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Electroless Plating Lead and Lead-Tin on Copper Using an Eco-Friendly Plating Bath

A. B. Abdel-Aziz[1*], M. M. B. El-Sabbah[2], I. M. Ghayad[3*], Adham A. El-Zomrawy[2*]

[1]October High Institute for Engineering & Technology, Giza Governorate, Egypt
[2]Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt
[3]Central Metallurigical R & D Institute, Cairo, Egypt
Email: *ighayad@yahoo.com, abdelazezbadawy3@gmail.com, *azomrawy.1@azhar.edu.eg

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Abstract

Copper serpentines used in gas heaters are currently coated with lead-tin alloy using hot-dip technology where copper is immersed in molten lead (98%)-Tin at about 400˚C. The major drawback of this technique is the pollution resulted from lead vapors which cause much harm to the labors in the unit. The present work investigates an eco-friendly plating technique to replace the currently used technology. Electroless plating of copper samples with lead or Lead (98%)-Tin alloy is carried out from a plating bath contained lead salt, tin salt, reducing agent and stabilizing agent. The parameters affecting the coating quality such as the plating time, temperature and bath composition were optimized. The chemical analysis and coating morphology of the formed coatings are examined by XRD, SEM and EDS to reach the best bath composition as well as the best conditions to coat copper with lead or lead-tin electrolessly. The electrochemical properties of copper and copper coated samples are also examined using electrochemical impedance spectroscopy.

Keywords

Copper Serpentine, Hot Dip Coating, Lead-Tin, Electro Plating, Electroless Plating

1. Introduction

Plating has been used for many years, it is critical for contemporary technology. Plating is applied for decorating objects, corrosion protection, improving solder ability, harden ability and wear ability, reducing friction, improving paint adhesion, altering conductivity, improving IR reflectivity, radiation shielding, and other purposes. Using environmentally friendly cheaper plating solutions is more favorable within the industrial purposes. In spite of the very fact that lead is pronouncedly susceptible to corrosion than copper, but lead and lead-tin alloy coatings have the advantageous to protect the base metal from oxidation especially at high temperature. Copper serpentines utilized in gas heaters are currently coated with lead-tin alloy using hot-dip technology. Historically, the hot-dip has been a very common coating method where copper is immersed in molten lead (98%)-Tin at about 400˚C. However, this method is accompanied with a dangerous pollution problem resulted from lead vapors which cause much harm to the labors. Pollution control policies do not allow lead emissions and should cause a financial penalty.

In order to solve the problem, alternative methods for plating lead-tin on copper should be proposed. Electroless and Electroplating are the two methods used for plating metal onto a substrate. Electroless plating lead or lead-tin on copper becomes an alternative coating method where copper is immersed in an electroless solution bath. These bathes consist of lead ions, tin ions, reducing agent, complexing agent, stabilizing agent and surfactant. Electroless plating technique produces compact, thin, smooth and adherent coat.

Examples of coating metals by lead or lead-tin using some eco-friendly plating techniques and the important additives of the bathes are reviewed. The electroless plating of copper by tin can be performed by immersion in tin plating bath of $SnCl_2 \cdot 2H_2O$, cyanide ion as complexing agent and $NaHCO_3$ for adjusting the pH of the solution [1]. Plating copper with an alloy of 60% Sn/40% Pb by immersion in plating bath has a composition comprising an organic sulfonic acid, divalent tin and lead salts of the organic sulfonic acid and thiourea at low temperature region within a short span of time [2]. The process for electroless plating lead on a metal such as copper comprises subjecting the metal to a solution consisting essentially of a lead salt and thiourea dissolved in dimethylsulfoxide. The lead salt may be, for example, lead nitrate, lead chloride or lead acetate [3]. Electroless plating tin, lead, or tin-lead alloy showed that the plating mechanism may be characterized in that copper is dissolved into the bath from copper or copper alloy and at the same time tin, lead or tin-lead alloy is deposited on the substrate [4]. Coating aluminum with lead or lead alloys are preferred so as to give a dense, adherent, fine-grained deposit of a lead alloy [5]. The electrode position of lead from electrolyte containing acetic acid, ammonium acetate and chloride ions at 25˚C under well stirring with the addition of organic additives like phenol, ethyl alcohol or gelatin to obtain a bright, smooth and compact lead deposited on copper electrode [6]. High speed plating using high current densities needs the addition of a defoaming agent comprised of silicone and silica and/or silicate in a polypropylene glycol to a bath comprised of tin and/or lead salt of alkane sulfonic acid, free alkane sulfonic acid, brightening agent and a surfactant consisting of an ethoxylatedarylphenol and an ethoxylated short-chain alcohol [7].

