JOURNAL OF MATERIALS SCIENCE **39** (2004) 495 – 499

Electrodeposition of composite copper/ liquid-containing microcapsule coatings

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This paper presents results on the preparation of microcapsules containing liquid organosilica, and their co-deposition with copper in an acidic copper electrolyte onto a carbon steel cathode to form a copper/microcapsule composite coating. Microscopic analyses of the surface and the cross-section of the coating confirm the incorporation of the liquid-containing microcapsules in the coating layer. The influence of microcapsules in the electrolyte on the cathode polarization, as well as that of process conditions on the microcapsule inclusion, is also discussed. © *2004 Kluwer Academic Publishers*

1. Introduction

Composites produced by electrolytic co-deposition of inert particles and metals find broad applications in space and automobile industries due to their better wear, friction and corrosion properties [1–3]. Most of the work deals with the co-deposition of metal with solid particles such as SiC, Al_2O_3, BC and ZnO_2 [4–9]. However, several publications on the incorporation of liquid-containing microcapsules into metal matrices have also appeared recently in the literature [1, 2, 10–12].

Composite coatings containing liquid microcapsules exhibit some distinctive advantages over those incorporating only solid particles. For example, if a liquid corrosion-inhibitor is encapsulated and incorporated in the coating, the release of the liquid inhibitor when the surface is locally damaged could partially repair the damage and protect the surface from corrosion. Further, if a liquid lubricant encapsulated in the coating, the continuous release of lubricant from the microcapsules due to surface wear thus breaking the wall of the capsules could reduce the friction between the contacting surfaces, bringing about a self-lubrication function of the coating.

Microcapsule/metal composite coatings are usually obtained from a two step process. The liquid to be encapsulated is first emulsified and stabilized in another immiscible liquid that would eventually form the wall of the microcapsules. The emulsion/dispersion is then added to and suspended in the electrolytic bath, and co-deposited with the metal ions onto the cathode to form the composite coating. To successfully produce the composite coating with desired properties, it is important that the following conditions are met: (1) the liquid core is emulsified to a size smaller than the intended coating thickness with a narrow size distribution, (2) the emulsion is stabilized against aggregation and coalescence to prevent the capsule size change over time during storage and electrolysis, and (3) the microcapsules are well dispersed and suspended in the electrolytic bath for their uniform incorporation into the coating.

The preparation of microcapsules and their co-deposition in electrolysis with metal ions are complex processes. Selection of the wall materials, stabilizers and the emulsification process is almost entirely dictated by the type of liquid to be encapsulated. Interactions of the microcapsules with metal ions and electrolyte are also strongly influenced by the physical and chemical properties of the microcapsules. This paper presents our results on the preparation of the microcapsules with liquid organosilica as the core and polyvinyl alcohol (PVA) as the wall material. It also discusses the behaviour of the microcapsules during their co-deposition with copper in an acidic copper electrolyte and their incorporation in the composite coating layer.

2. Experimental

2.1. Materials

The liquid core of the microcapsules was organosilica resin (W61-55). The wall material for the microcapsules was PVA. The stabilizer used to stabilize the oil-in-water emulsion in the preparation of microcapsules was an alkyl polyoxyethylene polyether type

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surfactant with a general molecular formula of R-O-$(CH_2CH_2O)_nH$, $n = 1–5$.

For the electroplating, the cathode was a 50 × 30 × 1 mm normal carbon steel plate. The electrolyte was an aqueous solution of $CuSO_4{\cdot}5H_2O$ (200 g/l) and H_2SO_4 (60 g/l). To prevent dissolution of iron from the cathode during electroplating, the steel plate was pretreated or electro-coated in a nickel Watts type bath for 10 min.

2.2. Preparation of microcapsules

There are many methods for the preparation of microcapsules including interfacial polymerization, *in-situ* polymerization, surface polymerization, solvent evaporation, phase separation in an aqueous solution and phase separation in an organic solvent [8, 13–18]. In this study, after many trials on several different methods, the phase separation in an aqueous solution method was chosen for the preparation of PVA-walled liquid organosilica microcapsules.

The preparation procedure used in this study was as follows. 100 ml of 0.5% (w/v) aqueous PVA solution was added to a 500 ml glass beaker and stirred at 900 rpm 10 ml of liquid organosilica was then slowly added dropwise to the PVA solution using a syringe. This process usually took around 30 min to complete. Immediately after completion of the liquid organosilica addition, 0.2 ml of stabilizer was added to the system and the mixture was stirred for a further 30 min. Due to its interfacial activity, PVA tends to accumulate and form a separate phase at the oil-water interface, producing PVA-walled organosilica microcapsules.

