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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 -Cu₆Sn₅, orthorhombic ε -Cu₃Sn, 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.

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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 highquality 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-40V 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, $5 \times 2.5 \times 0.5$ 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 3000H 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

 Table 1

 Specified composition of carbon steel substrate

1	1			
% C	% Mn	% S	% P	% Fe
0.063	0.23	0.03	0.011	Balance

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 $(1.0 \text{ cm}^2 \text{ exposed area})$ was immersed in the test solution of 3.5% w/v NaCl. Experiments were carried out at room temperature (28 °C).

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 (25g) 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

For a second	
CuSO ₄ 5H ₂ O	0.04 M
K ₂ SO ₄	0.06 M
SnSO ₄	0.19M
C ₆ H ₁₁ O ₇ Na	0.32M
Gelatin	10 g/l
pH	2
Bath temperature	28°C (RT)
Plating voltage	2 V
Duration	30 min
Anode	Graphite stylus



Fig. 2. Roughness profile of the brush plated Cu-Sn alloy film.

of 218 HV reported for the electrodeposited bronze coatings [15]. This higher value of hardness for the brush plated alloy coatings is due to the smaller grain size in the order of nanometer [16].

The uniform nature of these coatings on MS substrate with the thickness value of $24.4 \,\mu\text{m}$ was observed from Profilometric roughness and thickness measurement graph as shown in Fig. 2. This is in good agreement with the value of $24.7 \,\mu\text{m}$ obtained from weight difference method.

The plating thickness increases with increasing tin concentration and reaches a maximum value of about $24 \,\mu\text{m}$ at $40 \,\text{g/}$ l stannous sulphate, after which the deposition rate decreases at higher concentrations (Fig. 3). The decrease in deposition rate may be due to the limited solubility of stannous sulphate, observed by the turbidness of the solution.

The dependence of the amount of copper in the deposit as a function of the stannous sulphate concentration in the plating solution is shown in Fig. 4. Increasing the tin content in the bath decreases the copper content in the deposit. This may be due to the stability of copper gluconate complex and consequently inhibition of the reduction of copper at the expense of reduction of tin and hydrogen [17]. The deposit color changed from red to golden yellow when the stannous sulphate concentration was 40 g/l. When stannous sulphate concentration is greater than 40 g/l the plating solution becomes cloudy as the tin solubility limit is exceeded.

The effect of plating time on the plating thickness is shown in Fig. 5. It is seen that the coating thickness increases with increasing plating duration, reaching a maximum value at 30 min and remains constant thereafter. Attempts to prepare thicker

deposits have failed, since the deposits become darker and more porous with time.

3.1. Structure of the deposits

The X-ray diffractogram (XRD) obtained for the brush plated copper-tin alloy (62% Cu) plated from the bath under optimized conditions is shown in Fig. 6. The observed crystallographic distances, d (h k l), and expected values from phases described in JCPDS are in Table 3. The data show that the observed 'd' values are in very good agreement with the standard 'd' values and reported in the literature [17] of the corresponding phases. The presence of three intermetallic phases, the η -Cu₆Sn₅, ϵ -Cu₃Sn besides β -tin and copper phases are observed. The n-Cu₆Sn₅ has a hexagonal structure whereas the ϵ -Cu₃Sn phase has an orthorhombic structure. The β -tin phase possesses a tetragonal and Cu has a cubic structure. The lattice parameters for these phases are indicated in Table 4. The particle size (D) was calculated from line broadening β , under the simple assumption that line broadening is caused by the particle size alone [18].

$$D = 0.9\lambda/\beta\cos\phi \tag{1}$$

Where λ is the X-ray wavelength (1.514 A°) and ϕ is the Bragg angle. The crystallite sizes were calculated for different phases present in the film and given in Table 4. The crystallite sizes were found to be in the range of 8–20nm for Cu–Sn layers on mild steel substrates. The crystallite size was found to be in the range of 8–20nm. Such a small grain size contributes to the



Fig. 3. Plating thickness as a function of concentration of stannous sulfate in the plating solution.



