Effect of Thiourea on the Properties of a Cu–Al₂O₃ Coating Prepared via Jet Electrodeposition

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Cu–Al₂O₃ nanocomposite coatings were jet electrodeposited from an electrolyte containing Al₂O₃ nanoparticles and added thiourea. The effects of the thiourea concentration on the surface morphologies, microstructures, growth structures, incorporated Al₂O₃ nanoparticle contents, and mechanical performances of the composite coatings were examined. The results revealed that the adsorption of Al₂O₃ increased from 4.6 at% to 9.3 at% with the addition of thiourea, and grain refinement from 61 nm to 33 nm was achieved. Thiourea additions in the concentration range of 0–15 mg/L increased the microhardness by 79% compared with that of the coating fabricated without thiourea. The mechanisms by which thiourea influenced the deposition quality and mechanical properties of the coating are discussed. [doi:10.2320/matertrans.M2019024]

(Received January 21, 2019; Accepted February 22, 2019; Published April 25, 2019)

Keywords: jet electrodeposition, thiourea, coatings, mechanical properties

1. Introduction

Nanocomposite electrodeposition is a suitable technique for co-depositing a variety of nanoparticles (NPs) to improve the properties of coatings^{1,2)} and has gained widespread use for the protection of automotive engineering and the casting of moulds.^{3,4)} However, small ceramic powders including Al₂O₃ NPs are not easily included in deposited coatings since they disperse poorly in the electrolyte because of their tendency to agglomerate, which often leads to a significant decrease in the hardnesses and strengths of composite coatings.^{5–8)} Additionally, because of the uneven current distribution over the substrate, as the coating thickness increases during electrodeposition, the surface becomes rougher and tends to form nodules or dendrites, which affects the dimensional accuracy of an electrodeposited coating.^{9,10)} To enhance the performances of electrodeposited nanocomposites, it is essential to find a way not only to increase the NP content in the substrate material to promote the coating properties but also to reduce the coating roughness to obtain a good surface finish.

Currently, methods for improving the NP content in composite coatings and the surface finish have attracted much attention in the electrodeposition field. These methods include changing the direct current to a pulsed current (PC),¹⁰⁾ air agitation, supersonic vibration and the addition of surfactants.¹¹⁾ Thiourea (TU) is widely used as a levelling agent for copper electroplating and has the effect of regulating and refining the grains to produce a smooth and bright electroplated surface.^{12,13)} However, there are few studies on the use of thiourea for the preparation of nanocomposite copper coatings. Moreover, in a conventional watts-bath environment, the addition of both thiourea and NPs to the electrolyte has not been found to generate an optimal effect.

As an emerging coating method in recent years,^{14–16)} jet electrodeposition (JE) is expected to overcome the above challenges when applying thiourea as an additive. As shown

Fig. 1 Schematic of the high-speed selective jet electrodeposition process.

in Fig. 1, the current causes deposition at the impinging zone only, resulting in a high degree of locality, which is one of the key features of jet electrodeposition technology. On the other hand, since the electrolytic jet continuously supplies fresh electrolyte to the deposition area, it creates a hydrodynamic environment that forms a diffusion layer with a very small thickness,¹⁷⁾ which results in deposition of metal ions onto the surface at a substantially higher rate than in conventional electroplating. Therefore, JE also enables a much higher applied current density than conventional electrodeposition and generates novel material structures. For instance, micro/nanoscale porous surface microstructures can be formed, which can develop to act as pockets for storing lubricants, resulting in a self-lubricating and wear-reducing effect between components in contact. In addition, this process has been found to be rapid, simple, economical, cold working to avoid heating effects and flexible to changes in surface morphology by adjusting the deposition conditions.

During the JE process, as the electrolyte impinges on the cathode surface, a high rate of mass transport promotes the liquid-mass-transfer efficiency of the electrolyte.^{18–21)} Consequently, JE achieves a much higher applied current density and provides unique advantages over conventional electrodeposition. First, JE possesses a grain-refining effect since it uses a much higher overpotential and produces nanocrystalline structured materials. Second, the electrolyte impingement plays an intense steering and forced-circulation

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double role that highly favours a decrease in the agglomeration tendency of NPs, prompting more NPs in the electrolyte to co-deposit with the metallic atoms onto the substrate. Considering these characteristics, JE could be a desirable method for producing nanocomposite coatings along with thiourea as a key additive in the electrolyte to increase the NP content in nanocomposite coatings and achieve a good surface finish. However, when a high current density is applied, rougher surfaces and nodules or dendrites still exist and often result in a deterioration of the deposition quality. In this case, the deposition cannot continue. As a levelling agent for copper metal electrodeposition, thiourea may be used to suppress the adverse effects of cell protrusions, ensure the generation of nanocrystalline structures at high current densities, and enable the coating process to continue to produce a thick coating. To date, few works have been reported in this regard. Additionally, the mechanism for the effect of thiourea on deposition quality is not yet clear. The optimal additive concentration in the electrolyte that determines the deposition quality is still unknown.

