Electroless plating of Sn/Cu/Zn triple layer on AA6082 aluminum alloy

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1. Introduction

Different electroless plating techniques have been used for coating metals on substrates — the most widely applied being immersion and autocatalytic plating. Immersion plating enlists displacement reactions to deposit very thin coats [1]. In autocatalytic plating, redox reactions in the presence of a reducing agent deposit metallic elements on the surface [2,3]. Compared to immersion, autocatalytic plating yields thicker, more uniform layers of higher quality [1]. In layer depositions by electrical current (electroplating), deposited layer thickness outperforms electroless techniques. However, a non-uniform layer can form in electroplating due to uneven current densities [4,5] and to aggregation of electrons on surface edges and corners [5] that renders electroplating difficult for complex shapes.

Metallic coatings on aluminum alloys in contact with copper conductors are crucial for protection against galvanic corrosion and conductivity loss in the electrical industry [6]. Tin-plated Al parts offer: (1) good solderability, (2) high ductility, (3) oxidation resistance, (4) protection against galvanic corrosion, and (5) proper conductivity [7,8]. Superior adhesion of the Sn layer to the Al substrate requires pre-deposition of a Cu layer [9,10]. To eliminate interference of any surface Al2O3 on Cu deposition, the specimen is initially coated with a Zn layer [11,12]. Such triple metallic layering of Zn—Cu—Sn has generally been deposited on Al parts by electroplating.

While the main advantages of electroless plating are uniformity and high quality [13–16], electroless plating is limited by its low deposition rate and high cost of chemical components in mass production. Still, electroless plating becomes cost-beneficial in job shops (low production rates) where expensive equipment is avoided. Here, intricate parts should be thus plated [1,17].

Electroless plating solutions contain four main components: (1) the metal ion salt, (2) the pH adjustor, (3) the complexing agent, and (4) the reducing agent [1]. Furthermore, in some recipes, one or more additives are introduced, such as (1) stabilizing agents, (2) brightening agents, and (3) deposition rate-controlling agents [13,14,18,19]. Electroless plating of Sn on Al that features the three Zn—Cu—Sn stages will be briefly discussed next.

The first stage includes Zn-plating of Al in order to inhibit surface formation of aluminum oxide. Oxides impair plating quality and reduce adhesion of the deposited layer to the substrate [12,18].
2. Experimental procedure

Zinc-plating solutions dissolve aluminum oxide to deposit a thin, smooth, dense zinc layer on the aluminum substrate, making it suitable for subsequent plating either by electroplating or electroless plating [20–22]. With the increase of plating time, the thickness of the deposited layer would increase, and its uniformity would decrease with weak adhesion properties [21].

The second stage involves plating Cu on the Zn-deposited layer. Many researchers have studied electroless plating of Cu, mainly studying the effects of different types and concentrations of complexing agents and additives on the deposition process [9,23]. Pau-novic et al. tested different complexing agents to conclude that cyclohexane-1,2-diamine-N,N,N',N'-tetracetic acid (CDTA) leads to the highest deposition rate, while tartrate has been reported to be least effective [24]. Kondo et al. concluded that the presence of a single amine group amid hydroxy groups in the chemical structure of the complexing agent exerts a positive effect on the deposition rate, but the quality of the deposited layer remains low [25]. This quality limitation has been resolved in later work using triethanolamine (TEA) to deposit a compact, dense, thick layer on the substrate [26].

Electroless Sn-plating solutions have been divided into two subgroups, alkaline and acidic [27–29], where investigations have mainly focused on acidic, electroless Sn-plating baths [30], pioneered by Davis et al. [31] using chloride salts of Sn and Pb. In acidic baths, immersion plating occurs in the presence of a complexing agent that lowers the reduction potential value of Cu, which then activates a redox reaction between Sn ions and the Cu complex [30]. Alkaline electroless Sn-plating, known as autocatalytic Sn-plating, proceeds as the reducing agent undergoes further reduction under the disproportionation of Sn ions [10,32–34]. Unlike immersion plating (acidic bath), the autocatalytic plating method (alkaline bath) is capable of increasing the thickness of existing Sn layers [33]. Microstructural investigations have shown the Sn layer to deposit via nucleation of new grains and their growth [30,33].

