



A variable hydrophobic surface improves corrosion resistance of electroplating copper coating

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ABSTRACT

In this paper, Cu/liquid microcapsule composite coating was prepared by electroplating method. And a variable hydrophobic surface was obtained due to the slow release of microcapsules and the rough surface. The hydrophobic property and corrosion resistance of the composite was investigated by means of water contact angle instrument and electrochemical technique, respectively. The results suggest that the contact angle (CA) of composite increases gradually with the increasing storing time, and the stable super-hydrophobic property was exhibited after storing in air for 15 days. Meanwhile, the excellent corrosion resistance was displayed, which could be ascribed to the good stability of hydrophobic film on composite surface.

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1. Introduction

Electroplating copper coating as a protective layer has extensive application in modern material science, applied science and engineering due to its high electrical conductivity and low cost. However, a major disadvantage of copper coating is that it corrodes easily, especially in acid environment. Several studies show that the corrosion resistance of plating copper coatings can be significantly improved by modifying their surface with passivation [1,2], self-assembly technology [3,4], and especially by creating super-hydrophobic surface [5,6].

Currently, super-hydrophobic surfaces with the water contact angle (CA) higher than 150° have attracted more and more attention [7,8] and are widely applied in national defense, industries and daily life [9]. Conventionally, two main ways are adopted to obtain super-hydrophobic surfaces. One is to create a rough microstructure on the hydrophobic surface by etching [10,11], phase separation [12], molding [13], sol-gel [14] and so on [15–17]. The other way is to modify the surface with low surface energy materials, such as fluoroalkylsilane [18–20]. Yin et al. have successfully fabricated super-hydrophobic film by etching on the copper surface and obtained good corrosion resistance in seawater [5].

Based on a series of experimental trials in our research, the plating copper coating containing liquid microcapsules (Cu/microcapsules composite coating) was prepared by electroplating method. The aim of designing this coating is to obtain a variable hydrophobic surface on copper coating through the release of liquid core material of microcapsules. Meanwhile, these microcapsules can “bleed” core material and fix the surface damage when the composite is stressed or damaged. So a hydrophobic core material is necessary. In this study, BH-102 hydrophobic agent was chosen as the core material of microcapsule. One of the promising advantages of this composite is that the encapsulated hydrophobic agent can be released gradually and forms a low surface energy hydrophobic film on copper surface. So this composite coating will have widely application prospect in the field of textile industry, function coating and so on. In this paper, the hydrophobic property and corrosion resistance behavior of composite will be discussed in detail.

2. Experimental details

2.1. Cu/liquid microcapsule composite preparation

Firstly, the phase separation method was employed to prepare the liquid microcapsule. Methyl cellulose (MC, cP 15–25, supplied by Shanghai Chemicals Co. Ltd.) and liquid BH-102 hydrophobic agent (it is a mixture of KF-99 hydrogen-containing silicone oil and inhibitor 1H-Benzotriazole, purchased by a ShinEtsu Company in Japan) were used as the shell and core materials of microcapsule, respectively. Secondly, the copper/liquid microcapsules composite

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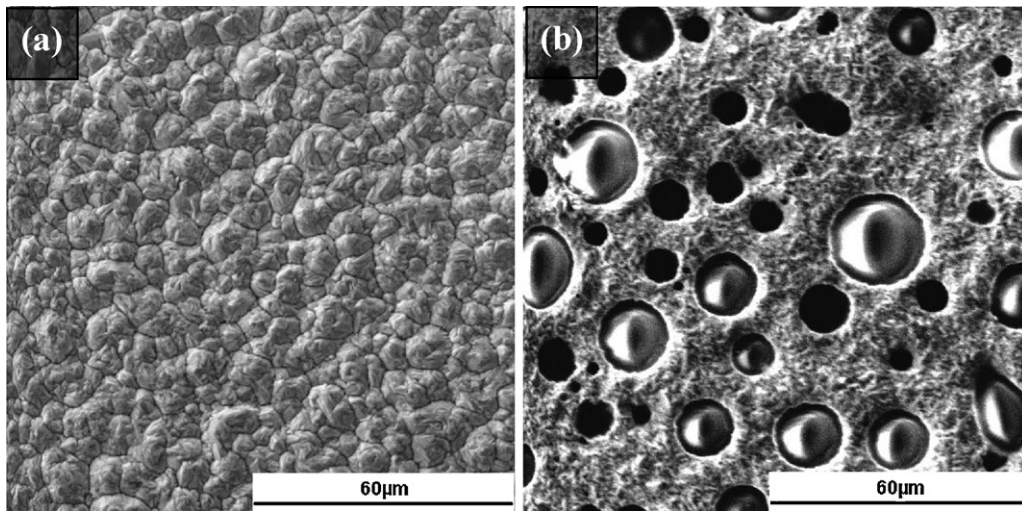


