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Short Communication

Influence of Preparation Processes on the Resistivity of Porous Ti Based ATO

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In order to avoid the mud cracks and decrease the resistivity, the ATO (antimony doped tin oxide) coating on Ti substrate is prepared by thermal decomposition method. The ATO coating was characterized and the preparation conditions were optimized. In the experiments, the sintering temperature and holding time both can promote the oxidization of the substrate Ti. Although the resistivity of ATO is higher than that of Ti, ATO coating can protect the substrate Ti from passivation. In this case, both uneven and excess thickness of the coating coverage will lead the resistivity increase. The results indicate that the Ti based ATO shows low resistivity with uniform and compact surface under the optimized experiment conditions (Sb doping content 15%wt, coating 20 times and sintering in 450 °C for 15 min).

Keywords: porous titanium; ATO; resistivity; preparation

1. INTRODUCTION

Antimony (Sb) doped tin oxide (ATO) is an excellent coating material to prepare anode with low resistance and good electric catalytic activity [1-3]. The Ti based ATO shows good stability and electrochemical performance, and it has been widely used in the electrochemical industry [4, 5]. In current study, the thermal decomposition method is one of the major method for preparing ATO layer on the surface of titanium substrate [6]. However, because of the difference of thermal expansion, the coating film based on the substrate often shows “mud cracks”, which is traditionally resulted from the serious internals tress during the preparation process [7-9]. In this case, the cracks will degrade the adhesion strength and the protective effects of the coating to the substrate [10, 11]. For this reason, many researchers have done works on material modification [12, 13].

Based on our previous works [14], we optimized the preparation process of the ATO film on the porous titanium substrate, and prepared the Ti based ATO coating without mud cracks.

2. MATERIAL AND METHODS

The porous Ti (plate, thickness 1 mm, porosity 21.6%, average pore size 2.76 μm) was prepared in our previous work [15]. The porous Ti based ATO coating was prepared as follows: (1) Pretreatment. Cutting porous titanium to desired size; ultrasonic cleaning in acetone 5 min and then cleared by deionized water; immersing in H_2SO_4 solution (80 °C, 20%wt) 30 min and then cleared by deionized water; dried and prepared for next step. (2) Preparing coating solution. 2.63 mol·L^{-1} $SnCl_4 \cdot 5H_2O$ and a certain concentration of $SbCl_3$ (the mass ratio of $SbCl_3$ in $SbCl_3/SnCl_4 \cdot 5H_2O$ 0 - 27%wt) are dissolved in 100 ml solution (N-Butanol 80%v/v, HCl 20%v/v) under ultrasonic. (3) Coating ATO. Coating the solution prepared in step 2 on the surface of the porous Ti substrate for a certain times (5, 10, 15, 20, 25, 30), then sintering in the air atmosphere at different temperature (400 °C, 450 °C, 500 °C, 550 °C), finally cooled and reserved.

XRD (D/max 2500 PC) was used to characterize the crystal structure of Ti based ATO coating. The morphology of the surface is presented by SEM (JSM-6360LA). The resistivity of the material is examined according to IEC 60468:1974 [16]. The mass loss of the material under the sintering conditions is characterized by TG (SDT-Q600).