This work investigated the possibility and features of electroless Sn-plating on AA6082 in the presence of two (Zn and Cu) interlayers. The final Sn layer is deposited using different times, temperatures and bath concentrations. Deposits were visualized by optical and scanning electron microscopy (SEM) to study the effects of processing parameters on thickness and microstructure. Electroless Sn-plating is described by the observed chemical equations. Finally, electrochemical tests have been carried out to characterize the corrosion properties of the coated samples.

2. Experimental procedure

Zn–Cu–Sn triple layering was applied to extruded AA6082 cylinders via the set of rinse and deposit stages shown in Fig. 1. Chemical baths featured analytical grade reagents and deionized water.

2.1. Sample preparation

Disks 30 mm diameter × 7 mm thick were cut from an AA6082 extruded with surface area 6314.6 mm². The samples initially underwent grinding in water under a consecutive set of sandpaper grit 400 to 2000. Next, surface-ground samples were cleaned ultrasonically for 5 min in 96% C₂H₅OH ethanol. Samples were finally treated in 5% NaOH solution for alkaline cleaning (5 min) and 2 min in 50% HNO₃ for acid pickling and surface activation.

2.2. Bath composition

After surface preparation, for the first step, all samples were treated in a zincating solution for 70 s to yield 1 μm Zn deposits on the Al substrate. Zn solution contained ZnO, NaOH, NaNO₃, NaKCa₄H₆O₆·4H₂O, and FeCl₃·6H₂O. Concentrations of each compound in this zincate bath are reported in Table 1. Potassium sodium tartrate (KNaCa₄H₆O₆·4H₂O) acted as complexing agent in the zinc-plating step.

For the second step, to deposit the Cu layer (6–8 μm), Zn-plated samples were immersed in the electroless Cu-plating solution for 15 min, followed by 15 min in 96% C₂H₅OH ethanol to expunge excess reagent lingering in surface micropores. The Cu-plating solution contained CuSO₄, formaldehyde, NaOH, TEA (triethanolamine), and other additives — all also reported in Table 1 [9,18,25]. For Cu-plating, TEA (triethanolamine) served as the complexing agent. Conventional electroless Cu-plating solutions formed layer thicknesses limited to 3 μm in 15 min [35]. Our enlisted bath composition was able to deposit Cu layers up to 10 μm thick in the mentioned time [25].

For the Third Step, fifteen identical samples were prepared according to procedure. To investigate the effects of plating parameters on the deposited layer, electroless deposition of Sn was performed under fifteen different conditions to be described later. The Sn deposition solution contained SnCl₂, NaOH, sodium citrate, and NaH₂PO₂·2H₂O [10]. Sodium citrate served as complexing agent in this tin-plating step [9,10,18]. Bath concentrations for Sn deposition are listed in Table 1.

2.3. Electroless plating conditions

As previously disclosed, Zn and Cu deposition stage parameters remained constant for all samples, and fifteen different parametric conditions were considered for Sn plating. Tin-plating experiments were divided into two sets focusing on the effects of:

- Sample set 1: variable temperature and bath concentration under constant deposition time. To vary bath composition, concentrations of all ingredients were scaled uniformly.
- Sample set 2: variable temperature and deposition time under constant bath concentration.

The two sample sets are shown in Fig. 2.

2.4. Characterization of deposited layers

The microstructures were studied via optical microscopy (Sino won 8502) and scanning electron microscopy (FEI Quanta 450) for both top surface and cross-sections. To study the cross-sections, samples were cut using wire electro-discharge machining (wire EDM). Chemical compositions of the deposited layers were studied using energy-dispersive X-ray spectroscopy (EDS) in SEM.

To study deposit layer anti-corrosion characteristics, electrochemical impedance spectroscopy was performed at the IVIUM Vertex electrochemical workstation. Coated samples were adjusted as the working electrode in the electrochemical cell, proximate to a platinum counter electrode and a saturated calomel electrode as the reference electrode (SCE). Pre-test, the working electrode was immersed in the test solution for 30 min at open circuit potential (OCP) to reach steady state. A 10 mV AC signal was used for EIS measurements at frequencies between 100 kHz and 10 MHz. A 3.5% NaCl solution acted as corrosive media on sample area 1 cm². UV–Vis spectrophotometry (PerkinElmer Lambda 25) was used to identify the presence of complexes in the electroless Sn-plating solution.

