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SYNTHESIS AND PROPERTY STUDY OF LAYERED Ti/TiB_2 COMPOSITE ELECTRODE MATERIALS FOR WET ELECTROLYTIC

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ABSTRACT

The structure and properties of the new Ti/TiB_2 composite based coating electrode materials prepared by the ion beam sputtering method was analyzed by the SEM, four-probe method and electrochemical workstation. The results show that the introduction of TiB_2 intermediate layer can be enhanced binding between the surface coating and the substrate with change the base material structure of electrode, and mud-crack shaped morphology of electrode surface is improved, in addition the resistivity of Ti/TiB_2 based coating electrical is reduced 16% than that of Ti-based electrode. Furthermore, the electrochemical behavior of the electrode can be improved by the use of TiB_2 intermediate layer, and that laying the foundation for energy-saving fall of the electrode in the practical application.

Keywords: Ion beam sputtering, TiB2 intermediate layer, Electrochemical performance, Composite electrode materials.

1. INTRODUCTION

Wet electrolytic (electro-winning) is one of the main methods and the future development direction in the field of extraction of nonferrous metals [1]. Electrolysis as the "heart" of the device in the electrode, its great influence on the electrolytic process [2]. So,the selection and preparation of electrode materials preparation is an important subject and difficult problem in wet electrolytic industry and electrochemical industry[1,3,4].

In hydrometallurgy industry, Ti based coating anode is expensive, the insulating layer was formed on the surface of Ti during the electro-deposition process which lead to coating failure [5-7]. Research shows that the base of electrode performance improvement is the change of the electrode matrix material [8-9], the researchers is so that prolong the service life of the electrode a middle transition layer to protect the substrate [10-14]. At present, due to emergence of many new metal ceramic, the selection of the anode material has been increasing steadily [15]. In practices, it can be proved that the advantages of the TiB2 metal ceramics has the merits of high stability, good conductivity and corrosion resistance. The TiB2 metal ceramics that has been successfully applied to the protective layer of carbon cathode in the electrolytic aluminum is the best candidate material for reinforcing agent for the preparation of metal ceramic composite materials [16].

Accordingly, this study proposes a new Ti base laminated layered composite materials which essentially a sandwich in which the core is TiB2. TiB2 that is the intermediate transition layer is not only a corrosion protection layer and an electron transport layer electrode matrix material, but also the link strengthened layer between the reactive coating and Ti matrix. In the preparation method, the Intermediate coating can be made in ion beam sputtering to TiB2 in our study.

2. EXPERIMENTAL PROCEDURE

Commercially pure Ti (TA1) and TiB2 sputtering target that the purity was 99.99% were employed in this study. The sizes of the samples were TA1 – 0.8mm×50mm×50 mm. Oxide films of Ti could form easily on each surface. The Ti surfaces were processed as follows: 10% of the alkaline solution→ distilled water→ 5%HF+15%HNO3→ distilled water→ vacuum oven dried.

The ion sputtering equipment was used in the experiments, the main parameters of the equipment were as follows: the flow of Ar was 8.5sccm, the electric voltage was 2.8KV, the beam current was 70mA and the sputtering time was 60min.

The active electrode surface coating of electrode are two element active coating, these substances are used in the preparation of coatings as follows: RuCl3•3H2O (ωRu=37%), C16H36O4Ti, HCl (36%), CH3 (CH2)3OH, The Ru and Ti molar ratio of coating is 3:7.

The microstructures and interface features of the Ti-TiB2 composite materials were observed using a Philips XL-30 ESEM scanning electron microscope (SEM). The resistivity of the Ti-TiB2 composite materials was measured by Four-probe method. The electrochemical performance of the Ti-Al composite materials were analyzed using a CHI600A electrochemical analyze instrument.

3. RESULTS AND DISCUSSION

3.1 The microstructure of micro bonding interface topography

The matrix Ti is coated with TiB2 to solve the problem of easy failure of coating. Study of TiB2 intermediate layer bonding interface effects on between coating and metal base by SEM. Fig.1 shows the scanning electron microscope (SEM) images of micro bonding interface topography, 1# is traditional Ti based anode coating materials, 2#is the research on the preparation of Ti /TiB2 based coating anode materials, where X is the surface active coating, Y is metal base, Z is the TiB_2 layer.