Fig. 1. SEM morphologies of (a) pure copper coating; and (b) Cu/liquid microcapsule composite coating.

coating was prepared from an acid sulfate bath containing 20 vol.% microcapsules emulsion. The preparation processes of liquid microcapsule and Cu/liquid microcapsule composite were described in detail in Ref. [21]. Ultimately, the composite containing microcapsule with the diameter of 2–20 μm was prepared.

2.2. Characterization

The surface morphologies and surface elemental composition of composite coating were analyzed by scanning electron microscope (SEM, HITACHI S-530, 20 kV) and energy dispersion spectrometry (EDS, Oxford Link Isis), respectively. The roughness of the pure copper and composite surfaces was measured by a TR110 roughometer.

The hydrophobic photos of composite coating were obtained by digital camera and the water contact angles θ were measured by an OCA-20 contact angle instrument. The corrosion behavior of samples was determined by electrochemical impedance spectroscopy (EIS) experiments using a CHI 604A three-electrode system. The electrolyte was 0.1 M H_2SO_4 solution prepared by using reagent grade chemicals dissolved in distilled water. The sample which had an apparent area of 1 cm^2 was used as working electrode, saturated calomel electrode (SCE) and platinum (Pt) were used as reference electrode and auxiliary electrode respectively. The EIS experiment was done at open circuit potential and the scan frequency of was from 10^{-3} Hz to 10^5 Hz .

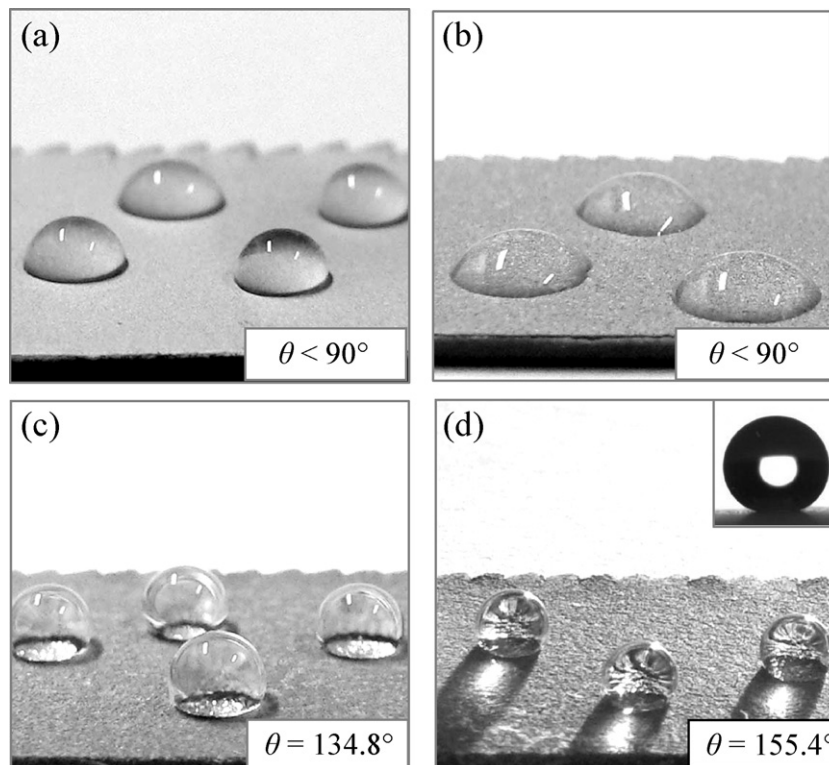


Fig. 2. Images of water droplet observed on the (a) pure copper surface; (b) newly prepared composite surface; (c) composite stored in air for 7 d; (d) composite stored in air for 15 d.

