

# Effect of TiO<sub>2</sub> Sol on the Microstructure and Tribological Properties of Cu-Sn Coating

Ying Lixia, Li Zhenghui, Wu Ke, Lv Xiupeng, Wang Guixiang

Harbin Engineering University, Harbin 150001, China

**Abstract:** In order to improve the hardness and wear resistance on condition that the self-lubricating property is ensured, Cu-Sn coatings were prepared and strengthened by combining sol-gel method and composite electroplating technology. TiO<sub>2</sub> sol was added to the Cu-Sn electroplating bath to obtain nano-particles reinforced Cu-Sn-TiO<sub>2</sub> composite coatings. The microstructure, composition, microhardness and tribological properties were analyzed. The results show that the introduction of the TiO<sub>2</sub> sol in the plating solution changes the composition and structure of the composite coatings. The co-deposited TiO<sub>2</sub> is uniformly distributed in the Cu-Sn matrix and greatly improves the microhardness and tribological properties of the Cu-Sn coating.

**Key words:** electrodeposition; Cu-Sn; TiO<sub>2</sub> sol; tribological properties

With excellent mechanical property, corrosion resistant and self-lubrication performance, Cu-Sn alloy is widely used in friction components<sup>[1-3]</sup>. However, Cu-Sn alloy has soft texture and weak carrying capacity, which leads to serious wear damage during the friction process. On the other hand, in order to improve the hardness and wear resistance and ensure the self-lubricating ability, the preparation of multiphase composite coatings has already become a significant research direction in the field of lubrication coatings<sup>[4,5]</sup>. The study of Cu-Sn-graphite plating showed that the graphite added in the plating decreased the hardness and frictional coefficient compared with Cu-Sn plating<sup>[6]</sup>. Cu-Sn-PTFE composite plating had better self-lubricating performance and higher wear resistance compared with the Cu-Sn alloy plating<sup>[7]</sup>. Researches on the Cu-Sn composite film which mixed with graphite and SiC showed that graphite and SiC together can reduce the frictional coefficient and the mass loss of wearing<sup>[8]</sup>. Furthermore, pulse electro deposition had significant effect on the microstructure of Cu-Sn alloy plating. The grain size of Cu-Sn alloy plating which was prepared by pulse electro deposition became smaller and showed the better mechanical property<sup>[9]</sup>.

In traditional composite electroplating, the nano powder was dispersed by surfactants firstly. Then the powder suspension was added into the plating solution. However, particles were prone to agglomerate in the bath and distributed unevenly in the coating. In order to overcome this problem and make the second-phase nano-particles highly disperse in the coating matrix, some novel methods have been adopted and studied. Sol-enhanced nanostructured Ni-TiO<sub>2</sub> and Ni-P-TiO<sub>2</sub> composites have been obtained<sup>[10-12]</sup>. Those research work shows that sol is a kind of highly dispersed system and the coating can be reinforced by adding nanoparticles in the form of sol. Furthermore, TiO<sub>2</sub> nanocrystalline particles have the performance of corrosion and wear resistance. TiO<sub>2</sub> sol is easy to synthesize and stably coexists with a lot kinds of plating bath<sup>[13,14]</sup>.

So, in the present paper, the electroplating Cu-Sn-TiO<sub>2</sub> composite coating was prepared by adding TiO<sub>2</sub> sol in the Cu-Sn plating bath. By comparing the properties between the Cu-Sn-TiO<sub>2</sub> composite coatings and the Cu-Sn alloy coatings, the effect of TiO<sub>2</sub> sol on the microstructure and properties of Cu-Sn coating had been studied.

Received date: October 16, 2016

Foundation item: National Natural Science Foundation of China (51305090)

Corresponding author: Ying Lixia, Ph. D., Associate Professor, College of Mechanical and Electrical Engineering, Harbin Engineering University, Harbin150001, P. R. China, Tel: 0086-451-82519710, E-mail: [yinglixia@hrbeu.edu.cn](mailto:yinglixia@hrbeu.edu.cn)

Copyright © 2017, Northwest Institute for Nonferrous Metal Research. Published by Elsevier BV. All rights reserved.