2.3. Co-deposition of copper and microcapsules

Electroplating of the sample carbon steel plate was carried out at room temperature in a bath of 500 ml in size. The electrolyte was an acidic aqueous copper solution of $CuSO_4{\cdot}5H_2O$ (200 g/l) and H_2SO_4 (60 g/l) into which a predetermined amount of microcapsule dispersion was added. The plating was performed at various cathode current densities and the bath being continuously stirred at different stirrer speeds.

2.4. Determination of cathodic polarization curve

For the determination of cathodic polarization curves at different microcapsule concentrations, a ZF-3 potentiostat, a ZF-4 scanning potential signal generator and a LM15-251 function recorder were used. The scanning speed was 5 mV/s. The auxiliary electrode was a Pt type, the reference a saturated calomel electrode, and the cathode a 10 mm × 10 mm nickel-plated carbon steel plate.

2.5. Analysis of composite coating

An S-530 scanning electron microscope (SEM) and a Link IsIs energy dispersion X-ray spectrometer (EDS) were used to determine the surface topology, topology of the cross-section and the elemental composition of the composite coating.

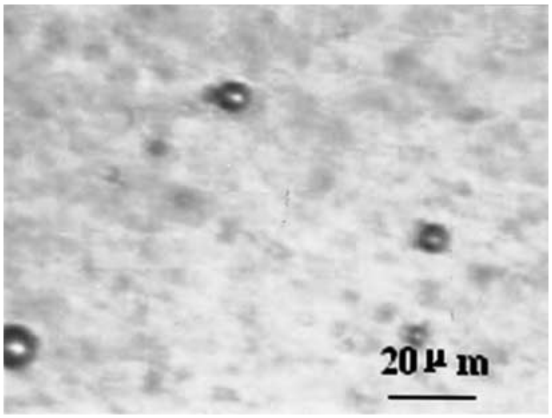


Figure 1 Microcapsules in dispersion.

3. Results and discussion

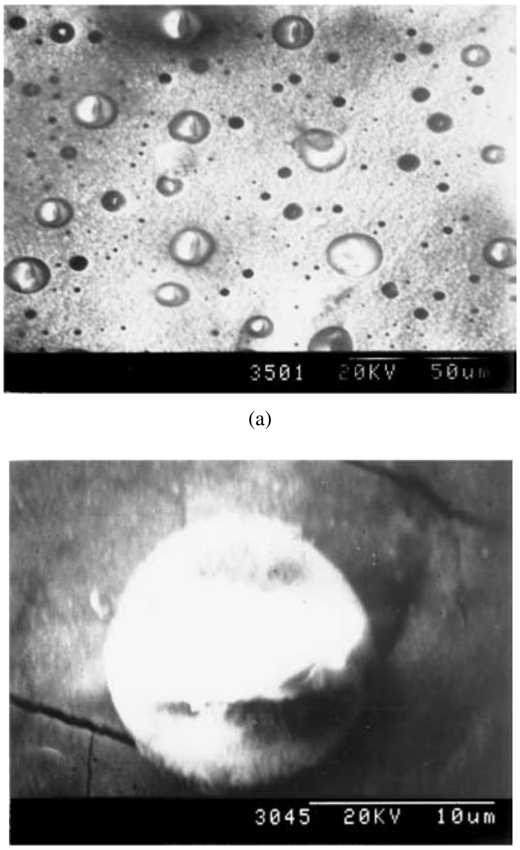
3.1. Microcapsules in dispersion

The appearance of the microcapsules in the emulsion/dispersion produced from the above described procedure is shown in Fig. 1. The picture was taken at the periphery of a sample dispersion spread on a microslide under an optical microscope. The reason for taking it at the periphery was that there were fewer number of microcapsules in the region, which made it easier to see the microcapsules. From the picture, it can be seen that the microcapsules are all spherical in shape in the dispersion. Observation of all the sample dispersion showed that most microcapsules were in the size range of 2–8 μm. Small mean particle sizes and narrow particle size distributions are necessary for the incorporation of the microcapsules in the composite coating during electroplating. Other methods to produce submicron microcapsules with very narrow particle size distributions are currently under investigation.