Table 1
Element quantitative analysis of the composites storing in air for different time.

Elements (wt.%)	C	O	Si	Cu
Newly prepared composite	11.91	0.46	0.60	87.02
Composite storing for 15 d	15.21	0.95	1.63	82.21
Composite storing for 30 d	16.40	2.75	9.59	71.27

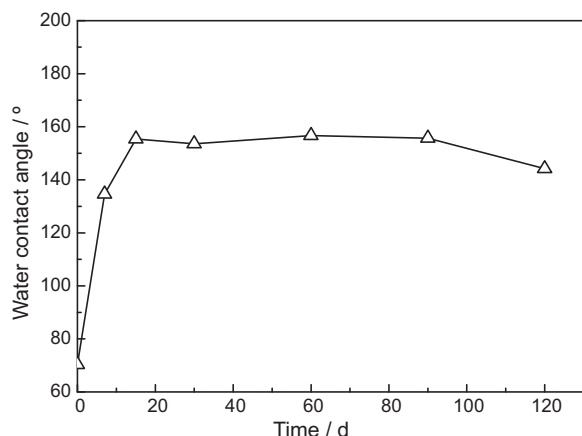


Fig. 3. The changes of contact angle with the storing time for composite surface in air.

3. Results and discussion

3.1. Surface characterization

Fig. 1 shows the SEM images of pure copper coating and Cu/liquid microcapsule composite. As observed in Fig. 1b, a great number of microcapsules are embedded in copper coating uniformly and most of them are of 2–20 μm in diameter. Storing in air for a period time, the content of composite surface elements has made some changes. Table 1 depicts the changes of the surface elements content with increasing time. It is obvious that the content of C, O and Si are enhanced gradually with the increasing storing time, which verifies the slow release of the core material (BH-102 hydrophobic agent) from microcapsules. And the released core material can form a protective film on composite surface, which has been proved by XPS result in Ref. [21].

3.2. Surface wettabilities

The results of time-dependent studies of the wettabilities of composite surfaces at room temperature are shown in Fig. 2. It is evidently found that the plating bare copper surface is very smooth and shows the water contact angle (CA) less than 90° (Fig. 2a). Fig. 2b–d display that the CAs of Cu/microcapsule composites sur-

Table 2
The roughness of the pure copper and different composites surfaces.

	Pure copper coating	Newly prepared composite	Composite storing for 15 d	Composite storing for 30 d
R_a	2.15	2.46	2.41	2.52

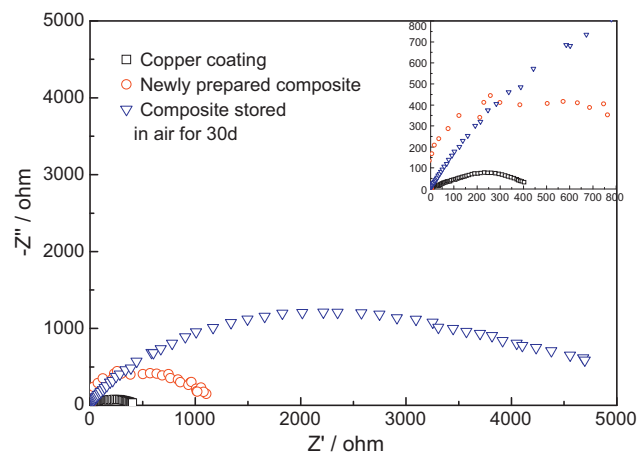


Fig. 5. Nyquist diagrams of copper coating and composite coatings in 0.1 mol/L H_2SO_4 solution. The inset is the amplified diagrams in the higher frequency range.

face increase with storing time and exhibit the super-hydrophobic property with the CA of 155.4° after 15 days. Meanwhile, the stability of the hydrophobic surface is evaluated, as seen in Fig. 3. There is no obvious fluctuation of the CAs on the composite surface after storage 15 days, showing the good stability of the hydrophobic film.