3. Results and discussion

3.1. Electroless deposition equations

It is well known that the standard reduction potential of Sn (Sn²⁺/Sn = −0.1375) is less than that for Cu (Cu²⁺/Cu = +0.34).
Based on the Gibbs free energy equation, Sn cannot be reduced in an electroless cell, and Cu cannot be oxidized thermodynamically [30]. However, three different electroless plating mechanisms remain to deposit Sn on Cu substrates: (1) displacement reaction [36], (2) reduction of a reducing agent, and (3) disproportionation of tin compounds in the solution.

The proposed displacement reaction yields two ways for a complex to form with either Cu or Sn. In acidic baths, Cu forms a ligand with the complexing agent where the reduction potential of this complex could undercut that of Sn, leading to the thermodynamically spontaneous reaction [30]. To ensure the prohibition of Cu complex formation in alkaline solution, UV–vis experiments were conducted [30]. A Cu sample size matching that of Al was put in the alkaline bath for 24 h at room temperature to observe any Cu complex formation with the bath (NaOH, NaH₂PO₂·H₂O, and sodium citrate). As results in Fig. 3 indicate, no perceptible peak was observed in the UV–vis data.

In alkaline baths (as used in this study), Sn either forms a ligand with a complexing agent or creates a compound, such as HSnO₂, with reduction potential above Cu’s [10]. To verify the displacement reaction hypothesis with the aid of complexing agents, Zn/Cu-plated samples were plated in the alkaline Sn-deposition bath at different plating conditions, and their cross-section microstructures were studied under an optical microscope.

The deposited Sn-layer thicknesses for all studied samples (sets 1 and 2 in Fig. 2) are presented in Fig. 4. As expected, results indicate that by increasing either temperature, bath concentration, or immersion time, Sn deposit layers thicken. Still, for high temperatures, concentrations and durations, layer homogeneity worsens, and large Sn crowns form and grow on the Cu substrate. In Fig. 5, the cross-section micrographs for the second sample set (Fig. 2) are presented. Heterogeneity in the Sn layer presents in the sample processed at the highest temperature for the longest time (Fig. 5i). As it is shown in Fig. 5, with the increase of temperature more Sn tend to deposit on the Cu layer, also, in higher plating times, more Sn tend to grow on the substrate. Importantly, extended plating time gradually thins the Cu layer (first row of Fig. 5), signaling the displacement reaction mechanism [3,36].
Notably, Cu layer thickness is a key factor in the Sn deposition process. When the Cu layer is too thin (1 \( \mu \)m), dissolution favors further thinning, cracking, and eventual layer shedding. When the bath solution contacts the Al substrate, H\(_2\) gas bubble pressure forms to detach the Cu.

In the displacement reaction, the alkaline pH of the bath exerts a crucial role. At lower pH levels (pH:8–11), Sn ions form Sn(OH)\(_2\)\[10\], which is ill-suited for activating a displacement reaction. However, at pH \( > 12 \), HSnO\(_2\)/C\(_0\) or Sn(OH)\(_3\)- forms (Equation(1)).

\[
\text{Sn(OH)}_2^+ + \text{H}_2\text{O} \rightarrow \text{HSnO}_2^- + \text{H}^+ + \text{OH}^- \quad \text{K} = 4.2 \times 10^{-15} \quad (1)
\]

Since the equilibrium constant for Equation (1) is very low, a rising bath pH yields more HSnO\(_2\). The presence of HSnO\(_2\) in solution drives continued displacement reactivity. In high values of pH, according to equation (2), displacement reaction is activated and Sn is deposited on the substrate.

\[
\text{Cu} + \text{HSnO}_2^- + \text{OH}^- \rightarrow \text{Sn}_{\text{deposited}} + \text{CuO}_2^{2-} + \text{H}_2\text{O} \quad (2)
\]