3.2. Microcapsules in coating

Fig. 2 shows the surface of the composite coating obtained from the co-deposition of copper and microcapsules by electroplating. In Fig. 2a, the microcapsules are seen to have been incorporated in the coating layer. Some of the microcapsules are only half-immersed in the coating with the remaining half protruding out of the surface; others completely submerged in the coating layer, leaving “holes” (depressions) on the surface. Fig. 2b is a picture of a single microcapsule on the surface of the coating, which shows that the spherical microcapsule has a yoke-like structure with the core material being different from that of the wall. Elemental composition analysis of these spheres and depressions using EDS suggests that they are all composed of Si, O and C (Fig. 3), which are the main elements of the liquid organosilica. When the spheres on the surface of the coating were cut open using a sharp knife under a microscope, surface wetting at the immediate vicinity of the sphere was observed. In addition, when the samples were subjected to wear tests, surface wetting was also apparent. All these indicate that the microcapsules were incorporated in the coating with a liquid core in them.

Results on an elemental composition analysis of the whole coating surface are presented in Fig. 4. The figure



(b)

Figure 2 SEM photomicrographs of (a) surface of composite coating incorporating microcapsules; (b) single microcapsule in coating layer.

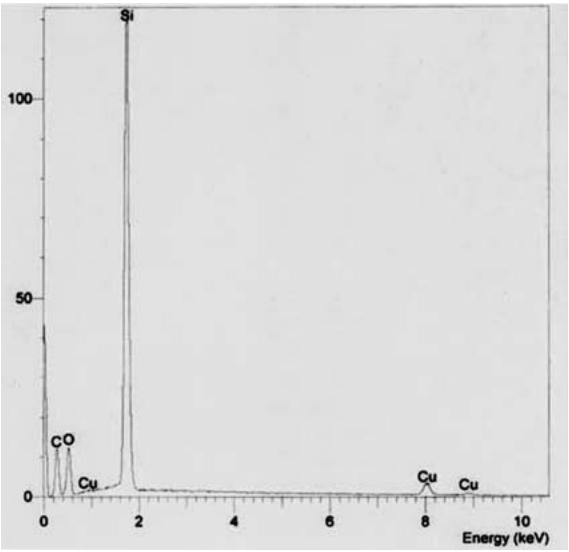


Figure 3 EDS spectra of a microcapsule in composite coating.

suggests that the surface consists predominantly of Cu with inclusions of Si, C and O. Based on the results presented in Figs 2–4, it may be concluded that the liquid organosilica containing microcapsules that we prepared in this study can be co-deposited with copper from a copper electrolyte to form a microcapsule/copper composite coating. The microcapsules are also seen to be evenly distributed in the surface of coating layer.

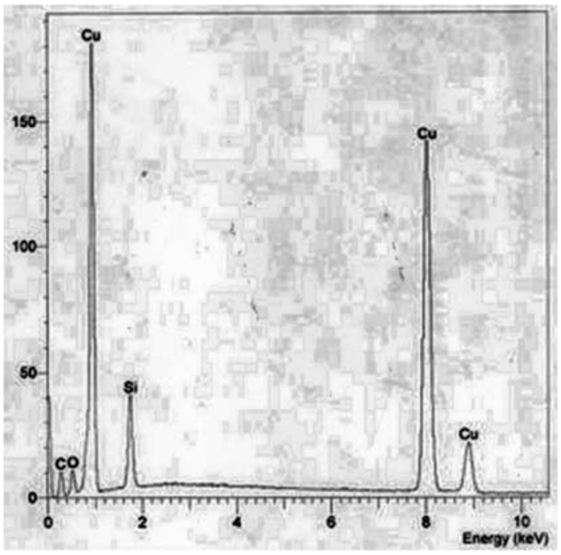
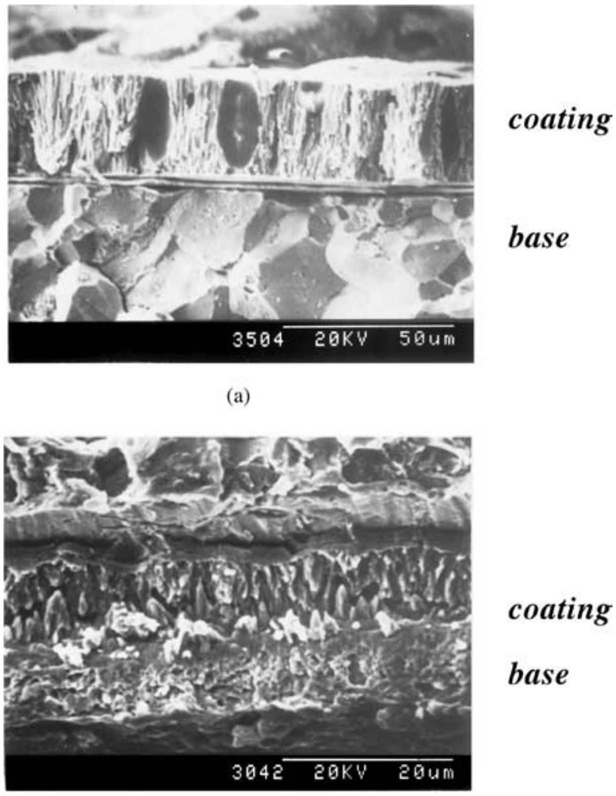


Figure 4 EDS spectra of composite coating surface.