Fig. 4. Copper content of deposit as a function of the concentration of stannous sulfate in the plating bath.



Fig. 5. Plating thickness as a function of plating time.

smooth surface morphology and also may have a beneficial effect on the improvement of the micro hardness of the coating [16]. Also the grain size reduction to the nanometer range results in considerable improvement in their resistance to localized corrosion [19].

3.2. Surface morphology

Optical micrograph of as plated Cu–Sn alloy is shown in Fig. 7. It indicates uniform coverage of the surface by micro crystallites without any cracks or pits. The granular morphology is observed from SEM picture taken for the same sample as shown in Fig. 8. A similar morphology exhibiting coalesced crystallites for the non-cyanide electrodeposited Cu–Sn films was reported [20].

Surface characterization of the brush plated Cu–Sn alloy sample was carried out using atomic force microscopy (AFM). Advantage of AFM is its capacity to probe into minute details related to the individual grains and inter-grain regions as well in

Table 3 Comparison of observed inter-planar distances and standard inter-planar distances of XRD pattern of brush plated Cu–Sn alloy

	-	-		
<i>d</i> —	d —	h k l	Relative intensity	Phase
observed	standard		%	
2.960	2.960	(101)	100	η-Cu ₆ Sn ₅
2.911	2.915	(200)	31.7	β-Sn
2.795	2.793	(101)	51.0	β-Sn
2.547	2.550	(002)	5.7	η-Cu ₆ Sn ₅
2.097	2.091	(110)	77.4	η-Cu ₆ Sn ₅
2.073	2.080	(2 12 0)	17.7	ε-Cu ₃ Sn
2.018	2.017	(211)	31.3	β-Sn
1.806	1.808	(200)	2.5	Cu
1.714	1.710	(201)	10.4	η-Cu ₆ Sn ₅
1.658	1.659	(301)	7.9	η-Cu ₆ Sn ₅

three dimensional form. AFM pictures scanned over an area of $1 \times 1 \,\mu\text{m}$ of the brush plated Cu and Cu–Sn alloy prepared under optimized conditions are shown in Fig. 9a and b, respectively. By comparing the two images, it is clear that the deposits consist of many small spherical particles corroborating the results of SEM analysis which are the structural characteristics of brush plated coatings.

Roughness analysis of these coatings was carried out and the value of the mean roughness R_a was calculated as the deviations in height from the profile mean value [21].

$$R_{\rm a} = \frac{1}{N} \sum_{\Delta}^{N} |Zi-Z| \tag{2}$$

where Z is defined as the sum of all height values divided by the number of data points (N) in the profile. Alloy deposit is more smooth than that of copper deposit as evident from a decrease in mean square root index of roughness value from 16 nm for the copper deposit to 3 nm for the alloy deposit. A higher value of 43.09 was observed for the electrodeposited Cu–Sn films [20].



Fig. 6. X-ray diffractogram of the brush plated Cu–Sn alloy film. $\Box = \eta$ -Cu₆Sn₅, $O = \epsilon$ -Cu₃Sn, $\bullet = -$ Cu, $\Delta = -$ Sn.

Table 4 Crystallite size and lattice parameters of Cu–Sn alloy

Phase	JCPDS card	Lattice p	parameters	Crystallite size	
		$a(A^{\circ})$	$b(A^{\circ})$	$C(A^{\circ})$	nm
η-Cu ₆ Sn ₅	2-0713	4.18	_	5.06	19.6
ε-Cu ₃ Sn	1-1240	5.520	38.21	4.319	12.4
β-Sn	4-0673	5.825	_	3.187	8.0
Cu	4-0836	3.609	-	-	11.6

3.3. Potentiodynamic polarization studies

The principal aim of this investigation was to study surface degradation resulting from electrochemical processes, and this necessitated an analysis of the surface deposit left after electrochemical reactions. The potentiostatic polarization experiments provided some idea of the electrochemical activity of the material. However, this necessitated scanning across a wide range of electrode potentials so that the surface of the material at the end of such polarization was the result of cumulative effects at different potentials. To analyze the surface, the material was subjected to potentiostatic polarizations, one specified potential being impressed on the material at a time. The potentials were either anodic or cathodic with respect to the primary electrochemical process occurring on the surface as indicated by the potentiostatic polarization curves.