The present research focuses on the effect of thiourea addition to the JE process and the mechanical properties of Cu–Al₂O₃ nanocomposite coatings. In this work, the surface morphology and the incorporation of Al₂O₃ NPs into the composite coatings for different levels of thiourea addition were observed. The effects of thiourea concentration on the mechanical properties of the coatings were evaluated and optimized.

2. Experimental Procedure

2.1 Experimental setup and conditions

The Cu–Al₂O₃ coatings were prepared using a self-developed JE experimental setup (see Fig. 2), mainly composed of a motion control system, flow control system, temperature control unit, nozzle, and DC power source. Table 1 shows the different compositions of the electrolyte (with 0, 5, 10, 15 and 20 mg/L thiourea additions). The α -Al₂O₃ NPs, with an average diameter of 35 nm, were added to the electrolyte at a concentration of 10 g/L. Prior to JE, the electrolyte must be stirred at 40°C for 1 h to ensure that the reagents are sufficiently dissolved. During JE, every solution

Table 1 Electrolyte composition and deposition conditions.

Electrodeposition bath and process	Composition and conditions
CuSO ₄ •5H ₂ O	250 (g/L)
H ₂ SO ₄	50 (g/L)
Al ₂ O ₃ nanoparticles	10 (g/L)
Thiourea	0–20 (mg/L)
Temperature	40±2 °C
Stirring speed during electrodeposition	100 rpm + ultrasonic agitation
Current density	200–500 (A/dm ²)
Deposition time	30 min

was mixed using ultrasonic agitation and a mechanical stirrer. A copper rod was added to the nozzle chamber as the anode, and a piece of 30CrMnSi stainless steel, with a size of 100 mm × 20 mm × 2 mm, was used as the matrix material. The samples were polished using sandpapers, cleaned with distilled water and immersed in acetone for 5 min. The experimental conditions were as follows: a rectangular nozzle (20 mm × 1 mm), an electrolyte flow velocity of 10 m/s, a scanning rate of 1000 mm/min, the number of scanning layers set to 800 and a spray distance of 5 mm. Every deposition continued for 30 min, and the coating thickness was approximately 300 µm.

2.2 Examination of the nanocomposite coatings

The coating surface morphologies and microstructures were observed by scanning electron microscopy with a LEO-1530 microscope, and the incorporated Al₂O₃ NP content in the coatings was determined using energy dispersive spectrometry (EDS). The grain size was calculated from the XRD patterns using the Scherrer equation. The coating hardness was measured with an HVS-1000A microhardness meter at a load of 100 g for 15 s. The tensile properties were tested by an electronic universal testing machine. Every sample was measured five times for the microhardness and tensile tests and the mean value was derived from the results.

3. Results and Discussion

3.1 Surface morphologies, microstructures and NP contents of the coatings

Figure 3 shows the effect of the thiourea content in the electrolyte on the surface growth morphology when the current density is 200 A/dm². It can be seen that in the range of 0–10 mg/L of added thiourea, the deposited surface has evident cellular-like nodules with sizes of 10–20 µm (see Fig. 3(a)), but as the thiourea content increases, the cellular nodules become smaller, and the flatness of the surface significantly improves. When the thiourea content is 10 mg/L, the deposited surface is the smoothest and flattest (see Fig. 3(c)). However, if the amount of added thiourea exceeds 10 mg/L, the coating does not notably change, as seen in Fig. 3(d). This indicates that a continuous increase in

Fig. 2 Experimental setup for the jet electrodeposition process.

Fig. 3 SEM images of the surface morphologies of the Cu-Al₂O₃ coatings with thiourea concentrations of (a) 0 mg/L, (b) 5 mg/L, (c) 10 mg/L, and (d) 15 mg/L.

Fig. 4 SEM images of the microstructures of the Cu-Al₂O₃ coatings with thiourea concentrations of (a) 0 mg/L, (b) 5 mg/L, (c) 10 mg/L, and (d) 15 mg/L.

the thiourea content of the electrolyte does not continuously influence the surface morphology. Further, this result indicates that 10 mg/L of thiourea in the electrolyte has the optimal morphological improvement.

