JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 147–153

Effect of codeposition of polymer on the morphology of electrodeposited copper

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Received 9 December 1977

Poly(4-vinyl pyridine-co-methyl methacrylate), which is soluble in water in its protonated form and insoluble as a neutral molecule, has been synthesized and introduced into an acid bath for copper deposition. Potential-sweep investigations have shown that the copolymer affects the electrocrystallization of copper on graphite by delaying nucleation even before conditions for codeposition of the polymer are reached. At overpotentials at which the diffusion limiting current of copper is reached and hydrogen evolution starts, alkalinity at the electrode surface causes precipitation of the polymer. This is found to affect the resistivity of the deposit. Electron microscopy revealed that under such conditions copper is deposited in the form of globular particles, the size of the globules being in the micron range and decreasing with increasing overpotential.

1. Introduction

The intimate mixing of metals and polymers is known to render composite materials with some special qualities arising from the inherent properties of the mixed components, such as, for example, good electrical conductivity together with plasticity enabling industrial moulding at relatively low temperatures.

The present work represents part of an attempt to learn what new qualities can be obtained in these composite materials if they are made by simultaneous deposition of both components by electrochemical processes. For a particular case one could expect to obtain protective and decorative coatings which would inherit the good properties of the parent materials. Hence, a series of new galvanic plating processes could be revealed.

The number of problems which are encountered in such an attempt have been summarized in a recent review [1]. In particular, the polymer must be of such a nature as to be soluble in the electrolyte in which the ions of the depositing metal are dissolved, and yet to deposit under conditions existing at the electrode surface during electrolysis. This can be achieved in a number of ways. In the present work a polymeric substance has been selected with a basic character which makes it soluble in a slightly acid electrolyte. The electrolysis conditions have been selected to promote powder formation and at the same time to achieve a simultaneous evolution of hydrogen with equivalent formation of OH^- ion at the electrode surface. The latter neutralize the acid and thus create conditions under which the polymer becomes insoluble and precipitates out of solution.

The proportions of the metal and polymer in the deposit can be varied in at least two ways: (a) by varying the concentrations of the depositing species and (b) by passing current densities in a varying degree of excess over the diffusion limiting current density of metal deposition. In this instance the low polymer content deposits have been investigated by using solutions of a relatively small concentration of the polymer. Using different overpotentials of deposition it was possible to overcome the diffusion limiting current for metal deposition to different extents, and hence obtain deposits of different character.

2. Experimental

2.1. *Synthesis and properties of the polymer*

2.1.1. Reactants. 4-Vinyl pyridine (Fluka AG, Buchs, Switzerland) was distilled at 12 Torr, boiling point 60° C, before use.

Methyl methacrylate (Fluka AG, Buchs, Switzerland) was washed twice with equal volumes of a 1 N NaOH solution and three times with equal volumes of distilled water, dried over sodium sulphate and distilled at 100 Torr, boiling point 47° C, before use.

Asobisisobutyronitrile (AIBN) (Fluka AG, Buchs, Switzerland) was recrystallized from ethanol and dried *in vacuo* before use.

2.1.2. Solvent. Glacial acetic acid (Merck AG, Darmstadt, Germany) was used without further purification.

2.1.3. Preparation of poly(4-vinyl pyridine-co-methyl methacrylate). Poly(vinyl alcohol) (1 g) dissolved in distilled water (400 ml), 4-vinyl pyridine (40 g), methyl methacrylate (60 g) and asobisisobutyronitrile (2 g) were added to a 100-ml four-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, a nitrogen inlet and a thermometer. The temperature of the suspension formed under stirring was raised to 70° C and maintained for 4 hours. The solid copolymer was filtered, washed with water and dried at 60° C *in vacuo*. The crude copolymer (94 g) was reprecipitated by dissolving it in glacial acetic acid (225 g), diluting to 3 N CH_3COOH with water (3500 ml) and pouring into a 3 N KOH solution (4000 ml). The copolymer was filtered again, washed with water and dried. The copolymer yield was 90 g.