The potentiodynamic polarization curves obtained for the mild steel (substrate), brush plated Cu, Sn, Cu–Sn alloy ($20 \,\mu m$ each) on mild steel in 3.5% w/v NaCl electrolyte are presented in Fig. 10. The current and potential of the corroding electrode is related by

$$i = i_{\rm corr} (e^{2.3 \ \eta/b_{\rm a}} - e^{-2.3 \ \eta/b_{\rm c}}) \tag{3}$$

Where i_{corr} — corrosion current; η — overpotential (*E*- E_{corr}), b_{a} and b_{c} — anodic and cathodic Tafel slopes. At high over potentials i.e.

 $n \gg RT/F$

 $i = i_{\rm corr} e^{2.3\eta/b_{\rm a}}$



Fig. 7. Optical micrograph under a low magnification (100×) for the brush plated Cu–Sn alloy film.



Fig. 8. Scanning electron micrograph of the brush plated Cu-Sn alloy film.

 $\log i = \log i_{\rm corr} + \eta/b_{\rm a}$

In the plot of η versus log *i*, extrapolation of linear line to corrosion potential gives a straight line and the slope gives both b_a and b_c and the intercept gives the corrosion current.



Fig. 9. AFM images (scan size $1 \times 1 \mu m$) showing the topography of (a) copper on MS and (b) Cu–Sn alloy film on Ms.



Fig. 10. Polarization studies of (a) blank MS, (b) Cu on MS, (c) Sn on MS and (d) Cu–Sn alloy film on MS in 3.5% w/v NaCl.

The $E_{\rm corr}$ and $I_{\rm Corr}$ values have been calculated using the Tafel extrapolation method and they are given in Table 5. There is an appreciable increase in corrosion resistance for the Cu–Sn alloy on mild steel substrate compared to bare mild steel substrate. $E_{\rm corr}$ and $I_{\rm Corr}$ values improve (a less negative value of $E_{\rm corr}$ and lower value of $I_{\rm Corr}$ signifies an improvement in corrosion) for Cu–Sn alloy on mild steel substrate. The $E_{\rm corr}$ values are shifted to near equilibrium value of Cu–Sn alloy system, which show the reduction of corrosion behavior of the system.

3.4. Electrochemical impedance

The electrochemical impedance spectra of brush plated Cu– Sn alloy system were measured in the same three electrode assembly, as used for the potentiodynamic polarization experiments. Impedance measurements were made at open circuit potential (OCP) applying an AC signal of 10mV in the frequency range 10Hz to 1MHz. The impedance results obtained from Nyquist plots for the samples used for corrosion tests in 3.5% w/v NaCl solution are shown in Table 6 and Fig. 11.

The $R_{\rm ct}$ can be related to $i_{\rm Corr}$ [22]

$$R_{\rm ct} = b_{\rm a} \times b_{\rm c}/2.3(b_{\rm a} + b_{\rm a})i_{\rm corr} \tag{4}$$

 $\begin{array}{ll} R_{\rm sol} & {\rm solution\ resistance} \\ R_{\rm ct} & {\rm charge\ transfer\ resistance} \\ b_{\rm a} \mbox{ and } b_{\rm c} \mbox{ anodic\ and\ cathodic\ tafel\ slopes} \end{array}$

Table 5				
Corrosion parameters obtained	from polarization	studies in	3.5%	w/v NaCl

