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The Role of Micelles of Multiblock Copolymers of Ethylene Oxide and Propylene Oxide in Ion Transport during Acid Bright Copper Electrodeposition

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Summary: The role of micelle formation in the levelling activity of electrolytes for copper electrodeposition was investigated. It was established that micelle formation in the electrolytes caused a dramatic increase in the degree of levelling. The effect takes places *via* the solubilization of the disodium bis(sulfopropyl) disulfide brightener in copolymer micelles and changes in the distribution of the brightener on cathode surface. The positive effect of a conducting-polymer additive, a colloidal polyaniline dispersion, on the brightness of electrodeposited copper coatings is discussed.

Keywords: block copolymer; conducting polymer; copper deposition micelles; polyaniline

Introduction

Surface-active agents and nitrogen- and sulfur-containing organic compounds are essential additives to non-cyanide electrolytes for copper electrodeposition[1]. These compounds control the structure, the physico-mechanical properties and anticorrosion resistance of electrodeposited metal coatings, and influence certain technological parameters of the cathode deposition of metals. Usually, copper coatings are used as a supportive underlayer for the multilayer copper–nickel–chromium coatings. They have to possess specific properties, the most important being the high degree of levelling. During the last few years, we have designed non-cyanide electrolytes for acid bright copper deposition with a high levelling activity[2] – above 90 %. This means that the surface structure becomes smooth and achieves a mirror-like appearance. The application of these

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electrolytes brings both ecological and economic benefits, because the high levelling activity allows elimination of all manual operations, including polishing, and provides the possibility of fully-automated processing. The surfactants used in these electrolytes were multiblock copolymers of ethylene oxide (EO) and propylene oxide (PO)[2] with a specific hydrophilic/hydrophobic balance, a low degree of crystallinity, and high solubilization performance. In aqueous solutions, they form micelles with a hydrophilic shell comprising poly(ethylene oxide) (PEO) segments and a hydrophobic core composed of poly(propylene oxide) (PPO) segments.

Unlike the currently-used wetting agents in electrolytes for copper electrodeposition – PEO and statistical copolymers of EO and PO – the multiblock copolymers are characterized by micelle formation, solubilization efficiency, and specific adsorption behaviour. The objective of this study is to investigate the role of copolymer micelles in the ion transport and electrochemical levelling of copper coatings during acid bright copper electrodeposition. The role of a conducting polymer colloid, a polyaniline (PANI) dispersion used as an additive, has also been studied.

Experimental

All materials and methods have been described in a previous paper[2]. The main electrolyte contained 220 g dm^{-3} copper sulfate pentahydrate, 50 g sulfuric acid (98 %) and 0.09 g dm^{-3} sodium chloride. A symmetrical pentablock copolymer of ethylene oxide and propylene oxide, $(EO)_8(PO)_{15}(EO)_{10}(PO)_{15}(EO)_8$ (EPEPE), was used as a wetting agent, disodium bis(sulfopropyl) disulfide (DS) as a brightener. Colloidal PANI particles were prepared by dispersion polymerization of aniline hydrochloride[3] using poly(*N*-vinylpyrrolidone) as stabilizer[4].

Results and discussion

Block copolymer micelles

The influence of the concentration of EPEPE on the degree of levelling of the copper coating at DS concentrations of 7 mg dm^{-3} and 17 mg dm^{-3}, and at a PANI concentration of 4.5 mg dm^{-3} has been studied (Fig. 1). It was established that, in the absence of EPEPE or at concentrations lower than the critical micellar concentration (cmc), the copper coatings were matt and rough. X-ray photoelectron analysis of these coatings revealed that, regardless of the DS concentration, sulfur was present both in the concavities and on the peaks of the uneven cathode surface. At an EPEPE concentration of 1.6 mg dm^{-3}, which corresponds to the cmc, sulfur was detectable only on the surface peaks. This change in sulfur distribution was parallelled by an abrupt increase in the degree of levelling. At EPEPE concentrations of 2.5–5 mg dm^{-3}, depending on the DS concentration, a plateau was reached and a further increase in the EPEPE concentration (even to 35 mg dm^{-3}) did not lead to a significant increase in the degree of levelling.