Figure 4 shows the influence of thiourea on the cross-sectional microstructures of the samples. When the thiourea concentration increases from 5 mg/L to 15 mg/L, the deposited layer gradually changes from a porous structure to a dense, even and fine structure. When the thiourea addition reaches 10 mg/L, the deposited layer has its densest state and forms a nanocrystalline microstructure (see Fig. 4(c)). Beyond this critical point, if the thiourea concentration continues to increase, small holes and cracks

begin to appear within the microstructure, and the deposited layer deteriorates (see Fig. 4(d)).

Figure 5 illustrates the effect of thiourea concentration on the coating grain size. It can be seen that the grain size decreases with increasing thiourea concentration. When 10 mg/L of thiourea is added, the average size of the deposited grains reaches a minimum of approximately 29 nm. However, if the thiourea concentration continues to increase, the grains begin to expand and attain their highest size of 36 nm.

The thiourea concentration has an obvious influence on the crystal orientation of the deposited layer. Figure 6 shows that when 5 mg/L of thiourea is added, the (220) plane is found to

Fig. 5 The grain sizes of coatings prepared with different concentrations of thiourea.

Fig. 6 Preferred orientation of the nanocrystals of the coatings prepared with different concentrations of thiourea.

have the maximum intensity and is the preferred orientation. When the thiourea concentration increases to 10 mg/L, the preferred orientation changes to be the (111) plane. As the thiourea concentration continues to increase to 15 mg/L, the preferred crystal plane orientation remains the (111) plane. Therefore, it is interesting to note that a 10 mg/L addition of thiourea results in similar crystal planes without an obvious preferred orientation.

Based on the above observations, it can be proven that the addition of an appropriate amount of thiourea has the evident effect of improving the deposition quality, not only producing a deposited surface that is smooth and flat but also favourably strengthening the inner-structure of the deposited coating and producing a more even and dense deposited coating, although an excessive addition of thiourea will deteriorate the deposition quality by increasing the protruding growths to increase the roughness of the surface and generate defects inside the coating. This improvement could be obtained in two ways.

First, the addition of thiourea has an obvious refining effect on the grains because thiourea can attach to and cover the growing point of the crystal, thus hindering the adsorbed atoms from diffusing to the growing point of the crystal and inhibiting the continuous growth of the crystal.¹⁵⁾ In addition, the thiourea additive can make discharging the entire crystal structure more difficult and increase the cathode overpotential, thereby promoting more nucleation and reducing the grain size. These compounding effects favour the

Fig. 7 The amounts of incorporated Al₂O₃ NPs in the coatings prepared with different concentrations of thiourea (at a current density of 300 A/dm²).

deposition of smooth and flat copper surfaces. However, too high a concentration of thiourea cannot provide the refining effect. Instead, the sulfur in the thiourea can introduce a high amount of stress to the coating and form micro-cracks and pores, making the coating brittle and inhibiting nucleation.^{12,13)} This is the reason for excessive thiourea increasing the grain size and deteriorating the deposited coating properties.

Second, thiourea addition changes the preferential orientation. When the concentration of thiourea is relatively low in the deposition of a copper composite, thiourea inhibits the growth of the (111) plane and significantly promotes the preferred orientation of the (220) plane. When the concentration of thiourea is relatively high, it inhibits the growth of the (220) plane and promotes the growth of the (111) plane. In other words, regardless of whether the thiourea content is low or high, only a single type of growth structure forms and preferred orientation growth is more likely to be generated. However, if a moderate amount of thiourea, for instance 10 mg/L, is added to the electrolyte, a balance between crystal planes without a preferred orientation structure can be obtained. At this optimum concentration, the deposited surface appears to be smoother and flatter.

Figure 7 shows the effect of thiourea concentration on the deposited Al₂O₃ contents of the composite coatings. It can be noted that with the addition of 5 mg/L of thiourea, the deposited Al₂O₃ content of the composite coating remains unchanged. However, by increasing to a 10 mg/L addition of thiourea to the electrolyte, the incorporated Al₂O₃ NP content is greatly increased from 6.4 at% to 9.3 at%, attaining its maximum value. When the thiourea concentration is increased to 20 mg/L, the incorporated Al₂O₃ NP content slightly declines. Therefore, it can be concluded that the thiourea concentration in the electrolyte strongly affects the incorporation of Al₂O₃ NPs into the composite coating.