## 1 Experiment

TiO<sub>2</sub> sol was prepared by hydrolytic and polymerization reaction. With tetrabutylorthotitanate (Ti(OBu)<sub>4</sub>) as precursor, the mixture of 10 mL Ti(OBu)<sub>4</sub> and 2 mL glacial acetic acid was dissolved into 30 mL ethanol. After magnetic stirring for 2 h, the mixture was hydrolyzed by gradually increasing mixture of 1 mL deionized water, 0.5 mL triethanolamine, 0.4 mL nitric acid and 10 mL ethanol. Then, the flaxen transparent TiO<sub>2</sub> sol was obtained and its particle size was measured by laser particle analyzer, as shown in Fig.1. It can be found that the average diameter of TiO<sub>2</sub> particles in the sol is about 300 nm (Fig.2).

In the investigation, a non-cyanide Cu-Sn plating bath containing pyrophosphate and stannate was adopted in the experiments. Sheet shape medium carbon steel with carbon content 0.42wt%~0.50wt% was used as the substrate. The dimension is 28 mm×24 mm×1 mm and the quenching HV hardness was about 4.5 GPa. TiO<sub>2</sub> was selected as the strengthening particle to prepare Cu-Sn-TiO<sub>2</sub> composite coatings, which was added to the plating solution in form of sol, as prepared above. At the same time, the TiO<sub>2</sub> sol was added into the Cu-Sn plating solution with surfactant TX-10. The compositions of electroplating bath and processing parameters are shown in Table 1.

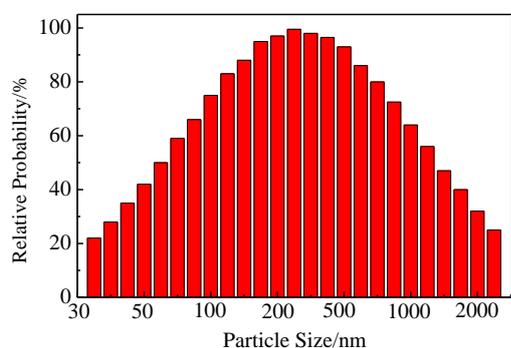


Fig.1 Particles size distribution of TiO<sub>2</sub> sol particle

**Table 1** Composition of electroplating bath and processing parameters

Deposition parameters	Value
Cu <sub>2</sub> P <sub>2</sub> O <sub>7</sub> 4H <sub>2</sub> O/g L <sup>-1</sup>	24~25
Na <sub>2</sub> SnO <sub>3</sub> 3H <sub>2</sub> O/g L <sup>-1</sup>	38~42
K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> 3H <sub>2</sub> O/g L <sup>-1</sup>	265~270
KNO <sub>3</sub> /g L <sup>-1</sup>	40
C <sub>4</sub> O <sub>6</sub> H <sub>4</sub> KNa 4H <sub>2</sub> O/g L <sup>-1</sup>	30
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> 2H <sub>2</sub> O/g L <sup>-1</sup>	20
TiO <sub>2</sub> Sol/mL L <sup>-1</sup>	(10~160)
Current density/A dm <sup>-2</sup>	2.5
Frequency/Hz	5000
Duty ratio/%	70
Time/h	1
pH	9.5
Stirring speed/r min <sup>-1</sup>	100
Temperature/°C	38

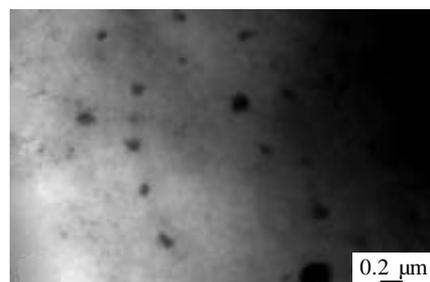


Fig.2 TEM micrograph of TiO<sub>2</sub> sol in the plating solution

The cross-section, surface morphologies and compositions of coatings were investigated using scanning electron microscopy (SEM) and X ray Fluorescence (XRF). Microhardness of the coatings was measured by Vickers HVS-1000. The load of 2 N was held for 15 s and an average value was obtained over 5 indents.

The tribological properties of coatings were characterized using a ball-disc tribological testing machine. The counterpart ball diameter was 5 mm which made of 9Cr18 was tempered. The hardness was between 5.5 GPa and 5.7 GPa. A load of 0.98 N and a stage rotate speed of 200 r/min were used at room temperature. The rotated radius was 4 mm and the total wear time was 10 min.