The other proposed mechanism for Sn electroless plating on Cu substrates features the reduction of Sn ions by hypophosphite. This mechanism is supported by the presence of HPO\(_2\)\(^-\) and the formation of HSnO\(_2\) in a highly alkaline medium (pH > 12) [8].

\[
\text{H}_2\text{PO}_2^- + \text{HSnO}_2^- \rightarrow \text{Sn}_{\text{deposited}} + \text{HPO}_3^{2-} + \text{H}_2\text{O} \quad (3)
\]

The third mechanism disproportionates Sn ions. According to research literature, different redox reactions support disproportionation as shown below in equation 4-a, 4-b and 4-c. According to Molenaar et al. [10], reaction (4-a) is not spontaneous thermodynamically [10]. On the other hand, reaction (4-b) is possible. However, the low concentration of Sn(OH)\(_2\) in high alkaline solutions [10] makes (4-b) unlikely per Equation (1) [10]. Here, redox reaction (4-c) is the favored reaction assumed to occur in solution [33].

\[
\begin{align*}
2\text{HSnO}_2^- & \rightarrow \text{Sn}_{\text{deposited}} + \text{SnO}_3^{2-} + \text{H}_2\text{O} \\
2\text{Sn(OH)}_2 + 2\text{OH}^- & \rightarrow \text{Sn}_{\text{deposited}} + \text{SnO}_3^{2-} + 3\text{H}_2\text{O} \\
2\text{Sn(OH)}_3^- & \rightarrow \text{Sn}_{\text{deposited}} + \text{Sn(OH)}_6^{2-}
\end{align*} \quad (4-a, 4-b, 4-c)
\]

### 3.2. Sn layer microstructure

Microstructures of deposited layers were studied using optical and scanning electron microscopy (SEM) on both top and cross-section surfaces. Optical micrographs of the top surface for both sample sets are presented in Fig. 6. The first sample set (Fig. 6a–e) shows the coating at the lowest temperature and bath concentration having red shades of Cu with almost no Sn deposition. By increasing temperature and bath concentration, samples gradually turn gray, and at the extreme conditions (Fig. 6f, h, i), Sn crystal laths form on the surface. A similar situation occurs in the second sample set when deposition time is increased (Fig. 6j–r).

To better see how Sn deposits on the Cu layer, the top surface of select specimens from the second sample set were studied via SEM and back-scattered electron (BSE). The distribution of elements is
revealed by EDS maps (Fig. 7). Fig. 7a–i shows the top surface microstructure of samples processed at constant time (t = 1200s) and bath concentration (C$_2$ = 1.5C). Fig. 7g shows that Sn was deposited on the surface as scattered islands. By heating bath temperature to 45 °C, the number of islands grew, yielding a more uniform distribution (Fig. 7h). Though deposition at 65 °C increased the homogeneity, Cu-rich regions still persisted around the large Sn crystals (Fig. 7i).

Effect of deposition time on the top coated surface appears in Fig. 7j–r. EDS results show that by extending deposition time (Fig. 7p–r), the Sn layer intensifies as remaining Cu valleys shrink.

Optical micrographs of layer cross-sections were previously exhibited in Fig. 5. Fig. 8 shows BSE and EDS results for cross-sections of selected samples from Fig. 6. BSE images indicate heterogeneous deposition of Sn. EDS maps portray the three Zn–Cu–Sn layers on the samples.

3.3 Electroless deposition mechanism

A comprehensive deposition mechanism is here proposed based on the deposition equations of section 3.1 and the observed microstructures of section 3.2. Fig. 7j shows a sample surface after 400 s of Sn deposition at T = 65°C and C$_2$ = 1.5C featuring vast numbers of tiny Sn crystals nucleated on top of the Cu layer. Fig. 7k indicates that after 1200 s, the small nuclei grew to larger crystals. After 3600 s (Fig. 7l), large crowns formed on the surface where many sharp edges distinctly emerged outlining crystallographic planes and directions. Figs. 7i and 8i depict Cu-rich valleys surrounding the tall Sn crowns. Per Von-Weimann precipitation theory, nucleation dominates the initial states of plating. As plating proceeds, the significance of growth gradually increases with temperature, exerting an inverse relationship with the nucleation rate. Heating the deposition process curbs nucleation in favor of growth [38,39]. These observed deposition mechanism are portrayed schematically in Fig. 9a.