2.1.4. Characterization of poly(4-vinyl pyridine-co-methyl methacrylate). The analysis of this copolymer was N = 5·24% corresponding to a 1 : 1·54 ratio of 4-vinyl pyridine and methyl methacrylate units. The initial molar ratio of the two monomers was 1 : 1·57. Essentially the same 4-vinyl pyridine content in the mixture of monomers and in the copolymer was to be expected from known reactivity ratios [2] and high conversion.

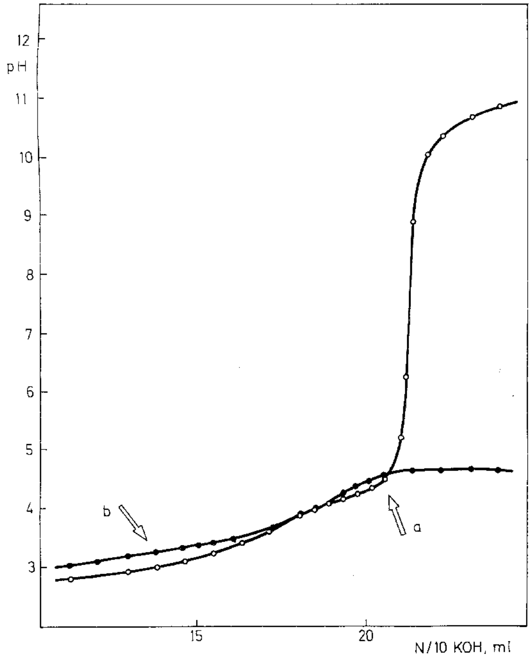

Fig. 1. Potentiometric titration curves for 1% KVPMM 40 in 0·1 N H_2SO_4 in the absence (a) and in the presence (b) of 0·1 M $CuSO_4$. Arrows indicate precipitation points.

The limiting viscosity number of the copolymer in tetrahydrofurane (THF) at 25° C was 0·92 dl g^{-1}.

The copolymer solubility as a function of the pH value was studied by potentiometric titration of an approximately 1% solution in 0·1 N H_2SO_4 by a 0·1 N KOH solution. The precipitation of the copolymer occurs at pH 4·4. In the presence of cupric ions (0·1 M $CuSO_4$) this value is shifted to 3·3. (Fig. 1).

From this behaviour electrodeposition of the copolymer from an acidic solution on the cathode during hydrogen evolution can be postulated [3].

2.2. *Method of investigation*

The effect of the presence of the dissolved polymer on the deposition of copper from 0·6 M copper sulphate solution in 0·005 M sulphuric acid on a graphite cathode was investigated. The concentration of the polymer in solution was 0·1 wt%. The cathode was placed in the cell horizontally, facing downwards, so that a relatively thick diffusion layer could develop without much convective disturbance. However, hydrogen bubbles developed in some instances after prolonged electrolysis at high cathodic overpotentials.

Potential sweep voltammograms and potentiostatic current–time response curves were recorded using standard apparatus (Elscint function generator model CHF-1, Wenking potentiostat model 61 RH and HP 7000 AM X–Y recorder). Potentials were measured versus a reference electrode made from a copper wire coated with freshly deposited copper placed in the same solution. The temperature was 22 ± 1° C.

Cathodic deposition was carried out in all cases at different constant overpotentials so as to obtain a deposit about 10 μm thick. Such deposits were observed with a scanning electron microscope GFM 35 in order to record their structure under appropriate magnifications (up to x 25 000).

3. Results

3.1. *Potential-sweep voltammograms*

Potential-sweep recordings were made using the graphite cathode in the copper sulphate–sulphuric acid electrolyte with and without the addition of the polymer. The potential was swept between a positive potential sufficient for all the copper deposit to be dissolved (around + 1 V versus the reversible potential of copper) and relatively small cathodic overpotentials (– 50 to – 100 mV), far below hydrogen evolution. A typical voltammogram, shown in Fig. 2, indicates that the presence of the polymer has a definite effect on the electrocrystallization process, although at these potentials it is not supposed to deposit by the neutralization mechanism. Hence, adsorption effects are indicated. It is seen that in the presence of the polymer the current during the cathodic sweep diverges from that in its absence around an overpotential of 50 mV. Since this seems to be a threshold of crystallization, it is obvious that once the latter starts, further deposition is slowed down when the polymer is present.

