Pulse Electro-deposition of TiB$_2$ onto Graphite from TiO$_2$-B$_2$O$_3$-KF-LiF Melts

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Abstract

Electrodeposition of TiB$_2$ coating provides a convenient and low-cost way in preparation of TiB$_2$ material. In this paper, TiO$_2$ and B$_2$O$_3$ were selected as the active components, KF-LiF as the supporting electrolyte, Ti^{4+} ions and B^{3+} ions reduction processes in TiO$_2$-B$_2$O$_3$-LiF-KF melts were investigated by cyclic voltammograms. Then electrodeposition of TiB$_2$ onto graphite substrate was carried out from TiO$_2$-B$_2$O$_3$-LiF-KF melts at 800 °C by using CCP (continuous current plating) and PCP (pulsed current plating). The TiB$_2$ coatings prepared by PCP exhibit uniform, dense and metallic surface with good dherence to the substrate, but with more cracks. compared with those obtained by CPC.

Introduction

TiB$_2$ has attracted much attention for being the most suitable cathode material in the aluminum electrolysis process because it comes closest to meet the strict requirements to an ideal cathode lining material of aluminum electrolysis cell[1]. But it is very expensive arising from the complicated production procedures. Compared with other possible techniques, electrochemical synthesis provides a simple way to directly prepare smooth coatings onto at a substrate with or without a regular geometric surface by using cheap raw materials at a relatively low temperature. Moreover, the composition of the deposit can be precisely controlled through electrodeposition parameters. Therefore, electrochemical synthesis of TiB$_2$ is regarded as a more attractive way from the economic point of view.

In fact, TiB$_2$ coatings have been prepared from kinds of molten salts with K$_2$TiF$_6$ and KBF$_4$ by continuous current plating and pulse current plating [2-6]. But if TiO$_2$ and B$_2$O$_3$ are selected as the raw materials instead of K$_2$TiF$_6$ and KBF$_4$, the preparation process will be more economic and convenient. According to literature [7], dendric or powder TiB$_2$ was obtained by electrodeposition from LiF-KF-B$_2$O$_3$-TiO$_2$ melts at 700-950 °C. In order to improve the quality of TiB$_2$ coating from LiF-KF-B$_2$O$_3$-TiO$_2$ melts, in this paper, Ti^{4+} ions and B^{3+} ions reduction processes in the melts were examined by electrochemical methods, and PCP were carried out to electrodeposit TiB$_2$ onto a graphite substrate at 800 °C.

Experimental details

All the chemicals used in the experiments including LiF, KF, TiO$_2$ and B$_2$O$_3$ were analytical pure. The LiF-KF mixture mixed in a graphite crucible was heated to 200 °C under vacuum and maintained for 2hrs for dehydration, then heated to 800 °C under pure argon atmosphere. After the mixture cooled down, a certain amount of TiO$_2$ and B$_2$O$_3$ were introduced to the melts and the same procedure was repeated.

Cyclic voltammetry (CV) was performed by typical three electrodes system using electrochemical device CHI1140. Pt wires (φ1 mm) were used as the working electrode and quasi-reference electrode, respectively, a spectrally pure graphite plate was served as the counter electrode. During electrodeposition two electrodes were applied, in which high-purity graphite sheet with dimension of 30 mm×10 mm×2 mm was used as cathode, and graphite with 30mm×20mm×3mm as anode. Electrodeposition were carried out by means of continuous current plating and pulse current plating at 800 °C for 30 min. All the experiments were performed under argon atmosphere.

Results and discussion

B$_2$O$_3$ reduction in the LiF-KF melts

After 6hrs pre-electrolysis at 0.01A/cm^2 in the LiF-KF melts at 800 °C, the background cyclic voltammogram on the Pt electrode is shown in Fig.1(a), giving a cathodic limit of 1.5 V corresponding to K ions reduction. When B$_2$O$_3$ was added to the purified Li-KF melts, a pair of redox peak at about -1.0V and about -0.65V in Fig.1(b) appeared corresponding to the reduction of B^{3+} and oxidation of B, indicating one-step reduction process of B^{3+}. As scan rate increased, the reduction and the oxidation peaks potentials do not shift significantly, and the plot of the reduction peak current against the scan rate gave a linear relationship passing through the origin, implying a reversible reduction process controlled by the ions diffusion process. Thus the electron transfer number for B^{3+} ions was calculated as 3.01 according to Eq.(1) by using the data obtained at scan rate of 0.2V/s in Fig.1(b).