## 2 Results and Discussion

### 2.1 Microstructure and composition of the coatings

Fig.3 is the cross-section of the composite plating coating, which shows that the coating bonds well with the substrate. The thickness of the coating is about 20 μm.

Fig.4 is the surface morphologies of Cu-Sn with different content of TiO<sub>2</sub> sol. On the surface of Cu-Sn coating(Fig.4a), many open- or sub-surface cavities are observed. On the surface of Cu-Sn-TiO<sub>2</sub> coatings, clusters of nodules are clear and crystal structure is arranged compactly. Moreover, there is no obvious cavity. The results indicate that appropriate amount of TiO<sub>2</sub> sol facilitates the formation of more compact coating.

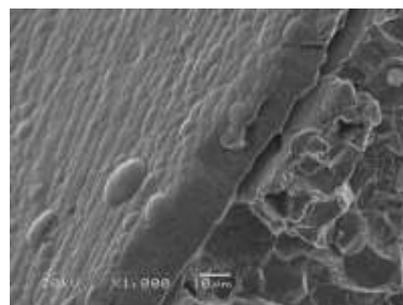


Fig.3 Cross-section of composite coating

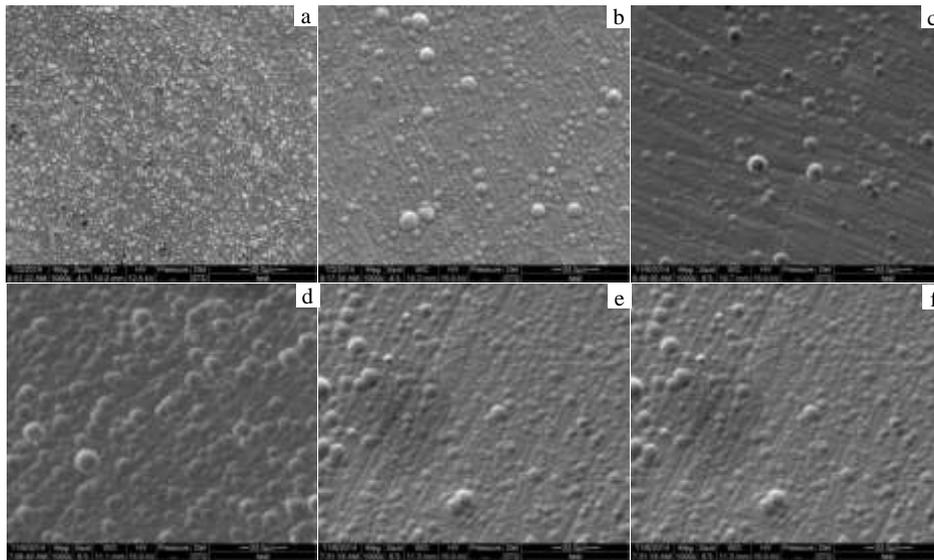


Fig.4 Surface morphologies of Cu-Sn coatings with different contents of  $\text{TiO}_2$  sol: (a) 0 mL/L, (b) 10 mL/L (c) 20 mL/L, (d) 40 mL/L, (e) 120 mL/L, and (f) 160 mL/L

Fig.5 is the content of Ti in the composite coatings as a function of  $\text{TiO}_2$  sol concentration in the bath. An increased concentration of  $\text{TiO}_2$  sol in the bath corresponds to an increased incorporation of  $\text{TiO}_2$  particles in the coating. When the concentration of  $\text{TiO}_2$  sol increases to 40 mL/L, the Ti percent in composite coating begins to descend. This can be due to the maximum particle absorption on the electroplated coating and deterioration of plating quality caused by high sol concentration. The determination by XRD shows that main components contain  $\text{Cu}_{81}\text{Sn}_{22}$ ,  $\text{Cu}_{42}\text{Sn}_{11}$  and Cu in Cu-Sn coatings (Fig.6). However, the addition of  $\text{TiO}_2$  sol makes no obvious effect on components, and the main components of the Cu-Sn- $\text{TiO}_2$  coatings include  $\text{Cu}_{81}\text{Sn}_{22}$ ,  $\text{Cu}_{42}\text{Sn}_{11}$ , Cu and  $\text{TiO}_2$ .