A schematic of the nanoparticles in a solution containing thiourea is presented in Fig. 8. When thiourea is added to the electrolyte, a number of thiourea molecules begin to complex with Cu²⁺ and cover the surface of the NPs as the jet electrolyte carrying a number of NPs impinges on the cathode surface. The positive surface charges of the Al₂O₃ NPs can be strengthened and correspondingly generate electrostatic repulsion between the NPs, thereby reducing the tendency of

Fig. 8 Schematic figure showing thiourea molecules around the Al_2O_3 particles.

the NPs to agglomerate as they are travelling to the cathode. On the other hand, as the NPs are covered by an increasing amount of metal ions, they will become increasingly positively charged, and more of the NPs will be electrostatically attracted to the negatively charged cathode and deposited on the cathode. This process can be seen as an effective strategy for preventing agglomeration and illustrates the mechanism behind the increasing content of Al_2O_3 in the composite coatings.^{13,14,20}

3.2 Effect of thiourea concentration on the mechanical properties of the composite coatings

Figure 9(a) shows the correlations between the microhardness and the current density and thiourea content of the electrolyte. In the range of 200–500 A/dm^2 , the microhardness continues to increase with increasing current density up to 400 A/dm^2 . Then, the microhardness decreases with increasing current density. The addition of thiourea to the electrolyte has an evident influence on the microhardness of the deposited coating. For a given current density, the microhardness increases with increasing thiourea addition. The highest microhardness of HV 261 is obtained at a current density of 400 A/dm^2 and a thiourea concentration of 10 mg/L , representing a 79% increase compared with the lowest microhardness of HV 146, which was obtained at a current density of 500 A/dm^2 without the addition of thiourea. These results show that the thiourea addition is very useful for increasing the microhardness of the composite coating. In fact, two factors contribute to the increasing hardness of the composite coatings: the first factor is the increasing Al_2O_3 NP content in the composite coating, which enhances the hardness and strengthens the composite coating, as shown in Fig. 7, where increasing thiourea, within a certain range, is beneficial for increasing the content of the Al_2O_3 nanoparticles. The second factor is that the high current density applied in JE is highly favourable for promoting the nucleation rate and achieving the grain refining effect, resulting in the dramatically improved microhardness of the composite coating. However, too high a current density has the negative effects of inducing the formation of a large number of large and cellular-like nodules on the deposited surface and generating cracks between

Fig. 9 Mechanical properties of the composite coating including (a) microhardness and (b) tensile strength.

larger Al_2O_3 particles, which contributes to the sharp decrease in microhardness as the current density exceeds 400 A/dm^2 .

Figure 9(b) shows the influence of the addition of thiourea on the tensile strength of the composite coating. The tensile strength has a similar trend as the microhardness in regard to its relationship with the current density and the amount of thiourea in the electrolyte. The tensile strength reached a maximum value of 586 MPa at a current density of 400 A/dm^2 and a thiourea concentration of 10 mg/L . The lowest tensile strength of 436 MPa is obtained at a current density of 500 A/dm^2 without the addition of thiourea.

These variations in the mechanical properties, including hardness and tensile strength, are mainly related to the surface morphology of the coating material and its density, and the mechanical properties are ultimately influenced by the JE conditions, especially the current density and amount of added thiourea. When the current density is less than 300 A/dm^2 , increasing the current density and amount of added thiourea causes the microstructure of the composite coating to gradually become denser and refines the grain size. Correspondingly, the mechanical properties of the coating can be highly strengthened. However, if the current density is greater than 300–400 A/dm^2 , the grain refining effect is weakened, and the grain size begins to increase. Moreover, the surface roughness increases and nodules grow on the coating surface. These effects will jointly lead to the mechanical properties of the deposited coating deteriorating.

4. Conclusion

A Cu–Al₂O₃ composite coating was prepared with the use of JE. The addition of thiourea significantly improved the surface morphology, microstructure and Al₂O₃ NP content of the composite coating. The composite coating prepared with a 10 mg/L addition of thiourea had an optimum surface morphology and a dense microstructure.

The Cu–Al₂O₃ composite coating produced using the optimized parameters (400 A/dm² current density and 10 mg/L of thiourea) contained a 9 at% Al₂O₃ NP content and had a high hardness of HV 263. Under the same optimized parameters, the tensile strength has a maximum value of 586 MPa. The jet electrodeposition method is proven to be effective and suitable for the joint addition of thiourea and Al₂O₃ NPs to the electrolyte and results in synergistic effects.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51305178), Natural Science Foundation of Jiangsu Provincial University (17KJD460005), Jiangsu Natural Science Foundation (BK20181473), Nantong 3D printing laboratory funding project (2018KFKT09/CP12016002), College Students' innovation and entrepreneurship training program (201810320112Y).

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