The formation of super-hydrophobic composite surface has two main reasons. On the one hand, hydrophobic agent is used as the core material of microcapsule, which is released slowly and forms a hydrophobic film on composite surface. On the other hand, the composite surface becomes coarse due to the participation of liquid microcapsules. Table 2 expresses the surface roughness of pure coating and composite. As shown, the roughness of the composite surface increases compared with that of pure copper coating. However, the surface roughness does not change obviously with the increasing time. Under these two synthetical factors, the super-hydrophobic surface is obtained.

3.3. Corrosion behavior of composite with variable hydrophobic surface

As we known from above, the liquid core material of microcapsules can be released slowly and further form a hydrophobic film on composite surface when it is stored for a period time. The oil film can greatly improve the oxygen resistance and tarnish resis-

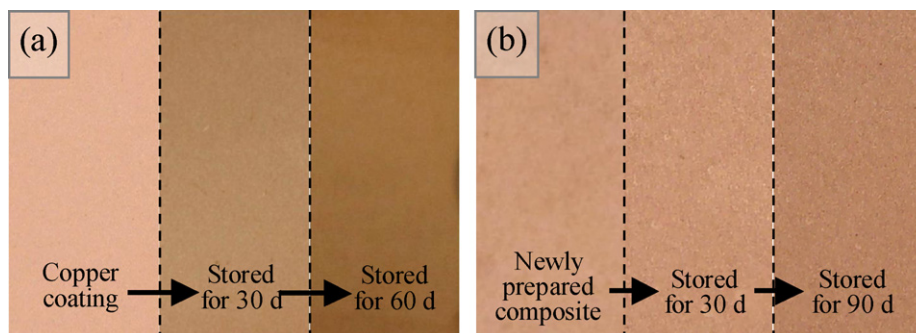


Fig. 4. Surface images of copper coating and composite stored in air for different days.