However, the anodic sweep shows that the presence of the polymer promotes the formation of a deposit of higher activity since a significant portion of it dissolves before the potential crosses to positive values with respect to the copper reference electrode in the same solution, and also before the deposit obtained in the absence of the polymer starts dissolving (the latter also has some portion of higher activity).

3.2. *Potentiostatic recordings*

Current–time responses during the application of potential steps of relatively long duration are examplified by those in Fig. 3. Steady-state currents characteristic of activation control of the deposition process are reached at low overpotentials (– 100 mV) soon after the application of the potential step (within 10 s). At high overpotentials (– 700 mV) however, a steady decline typical of diffusion control is observed with no tendency towards a steady state. Moreover, after some time the current response at higher overpotentials (e.g.

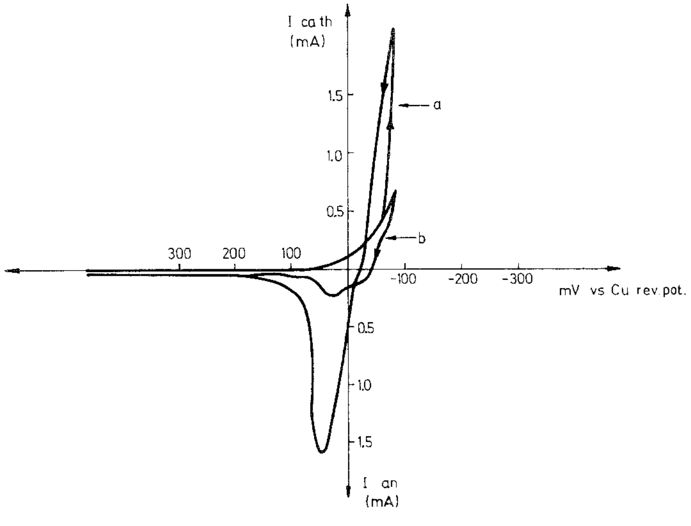

Fig. 2. Cyclic voltammograms for the deposition and dissolution of copper on graphite (a) in the absence and (b) in the presence of KVPMM 40 in solution (sweep rate 10 mV s^{-1}).

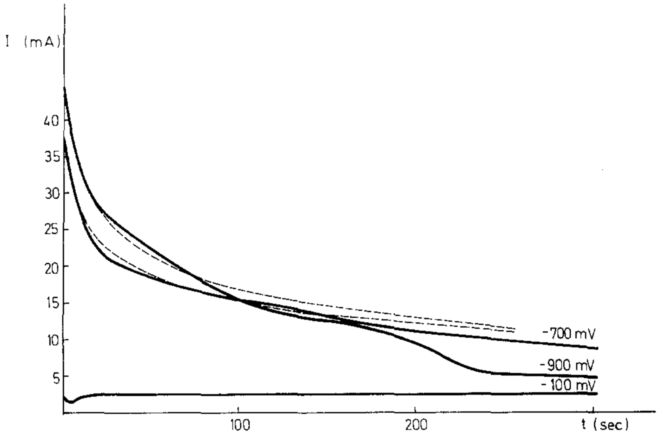

Fig. 3. Chronoamperograms for the deposition of copper onto graphite in the presence of KVPMM 40 in solution at different constant overpotentials.

— 900 mV) exhibits a faster decrease than that at lower overpotentials (e.g. — 700 mV), crossing the latter at some point and leading to slower deposition further on.

3.3. *Electronmicrography*

Figs. 4 and 5 show typical electronmicroscopic views of the copper deposits on graphite obtained from pure copper salt solution under different conditions of deposition. The first deposit is obtained under conditions of dominant activation control. The grain structure is clearly visible and coalescence is almost complete to the extent that, without magnification, the deposit appears fairly smooth. However, at overpotentials at which inhibited transport of depositing ions by diffusion controls the rate of deposition, a dendritic deposit is obtained.