## 2.2 Hardness of coatings

Fig.7 shows the relationship between the microhardness of the coatings and the concentration of  $\text{TiO}_2$  sol in the plating solution. It can be found that the hardness of the Cu-Sn- $\text{TiO}_2$  composite coatings is higher than that of Cu-Sn coating without  $\text{TiO}_2$ . The hardness of the Cu-Sn- $\text{TiO}_2$  composite coatings depends on the percent incorporation of  $\text{TiO}_2$  particles.

Higher  $\text{TiO}_2$  content in the coatings leads to higher hardness of the composite coatings, which is corresponding with the result in Fig.5. The enhancement in the hardness of Cu-Sn- $\text{TiO}_2$  composite coatings is related to the dispersion-strengthening effect caused by  $\text{TiO}_2$  particles in the composite coatings, which impede the motion of dislocations in metallic matrix. This indicates that the  $\text{TiO}_2$  particles in the sol-enhanced nano-composite coatings play an important role in strengthening the microhardness. It is very encouraging to find that the Cu-Sn- $\text{TiO}_2$  composite coating exhibits higher hardness value 4.9 GPa (Fig.7) when the

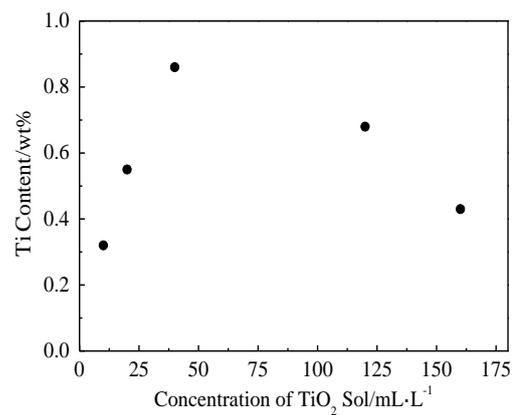


Fig.5 Content of Ti in the coatings as a function of  $\text{TiO}_2$  sol concentration

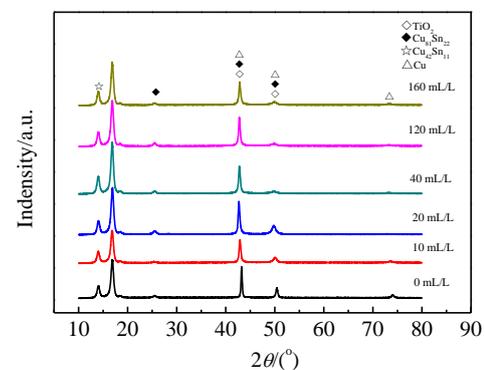


Fig.6 XRD patterns of coatings with different contents of  $\text{TiO}_2$  sol

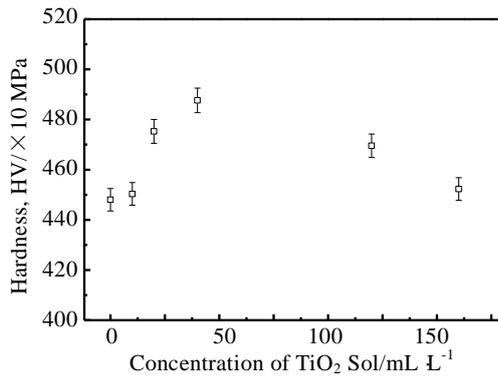


Fig.7 Microhardness of Cu-Sn-TiO<sub>2</sub> coatings

concentration of TiO<sub>2</sub> sol is 40 ml/L. Accordingly, the improved friction and wear properties are expected from the hardened composite coatings.

### 2.3 Tribological properties

Friction coefficient of the composite coatings with different content of TiO<sub>2</sub> are shown in Fig.8. It is suggested that the friction and wear behaviors of Cu-Sn-TiO<sub>2</sub> composite coatings are closely related with TiO<sub>2</sub> content. On one hand, the composite coatings with TiO<sub>2</sub> sol concentration 20 mL/L and 40 mL/L in the plating solution both show better tribological properties than Cu-Sn coating. The friction coefficient of Cu-Sn-TiO<sub>2</sub> composite coating obtained with 20 mL/L TiO<sub>2</sub> sol in the plating bath is 0.15 (Fig.8c) and with 40 mL/L TiO<sub>2</sub> sol in the plating bath is 0.1 (Fig.8d), which is significantly reduced compared with the Cu-Sn coating, 0.25 (Fig.8a). At

the same time, the friction processes become stable. On the other hand, the composite coatings with a lower and higher TiO<sub>2</sub> sol concentration show somewhat increase of friction coefficient compared with that of Cu-Sn coating. Particularly, when the concentration of TiO<sub>2</sub> sol increases to 160 mL/L in the bath, the tribological properties deteriorate. In the 10 min friction process, the friction coefficient keeps on a rise from 0.1 to 0.9. So, it is believed that an appropriate TiO<sub>2</sub> sol concentration in the bath is important to reduce the friction coefficient of the composite coating.