Fig. 9a shows that activation of the displacement reaction (Equation (2)) forms Sn nuclei on the surface by consuming Cu to leave small pits on the surface. As this reaction gradually ensues, Sn nuclei grow and Cu pits deepen around Sn crystal “teeth” (Fig. 9b) as displacement consumes $\text{HSnO}_2^{-}$ to produce $\text{CuO}_2^{2-}$ ions. This yields concentration gradients in areas near the Sn crowns. $\text{HSnO}_2^{-}$ depletion and $\text{CuO}_2^{2-}$ enrichment both deter displacement.

Meanwhile, reduction and disproportionation reactions deposit more Sn on the crowns far above the surface (Fig. 9c) [10] as surrounding valleys also coat with Sn atoms, thus blocking the path between Cu and the solution. Elapsed time curtails the significance of the displacement reaction through: (1) $\text{HSnO}_2^{-}$ and $\text{CuO}_2^{2-}$ concentration gradients and (2) Cu-solution connection loss as contribution from reduction and disproportionation accelerates.

As previously mentioned, Sn crowns showed clear signs of sharp edging typical of crystallographic planes and directions. This morphology suggests a preferred orientation for growth labeled as fast growth direction “FGD” in Fig. 9b and c encircling the slow-growing planes (labeled “SGP”).

Fig. 10 shows SEM imagery of one Sn crown and a schematic view of the successive stages in its growth. According to Von-Weimann theory for diluted bath concentrations, the layer tends to grow crystalline [37]. In the studied samples, the Sn crystal expanded in its fast growth directions (FGD) encircling the high-packing, slow-growing planes (SGP). The micrograph also shows deep valleys surrounding the large central crown. As deposition proceeded, these valleys became dilute of $\text{HSnO}_2^{-}$ and enriched by $\text{CuO}_2^{2-}$, both reducing the rate of the displacement reaction.

3.4 Corrosion characterization

To evaluate the coating efficiency, the corrosion behavior of a Zn/Cu/Sn-plated sample (T = 65 °C, C$_2$ = 1.5C, and t = 1200s) was compared to a sample with no Sn coating. Fig. 11a features the Nyquist plots of Zn/Cu- and Zn/Cu/Sn-plated samples. The larger the diameter of the Nyquist plot, the better the corrosion resistance of the sample [40,41]. Consequently, the corrosion resistance of the Zn/Cu/Sn sample proved superior to the Zn/Cu sample.

The effect of frequency on corrosion behavior for the two samples appears in the BODE diagram of Fig. 11b. Impedance at low frequency indicates total system resistance [41]. BODE curves confirm Zn/Cu/Sn corrosion resistance outperforming the Zn/Cu sample. System equivalent circuitry can be estimated according to the number of peaks in the BODE-Theta diagram [41].

The equivalent circuit of the system appears in Fig. 11a where Rs is the solution resistance in series with the surface shunt elements: coating resistance Rc, coating capacitance CPEc, the defect corrosion charge-transfer resistance Rct, and defect corrosion double-layer capacitance CPEdl. Values of each parameter for the two layers are summarized in Table 2. Total surface resistance of the samples is denoted as Rt – the sum of Rc and Rct for each. High values of Rt
indicate good corrosion resistance. Table 2 shows that the Zn/Cu/Sn-coated sample enjoys threefold superior $R_t$.