3. RESULTS AND DISCUSSION

3.1. The Influence of Sb doping on the resistivity of Ti based ATO

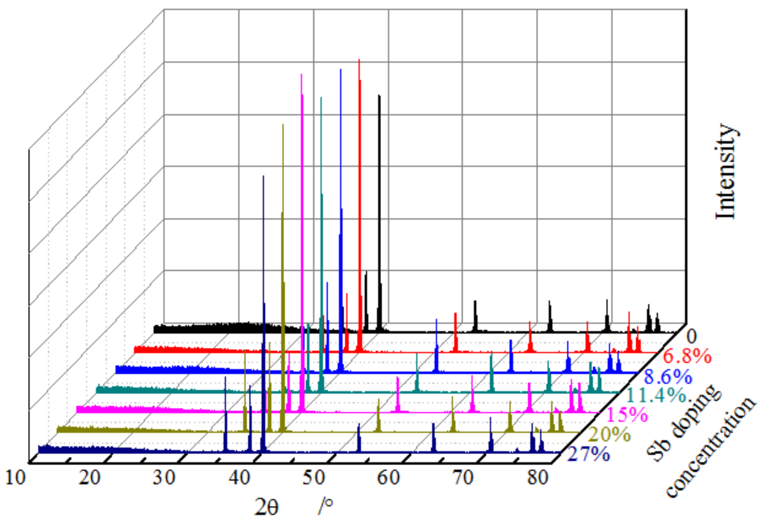

Figure 1. The XRD results of Ti based ATO with different Sb doping

In the ATO crystal, Sb is mainly as Sb^{5+} to dope into SnO_2 crystal. When ATO was coated on the porous Ti substrate, it is usually formed Sn-Ti solid solution [14]. Therefore the doping concentration of Sb showed effects on the material's crystalline structure. The XRD results of different Sb-doped Ti based ATO can be clearly seen in Figure 1. It can be confirmed from the results, that the diffracted intensity of the materials enhanced with the increasing of Sb doping concentration, and the peak appeared at 15%wt.

Moreover, it can be seen from the relationship between the resistivity and Sb doping concentration (Figure 2) that the resistivity of the materials decreased till 15%wt Sb-doping but increased with further doping. When the Sb doping concentration is low, the state of Sb is mainly in Sb^{5+} [17], and in this case the resistivity decreases with the increase of doping concentration. However, the portion of Sb^{5+} may transfer to Sb^{3+} when the Sb doping concentration is higher than 15%wt [18], which finally leading to an increase in the resistivity.

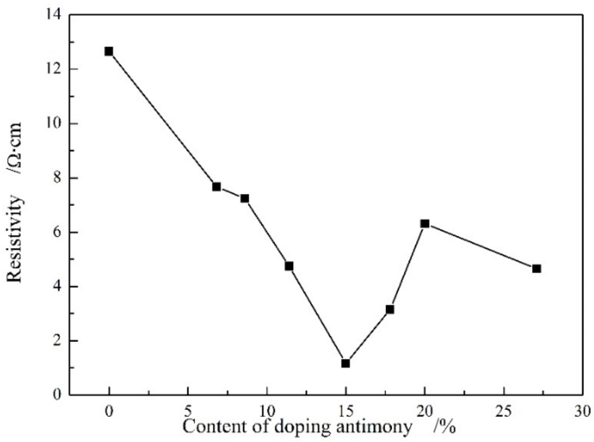

Figure 2. The influence of Sb doping on the resistivity of Ti based ATO (coating 20 times and sintering in 450 °C for 15 min)

3.2. The Influence of coating times on the resistivity of Ti based ATO

Figure 3 represents the XRD of Ti based ATO with different coating times. According to the XRD pattern, the effect of the coating times on the diffracted intensity can be concluded as the order: 20 times > 15 times > 10 times > 5 times > 0 times. Comparing with the sample without coating, the peak shifting appeared in the XRD patterns of the samples with ATO coating, which implied that the solid solution is formed [19, 20].

Furthermore, it can be seen from Figure 4 that the resistivity rapidly decreased along with the increasing of the coating times, and reaching a shallow minimum around 20 coating times. The SEM results (Figure 5) presented the morphology of the Ti based ATO. It can be seen from Figure 4 that the ATO layer coating 20 times was more uniform and thicker than that of the ATO layer coating 10 times. Although the resistivity of ATO is higher than that of Ti ($0.421\sim0.478\times10^{-6}\Omega\cdot m$), ATO coating can protect the substrate Ti from passivation. In this case, both uneven and excess thickness of the coating coverage will lead the resistivity increase.