This result further indicates that B^{3+} is reduced in one step.

$$E_p\text{-}E_{P/2}=2.2RT/nF \tag{1}$$

where Ep is peak potential, Ep/2 the potential where the current is equal to half of peak current, R the ideal gas constant, T the temperature, F the Faraday constant.

The effects of B/Ti molar ratio on B$_2$O$_3$ reduction in the LiF-KF-TiO$_2$-B$_2$O$_3$ melts.

In order to understand the reduction process of Ti^{4+} and B^{3+} ions in LiF-KF-TiO$_2$-B$_2$O$_3$ melts, the effects of B/Ti molar ratio on the B$_2$O$_3$ reduction process was characterized in the melts with a fixed TiO$_2$ concentration of 0.3 mol/l .When the molar ratio of B/Ti is 2.5, Fig.2(a) clearly shows that the reduction peak at about -1.0V disappeared and the reduction potential for B^{3+} shifted to more negative one compared with the one in Fig.1(b), and three new reduction peaks were observed caused by the addition of TiO$_2$ in the LiF-KF-B$_2$O$_3$ melts. As the molar ratio of B/Ti increased to 5, the three reduction peaks for Ti^{4+} ions shifted to positive values in

Fig.2(b), and the second reduction peak disappeared when the molar ratios of B/Ti were 7.5 and 10 in Fig.2(c) and (d). Distinctly, the deposition of B facilitated Ti^{4+} ion reduction resulting from depolarization effects caused by formation of TiB_2 compound. At the B/Ti molar ratio of 10, the reduction current reached the biggest value and codeposition potential for B and Ti ions was about -1050V. Also the corresponding oxidation peaks change with the molar ratio of B/Ti, two oxidation peaks at about -0.8V and -0.4V corresponded simultaneous oxidation of Ti and B and further oxidation of Ti ions, respectively at the B/Ti molar ratio of 2.5, the two oxidation peaks shifted to more positive potential values at the B/Ti molar ratio of 5 and 7.5, while only one oxidation peak can be seen at the B/Ti molar ratio of 10, which suggested an appropriate molar ratio for Ti and B codeposition

Electroposition of TiB_2 in $LiF-KF-TiO_2-B_2O_3$ melts

The effects of B/Ti molar ratio on the deposits have been tested on the graphite substrate under an average current density of 0.6 A/cm^2 at 800 °C by using CCP and PCP. No any deposits were obtained at the B/Ti molar ratio of 5 either by CCP or PCP, and some loosen deposits were formed on the cathode at the B/Ti molar ratio more than 20. Compact and flat TiB_2 coatings with metallic luster appeared at the B/Ti molar ratio range from 10 to 20 regardless of the CCP or PCP, well in agreement with the results in the CV measurements.

Current density effects by Continuous current plating

The suitable current density was 0.45 to 0.6 A/cm^2 determined by continuous current plating in the melts with B/Ti molar ratio of 15 at 800 °C.while the deposits were composed of coarse and large particles packed with salts as the current density was more than $0.65A/cm^2$. In fact, a smaller current density is subject to nuclei growth and a larger one is propitious to new nuclei formation. Therefore, a higher current density is expected to increase nuclei number to form compact surface. But the current density can not exceed a limit value at which the electrodeposition process is controlled by ion diffusion in the melts (concentration polarization) that will result in the formation of dendrites. A greater electrochemical overpotential can produce a larger nucleus formation rate , therefore, leading to a smaller grain size, and also can help to improve surface morphology. However, as the electrodeposition proceeds, the further increase of the current density will cause the concentration decrease of titanium and boron ions on the electrode surface because the mass transport of the ions can not match the rate of reduction. During the direct-current deposition it is unable to continuously maintain a stably greater overpotential value for long time. Pulse-current plating provides a possibility of maintaining a relatively higher and stable overpotential cross the whole electrodeposition process by applying a pulsed current on /off duration.

