electrochemical Society, 1996.
5. Yu. V. Borisoglebskii, M. M. Vetyukov, and M. I. Karimov, *Cvetnye Metally* **2,** 36–37 (1992). [In Russian]