A completely different picture is obtained in the presence of the polymer in solution. At low overpotentials a granular deposit is obtained as seen in Fig. 6, in which the grains have a similar shape to those in the deposit without the polymer, but with much less coalescence. Also, since in Figs. 4 and 6 the grains appear to be on average of a similar size, considering the difference in magnification, one can conclude that the presence of the polymer leads to the production of grains which are about five times smaller than those obtained from pure solution.

At increasing overpotentials, in the diffusion controlled region, the grains tend to spheroidize, as seen in Figs. 7–9. Considering again the different magnification of the three electronmicrographs it is seen that the increase of overpotential leads to a reduction in grain size (about 5 times between — 700 and — 1100 mV).

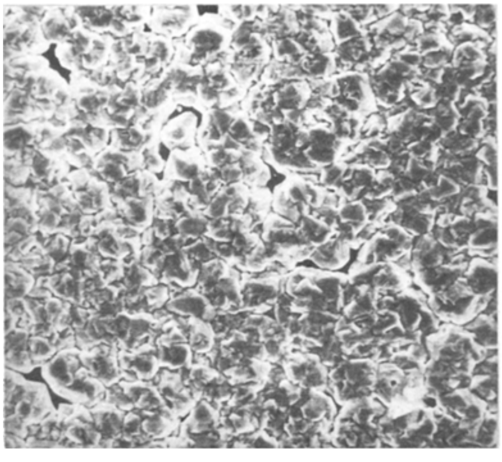

Fig. 4. Overpotential — 100 mV, without polymer (X 640).

Fig. 5. Overpotential — 900 mV, without polymer (X 1040).

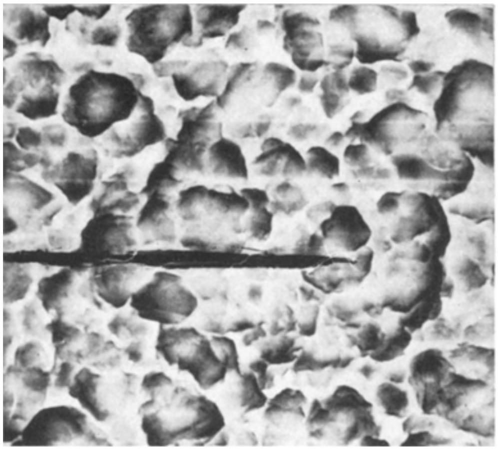

Fig. 6. Overpotential — 100 mV, with polymer (X 3200).

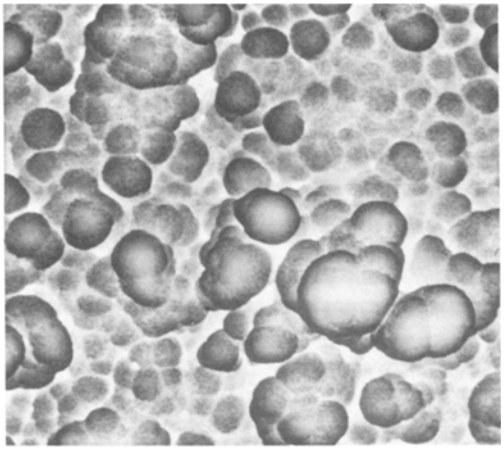

Fig. 8. Overpotential — 900 mV, with polymer (X 2400).

The shape of the grains remains the same, i.e. almost perfect globulae as seen in Fig. 10.

However, if the overpotential is increased further, polyhedral grains are again obtained, Fig. 11.

4. Discussion

Addition of a relatively small amount (0·1%) of the polymer to the solution inhibits nucleation of electrodeposited copper. This is reflected in the fact that attaining a certain cathodic overpotential (e.g. about -60 mV at 10 mV s^{-1}) in pure acidic copper sulphate solution triggers a fast rise of the rate of deposition (Fig. 2) as a consequence of the formation of the necessary crystallization centres (nuclei). In the presence of the polymer this process occurs with a delay after the electrode has reached higher overpotentials (in this case some 3 s later after the -80 mV limit has been reached and the potential had started changing in the anodic direction). Several monolayers can be deposited and redissolved without signs of crystallization being detected in the above sense. This indicates that, although in cationic form, the polymer is strongly adsorbed at the graphite surface which is still positive with respect to the pzc. Hence, strong specific adsorption forces are likely to be active. It is questionable in what state the deposited metal exists on the surface. Amorphous agglomeration of copper adatoms mixed with adsorbed polymer molecules is likely, particularly in view of the fact that the majority of the material dissolves anodically at potentials negative