Fig.9a~9f show the SEM morphologies of the worn surfaces. It is seen that the wear track of the Cu-Sn coating shows signs of severe plastic deformation, adhesion and scuffing (see Fig.9a), which is usually related to adhesive wear mechanism for the Cu-Sn electroplated coating. A small quantity of TiO<sub>2</sub> sol in the bath has no significant effect on the hardness of composite coating (Fig.9b) and its wear mechanism is analogous to Cu-Sn coating.

However, narrow parallel scratches implying abrasive wear mechanism are observed in worn surfaces of Cu-Sn-TiO<sub>2</sub> composite coatings (Fig.9c and 9d). For high hardness and evenly spread nano-particles, the adhesion and scuffing on the worn surface of the Cu-Sn-TiO<sub>2</sub> composite coating are significantly abate, though the scuffing still remain in the latter case. According to Archard law, the wear resistance of Cu-Sn-TiO<sub>2</sub> increases evidently due to high dispersive TiO<sub>2</sub> particles and their strengthening effect. On the other hand, with higher TiO<sub>2</sub> sol concentration, 120 ml/L and 160 ml/L, the wear scars become rough and unconsolidated (Fig.9e and 9f).

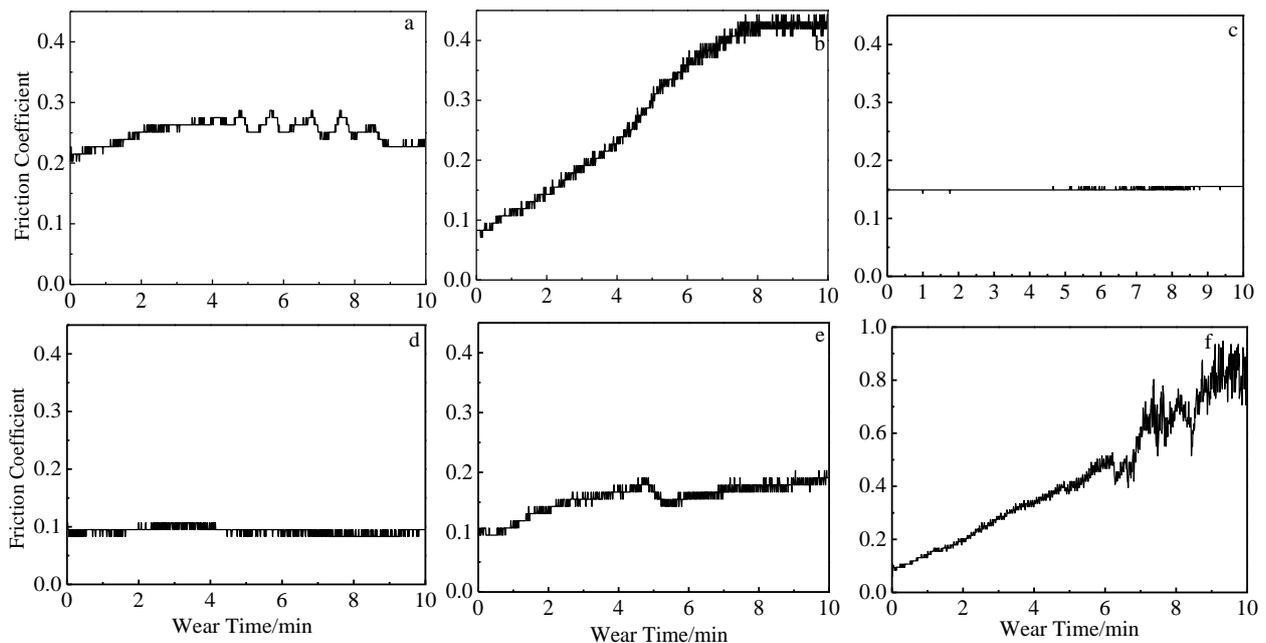


Fig.8 Friction coefficient of Cu-Sn-TiO<sub>2</sub> composite coatings with different concentrations of TiO<sub>2</sub> sol in the plating bath: (a) 0 mL/L, (b) 10 mL/L (c) 20 mL/L, (d) 40 mL/L, (e) 120 mL/L, and (f) 160 mL/L

