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Bronze electrodeposition from an acidic non-cyanide high efficiency electrolyte: Tribological behavior

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ABSTRACT

Bronze coatings were electrodeposited onto a rotating cylinder electrode from a novel non-cyanide acid plating bath with high efficiency (92%). Deposits were obtained from a phenol sulfonic acid bath and their morphology, phase composition and tribological behavior were characterized. Cyclic and linear sweep voltammetries were used to study the effect of organic additives on the reduction processes to achieve an adequate formulation. The resulting bronze deposit consisted of a mono α-phase matrix with a 78% Cu and 22% Sn composition. Dry sliding wear tests were carried out employing a homemade ball on ring system and the coefficient of friction and wear resistance were quantified at different normal loads. Surface characterization of the bronze coatings showed that the resulting roughness is detrimental for the wear resistance of the deposit. This is evidenced by a higher friction coefficient and wear volume of Cu/Sn compared to a conventionally electrodeposited copper coating.

1. Introduction

Electrodeposited Cu–Sn alloys, commonly known as bronze, are widely used as protective and decorative coatings due to their good corrosion resistance and appearance [1,2]. For several years bronze plating has been carried out in an alkaline cyanide-based electrolyte [1–4], which produces high quality deposits but causes several environmental problems, during use and disposal, owing to its high toxicity [5]. The latter, together with increasing environmental regulations, have encouraged the development of a large number of cyanide-free baths for Cu–Sn alloys electrodeposition.

Most formulations reported so far have been achieved by the addition of a tin salt to electrolytes used for copper plating. Among these, sulfate solutions containing organic additives have been by far the most widely studied [6–13], though some pyrophosphate-based [14] and non-cyanide alkaline baths have also been developed [15]. In all these cases the addition of such organic compounds is necessary to attain high quality bronze coatings. For example, surface active substances, mainly polyethers or polyesters, are added as they act as wetting agents and inhibitors (leveling agents) [7,8] producing smooth surfaces. In addition, a second organic substance containing double bonds or aromatic rings is usually used as a brightener to obtain lustrous coatings [8,16]. Such is the case of benzyl alcohol (BA), which has been used to obtain bright bronze coatings with 20% of tin [13], and benzaldehyde, whose effect on sulfate electrolytes has been studied by Survila et al. [8]. Regardless the vast variety of organic compounds that have been evaluated, there are some common features that can be remarked. One of them is the deposition of tin at potentials less cathodic than the equilibrium reduction potential of Sn^{+2}, which can be attributed to an under potential deposition (UPD) mechanism. The other one is related to the formation of various bronze phases, stable only at high temperatures, whose content in the deposit strongly depends on the electrodeposition conditions [17].

Although good quality bronze coatings have been plated from sulfate solutions, these electrolytes have a major drawback: an important loss of tin by spontaneous oxidation of Sn^{+2} as SnO_2 [9,13,18]. An alternative to overcome this problem is the development of new baths based on commercially used tin plating electrolytes, which have been formulated taking this issue into consideration. Some authors have already considered the use of methane sulfonic acid (MSA) as a suitable electrolyte for Cu–Sn alloys deposition [19,20]. Another chemistry which has been used for decades in tinplate production, is the phenol sulfonic acid (PSA) based electrolyte [21–23]. It is worth noting that the electrolyte's formulation usually includes a surface active substance as an additive. One of them is Diphone VI (D6), a sulfonate compound containing aromatic rings. It is important to recall that little attention has been paid to additives with such a structure and their effect on Cu–Sn electrodeposition process.

As has been mentioned, bronze deposits have several uses as protective and decorative coatings. In addition, they have been proposed as an alternative to copper coatings in some industrial applications due to

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their higher hardness. For example, Cu–Sn alloys electrodeposited from a cyanide electrolyte have proved to be a suitable option when plating threaded joints [24], which means that these coatings are able to withstand high loads for short times without undergoing galling. Although many authors have studied the electrodeposition of Cu–Sn from non-cyanide electrolytes, little efforts have been put in evaluating the mechanical performance of the resulting deposits.

The present paper deals with the study of Cu–Sn alloys electrodeposition from a PSA based electrolyte to which small amounts of BA are added. Special attention was paid to the mechanical and tribological properties of the resulting coatings in order to evaluate their performance at similar experimental conditions as those found during the make-up and break-out of threaded joints.

