Electrochemical Preparation of Carbon Films with a Mo₂C Interlayer in LiCl-NaCl-Na₂CO₃ Melts

Jianbang Ge ^a, Shuai Wang ^a, Feng Zhang ^a, Long Zhang ^a, Handong Jiao ^a, Hongmin Zhu ^b, Shuqiang

Jiao ^{a,*}

^a *State Key Laboratory of Advanced Metallurgy, University of Science and Technology*

Beijing, Beijing, 100083, P.R. China

^b *Department of Metallurgy, Materials Science, and Materials Processing, Tohoku university,*

Sendai 980-8579, Japan

Abstract

The electrodeposition of carbon films with a Mo₂C interlayer was investigated in LiCl-NaCl-Na₂CO₃ melts at 900 °C. Cyclic voltammetry was applied to study the electrochemical reaction mechanism on Mo and Pt electrodes, indicating that, two reduction reactions including carbon deposition and carbon monoxide evolution, may take place on the two electrodes simultaneously during the cathodic sweep. Carbon films with a continuous Mo₂C interlayer were prepared by constant voltage electrolysis, showing a good adhesion between Mo substrate and carbon films. The carbon films with a Mo₂C interlayer were characterized using X-ray diffraction measurement, Raman spectroscopy, scanning electron microscopy and transmission electron microscopy. The results reveal that carbon materials deposited on the electrodes are mainly composed of graphite and carbon diffusion in Mo (or Mo₂C) leads to the formation and growth of Mo₂C interlayer.

Keywords: Molten Salts; Thin films; Electrodeposition

1. Introduction

Carbon film is a promising candidate for the protective films or coatings on the working surfaces due to its unique chemical and physical properties [1,2]. Carbon films on Mo substrate improve the corrosion resistance, thermal resistance and tribological performance of the substrate. Nevertheless, the adhesion between carbon films and metal substrate is a big challenge due to the difference in their thermal properties such as thermal expansion. Mo_2C is widely used as interlayer due to its high hardness and melting point, good thermal stability, electrical conductivity on the carbon and Mo substrate, respectively [3-5].

It has been reported that carbon films can be successfully obtained on various working electrodes such as copper, gold, aluminum, mild steel, etc [6-8], and an interlayer could also be easily prepared on the substrate by electrochemical reactions, which enhanced the adhesion of the carbon film to the metal substrate [9-13]. Massot and his co-workers investigated the electrodeposition of carbon films from carbon ions in molten alkaline fluorides on copper and gold electrodes at a temperature range of 700-800 °C using cyclic voltammetry and chronopotentiometry [6]. Kawamura and Ito studied the electrodeposition of carbon films on aluminum electrode in a $\text{LiCl-KCl-K}_2\text{CO}_3$ melt by cyclic voltammetry and potentiostatic electrolysis at 450 °C [7]. Siambum et al reported the utilization of carbon dioxide for electro-carburisation of mild steel in two different molten salts, $\text{Na}_2\text{CO}_3\text{-NaCl}$ and $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$, at 800 °C [8]. Song et al conducted a series of experiments in molten $\text{LiCl-KCl-K}_2\text{CO}_3$ to prepare a Ti-O-C gradient on titanium electrode and a carbon/Cr-O-C bilayer film on stainless steel respectively at 500 °C [9-11]. Kalpan et al obtained titanium carbide coating on a titanium electrode by cathodic deposition in molten Li_2CO_3 at 900 °C

and the reaction mechanism was investigated in detail [12]. Lv et al obtained cohesive and well-crystallized graphite films on 304 stainless steel with a multi-arc ion plated Cr or Ti coating in molten $\text{Na}_2\text{CO}_3\text{-NaCl}$ at 900 °C, and a chromium carbide interlayer was observed when 304SS with a Cr coating was served as the cathode [13]. These studies demonstrated that carbon films or/and carbides of metals could be prepared in an electrochemical way which had a lower cost compared to chemical vapour deposition.

In the present study, our purpose is to prepare a Mo_2C gradient between carbon film and Mo substrate by electrochemical reduction of CO_3^{2-} in molten $\text{LiCl-NaCl-Na}_2\text{CO}_3$. This process can also be used to other metal substrates such as Cr and W, which have similar chemical properties to Mo.