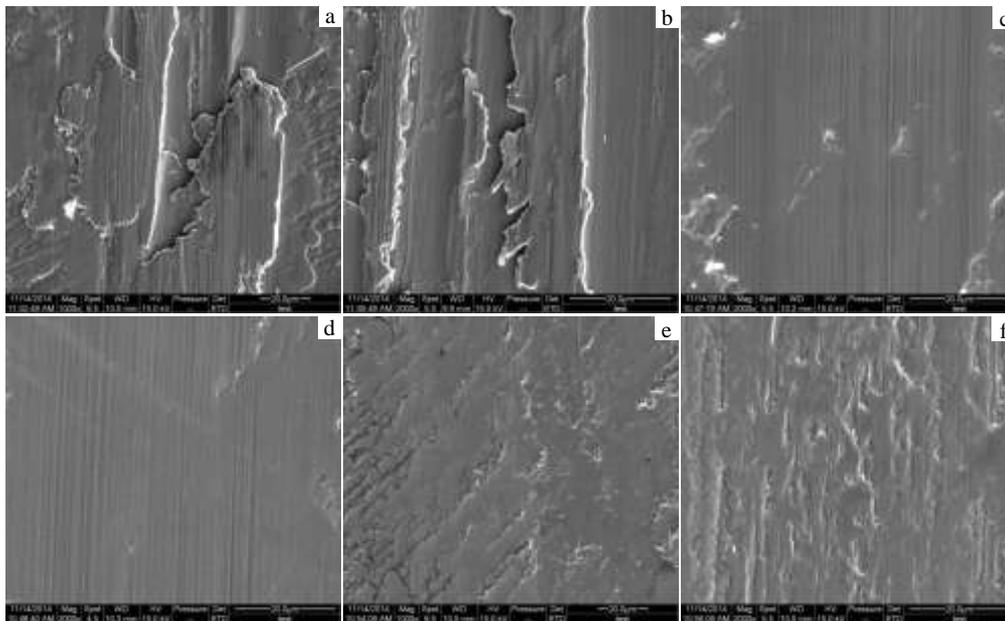


Fig.9 SEM morphologies of the worn surfaces of coatings with different concentration of  $\text{TiO}_2$  sol in the plating bath: (a) 0 mL/L, (b) 10 mL/L (c) 20 mL/L, (d) 40 mL/L, (e) 120 mL/L, and (f) 160 mL/L

Compared with Fig.4~9, it can be found that when the concentration of  $\text{TiO}_2$  sol is 40 mL/L, the coatings have fine microstructure. The more the content of  $\text{TiO}_2$  is in the coating, the higher the hardness is. The small and uniform microstructure and high hardness lead to lower friction coefficient and high wear resistance. In particular, the coating obtained with 40 mL/L Ti sol in the electroplating bath has the highest Ti content, which leads to the excellent tribological properties.

When the concentration of  $\text{TiO}_2$  sol exceeds 120 mL/L, increased solution viscosity leads to maldistributing current density and poor coating quality. Moreover, the sol in the plating solution is prone to agglomerate. The quality of the coatings deteriorates. Coarse and loose microstructure and high  $\text{TiO}_2$  content make the friction coefficient go up. The serious wear begins to occur. So,  $\text{TiO}_2$  content in the composite coating plays an important role in improving the tribological properties rather than the  $\text{TiO}_2$  sol concentration in the plating solution.

The mechanical properties of Cu-Sn- $\text{TiO}_2$  composite coatings are obviously improved, and the strengthening mechanisms can be described as two aspects: grain refinement strengthening effect and dispersion strengthening effect<sup>[15]</sup>. According to the Hall-Petch theory, the microhardness of Cu-Sn coating increases when the  $\text{TiO}_2$  grains are refined. And Fig. 2 provides the evidence that  $\text{TiO}_2$  nano-particles are highly dispersed in the Cu-Sn coating matrix with a size 300 nm, and the percent content

can reach 0.9wt%, contributing to a large dispersion strengthening effect.