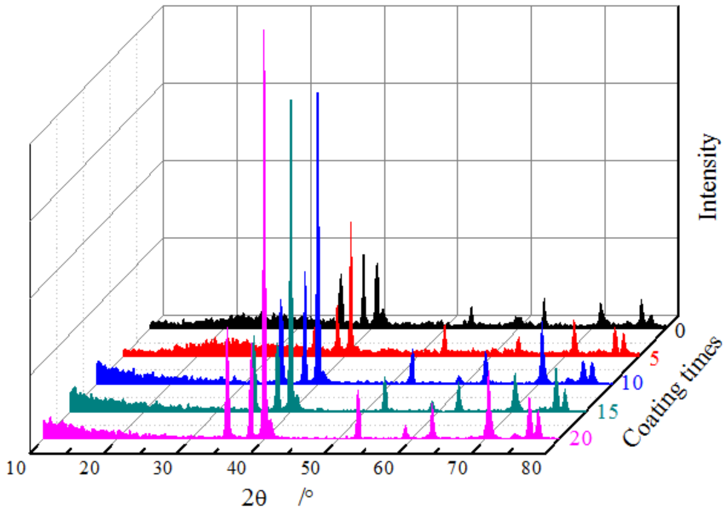

Figure 3. The XRD results of Ti based ATO with different coating times

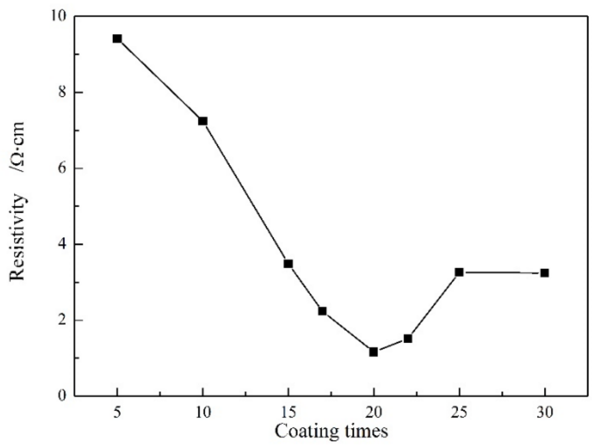

Figure 4. The influence of coating times on the resistivity of Ti based ATO (Sb doping content 15%wt and sintering in 450 °C for 15 min)

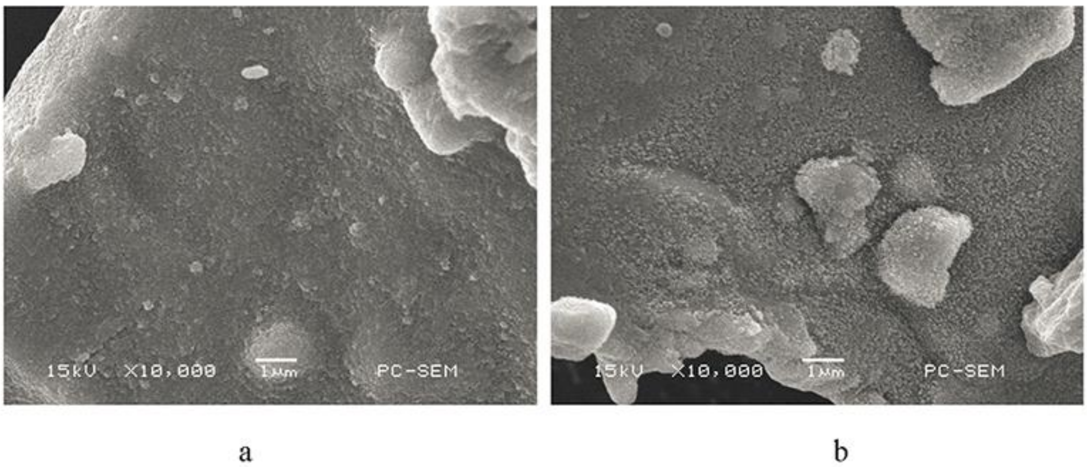

Figure 5. The SEM results of Ti based ATO with different coating times (a-10 times; b-20 times)

3.3. The effect of Sintering conditions on the resistivity of Ti based ATO

Sintering conditions are important for the preparation process of Ti based ATO [21]. In this work, the effects of the sintering temperature and time on the resistivity of the materials were investigated.