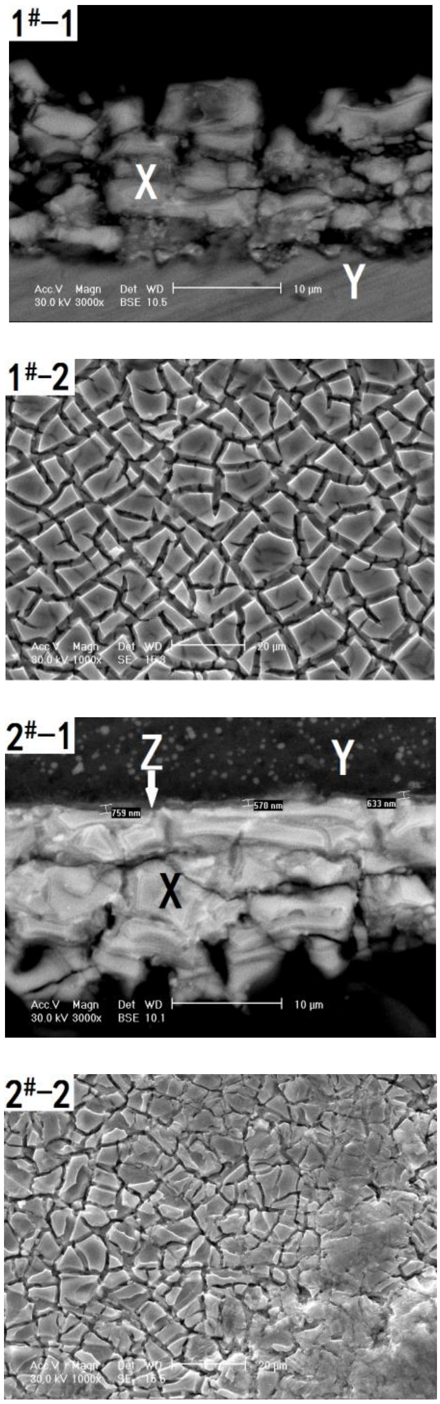

Figure 1. The SEM images of the bonding interface and coating surface morphology

The image of bonding interface indicate in Fig.1 that 1-1# is an image of bonding interface traditional Ti based coating anode, it has so long and narrow crack from the coating surface to the substrate of Ti that Ti matrix is directly exposed to the outside. It is not only the electrolyte can make coating and substrate occurs corrosion through these cracks into the coating, but also bubbles that is produced in the reaction generated stress effect on crack to peeling of the coating during the process of electrochemical reaction. Moreover, oxygen that is produced in the oxygen evolution reaction will be combined with the substrate to generate the TiO2 insulating layer what cause the failure of high active oxide coating.

The image of bonding interface indicate in Fig.1 that 2-1# is an image of bonding interface of based coating anode on Ti /TiB2 laminated composites, the thickness of coating is about 12μm and the average thickness of TiB2 intermediate layer is about 653nm. Furthermore, it has no gaps appear between the middle layer and the substrate, and the coating is a tightly coupled state on the surface of the substrate is about 3μm. From the above, it is clear that, excellent binding effect between coating and metal base, it is better to protect the substrate and to prevent the failure of coatings for the life of electrode prolongs.

Both the surface of Ti based coating materials and the Ti/TiB2 based coating material are showing a typical mud crack morphology with reference to surface morphology in the Fig.1 1#-2 and 2#-2. There are a large number of first cracks in the coating surface, and a few small second cracks appeared the mud crack block. The formation of first crack is mainly the difference in thermal expansion between the coating and Ti matrix, the thermal stress which leads to cracks generated between them. The formation of second crack is caused by the uneven stress distribution which due to precipitation of TiO2 and RuO2 in coating in Ru-Ti oxide coating. We can see from the Fig.1 1#-2 and 2#-2, the crack width of Ti/TiB2 matrix(＜1μm) anodes smaller than that of traditional Ti matrix(about 3.11μm) anodes in the surface morphology of the coating. The mud crack block are uniform in size.

It can be seen from Fig.1 that the TiB2 middle layer can improve the status of combined with the surface coating and substrate by changing the structure of the electrode matrix material. TiB2 intermediate layer protects the Ti matrix so that it does not react with oxygen ions in the reaction to prevent the emergence of TiO2 insulation layer. Moreover, the introduction of TiB2 intermediate layer reduced the binding interface crack, thereby prolonging the service life of the electrode.

3.2 The resistivity of the composite materials

According to electrode material the path of the electric current import and export in actual use and the principle of four-probe resistance measurement. In this study, the current flows from the Ti layer to the sample, through the interface between Ti/ TiB2, finally flows out from the surface of the TiB2.The results from four-probe resistance measurement, Table 1, show that there is the resistivity of Ti/ TiB2 composite electrode and Ti electrode.

