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Structural, microstructural and corrosion properties of brush plated copper–tin alloy coatings

B. Subramanian *, S. Mohan, Sobha Jayakrishnan

EMFT Division, Central Electrochemical Research Institute, Karaikudi-630 006, India

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Abstract

Cu–Sn alloy coatings on mild steel substrates produced by the brush plating process have been investigated using XRD, SEM and AFM. X-ray diffraction analysis revealed that the brush plated Cu–Sn alloy was heterogeneous and composed of hexagonal η-Cu_6Sn_5, orthorhombic ε-Cu_3Sn, tetragonal β-Sn and cubic Cu phases. Uniform surface coverage of the substrate by granular morphology was observed from SEM and AFM. The alloy composition was determined from atomic absorption spectroscopy (AAS). The corrosion protection performance of brush plated Cu–Sn alloy on mild steel has been assessed using salt water immersion and electrochemical corrosion tests. The results indicated a high charge transfer resistance and very low I_{Corr} for the alloy system comparing with that of individual elements on the substrate and the mild steel substrate.

Keywords: Brush plating; XRD; Cu–Sn alloy; Corrosion resistance

1. Introduction

Copper–tin alloy is used in industry because of its excellent wear properties, attractive appearance, good corrosion resistance, excellent machinability and solderability [1,2]. The baths used for electrodeposition of Cu–Sn alloy are phosphate [3], fluoborate [4], boron–fluoride [5], pyrophosphate [6] and cyanide based [7,8]. These electrolytes are not recommended because of its toxicity and corrosive nature. The sulphate electrolytes are promising alternatives for these electrolytes [1,9,10].

It was shown that electrodeposited coatings can comprise a solid solution of tin and copper, which can be super saturated, sometimes along with a number of intermetallic compounds such as Cu_6Sn_5 or $Cu_{31}Sn_8$ [11,12]. Electroless plating of steel with a copper–tin alloy was investigated by Duncan and Banter [13]. Immersion Cu–Sn alloy using sulphate bath was formulated [14] to study the influences of solution composition and operating parameters.

Brush plating is a portable process for accurately applying plated deposits onto localized areas. It differs from traditional tank or bath plating in that the work piece is not immersed in a plating solution (electrolyte). Instead, the electrolyte is brought out to the part to be plated and applied by a hand held anode or stylus, which incorporates an absorbent wrapping for applying the solution to the work piece (cathode). A DC power pack drives the electrochemical solution, depositing the desired material on the substrate. A schematic of the brush plating process is shown in Fig. 1. It offers portability, flexibility and high-quality deposits. The present work deals with the brush plating of copper–tin alloys on steel substrates from acidic sulphate solutions containing sodium gluconate complexing agent and studying the influences of solution composition and operating parameters. The morphology, elemental composition and corrosion resistance of the Cu–Sn alloy coating were also determined.

2. Experimental

The Cu–Sn alloy coatings were brush plated on mild steel (MS) substrates. The composition of the low carbon steel substrate used in this study is shown in Table 1. In this work,

* Corresponding author. Tel.: +91 4565 227555; fax: +91 4565 227779.
E-mail address: tspsenthil@yahoo.com (B. Subramanian).

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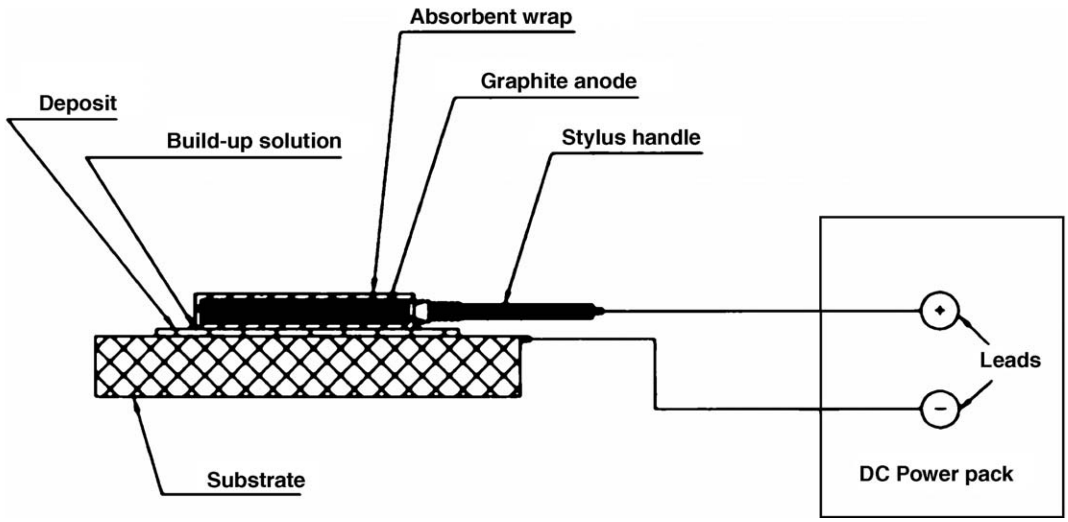