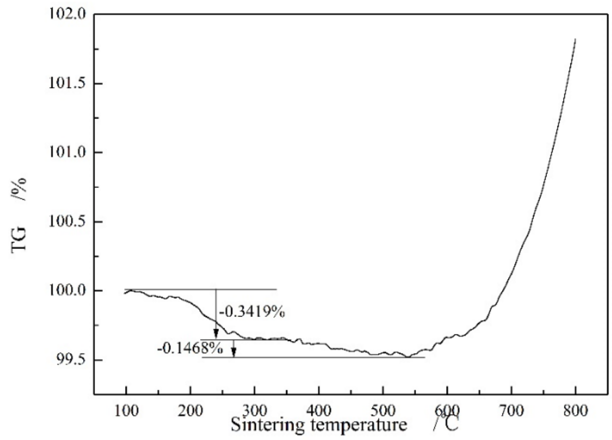

Figure 6. The TG curve of the Ti based ATO (Sb doping content 15%wt, coating 20 times)

As can be seen from the TG curve in Figure 6, there are two obvious weight loss steps from 100 °C to 550 °C (0.3419% from 100 °C to 350 °C, and 0.1468% from 350 °C to 550 °C). When the temperature is higher than 550 °C, the ATO layer began to sublimate and the substrate Ti came into oxidize, therefore the weight gradually increases.

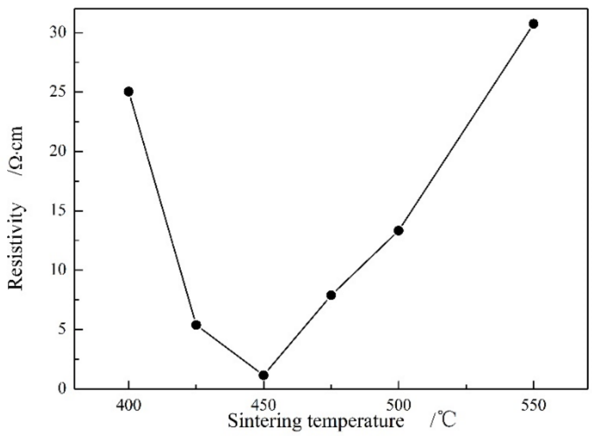

Figure 7. The effect of sintering temperature on the resistivity of Ti based ATO (Sb doping content 15%wt, coating 20 times and holding 15 min)

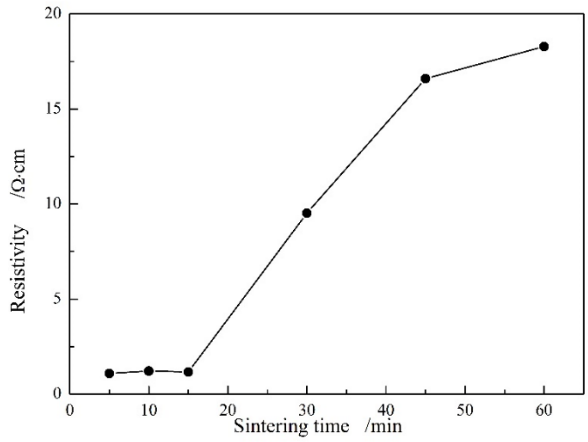

Figure 8. The effect of holding time on the resistivity of Ti based ATO (Sb doping content 15%wt, coating 20 times and sintering in 450 °C)

In the process of sintering, the sintering temperature and holding time both can promote the oxidization of the substrate Ti. As a result, the resistivity value of the porous Ti based ATO shows a minimum which sintering in 450 °C for 15 min (Figure 7). Moreover, the effect of holding time on the resistivity can be seen from Figure 8, the resistivity is stable at the beginning, while it increased sharply after 15 min. According to the result, the sintering temperature and the holding time was determined at 450 ℃ and 15 min respectively.