2. Experimental Section

Anhydrous LiCl , NaCl and Na_2CO_3 with a mole ratio of 1:1:0.1 were put into an alumina crucible which was placed in a sealed vertical tubular reactor. The external diameter of the crucible was 75 mm and the wall thickness was 3 mm. Then the salt (about 170 g) was dried at 300 °C for 10 h under vacuum to remove moisture before it was heated up to 900 °C under argon atmosphere. It would need to be declared that a eutectic mixture of LiCl and NaCl (1:1 in mole fraction) purified in the same procedure was also used for cyclic voltammetry measurements mentioned below. Molybdenum rod and platinum wires served as electrodes in the melt were of more than 99.9% purity.

Cyclic voltammetry tests in a three-electrode cell were used to investigate the electrochemical reactions in the eutectic melt at 900 °C. A Mo rod (3 mm in diameter, 0.32

cm² in area) and a Pt wire (0.6 mm in diameter, 0.188 cm² in area) were used as working electrodes, respectively. A graphite rod (6 mm in diameter, 4.9 cm² in area) was served as the counter electrode. The reference electrode used was a Pt wire (1 mm in diameter). Constant voltage electrolysis was carried out in a two-electrode cell, in which a Pt wire (1 mm in diameter, ≈ 1.9 cm² in area) and a Mo rod (3 mm in diameter, ≈ 2.2 cm² in area) was employed as anode and cathode. The effluent gas from the reactor was monitored by resolution mass spectra (Hidden, SPR-30). After electrolysis, the cathode was taken out and immersed into 1M HCl solution to remove the frozen electrolyte, and then dried in a drying oven at 150 °C. All the electrochemical tests were carried out using the power supply (Solartron 1287).

The as-prepared carbon films were analyzed by X-ray diffraction analysis (XRD, Rigaku-TTRIII), scanning electron microscopy (SEM, JEOL-JSM-6701F and ZEISS-EVO 18), energy dispersive X-ray spectroscopy (EDS, Xflasher detector 5010) and transmission electron microscopy (TEM, JEOL, JSM-2010).

3. Results and discussion

To provide a wide enough potential window to study of all possible reactions and be served as a reference for comparison with Mo electrode, Pt was first employed as working electrode in the eutectic salt. **Fig. 1** shows the cyclic voltammograms obtained on a Pt wire in the eutectic mixture of LiCl-NaCl and LiCl-NaCl-Na₂CO₃ at 900 °C. Apparently the redox peaks, C₄ and O₄, represent the redox reactions of alkali chloride in LiCl-NaCl molten salt. As can be seen in **Fig.1a**, after the addition of sodium carbonate to the LiCl-NaCl melt, there is no appreciable reductive peak but a continuous increase in cathodic current (C₁) during the

cathodic sweep from -0.5 V to -1.0 V. This phenomenon can be explained by the reduction mechanism of carbonate ions in molten salt as below. Reactions (1) and reaction (2) would occur in the cathode and the potentials of two reactions are very close at 900 °C, indicating that those two reactions may take place simultaneously during the cathodic sweep and then lead to the complex increasing cathodic current. When the cathodic sweep is limited at -0.5 V, two anodic peaks (O₃ and O₄) in **Fig. 1b** nearly disappear compared to **Fig. 1a**, showing that the occurrence of these two oxidation peaks are due to re-oxidation of the deposited carbon and could be attributed to reactions (3) and (4) [14]. It is assumed that carbon monoxide gas will soon escape from the fused molten salt at such a high temperature.

If the reduction peak C₃ correspond to the reduction of carbonate ions in the melt, which includes reactions (4) and (5), then peak C₂ may represent either of the two reactions. To confirm this, further analysis should be carried out by comparing the charges passed during the cathodic and anodic potential scans in LiCl-NaCl-Na₂CO₃ melt. Integration of the reduction current until the cathodic limit in **Fig. 1a** revealed a total charge of 4.301 C, which is 0.158 C in **Fig. 1b**. And their corresponding anodic charges are 1.422 C and 0.120 C, respectively. The ratio of anodic and cathodic charges in **Fig. 1a** and **1b** are 0.33 and 0.76 respectively. This phenomenon shows that carbon may first deposit on the Pt electrode rather than carbon monoxide, meaning that C₂ should correspond to reaction (1). The anodic peak O₃

should be attributed to the evolution of oxygen and the cathodic peak C₁ may be related to the reduction of platinum oxide or other platinum compounds.