To assess the effect of microcapsules' incorporation in the coating on the grain structure of the coating, electroplating onto steel saw blades was carried out with and without microcapsules in the electrolyte. The plated saw blades were then bent broken and the cross-section of the blades examined under microscope.

The grain structures of the coatings obtained from electroplating with and without microcapsules added to the bath solution are similar, as shown in Fig. 5a and b, respectively. The microcapsules can be seen to have physically included and almost completely submerged in the coating layer. However, due to the growth of



(b)

Figure 5 SEM photomicrographs of cross-sections of (a) normal copper coating and (b) copper/microcapsule composite coating on a carbon steel blade.

the copper grains during electroplating, the shape of the microcapsules has distorted somewhat from being spherical in the dispersion to ellipsoidal in the coating. Compositional analysis of these ovals by EDS showed that they were composed of Si, O and C, confirming again that the microcapsules incorporated in the coating layer contained a liquid organosilica core.

After the plated saw blades were bent broken, the cross-section of the normal coating showed some irregular micro-cracks (not shown in the photo). In contrast, no such cracks were observed in the microcapsule-containing coating. This implies that the coating with microcapsules possesses better mechanical toughness.

3.3. Influence of microcapsules on cathodic polarization

The influence of microcapsule concentration in the acidic copper electrolyte on the cathodic polarization has also been investigated. The results are presented in Fig. 6. It can be seen that, addition of microcapsules to the electrolyte, even at a low 4 vol% concentration, caused the cathode to polarize, making the cathodic potential more negative. Although the negative shift of the cathodic potential seemed to be insignificant and with no definite trend in the microcapsule concentration range from 4–12%, the overall trend seemed to be that, the higher the microcapsule concentration in the electrolyte, the more the negative shift of the cathodic potential. This is beneficial for the electrodeposition of copper as higher cathodic polarization generally causes higher nucleation rate thus producing finer grains in the coating. Microscopic examination of the grain structures of the coating also confirmed that the higher the microcapsule concentration in the electrolyte, the finer the copper grains in the coating, consistent with the observations mentioned in Section 3.2.

In general, addition of certain volume of microcapsules into the electrolyte lowers the concentration of the metal cation in the electrolyte, favoring cathodic polarization. In addition, microcapsules in the copper electrolyte might also be preferentially adsorbed onto the nickel/electrolyte interface (the carbon steel cathode was nickel plated), further promoting the cathodic polarization of the composite electrolyte.

TABLE I Effect of microcapsule concentration in electrolyte on number of microcapsules incorporated in composite coating (cathode current density: 30 mA/cm^2; stirring speed: 100 rpm)

Microcapsule concentration in electrolyte (Vol %)	6	10	14	18	22
Number of microcapsule in coating (1/mm^2)	20–30	50–60	70–80	80–90	60–70

TABLE II Effect of cathode current density on number of microcapsules incorporated in composite coating (microcapsule concentration in electrolyte: 15 vol%; stirring speed: 100 rpm)

Cathode current density (mA/cm^2)	10	20	30	40	60
Number of microcapsule in coating (1/mm^2)	20–30	50–60	70–80	40–50	2–5

3.4. Influence of process conditions on microcapsule inclusion

Table I presents the result on the relationship between the microcapsule concentration in the electrolyte and that in the coating. It can be seen that, all other condition being kept the same, the number of microcapsules incorporated in the coating increased with increasing microcapsule concentration in the electrolyte. However, when the microcapsule concentration in the electrolyte reached 20% by volume, the number of microcapsules in the coating decreased. At the present, no substantial explanation can be offered for this sudden change of trend.