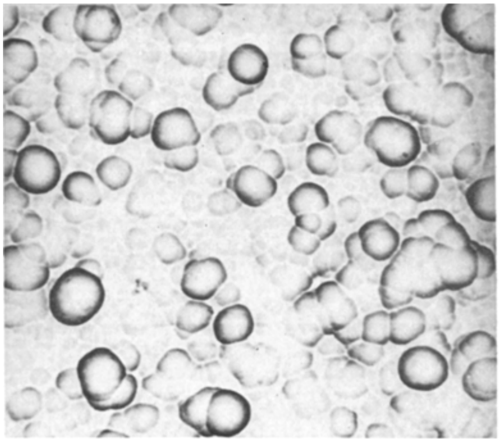

Fig. 7. Overpotential — 700 mV, with polymer (X 640).

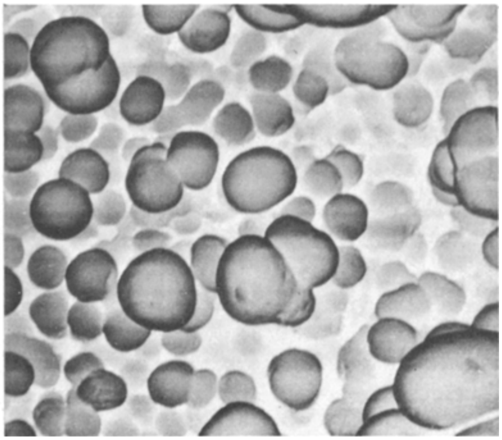

Fig. 9. Overpotential — 1100 mV, with polymer (X 3200).

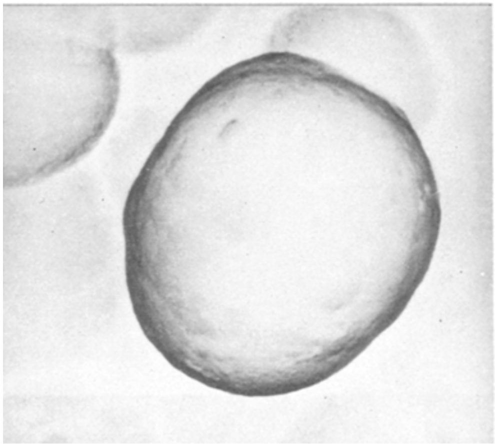

Fig. 10. Typical grain at overpotential of – 700 mV, with polymer (× 4000).

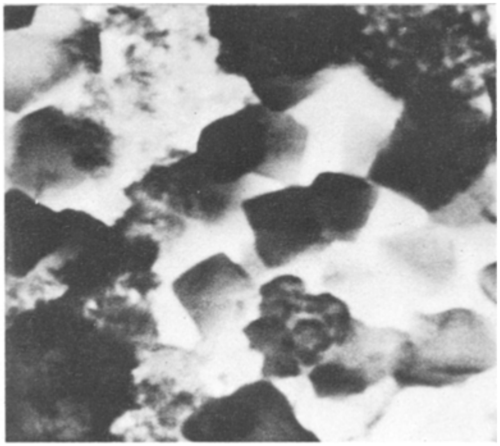

Fig. 11. Overpotential – 1300 mV, with polymer (× 6400).

with respect to the reversible potential of copper.

Adsorption is further stimulated by increasing negative overpotential. It affects the morphology of the deposit already at relatively low overpotentials as seen by comparing Figs. 4 and 6.

However, dramatic effects are obtained at higher overpotential values, at which concentration polarization with respect to cupric ions favours outward growth of the metal [4] and co-evolution of hydrogen causes an increase of pH at the electrode surface and thus creates conditions for deprotonation and precipitation of insoluble polymer. Instead of the dendritic growth normally obtained under such conditions [4] (Fig. 5), globular metal particles are formed as seen in Figs. 7–9. The decrease in particle size with increasing overpotential suggests an increased nucleation rate of new grains. In this case, one and the same rate of arrival of depositing material by linear diffusion from the bulk of solution, must supply a larger number of growing grains. Hence, each grain grows to a correspondingly smaller size before new nuclei start consuming the material.