After Mo electrode was used to replace the Pt electrode, great changes in anodic sweep of cyclic voltammogram took place on the Mo electrode. As can be seen in **Fig. 2**, the anodic potential was limited at 0.5 V and the reason should be the oxidation of Mo substrate (peak O₆) via reaction (5) and hence leads to the anodic dissolution in the molten salt. The CV obtained in LiCl-NaCl-Na₂CO₃ melt in **Fig. 2** also shows a significant reduction peak C₅, which, as discussed above, represents the reduction of carbonate ions. Besides, the small current fluctuation observed under low potential also indicates the evolution of carbon monoxide. Obviously, peak C₆ obtained in LiCl-NaCl melt is related to the alkali deposition. The anodic peak O₅ is related to the oxidation of carbon deposited on Mo electrode.

When a constant voltage electrolysis is performed at 2.2 V between the Mo cathode and Pt anode for 1 h, it is noticeable that there is little change in the concentration of carbon monoxide as shown in **Fig. 3**, which also has been observed in previous work [15]. This observation is not in accordance with the results which have been discussed above and may be explained as follows. Carbon deposition and evolution of carbon monoxide may occur on the fresh Mo rod simultaneously, but after the Pt anode covered by deposited carbon, carbon deposition dominates compared to other competing reactions. Besides, the variation of oxygen is well consistent with the current curve, indicating that Pt electrode can be used as an inert anode for the electrochemical generation of oxygen in this fused salt system. A rational explanation to the current changes during the electrolysis in **Fig. 3** is given as below. At the

initial stage, the current ascends with time due to the carbon deposition and the growth of cathodic surface area. Then it comes to a “quasi-platform” stage with some fluctuation, which caused by the combined effect of both the increase of cathodic surface area and the decrease of carbonate ions concentration. At last, apparently, the current diminishes because of the low carbonate ions concentration in the molten salt.

After the electrolysis, a carbon coating was clearly seen on the Mo rod, and the XRD pattern of the surface material was shown in **Fig. 4a**. The peak at $2\theta = 26^\circ$ is related to the presence of graphite structure. Besides, Mo_2C can also be detected due to that the graphitic carbon can react with the Mo substrate to form Mo_2C at working temperature ($\Delta G = -60.362$ kJ/mol). Raman spectroscopy was used to provide the cathode product information of graphitized degree. As shown in **Fig. 4b**, the G-band at about 1575 cm^{-1} is associated with sp^2 vibrations of a perfect graphite, while the D-band at 1360 cm^{-1} is closely related to the disorder-induced scattering resulting from imperfections [16]. The I_G/I_D value is 2.16 for the graphite, meaning a high degree of graphitization in the composite. In addition, sharp and symmetric 2D-band at around 2750 cm^{-1} is obviously seen, being consistent with the literatures' reports of graphitic carbon [17]. Combined with the XRD and Raman results, the cathode products is favoured to form graphitic carbon than amorphous carbon at higher temperature [18-20]. The SEM photograph of the outermost carbon materials were presented in **Fig. 4c**. As observed by SEM, the deposited carbon materials exhibits “quasi-spherical” microstructures with particle size between 3 and 5 μm . The HRTEM photograph presented in **Fig. 4d** shows well crystallized graphite in deposited carbon materials.

In addition to that, it is well-known that C can react with CO_2 to generate CO at high

temperature. By controlling of the constant cell voltage of the electrolysis, it is expected that a thin carbon film can be obtained under CO₂ atmosphere. Once the electrolysis is completed, the thin carbon film may disappear quickly due to the reaction with CO₂ (or CO₃²⁻) to form CO under CO₂ atmosphere in high temperature, while Mo₂C layers remains unchanged according to the reaction (6) - (7). However, this phenomenon was not observed in our experiment, implying that the reaction may need a higher temperature.