The variation in the number of microcapsules included in the coating with the cathode current density is shown in Table II. In the density range of 10

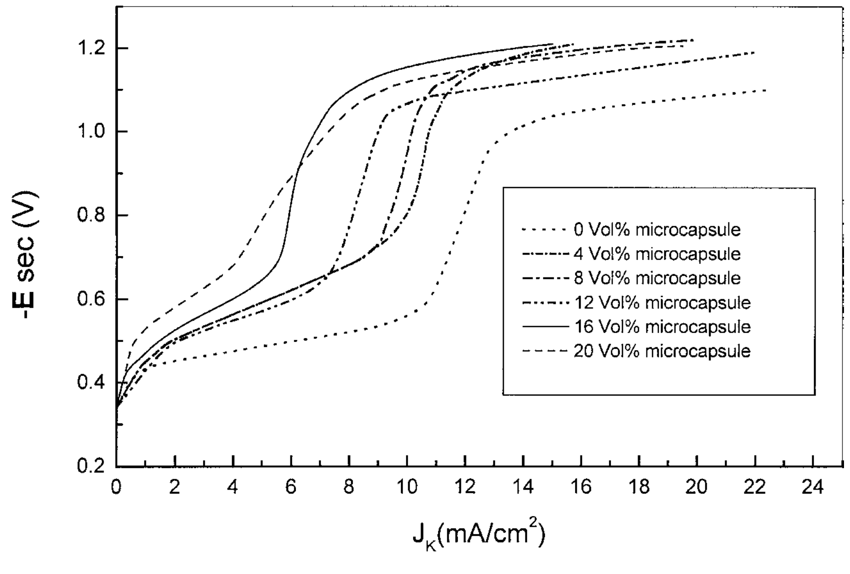


Figure 6 Cathodic polarization behaviour as a function of microcapsule concentration in electrolyte.

TABLE III Effect of stirring speed on number of microcapsules incorporated in composite coating (microcapsule concentration in electrolyte: 15 vol%; cathode current density: 30 mA/cm^2)

Stirring intensity (rpm)	None	Medium (100)	High (300)
Number of microcapsule in coating (1/mm^2)	80–90	50–60	30–40

to 30 mA/cm^2, the number of microcapsules in the coating increased with increasing current density. However, when the current density was further increased to the range of 40–60 mA/cm^2, the number microcapsules in the coating decreased significantly. This is probably because at high current densities, noticeable amount of hydrogen evolved from the cathode, which could have significantly affected the co-deposition of the microcapsules.

When carrying out composite electroplating of metal ions with solid particles, mixing of various forms are required to keep the particles in the composite electrolyte suspended, enhancing their collision with and adsorption onto the cathode, and co-deposition with the cation(s) thus obtaining the desirable composite coating. In our case, however, the microcapsules with liquid organosilica cores can easily be suspended in the electrolyte without stirring, due to their comparable density with the electrolyte. As such, one would expect to obtain good composite coating without stirring at all. The effect of stirring of the composite electrolyte in the plating bath on the inclusion of the microcapsules in the coating is presented in Table III. It can be seen that the number of microcapsules incorporated in the coating decreases significantly with increasing stirring speed. Increasing stirring intensities have adverse effect on the inclusion of the microcapsules in the coating possibly because the shear force generated by the stirring not only could sweep off some microcapsules already adsorbed on the cathode, thus directly lowering the number of microcapsules incorporated in the coating, but also could break some microcapsules in the electrolyte hence lowering its concentration in the electrolyte.

The study has also found that, in the room temperature range in which electroplating is normally conducted, the temperature has negligible effect on the number of microcapsules incorporated in the coating layer.

Series of tests on the composite coating have been carried out. Results of the tests, which will be published in a following up paper, show that the incorporation of liquid-containing microcapsules in the coating layer improves the corrosion and wear properties of the coating. Trials on the composite electroplating of iron-phosphate and microcapsules also prove that the technique developed in this study can easily be applied to the composite coating of other metals with only minor modifications. There is no doubt that composite electroplating incorporating liquid-containing microcapsules will find broad application in various industries.

4. Conclusion

From the experimental results obtained in this study, the following conclusions can be made:

1. Microcapsules with a liquid core of organosilica and PVA as wall material have been successfully made and stabilized by the method developed in this study. In dispersion, the microcapsules are spherical in shape with their diameter ranging from 2 to 8 μm.
2. Co-deposition of the microcapsules with copper onto a carbon steel plate has been achieved through electroplating in an acidic copper electrolyte to form a copper/microcapsule composite coating.
3. SEM and EDS and optical microscopic analyses of the composite coating show that the microcapsules are physically included in the coating, though shape distorted somewhat to an oval, maintaining their original chemical compositions and the liquid core physical state.
4. The amount of inclusion of the microcapsules into the coating layer can easily be tailored to suit application purposes through changing process conditions of plating.

Acknowledgement

The work is supported by the National Natural Science Foundation of China, Grant No. 50171002.

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Received 26 February
and accepted 16 September 2003