Pulse urrent plating of TiB_2 in $LiF-KF-TiO_2-B_2O_3$ melts

Under the average current density of $0.6A/cm^2$, the effects of PCP parameters such as the ratio of t_{on}/t_{off} and frequency were examined with B/Ti molar ratio of 15 in $LiF-KF-TiO_2-B_2O_3$ melts at 800 °C.The deposits were composed of TiB_2 identified by XRD (did not shown here). The surface and cross-section morphology of the deposits were shown in Fig.3. Compared with the deposits by CCP in Fig.3 (a) and (b), the surface morphology of deposits

by PCP in Fig.3 (c) and (d) did not show much difference, but the cross-section morphology for deposit exhibited a better coherence with the substrate, more compact, homogenous and metallic surface with a higher thickness of 75 μ m, but showing more cracks maybe due to the formation of etch crack. And its microhardness of 4305 HV was much higher than the deposits by CCP of 3363 HV, implying a more compact coating.

Conclusions

In $TiO_2-B_2O_3-LiF-KF$ melts, B^{3+} ion was reduced in one step with three electron transfer, and B/Ti molar ratio had much effects on Ti^{4+} and B^{3+} ions reduction process, the codeposition potential for B and Ti ions was about -1050V at the B/Ti molar ratio of 10. The pulse current plating at t_{on}=7.5ms, t_{off}=2.5ms and i=0.6A/cm² at 800 °C gave deposits with a good coherence with the substrate, more homogenous, compact and metallic sueface with a higher thickness of 75 μ m, and a microhardness of 4305HV, but showing more cracks.
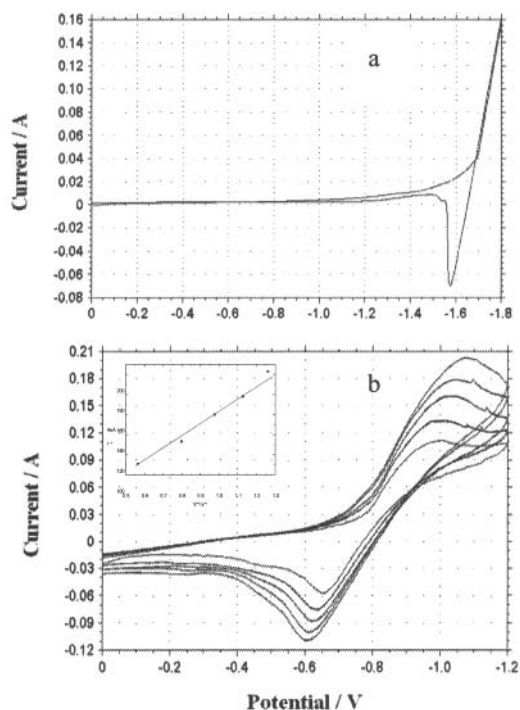
Acknowledgements