To investigate the formation mechanism of the Mo₂C interlayer further, electrolysis was performed at 2.2 V for 15 min, 1 h and 4 h with the SEM images and EDS lines of the cross section of the Mo electrodes show in **Fig. 5**. As observed from **Fig. 5a**, there is no apparent interlayer between carbon and molybdenum at short time (15 min), which is well in accordance with the results of EDS line (**Fig. 5d**). After 1 h electrolysis, the SEM image in **Fig. 5b** of the polished cross-section of the Mo electrode clearly shows that two layers coat on the surface of the Mo substrate. It can be seen that a Mo₂C interlayer exists between the carbon layer and Mo substrate, and the thickness of the Mo₂C layer is about 10 μm. In addition, the SEM image (**Fig. 5c**) and EDS line (**Fig. 5e**) measured after 4 h electrolysis reveal the presence of a ~30 μm Mo₂C layer, showing that the intermediate layer grows as time evolves. This phenomenon can be explained by the carbon diffusion in Mo (or Mo₂C) substrate to form the solid solution phase, which has been pointed out by previous work [21]. Furthermore, the continuous three layers imply that Mo₂C interlayer offers a good adhesion surface to the other two layers.

4. Conclusion

Carbon films with a Mo₂C interlayer on Mo substrate has been obtained during electrolysis in LiCl-NaCl-Na₂CO₃ molten salt. XRD and Raman results show that carbon products are mainly composed of graphite. The continuous Mo₂C interlayer reveals a good adhesion between the other two layers. Carbon diffusion in Mo/Mo₂C substrate engenders the formation and growth of Mo₂C interlayer. This electrochemical method can also be applied to other metal which has similar chemical properties to molybdenum, such as tungsten and chromium. In addition, this process may be extended to prepare Mo₂C layer on Mo substrate at higher temperature.

Acknowledgements

This work was supported by the National Science Foundation of China (No. 51322402).

References

- [1] K. C. Paul, L. H. Li, Mater, Characterization of amorphous and nanocrystalline carbon films, *Mater. Chem. Phys.* 96 (2006) 253.
- [2] Y. X. Wang, L. P. Wang, G. G. Zhang, S. C. Wang, R. J. K. Wood, Q. J. Xue, Effect of bias voltage on microstructure and properties of Ti-doped graphite-like carbon films synthesized by magnetron sputtering, *Surf. Coat. Technol.* 205 (2010) 793.
- [3] M. Rasinski, H. Maier, C. Ruset, M. Lewandowska, K. J. Kurzydowski, Carbide formation in tungsten coatings on carbon-fibre reinforced carbon substrates, *Thin Solid Films* 531 (2013) 21.
- [4] Q. Liu, X. B. He, S. B. Ren, T. T. Liu, Q. P. Kang, X. H. Qu, Fabrication and thermal conductivity of copper matrix composites reinforced with Mo₂C or TiC coated graphite fibres, *Mater. Res. Bull.* 48 (2013) 4811.
- [5] J. Liu, Q. M. Gong, Y. Shao, D. M. Zhuang, J. Liang, In-situ fabrication of MoSi₂/SiC-Mo₂C gradient anti-oxidation coating on Mo substrate and the crucial effect of Mo₂C barrier layer at high temperature, *Appl. Surf. Sci.* 308 (2014) 261.
- [6] L. Massot, P. Chamelot, F. Bouyer, P. Taxil, Studies of carbon nucleation phenomena in molten alkaline fluoride media, *Electrochim. Acta* 47 (2002) 1949.
- [7] H. Kawamura, Y. Ito, Electrodeposition of cohesive carbon films on aluminum in a LiCl-KCl-K₂CO₃ melt, *J. Appl. Electrochem.* 30 (2000) 571.
- [8] N. J. Siambum, H. Mohamed, D. Hu, D. Jewell, Y. K. Beng, G. Z. Chen, Utilisation of carbon dioxide for electro-carburisation of mild steel in molten carbonates salts, *J. Electrochem. Soc.* 158 (2011) H1117.