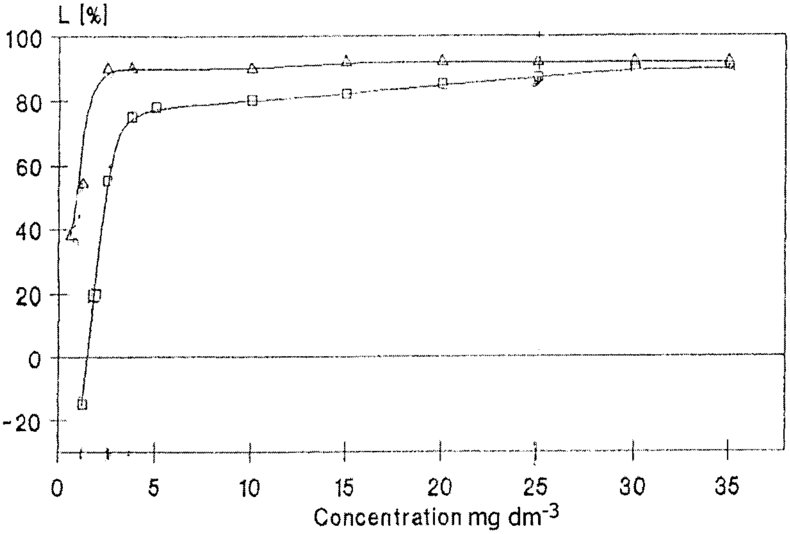

Figure 1. Influence of the EPEPE concentration on the degree of levelling L estimated by profilometry[2] at DS concentrations of 7 mg dm^{-3} (□) and 17 mg dm^{-3} (Δ).

For electrolytes containing PEO instead of EPEPE, no dramatic increase in the degree of levelling, nor changes in the sulfur distribution were observed[5]. In our opinion, this is due to the fact that poly(ethylene oxide) does not form micelles. The DS concentration has an influence on the degree of levelling only in the lower EPEPE concentration range (up to *ca* 10 mg dm^{-3}).

Effect of colloidal polyaniline particles

We have also studied the adsorption of dispersed PANI particles. X-ray photoelectron analyses showed that nitrogen from PANI was present only at the peaks of the cathode surface[5], independently of the presence of EPEPE and DS. The dominant adsorption of PANI particles, which had a hydrodynamic radius of $R_h = 185$ nm, was observed by scanning electron microscopy (Fig. 2). In acid electrolytes, protonated PANI is a polycation and therefore PANI particles are attracted to the cathode; they adsorb at the peaks of the cathode surface and block copper deposition at those sites. Because PANI is electrically conducting, this process does not result in the passivation of the electrode. During PANI adsorption from copper electrolytes containing EPEPE and DS, the dominant adsorption of colloidal PANI on the peaks persists but the adsorption layer formed is denser and continuous due to the DS-loaded EPEPE micelles chemisorbed on the peaks[2].

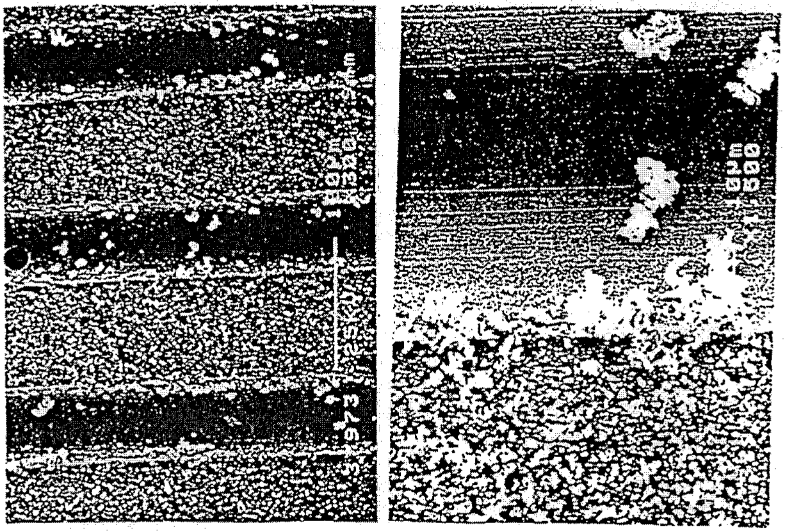

Figure 2. A micrograph of cathode surfaces with PANI particles adsorbed on the surface peaks (two different magnifications).