Table 1. The contrast of different samples resistivity

No.	ρ/μΩ•cm
$1^{\#}$	51.16
$2^{\#}$	42.23

Table 1 show that the Ti/TiB_2 composite electrode material had dropped. By comparison with the resistivity of Ti based coating electrode, that of Ti/TiB_2 based coating electrode decreased by 16%, it shows that the conductive properties of the electrode have been improved. As can be seen from the Fig.1 and Table1, the number of cracks in the coating was be reduced by a large degree to the coating and matrix is closely bonded, so that the resistance decreases in the electrons transmission process to reduce the resistivity of the composites, and excellent conductive properties is the basis of electrochemical performance.

3.3 The electrochemical properties of the composite materials

Excellent electrochemical performance has a vital role to the application of electrode material. Therefore, the electrochemical properties of the composites were tested by the electrochemical analyze instrument. We tested the steady-state anodic polarization curve by the Linear sweep voltammetry (LSV) in the saturated KCl solution. The results shown in Fig.2, where the $1^{\#}$ sample is Ti matrix and there is a TiB_2 intermediate layer in $2^{\#}$ sample.

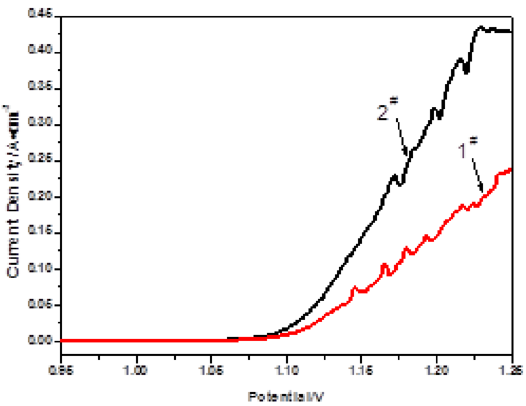

Figure 2. Linear Sweep Voltammetry (LSV) of different

As can be seen from the Fig.2, when the potential is less than 1.06V, the density of current does not change, but when the potential is greater than 1.06V, all the electrodes of the current changes are obvious with the potential rise, and the density of current of Ti/TiB_2 composite electrode increases much faster than that of Ti electrode. That is to say, the density of work exchange current of Ti/TiB_2 based coating anode was significantly higher than that of Ti based coating anode in the same electrode potential, and the polarization potential of Ti/TiB_2 based coating anode was significantly lower than that of Ti based coating anode in the same density of current. For example, the density of current of $1^{\#}$ sample is $0.1074 A•cm^{-2}$ and that of $2^{\#}$ sample is $0.3189 A•cm^{-2}$ when the polarization potential is 1.20V, the density of current Ti/TiB_2 based increased nearly two times than that of Ti based, moreover, the polarization potential of $1^{\#}$ sample is 1.197V and that of $2^{\#}$ sample is 1.137V when density of current is $0.10 A•cm^{-2}$. In actual use, the polarization potential reduction means a lower cell voltage, this is also the basis of saving energy and reducing consumption of the electrode materials.

The surface of metal anode can have a large number of electronic, the electrochemical reactions occurring completely on the surface and the rate of reaction increased. The potential of electrode changes 100mV, the activity of electrocatalytic can be increased by 10 times in electrochemical etching course. Therefore, Ti/TiB2 based anode coating has a more excellent electrochemical polarization performance than that of Ti based coating anode. From the viewpoint of electrochemical kinetics [7, 17], the steady polarization curves actually reflect the characteristics of relationship between the electrode reaction velocity and electrode potential (the overpotential), and it points out that the potential is the driving force to the electrochemical reaction of electrode, the electrode reaction is easy to happen for the driving force is small and the overpotential is low. Therefore, the electrochemical reaction rate of Ti/TiB2 based coating electrode faster than that of Ti based coating anode, the positive charge accumulated less in the reaction interface of Ti/TiB2 based coating electrode to reduce the electrode reaction force and to improve the electrocatalytic activity of the electrode.

Add it all up, we can see combined with Fig.1 and Table1 that the introduction of TiB_2 intermediate layer on the electrochemical properties and resistivity of the composite materials has the impact of the same law, because of the boride intermediate layer plays a key role to improve the bonding conditions between the electrode coating and substrate, and stable binding interface has a protective effect on the performance of electrode. In addition, it is a problem that must be considered which is different interfacial wettability and interfacial characteristics in the preparation of intermediate layer for electrode materials process.