Sample	$\frac{E_{\rm corr}}{{ m Vs}}$	$b_{\rm a}$	$b_{\rm c}$	I _{Corr}	Corrosion rate
	SCE/mV	V/dec	V/dec	A/cm ²	mpy
MS panel	-0.680	0.118	-0.196	1.26×10^{-4}	0.57×10^{-6}
Sn on MS	-0.570	0.154	-0.057	7.22×10^{-5}	7.55×10^{-7}
Cu on MS	-0.565	0.418	-0.240	5.59×10^{-5}	2.55×10^{-7}
Cu-Sn alloy on MS	-0.527	0.118	-0.226	0.57×10^{-5}	0.37×10^{-7}

Table	6
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Corrosion parameters	obtained from	impedance measurements	by	Nyquist	plots
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Sample	OCP	$R_{\rm ct}$	$C_{\rm dl}$
	V	$\overline{\Omega \ \mathrm{cm}^2}$	F/cm ²
MS panel	-0.655	93.8	0.056
Sn on MS	-0.408	291.7	0.012
Cu on MS	-0.549	1111.7	0.003
Cu-Sn alloy on MS	-0.483	1382.4	0.0004

The double layer capacitance C_{dl} value is obtained from the frequency at which Z imaginary is maximum [22]

$$\omega(Z_{\rm (im)} \max) = 1/C_{\rm dl} R_{\rm ct} \tag{5}$$

The increased R_{ct} values and decreased C_{dl} values for the Cu–Sn alloy clearly confirm the better corrosion resistance



Fig. 11. Nyquist plots for corrosion measurements of (a) blank MS, (b)Cu on MS, (c) Sn on MS and (d) Cu–Sn alloy film on MS in 3.5% w/v NaCl.



Fig. 12. Bode plots for corrosion measurements of (a) blank MS, (b)Cu on MS, (c) Sn on MS and (d) Cu–Sn alloy film on MS in 3.5% w/v NaCl.

 Table 7

 Results of tarnishing/rusting level after salt water dipping

Sample	8 h	1 day	4 days	7 day
Blank MS	5%	40%	75%	100%
Copper on MS	No	No	20%	30%
Cu-Sn alloy on MS	No	No	1%	3%

of these systems compared to individual species and bare mild steel substrate. Also it is observed a more pronounced semicircular region in the case of Cu–Sn alloy indicating that the alloy system has maximum corrosion resistance as observed from the high frequency region of the impedance spectra. The corrosion rate (CR) is expressed in mills per year.

$$CR = 0.1288 \times i_{corr} \times w/\rho \tag{6}$$

where i_{Corr} = corrosion current in A/cm², w= equivalent weight of metal, ρ = density.

The corrosion rate observed on alloy plated sample was significantly lower than that of the steel substrate and individual species on the substrate exhibiting the lowest corrosion rate of brush plated Cu–Sn alloy of all the four samples.

The corrosion behavior of the brush plated Cu–Sn alloy system is further illustrated by Bode plots in Fig. 12 where it can be seen that the mild steel has the lowest absolute impedance. The values of |z| of the alloy system are significantly higher than that of the mild steel substrate. This confirms that the Cu–Sn alloy plating provides better corrosion protection to the steel substrate.

The corrosion resistance of the Cu–Sn alloy deposit was assessed by salt water immersion test also. The deposits were dipped in a 3.5% w/v NaCl solution at room temperature. The appearance of surface after different times of dipping in 3.5% w/v NaCl solution is presented in Table 7. Comparing the corrosion resistance of the blank mild steel panel and brush plated copper on mild steel, the Cu–Sn alloy deposit appears to be more resistant to corrosion.

4. Conclusions

Adherent, smooth, bright deposits of Cu–Sn alloy deposits were brush plated successfully on low carbon steel substrates from gluconate-based sulphate baths. The brush plated Cu–Sn alloy films are heterogeneous systems comprised of intermetallic compounds (η -Cu₆Sn₅, ϵ -Cu₃Sn and β -tin). Uniform coverage with the spherical nodular morphology of these coatings is observed from microstructure analyses. The golden Cu–Sn alloy deposit, obtained from the bath composition and bath parameters mentioned in Table 2, demonstrated excellent corrosion protective performance.

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