A blown-up picture of a single globula (Fig. 10) reveals no crystal structure effect on the morphology..The spherical shape could be due to two factors: (a) this could be an indication of a prevalence of surface tension over crystal lattice forces, indicating a high degree of disorder, or else (b) strong adsorption makes rates of growth of all possible crystal planes equal and hence a sphere results. Since preliminary X-ray investigations of the deposit reveal the existence of crystal structure over relatively large regions of the spheres, the second effect appears more likely.

Linear diffusion control over the rate of deposition can be established by analysing the potentiostatic chronoamperograms shown in Fig. 3. The theory of mixed activation and diffusion control gives for the time dependence of the current density [5]

$$i = i_\mathrm{d}\lambda \exp(\lambda^2) \operatorname{erfc}(\lambda) \qquad (1)$$

with

$$i_\mathrm{d} = nFAD^{1/2}C^0/t^{1/2} \qquad (2)$$

and

$$\lambda = k_{\mathrm{f,h}}t^{1/2}/D^{1/2} \qquad (3)$$

where D is the diffusion coefficient of cupric ions and $k_{\mathrm{f,h}}$ is the electrochemical (potential-dependent) rate constant of their reduction. All other constants being known and with $D = 0{\cdot}38 \times 10^{-5}$ cm^2 s^{-1} and $C^0 = 6{\cdot}3 \times 10^{-4}$ mol cm^{-3}, $k_{\mathrm{f,h}}$ can be found at each overpotential from a single point in the corresponding chronoamperogram. The λ value for that point can be found graphically from a graph of i/i_d versus λ, since i is measured and i_d can be calculated. $k_{\mathrm{f,h}}$ is then calculated using Equation 3. Once this is known Equations 3 and 1 can be used to calculate i as a function of time and compare it with the experimentally obtained chronoamperograms as is done in Fig. 3. Two conclusions can be drawn:

(a) the $k_{\mathrm{f,h}}$ values for overpotentials of – 700 mV and – 900 mV (being $1{\cdot}94 \times 10^{-4}$ and $2{\cdot}67 \times 10^{-4}$, respectively) do not increase exponentially with overpotential as should be the case if the charge transfer was simply activation controlled. It is clear that adsorption of the polymer increases with overpotential and hence increasingly inhibits the charge-transfer step,

(b) the experimental chronoamperogram at − 700 mV practically coincides with the theoretically calculated one up to rather large deposition times. At − 900 mV, however, the experimentally measured current diverges from the theoretical one after a relatively short period of deposition, decreasing much faster than the theory predicts. This can be explained in terms of the increasing resistance of the deposit which may be due to the coprecipitation of the non-conducting polymer and its incorporation into the deposit.

Finally, one can observe (Fig. 11), that deposition at overpotentials larger than − 1100 mV restores crystalline properties to the deposited copper particles.

This is an indication that the polymer itself is consumed at the electrode surface by incorporation into the metal particles. Hence, as the rate of charge transfer exceeds a certain value at relatively low concentrations of the polymer as used in these experiments, the supply of codepositing polymer becomes insufficient for causing spheroidization.

5. Conclusions

On the basis of the above experimental results one can draw the following conclusions:

(a) Addition of poly(4-vinyl pyridine-co-methyl methacrylate) to an acid bath for the electrodeposition of copper has a pronounced effect on the nucleation of copper grains on a foreign substrate. At the same and relatively low overpotentials, at which there can be no coprecipitation of the polymer, it delays nucleation but leads to a formation of a larger number of nuclei.

(b) At higher overpotentials at which dendritic growth appears in a pure acid bath, the polymer provokes the growth of a deposit consisting of spherical copper particles.

(c) Prolonged deposition at high overpotentials leads to an increase of the resistance of the deposit which indicates codeposition of the polymer with the metal.

Acknowledgements

The authors are indebted to the NSF (USA) and the Research Fund of Serbia whose material support made this work possible.

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