### 3 Conclusions

1) Strengthened composite coatings Cu-Sn- $\text{TiO}_2$  may be obtained by adding  $\text{TiO}_2$  sol in the electroplating bath. This method overcomes the problems that the strengthening particles are easy to agglomerate and couldn't be dispersed well in plating process.

2) When the concentration of  $\text{TiO}_2$  sol is 20 mL/L and 40 mL/L, the coatings have fine microstructure, high Ti content and hardness. With the further improvement of sol concentration, the sol in the plating solution is prone to agglomerate. The coating quality, Ti content and hardness all come down. So, appropriate sol concentration in the plating solution plays an important role in improving the quality of coating.

3) When the concentration of  $\text{TiO}_2$  sol in the plating bath is 40 mL/L, the Ti content in the coating is the highest and the hardness of composite coating reaches the highest point, 4.9 GPa. The friction coefficient decreases to 0.1. However, when sol content is more than 120 mL/L, the coating's microstructure becomes loose. The tribological properties deteriorate.

### References

- 1 Pewnim N, Roy S. *Electrochemical Acta*[J], 2013, 90(15): 498
- 2 Zanella Caterina, Xing Sujie, Deflorian Flavio. *Surface &*

- Coatings Technology[J], 2013, 236(15): 394
- 3 Cui Gongjun, Bi Qinling, Zhu Shengyu et al. *Tribology International*[J], 2012, 53: 76
- 4 Ma Guozheng, Xu Binshi, Wang Haidou. *Rare metal Materials and Engineering*[J], 2012, 41(S1): 331 (in Chinese)
- 5 Afsaneh Dorri Moghadam, Emad Omrani, Pradeep L. *Composites Part B*[J], 2015, 77: 402
- 6 Nickchi T, Ghorbani M. *Surface and Coatings Technology*[J], 2009, 203(20-21): 3037
- 7 Balaji R, Pushpavanam M, Kumar K Y et al. *Surface and Coatings Technology*[J], 2006, 201(6): 3205
- 8 Asnavandi M, Ghorbani M, Kahram M. *Surface and Coatings Technology*[J], 2013, 216: 207
- 9 Zanella C, Xing S, Deflorian F. *Surface and Coatings Technology*[J], 2013, 236: 394
- 10 Weiwei Chen, Wei Gao. *Composites: Part A*[J], 2011, 42:1627
- 11 Chen Weiwei, Gao Wei. *Electrochimica Acta*[J], 2010, 55: 6865
- 12 Wang Y, Ju Y, Wei S et al. *Journal of The Electrochemical Society*[J], 2014, 161(14): D775
- 13 Wei Zhihao, Zhong Min, Dai Peipei et al. *Rare metal Materials and Engineering*[J], 2012, 41(S3): 599
- 14 Liu Xiangchun, Feng Xueli, Zhou Kaixuan et al. *Rare metal Materials and Engineering*[J], 2016, 45(2): 436 (in Chinese)
- 15 Low C T J, Wills R G A, Walsh F C. *Surface & Coatings Technology*[J], 2006, 201: 371

## TiO<sub>2</sub> 溶胶对 Cu-Sn 镀层微观组织和性能的影响

应丽霞, 李正辉, 吴珂, 吕秀鹏, 王桂香

(哈尔滨工程大学, 黑龙江 哈尔滨 150001)

**摘要:** 为了进一步提高Cu-Sn镀层的硬度和耐磨性, 在保持镀层自润滑性能的基础上, 采用纳米溶胶技术与复合电镀技术相结合的方法, 将纳米TiO<sub>2</sub>溶胶加入到电解液中, 制备了TiO<sub>2</sub>纳米粒子强化的Cu-Sn-TiO<sub>2</sub>复合镀层。通过对微观组织、成分、显微硬度和摩擦学性能的分析表明, 适量纳米TiO<sub>2</sub>溶胶的加入, 细化了Cu-Sn镀层组织, 提高了镀层的致密性, 其硬度和耐磨性均较Cu-Sn镀层显著提高。

**关键词:** 电镀; Cu-Sn; TiO<sub>2</sub>溶胶; 摩擦学性能

作者简介: 应丽霞, 女, 1978年生, 博士, 副教授, 哈尔滨工程大学机电工程学院, 黑龙江 哈尔滨 150001, 电话: 0451-82519710,

E-mail: yinglixia@hrbeu.edu.cn