Thus, there are three types of positively charged particles, which travel during electrolysis to the cathode at different speeds depending on their size and their relative charge density (Fig. 3). The micelles of EPEPE containing adsorbed copper ions are the smallest objects and have the highest relative charge density. Therefore, they travel to the cathode rapidly. Having lost their copper ions, they are desorbed and redirected back into the electrolyte, where they are again positively charged by interaction with copper ions. Larger micelles, with a lower relative charge density, containing in addition to copper ions also the solubilized DS, reach the cathode more slowly and adsorb predominantly at the peaks of the cathode surface. After losing their copper ions and positive charge, they remain attached by chemisorption of DS to the metal surface and block copper deposition at those sites. The higher the DS content, the larger is the size of the micelles and, hence, the larger the area of cathode where copper deposition at peaks is prevented and surface brightness increases. This may explain the influence of the DS concentration on levelling (Fig. 1). Colloidal PANI particles are the largest and they also adsorb at the cathode peaks. Therefore, a dense non-interrupted layer – with a specific composition and structure – is formed at the cathode; this hampers electron transport and the free access of copper ions, and affects the nucleation of the metal phase.

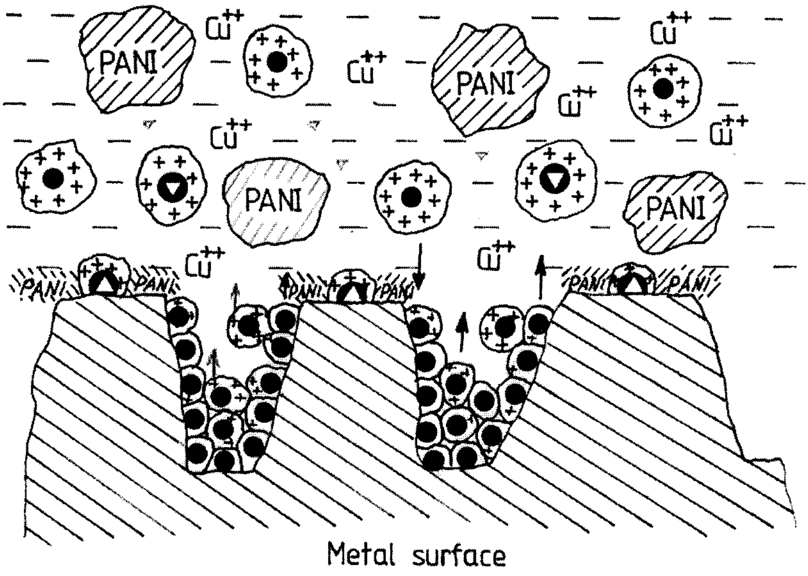

Figure 3. A proposed model of ion transport by EPEPE micelles during copper electrodeposition: DS brightener molecules (open triangles), the hydrophobic cores of EPEPE micelles (full circles), the copper ions in the micellar shell (crosses), and colloidal polyaniline particles (PANI) participate in the copper deposition.

Conclusions

The formation of a dense continuous adsorbed layer of a brightener and colloidal PANI particles at the peaks of cathode surface impedes electron transport and the free passage of copper ions to the cathode surface during electrodeposition of copper. This results in the formation of highly levelled copper layers. The proposed model is in good agreement with all the experimental findings and serves to explain the importance of micelle-forming surfactants in obtaining mirror-bright copper layers and its role in ion transport. The EPEPE, in addition to its micelle-forming properties in aqueous media, is also non-toxic, it does not foam, and is commercially available. These properties make it a suitable surfactant in electrolytes for copper electrodeposition. Moreover, the introduction of a conducting-polymer colloid, a PANI dispersion, can substantially improve the levelling of electrodeposited copper coatings and thus their brightness.

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