2. Materials and methods

PSA electrolytes were prepared for electrodeposition of Cu/Sn alloys. PSA and Sn^{+2} concentrations were similar to those usually found in tin-plating industry [22,23,25], while Cu^{+2} concentration was defined considering values found in the literature for the deposition of bronze from acid baths [6–13]. The chemicals used to prepare the baths and their concentrations are listed in Table 1.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out using an EG&G Princeton Applied Research Potentiostat/Galvanostat (Mod. 273A) coupled to a personal computer controlled by CorrWare2® software. The working electrode was a Pt rotating disk electrode (RDE), with an active surface area of 0.041 cm^2, while the counter electrode was a Pt wire (1.6 cm^2). A standard saturated calomel electrode (SCE) was used as reference electrode and all the electrochemical potential values in this work are expressed in this scale. The potential window examined was between −0.75 V and 0.15 V vs SCE. All CV curves were recorded at a scan rate of 20 mV/s and 500 rpm. In contrast, LSV was performed at several scan rates (1–20 mV/s) and rotation speeds (100–1500 rpm) to identify the charge-transfer and mass-transport controlled processes. The temperature was fixed at (30 ± 0.2 °C). Galvanostatic deposits were obtained on low carbon steel rotating cylinder electrodes (RCE) 5 cm long and 0.8 cm diameter. This geometry was chosen to meet the requirements of the homemade ball on ring system used in the tribological experiments (described later). Before plating, the steel substrates were electrochemically degreased in a 30 g/L NaOH solution at a cathodic current density of 64 A/dm^2 at room temperature and then pickled in 10% sulfuric acid at 70 ºC. A very thin deposit of nickel (nickel strike) was electrodeposited on the steel cylinders before co-deposition of tin and copper to avoid the Cu^{+2} cementation reaction. To that end, a Woods solution (240 g/L $NiCl_2 \cdot 6H_2O$, 126 mL/L HCl) was prepared and electrodeposition was carried out at room temperature for 3 min at 13 A/dm^2 [26]. For tin–copper electrodeposition a copper anode was used instead of a bronze one because of the short electrolysis time of each experiment and the relative high tin concentration in the electrolyte. During galvanostatic deposition experiments, the cathode was rotated at 500 or 800 rpm and the temperature was set to a value of (30 ± 0.2 °C). Current density was varied between 2.5 and 3.75 A/dm^2 and the electrodeposition time was adjusted to obtain approximately 50 μm thick deposits. For reference, some cylinders were coated with copper using a traditional sulfate bath containing 117.9 g/L $CuSO_4 \cdot 5H_2O$, 120 g/L H_2SO_4 and 70 ppm Cl^-. These samples were plated at the same temperature and rotation speed used in the other experiments, while the current density was set at 8 A/dm^2.

SEM micrographs were recorded with a Quanta200 FEI equipment (Tungsten filament source). The composition of the coatings was evaluated using EDS. XRD spectra of the coatings were determined with an equipment Phillips X'Pert diffractometer with a CuKα = 1.5405 Å. The detector scan mode with a step size of 0.05° and a sampling time of 3 s was used (scan rate 0.0167 º/s). Coating surface roughness was evaluated according to ISO 3274:1996 by means of a profilometer Hommel Etamic T500 and Etamic software. In addition, hardness measurements were made with a Vickers microhardness measuring device. The reported values for each sample are the results of at least 10 measurements.

Samples were embedded in an epoxy resin and mechanically ground with 800 to 2500 grade silicon paper. Finally, the samples were polished with 6 μm and 1 μm diamond paste and faradaic efficiency (FE) of the electrolytes was quantified through coating thickness measurements from optical micrographs of the cross sections.

Dry sliding wear tests were carried out by employing a homemade ball on ring system. The coated samples were rotated at a constant speed of 12 rpm (0.3 m/s) against a 6.35 mm diameter SAE 52100 steel ball used as the counter-body. The contact load was 5 and 10 N of normal force and the total sliding distance was of 170 cm. These experimental conditions were carefully chosen with the aim of reproducing the industrial make up and break out process. All the sliding wear experiments were run in a controlled environment: (25 ± 1 °C) and 50%–55% relative humidity. Wear quantification was achieved measuring the width of wear track from optical microscopy (OM) images and the coating volume damage was calculated assuming that the counter-body remains unchanged. The reported results are an average of at least two tests. COF was recorded during the test and the value was defined according to standard ASTM G 115-04.

3. Results and discussion

3.1. Cu/Sn alloy electrodeposition

LSVs of Cu^{+2}, Sn^{+2} and mixed Cu^{+2}/Sn^{+2} in a PSA electrolyte are shown in Fig. 1. For the Cu^{+2} solution, copper deposition starts at approximately $E_{Cu} = 0.12$ V. Once Cu^{+2} discharge begins, the current density increases reaching a limiting current plateau at an electrode potential of $E = -0.26$ V. On the other hand, for the Sn^{+2} electrolyte, tin reduction does not occur until the electrode potential reaches a value of $E_{Sn} = -0.47$ V. A similar value for tin discharge in an MSA electrolyte was reported by Pewnim and Roy [19]. At approximately $E = -0.50$ V a small shoulder can be appreciated, after which the current rises linearly. A similar behavior was observed by Wen and Szpunar [27] who attributed the peak to the existence of a nucleation and growth mechanism controlled by mass transfer.

When both ions are present in the solution the reduction process starts at $E_{CuSn} = -0.04$ V, which is more cathodic than the deposition

Table 1
Chemicals used and their concentrations in the bath.

Chemical component	Nomenclature	Concentration in the bath
$SnSO_4$ Sigma-Aldrich 95%	–	0.253 mol dm^{-3}
$CuSO_4 \cdot 5H_2O$ Cicarelli 100%	–	0.063–0.126–0.189 mol dm^{-3}
Phenol sulfonic acid (acidity 234.53 gr H_2SO_4/L)	PSA	0.115 mol dm^{-3}
Diphone VI	D6	8 g/L
Benzyl alcohol Fisher Scientific 99%	BA	3 mL/L

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