- [9] Q. S. Song, Q. Xu, Y. Wang, X. J. Shang, Z. Y. Li, Electrochemical deposition of carbon films on titanium in molten LiCl-KCl-K₂CO₃, *Thin Solid Films* 520 (2012) 6856.
- [10] Q. S. Song, Q. Xu, C.Y. Xing, Preparation of a gradient Ti-TiOC-carbon film by electro-deposition, *Electrochem. Commun.* 17 (2012) 6.
- [11] Q. S. Song, Q. Xu, Y. Wang, X. J. Shang, Z. Q. Ning, Y. Qi, K. Yu, Electrochemical preparation of a carbon/Cr-O-C bilayer film on stainless steel in molten LiCl-KCl-K₂CO₃, *J. Electrochem. Soc.* 162 (2015) D82.
- [12] V. Kaplan, E. Wachtel, I. Lubomirsky, Titanium carbide coating of titanium by cathodic deposition from a carbonate melt, *J. Electrochem. Soc.* 159 (2012) E159.
- [13] W. Y. Lv and C. L. Zeng, Preparation of cohesive graphite films by electroreduction of CO₃²⁻ in molten Na₂CO₃-NaCl, *Surf. Coat. Tech.* 206 (2012) 4287.
- [14] H. V. Ijije, R. C. Lawrence, N. J. Siambum, S. M. Jeong, D. A. Jewell, D. Hu and G. Z. Chen, Electro-deposition and re-oxidation of carbon in carbonate molten salts, *Faraday Discuss.* 172 (2014) 105.
- [15] J. B. Ge, L. W. Hu, W. Wang, H. D. Jiao, S. Q. Jiao, Electrochemical conversion of CO₂ into negative electrode materials for Li-ion batteries, *Chemelectrochem.* 2 (2015) 224.
- [16] Raman spectroscopy in carbons: from nanotubes to diamond, ed. A.C. Ferrari and J. Robertson, Royal Society, London, 2004.
- [17] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, Raman spectrum of graphene and graphene layers, *Phys. Rev. Lett.* 97 (2006) 187401.

- [18] H. Y. Yin, X. H. Mao, D. Y. Tang, W. Xiao, L. R. Xing, H. Zhu, D. H. Wang, D. R. Sadoway, Capture and electrochemical conversion of CO₂ to value-added carbon and oxygen by molten salt electrolysis, *Energy Environ. Sci.* 6 (2013) 1538.
- [19] H. V. Ijje, C. G. Sun, G.Z. Chen, Indirect electrochemical reduction of carbon dioxide to carbon nanopowders in molten alkali carbonates: Process variables and product properties, *Carbon* 73 (2014) 163.
- [20] K. Le Van, H. Groult, F. Lantelme, M. Dubois, D. Avignant, A. Tressaud, S. Komaba, N. Kumagai, S. Sigrist, Electrochemical formation of carbon nano-powders with various porosities in molten alkali carbonates, *Electrochim. Acta* 54 (2009) 4566.
- [21] B. M. Warnes, G. Simkovich, Carbon diffusivity in Mo₂C from 800 to 1000 °C, *J. the Less Common Met.* 106 (1985) 241.

Figure Captions

Fig. 1 Cyclic voltammograms of LiCl-NaCl and LiCl-NaCl-Na₂CO₃ melts at 900 °C on a Pt working electrode. (a) A broad sweep range of potential, cathodic limit = -1.0 V. Dashed line: Cyclic voltammogram obtained in LiCl-NaCl melt. (b) Sweep confined to a narrow range of potential, cathodic limit = -0.5 V. Scan rate = 100 mV/s.

Fig.2 Cyclic voltammograms of LiCl-NaCl and LiCl-NaCl-Na₂CO₃ melt at 900 °C on a Mo rod working electrode. Scan rate = 50 mV/s.

Fig .3 The current profile and oxygen evolution of constant voltage electrolysis between a W cathode and a Pt anode in LiCl-NaCl-5% Na₂CO₃ molten salt at 900 °C.

Fig. 4 XRD pattern (a), Raman spectra (b) SEM photograph (c) and HRTEM photograph (d) of the surface material deposited at 2.2 V for 1 h.

Fig. 5 SEM images of the cross section of Mo electrode after 15min (a), 1 h (b) and 4 h (c) electrolysis at 2.4 V; the EDS line scans of the cross section of Mo electrode after 15min (d) and 4 h (e) electrolysis.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5