Figure.1(a) Background Cyclic Voltametric curves in the system LiF-KF at 800 °C, 0.1V/s. (b) Cyclic voltammograms in the B_2O_3-KF-LiF system at various scan rates, at 800 °C, C_{B2O3}=1.5mol/l. WE: Pt (0.314cm²), RE: Pt, CE: graphite. Inset: Peak currents as a function of scan rates.
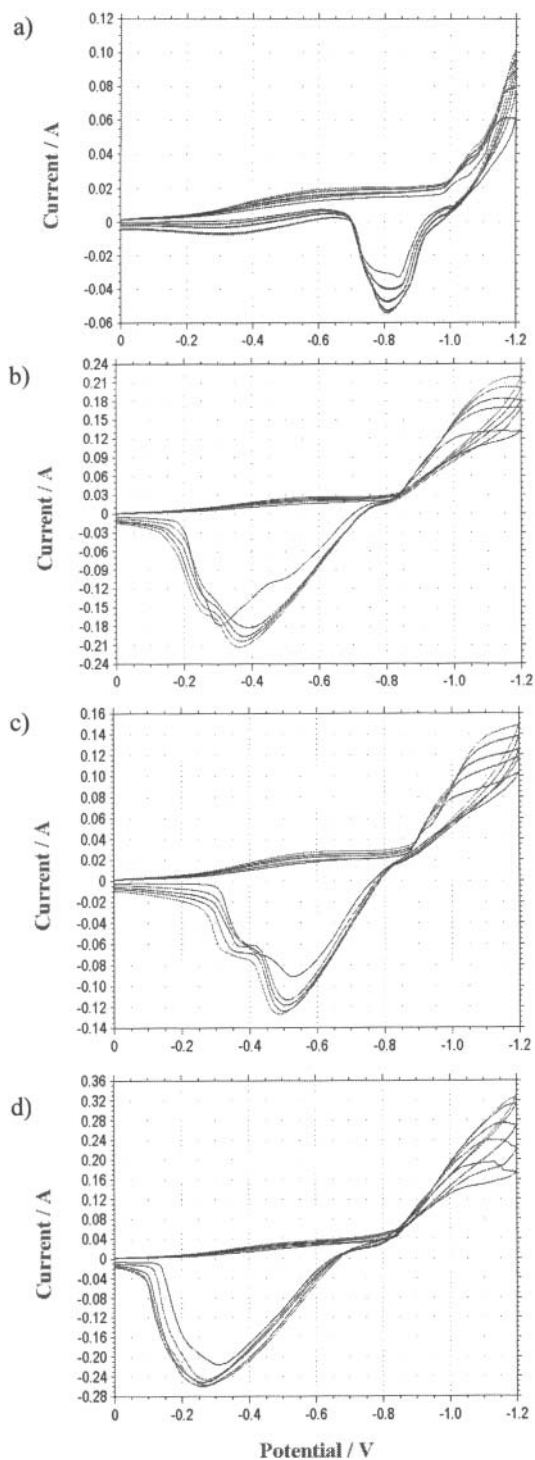
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Figure. 2 Cyclic voltammograms on the Pt electrode in the B_2O_3-TiO_2-LiF-KF system at 800 °C, (a) C_{B2O3}=0.75 mol/l; (b) C $_{B2O3}$=1.5 mol/l; (c) C $_{B2O3}$ =2.25 mol/l; (d) C $_{B2O3}$=3.0 mol/l
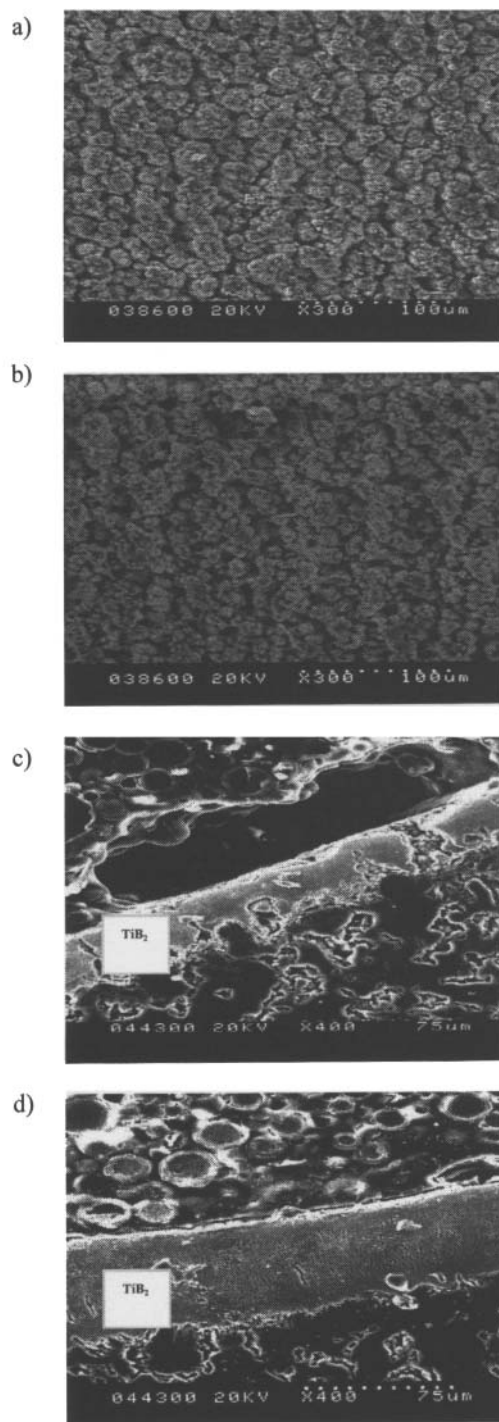
Figure.3 (a) and (b) Surface and Cross-section SEM micrograph (etched) (CCP .6A/cm^2 , CCP, 0.6A/cm^2), (c) and (d) Surface and Cross-section SEM micrograph (etched) (PCP, t_{on}=7.5ms, t_{off}=2.5ms,

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