4. CONCLUSIONS

(l) The combination have obvious improvement between the coating and substrate by introduce the TiB_2 intermediate layer to Ti based coating electrode, it is better to protect the substrate and to prevent the failure of coatings for the life of electrode prolongs.

(2) By comparison with the resistivity of Ti based coating electrode, that of Ti/TiB_2 based coating electrode decreased by 16%, and the resistance decreases in the electrons transmission process to reduce the resistivity of the composites, and excellent conductive properties is the basis of electrochemical performance.

(3) In electrochemical performance, Ti/TiB_2 composite materials has excellent electrochemical properties to pure Ti, the polarization potential of the Ti/TiB_2 composite based decreased about 60mV to the polarization potential of Ti based, the density of current the Ti/TiB_2 composite based increased nearly two times than that of Ti based.

Therefore, the introduction of TiB_2 can improve the interface bonding state and micro structure of coating electrode to directly influence the conductivity and electrochemical performance of the electrode, so that it improve the catalytic activity and service life of the electrode.

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REFERENCES

1. Zhang Zha-xian, Zhao Guo-Pei and Luo Xiao-jun, Introduction of Titanium Electrodes, Metallurgical Industry Press, Beijing, 2008.
2. S. Trasatti, Electrocatalysis in the Anodic Evolution of Oxygen and Chlorine, *Electrochim Acta*, vol.29, pp.1503-1512, 1984.
3. Ma Fu-kang, Rare Metal Handbook, Metallurgy Industry Press, Beijing, 2008.
4. Electroplating Manual Compilation Group, Electroplating Handbook, National Defence Industrial Press, Beijing, 1980.
5. Liang Zhen-hai, Study on Ti/MO_2 Anode with Intermediate Layers of Oxide Solid Solution, Ph.D. thesis, Taiyuan University of Technology, Taiyuan, 2006.
6. Wang Ling-li, Peng Qiao, Advances in Research On Ti Anodes Coating with RuO_2, Liaoning Chemical Industry, vol.35, pp.485-487, 2006.
7. Zhang Zhao-xian, Engineering of Titanium Electrode, Metallurgy Industry Press, Beijing, 2003.
8. Liang Fang, Zhu Pei-xian, Zhou Sheng-gang, Sun De-lin and Ma Hui-yu, Influence of Tin on Improving Bonding Interface and Performance of Lead-Steel Laminated Composites, *The Chinese Journal of Nonferrous Metals*, vol.22, pp.3094-3099, 2012.
9. Han Zhao-hui, Zhu Pei-xian and Ma Hui-yu, A Study of the Performance of the Ti-Al Composite Electrode Materials in the Hot-Pressing Diffusion Bonding Method, *Acta Materiae Compositae Sinica*, vol.29, pp.129-134, 2012.
10. Cao Mei. The Preparation and Application of Al Base $SnO_2 + Sb_2O_3$ / $SnO_2 + Sb_2O_3 + MnO_2$ Coating of Lead Dioxide Electrode, Master Thesis, Kunming University of Science and Technology, Kunming, 2005.
11. D. Devilliers, M. T. D. Thi, E. Mahé and Q. L. Xuan, Cr (111) Oxidation with Lead Dioxide-Based Anodes, *Electrochim Acta*, vol.48, pp.4301-4309, 2003.
12. Tao Zi-chun, Pan Jian-yue and Luo Qi-fu, Study on Preparations of Pt Inter-Media and Effects of the Inter-Media on the Performances of Ti-Substrate Iro_2-Ta_2O_5 Coating Anodes, *Journal of Materials Science and Engineering*, vol.22, pp.240-244, 2004.
13. N. Munichandraiah, Insoluble Anode of Porous Lead Dioxide for Electro-Synthesis: Preparation and Characterization, *J. Appl Electrocheml*, vol.17, pp.22-23, 1987.
14. Ch. Comninellis and E. Plattere, The Preparation and Behaviour of Ti/Au/Pbo_2 Anodes, *J. Appl Electrochem*, vol.12, pp.399-404, 1982.
15. Guo Hong-qiang, Progress in the Selection of Inert Anode Materials for Aluminum Electrolysis, Sichuan Chemical Industry, vol.15, pp.19-21, 2012.
16. Fu Zheng-yi, Wang Wei-min and Wang Hao, Proposal of Structure Formation in Self-Propagating High Temperature Synthesis of Tib_2-Xal Composites, *Acta Metallurgica Sinica*, vol.30, pp.373-378, 1994.
17. Zha Quan-xing, The Introduction of Electrode Dynamic Process, Science Press, Beijing, 2007.6.

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