Polarization plots (TAFEL test results) of the two studied samples are showcased in Fig. 12. The intersection of the anodic and the cathodic branches in the Zn/Cu/Sn-coated sample permits a lower current density versus the Zn/Cu-coated sample. This also indicates a lower corrosion rate for the Zn/Cu/Sn sample. In the TAFEL extrapolation results of Fig. 12, $\beta_a$ and $\beta_c$ are the slopes of anodic and cathodic branches, respectively. $E_{\text{corr}}$ and $I_{\text{corr}}$ denote corrosion potential and current density, respectively. The Stern-Geary equation has been used to calculate polarization resistance ($R_p$) [41]. Calculated results indicate the Zn/Cu/Sn-coated sample permitting the lower corrosion current density. The corrosion resistance has been reported in terms of $I_{\text{corr}}$ which is inversely proportional to polarization resistance ($R_p$). By introducing a constant element phase, the inhomogeneity in the coatings was accounted in the calculations. The difference in polarization resistance of the samples further signals a corrosion rate in the Zn/Cu/Sn sample 27.5% lower than that of the Zn/Cu sample.

The corrosion characterization results indicate that, although the proposed electroless deposition technique coated a rough heterogeneous Sn surface, corrosion resistance significantly improved. Cu-rich valleys encircling nearby Sn crowns were initially considered a problematic source in the corrosion

**Fig. 5.** Optical micrographs showing cross-sections of Zn/Cu/Sn-plated samples at various Sn-plating conditions for $C_2 = 1.5C$ (quantitative data is presented in Fig. 4).

**Fig. 6.** Optical micrographs of the top surface after Sn plating in (a–i) sample set 1 (constant time) and (j–r) sample set 2 (constant bath concentration).
Fig. 7. SEM, BSE, and EDS images of the top surface of deposited layers (a–i) at constant bath concentration and time, (j–r) at constant temperature and bath concentration.

Fig. 8. Cross-section SEM and EDS maps of electroless tin plating on the substrate for $C_2 = 1.5C$ and $t = 1200s$ at different temperatures, magnified 4000×. (Must be printed in colors).

Fig. 9. Schematic depiction of deposition stages and mechanisms including displacement, reduction, and disproportionation reactions.
resistance. However, corrosion experiments confirmed the Cu path to the surrounding environment to have been successfully eliminated. Signs of Cu surface presence in the EDS results of Fig. 7 probably originated as X-ray emissions from deeper regions.

A triple-layer coating has been successfully deposited on the Al substrate in the present study, which successfully boosted corrosion resistance. Proposed micro-mechanisms have been based on various observations and characterizations. New findings will foster development of even more effective electroless deposition procedures in the future.

4. Conclusions

An electroless deposition technique coating an AA6082 alloy with a triple Zn–Cu–Sn layer has been shown to enhance corrosion resistance. Electroless deposition parameters of the Sn layer were varied to study the deposition reactions and micromechanisms. Main conclusions are as follows.

- Fifteen different Sn layers were deposited on Zn–Cu substrates subject to various times (400s–3600s), temperatures (25–65 °C), and bath concentrations (C, 1.5C, and 2C). Peak layer quality was deposited at T = 45 °C, C = 1.5C for 1200s. EIS analysis shows substantial corrosion resistance for the aluminum samples coated by this procedure.
- The Sn layer nucleates and expands heterogeneously from small isolated bulges into large crystal crowns as they outgrow the nearby trenches of lower Sn concentration levels. Microstructural observations indicate evidence of growth in crystallographic planes.
- Sn deposition activates via three reactions: displacement, reduction and disproportionation. Displacement initiates until bath solution engages the Cu substrate. As the Cu substrate gradually coats with Sn, displacement subsides in favor of the remaining two reactions that supply Sn directly from solution.
- The island type Sn electroless plating layer on Cu is an evidence that the Cu dissolution control the electroless plating, and the plating bath could not give a dense Sn layer. However, micro porous Sn coating may offer a better corrosion resistance due to the cathodic protection.

Fig. 10. SEM micrograph showing the top view of a tin crown, and schematic drawing showing successive stages in the crystal’s growth.

Fig. 11. (a) Nyquist plots and EIS Equivalent circuit, (b) BODE diagram of Zn/Cu- and Zn/Cu/Sn-coated samples. (This must be printed in colors).
Table 2
Simulation and fit results of EIS equivalent circuit for Zn/Cu and Zn/Cu/Sn samples.

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<th>Parameter</th>
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Fig. 12. EIS polarization plots and TAFEL extrapolation results of the two Zn/Cu and Zn/Cu/Sn samples.

Conflicts of interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References