Fig. 1. Schematic of brush plating process.

commercially available brush plating equipment, Selectron power pack, USA, Model 150A-40 V was utilized. The bath composition and bath parameters used for the Cu–Sn alloy deposition are shown in Table 2. Solutions were prepared from reagent grade chemicals and distilled water. The pH was adjusted using either sulphuric acid or sodium hydroxide. Mild steel specimens, 5 × 2.5 × 0.5 cm, were polished mechanically using polishing wheel with 80 emery alumina powder and degreased with acetone. Following ultrasonic cleaning in acetone and washing in DI water the specimens were used for brush plating. The deposit thickness was determined using Mitutyo profilometer. It is useful for measuring surface roughness profiles of the coatings. However, they can be used to measure the step height between the substrate and the adjacent coating. A region of the mild steel substrate was masked before brush plating. A stylus made of stainless steel with a diamond tip is drawn across the step from the substrate to the coating and both the vertical and horizontal motion of the stylus are amplified and recorded. The composition of the deposit was analyzed by atomic absorption spectroscopy (AAS) after the coating was stripped from specimens by dissolving in 1 : 1 HCl. Effect on stannous sulphate concentration on copper content of the deposit and plating thickness and plating time versus plating thickness were studied to find the optimum condition for obtaining golden Cu–Sn alloys with tin content arrived at. Structural characterization of the deposit was carried out by XRD using Philips Diffractometer. Surface morphological examinations were carried out by employing Hitachi S 3000 H Scanning Electron Microscope (SEM) and Molecular Imaging Atomic Force Microscope (AFM). The micro hardness of the brush plated samples was determined using a Micro hardness Testing Machine Leco DM 400 with a Vickers indenter and a load of 25 g. The corrosion resistance of the deposit was assessed by electrochemical polarization studies and AC Impedance measurement using BAS IM6 Electrochemical analyzer. Experiments were carried out using the standard three-electrode configuration, saturated calomel as a reference electrode with a platinum foil as a counter electrode and the sample as a working electrode. Specimen (1.0 cm^2 exposed area) was immersed in the test solution of 3.5% w/v NaCl. Experiments were carried out at room temperature (28 °C).

Table 1
Specified composition of carbon steel substrate

% C	% Mn	% S	% P	% Fe
0.063	0.23	0.03	0.011	Balance

3. Results and discussion

The copper–tin alloy brush plated from the sulphate bath containing sodium gluconate under optimum conditions was adherent, smooth and bright in appearance. When the tin content as observed from AAS varies from 10% to 15%, the alloy coatings of golden color were obtained. Increasing the tin content, the coatings acquire grey-white color, whereas decreasing the tin content, they become reddish in color.

The brush plated Cu–Sn alloy samples were bent through an angle of 180° repeatedly as required by BS 5411 standards and found no lifting and peeling which showed good adhesion of these coatings to the mild steel substrates. Deposits with a Vickers hardness of 357 HV (25 g) were obtained for the optimized Cu–Sn alloy sample which is higher than the value

Table 2
Bath parameters for the brush plating of Cu–Sn alloy bath composition and bath parameters

$CuSO_4$ 5 H_2O	0.04 M
K_2SO_4	0.06 M
$SnSO_4$	0.19 M
$C_6H_{11}O_7Na$	0.32 M
Gelatin	10 g/l
pH	2
Bath temperature	28 °C (RT)
Plating voltage	2 V
Duration	30 min
Anode	Graphite stylus