4. CONCLUSIONS

1) The porous titanium based ATO coating was prepared by thermal decomposition method. The SEM results showed that the morphology the ATO layer was uniform and without mud cracks.

2) Comparing with the sample without coating, the peak shifting appeared in XRD patterns implied that the solid solution is formed on the surface of the Ti based ATO.

3) Both uneven and excess thickness of the coating coverage will lead the resistivity increase. Under the experiment conditions, Sb doping content 15 %wt and coating 20 times can take advantages for preparing Ti based ATO with low resistivity.

4) Increasing sintering temperature or holding time can promote the oxidization of the substrate Ti, which will decrease the resistivity of the Ti based ATO. In this case, sintering in 450 °C for 15 min can be obtained as the optimum conditions for Ti based ATO preparation.

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References

1. Y. Li, J. Wang, B. Feng, K. Duan and J. Weng, *J. Alloy. Compd.*, 634 (2015) 37.
2. J. López-García, J. Montero, C. Maffiotte, C. Guillén and J. Herrero, *J. Alloy. Compd.*, 648 (2015) 104.
3. R.M.Piasentin, R.F.B. de Souza, J.C.M. Silva, E.V. Spinacé, M.C. Santos and A.O. Neto, *Int. J. Electrochem. Sci.*, 8 (2013) 435.
4. Y. Wang, Q. Zhang, Y. Wang, L. Jiao and H. Yuan, *J. Alloy. Compd.*, 645 (2015) S509.
5. J. Sun, H. Lu, H. Lin, W. Huang, H. Li, J. Lu and T. Cui, *Mater. Lett.*, 83 (2012) 112.
6. H. Xu, W. Yan and C. L. Tang, *Chinese. Chem. Lett.*, 22(2011) 354.
7. R. Grilli, D. Di Camillo, L. Lozzi, I. Horovitz, H. Mamane, D. Avisar and M. Baker, A. *Mater. Chem. Phys.*, 159 (2015) 25.
8. S. Kumar and A. C. Cocks, *J. Mech. Phys. Solids.*, 60 (2012) 723.
9. J. Yang, X. Zhao, Y. An, N. Liu, H. Zhou and J. Chen, *Mater. Manuf. Process.*, 29 (2014) 1126.
10. C. Q. Hu and Y. H. Song, Beijing: *Chemical Industry Press*, 2000.
11. G. Rivero, L. A. Fasce, S. M. Ceré and L. B. Manfredi, *Prog. Org. Coat.*, 77 (2014) 247.
12. L. Bao, J. Liu, F. Shi, Y. Jiang and G. Liu, *Appl. Surf. Sci.*, 290 (2014) 48.
13. Y. Chen, W. C. Xu and T. G. Duan, *Chinese. J. Inorg. Chem.*, 29 (2013) 243.
14. L. Wang, F. Pan and L.Wang, *Mater. Lett.*, 136 (2014) 195.
15. L. Wang, P. Liu, L. Wang, W. Xing, Y. Fan and N. Xu, *Mater. Manuf. Process.*, 28 (2013) 1166.
16. 16 IEC 60468: 1974. Method of measurement of resistivity of metallic materials.
17. E. Elangovan and K. A *Ramamurthi, Appl. Surf. Sci.*, 249 (2005) 183.
18. Y. Hu, H. Zhang and H. Yang, *J. Alloy. Compd.*, 453 (2008) 292.
19. J. Li, L. Wang, Y. Wang, J. Li, L. Wang and X. He, *Int. J. Electrochem. Sci.*, 10 (2015) 805.
20. S. Yang, T. Chen, Y. Wang, Z. Peng and W. Wang, *Int. J. Electrochem. Sci.*, 8 (2013) 2330.