Effect of TiO_2 Sol on the Microstructure and Tribological Properties of Cu-Sn Coating

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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_2 sol was added to the Cu-Sn electroplating bath to obtain nano-particles reinforced Cu-Sn- TiO_2 composite coatings. The microstructure, composition, microhardness and tribological properties were analyzed. The results show that the introduction of the TiO_2 sol in the plating solution changes the composition and structure of the composite coatings. The co-deposited TiO_2 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_2 sol; tribological properties

With excellent mechanical property, corrosion resistant and self-lubrication performance, Cu-Sn alloy is widely used in friction components^[1-3]. 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^[4,5]. 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^[6]. Cu-Sn-PTFE composite plating had better self-lubricating performance and higher wear resistance compared with the Cu-Sn alloy plating^[7]. 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^[8]. 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^[9].

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_2 and Ni-P- TiO_2 composites have been obtained^[10-12]. 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_2 nanocrystalline particles have the performance of corrosion and wear resistance. TiO_2 sol is easy to synthesize and stably coexists with a lot kinds of plating bath^[13,14].

So, in the present paper, the electroplating Cu-Sn- TiO_2 composite coating was prepared by adding TiO_2 sol in the Cu-Sn plating bath. By comparing the properties between the Cu-Sn- TiO_2 composite coatings and the Cu-Sn alloy coatings, the effect of TiO_2 sol on the microstructure and properties of Cu-Sn coating had been studied.

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1 Experiment

TiO₂ sol was prepared by hydrolytic and polymerization reaction. With tetrabutylorthotitanate (Ti(OBu)₄) as precursor, the mixture of 10 mL Ti(OBu)₄ 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 TiO₂ 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 TiO₂ 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. TiO₂ was selected as the strengthening particle to prepare Cu-Sn-TiO₂ composite coatings, which was added to the plating solution in form of sol, as prepared above. At the same time, the TiO₂ 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 TiO₂ sol particle

Table 1 Composition of electroplating bath and processing parameters

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

Fig.2 TEM micrograph of TiO₂ 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 TiO₂ sol. On the surface of Cu-Sn coating(Fig.4a), many open- or sub-surface cavities are observed. On the surface of Cu-Sn-TiO₂ 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 TiO₂ 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 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 TiO_2 sol concentration in the bath. An increased concentration of TiO_2 sol in the bath corresponds to an increased incorporation of TiO_2 particles in the coating. When the concentration of 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 TiO_2 sol makes no obvious effect on components, and the main components of the Cu-Sn- TiO_2 coatings include $\text{Cu}_{81}\text{Sn}_{22}$, $\text{Cu}_{42}\text{Sn}_{11}$, Cu and TiO_2 .

2.2 Hardness of coatings

Fig.7 shows the relationship between the microhardness of the coatings and the concentration of TiO_2 sol in the plating solution. It can be found that the hardness of the Cu-Sn- TiO_2 composite coatings is higher than that of Cu-Sn coating without TiO_2 . The hardness of the Cu-Sn- TiO_2 composite coatings depends on the percent incorporation of TiO_2 particles.

Higher 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- TiO_2 composite coatings is related to the dispersion-strengthening effect caused by TiO_2 particles in the composite coatings, which impede the motion of dislocations in metallic matrix. This indicates that the 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- 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 TiO_2 sol concentration

Fig.6 XRD patterns of coatings with different contents of TiO_2 sol

Fig.7 Microhardness of Cu-Sn-TiO₂ coatings

concentration of TiO₂ 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 TiO₂ are shown in Fig.8. It is suggested that the friction and wear behaviors of Cu-Sn-TiO₂ composite coatings are closely related with TiO₂ content. On one hand, the composite coatings with TiO₂ 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-TiO₂ composite coating obtained with 20 mL/L TiO₂ sol in the plating bath is 0.15 (Fig.8c) and with 40 mL/L TiO₂ 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 TiO₂ sol concentration show somewhat increase of friction coefficient compared with that of Cu-Sn coating. Particularly, when the concentration of TiO₂ 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 TiO₂ 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 TiO₂ 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-TiO₂ 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-TiO₂ composite coating are significantly abate, though the scuffing still remain in the latter case. According to Archard law, the wear resistance of Cu-Sn-TiO₂ increases evidently due to high dispersive TiO₂ particles and their strengthening effect. On the other hand, with higher TiO₂ 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-TiO₂ composite coatings with different concentrations of TiO₂ 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 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 TiO_2 sol is 40 mL/L, the coatings have fine microstructure. The more the content of 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 TiO_2 sol exceeds 120 mL/L, increscent 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 TiO_2 content make the friction coefficient go up. The serious wear begins to occur. So, TiO_2 content in the composite coating plays an important role in improving the tribological properties rather than the TiO_2 sol concentration in the plating solution.

The mechanical properties of Cu-Sn- 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^[15]. According to the Hall-Petch theory, the microhardness of Cu-Sn coating increases when the TiO_2 grains are refined. And Fig. 2 provides the evidence that 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- TiO_2 may be obtained by adding 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 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 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.

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TiO₂ 溶胶对 Cu-Sn 镀层微观组织和性能的影响

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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TiO₂溶胶加入到电解液中, 制备了TiO₂纳米粒子强化的Cu-Sn-TiO₂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TiO₂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; TiO₂ 溶胶; 摩擦学性能

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