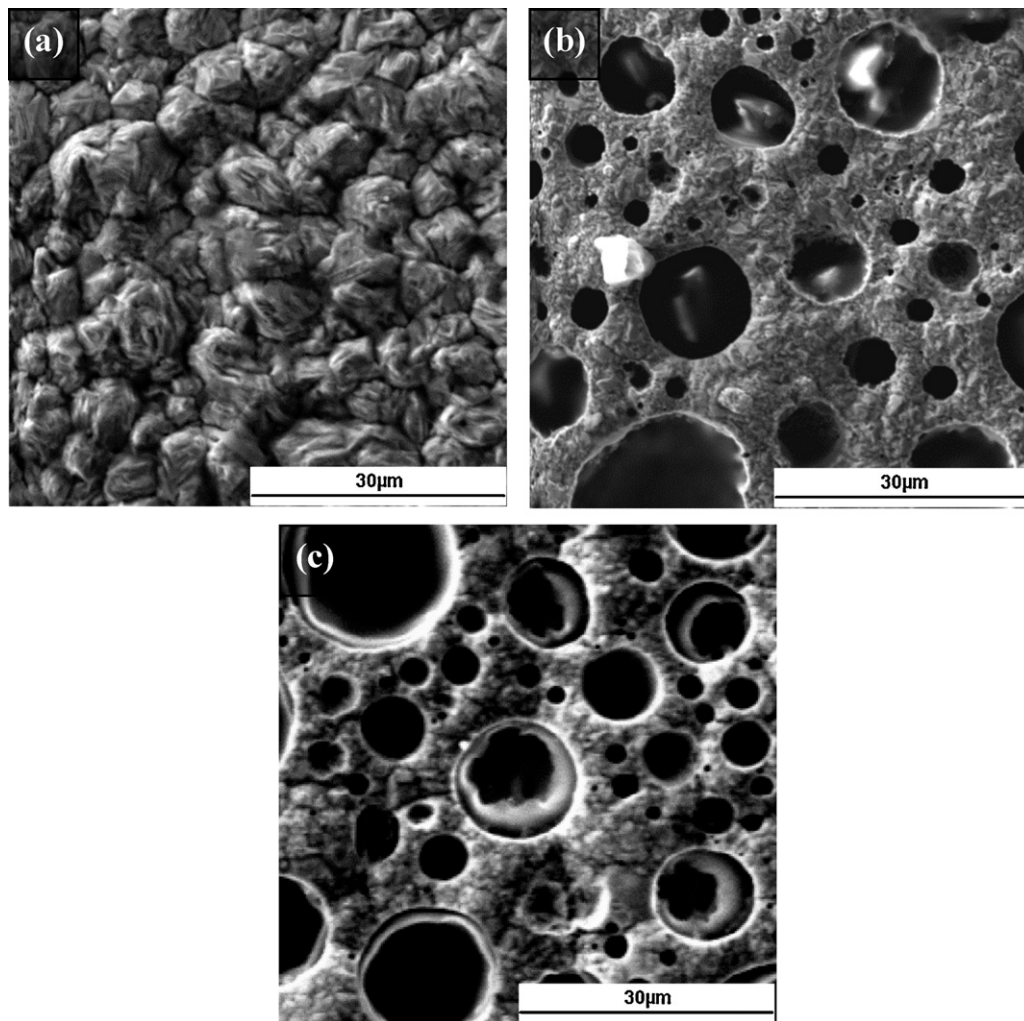


Fig. 6. Surface images of coatings after EIS experiment: (a) copper coating; (b) newly prepared composite; and (c) composite stored in air for 30 d at 25 °C.

tance capacity of copper. The pure copper coating has been oxidized obviously when it is placed in air for 30 d at 25 °C, as shown in Fig. 4a. After 60 d, the oxidation phenomenon of copper becomes more serious. However, little color change is observed on the composite surface within 90 d at the same condition (Fig. 4b). This phenomenon exhibits the protective effect of the oil film on the coating. This hydrophobic film as a barrier layer can effectively isolate the oxygen and water vapor from environment.

In order to further estimate the corrosion resistance ability of the hydrophobic composite coating, the electrochemical impedance spectroscopy (EIS) is measured. Fig. 5 depicts the Nyquist plots for the bare copper coating and composites in 0.1 mol/L H_2SO_4 solution. As seen, the impedance spectra of bare copper coating contains not perfect semicircles whose center lies below the real axis, this phenomenon is known as the dispersing effect [22]. For the Cu/liquid microcapsule composite, the impedance semicircles enlarge markedly compared with that of bare copper coating. On the one hand, the presence of microcapsules increases the charge transfer resistance in the course of electrochemical test. On the other hand, the hydrophobic film on the composite surface hinders the corrosion, which makes the corrosion resistance improvement of composites compared with that of copper coating. Especially, the corrosion speed of composite greatly decreases after storage in air for 30 d at 25 °C. We have reason to believe, the excellent corrosion resistance of composite will maintain for a long time due to the stable super-hydrophobic property.

Fig. 6 shows the surface images of coatings after EIS experiment. As seen in Fig. 6a, the pure copper coating is corroded evenly in 0.1 mol/L H_2SO_4 solution. Comparatively, because of the microcapsules in newly prepared composite release partially during the electrochemical test (Fig. 6b), the corrosion resistance of composite improves slightly. When composite coating is stored in air for 30 d at 25 °C, the formed hydrophobic film through the release of microcapsules can inhibit effectively the corrosion. It is also observed from Fig. 6c that most of microcapsules have released and the composite surface has no evidence of corrosion.

In a word, both the Nyquist plot and the SEM morphologies after EIS experiment indicate that super-hydrophobic surface can improve the oxygen resistance and corrosion resistance of copper significantly although the super-hydrophobic property is not always maintained.

4. Conclusion

The present work shows that Cu/liquid microcapsules composite coating is prepared using a simple and inexpensive electroplating method. And the super-hydrophobic film on copper surface was created through the slow release of core material from microcapsules and the coarse surface. This functional film keeps the long-term stability in air or acid medium and the superior corrosion resistance property and can be widely applied in corrosion protection of various engineering materials.

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