The present work investigated the electroless plating of lead or lead (98%)-tin on copper using an ecofriendly-plating bath. The work aims to replace the currently used environmentally polluted technique of lead (98%)-tin coating on copper pipes of gas heaters by an ecofriendly technique.

2. Experimental

Experimental work involves electroless plating of copper by lead or lead-tin alloy using different bathes so as to reach a more efficient and easier electroless plating method. Copper samples measures 2 cm × 2 cm × 1 mm were used as substrates in the electroless plating experiments. Copper samples were degreased in a commercial degreaser and then activated in 20% H_2SO_4 for 10 min. Activated copper samples were immersed in the electroless plating bathes as shown below. All plating experiments were carried out at 70˚C for 1 hr.

In lead plating bath (**Table 1**) lead acetate was used as the source of lead, thiourea was used as reducing agent, EDITA was used as complexing agent, and

Table 1. Electroless lead and lead-tin plating bathes.

Bath (1)		Bath (2)	
Bath composition	**Concentration g/l**	**Bath composition**	**Concentration g/L**
Lead acetate	200	Lead acetate	200
Thiourea	70	Thiourea	70
EDTA	5	Stannous chloride	10
Gelatin	5	EDTA	5
		Gelatin	5
Bath (3)		**Bath (4)**	
Bath composition	**Concentration g/l**	**Bath composition**	**Concentration g/l**
Lead nitrate	200	Lead nitrate	200
Thiourea	70	Thiourea	70
EDTA	5	Stannous chloride	10
Gelatin	5	EDTA	5
		Gelatin	5
Bath (5)		**Bath (6)**	
Bath composition	**Concentration g/l**	**Bath composition**	**Concentration g/l**
Lead oxide	140	Lead oxide	140
Acetic acid	80 ml/l	Acetic acid	80 ml/l
Thiourea	70	Thiourea	70
EDTA	5	Stannous chloride	10
Gelatin	5	EDTA	5
		Gelatin	5

gelatin was used to increase the adhesion of coating on copper surface. Lead nitrate was used as an alternative source of lead to be plated on copper. Lead acetate can be prepared insitu by the reaction of lead oxide and acetic acid. In lead-tin plating bath (**Table 1**) stannous chloride was added as a source of tin so as to give a bright, smooth, adherent and more corrosion resistant coat.

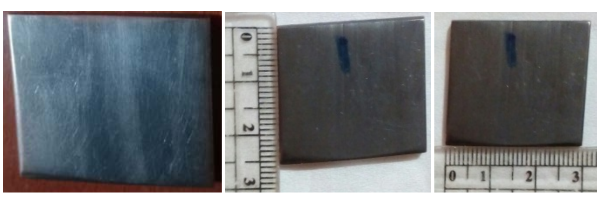
Scanning electron microscope (SEM) was used to examine the surface morphology of coated samples. Prior to SEM investigation, samples were washed with deionized water and cleaned ultrasonically in acetone to improve the images quality. Cross sections of coated samples were also investigated under the SEM to determine the coating thickness. The elemental analysis of the coatings was performed using electron dispersive spectroscopy (EDS) unit attached with the SEM instrument.

Electrochemical impedance (EIS) technique was used to evaluate the electrochemical behavior of the uncoated and coated samples in different conditions. Tests were performed using three electrodes corrosion cell. The coated sample was used as the working electrode with a 0.785 cm^2 exposed area, a saturated calomel electrode (SCE) was used as the reference electrode and a platinum sheet as the counter electrode. Tests were carried out using a computerized potentiostat (Autolab PGSTAT 30).EIS experiments were performed at room temperature over the frequency range between 1 Hz and 65 kHz at open circuit potential. The amplitude of the sinusoidal voltage signal was 10 mV.

3. Results and Discussion

Preliminary investigations showed that the saturated bath solutions containing lead source and reducing agent yields dense and thick coat under optimized conditions of temperature and time. Photographs of plated samples are shown in **Figure 1**.

SEM was used to examine the surface morphology of coated samples [8] [9]. SEM images of lead-plated copper samples are shown in **Figure 2** while **Figure 3** represents SEM cross section of the plated samples. The lead coating formed using lead acetate as a source of lead shows smooth surface and compact coating layer (**Figure 2(a)**). The cross section of the coating shows regular morphology with average thickness 15.20 μm (**Figure 3(a)**). On the other hand, the lead coating formed using lead nitrate as a source of lead shows non smooth surface while the deposited layer shows elongated non connected granules arranged in an ordered



(a)

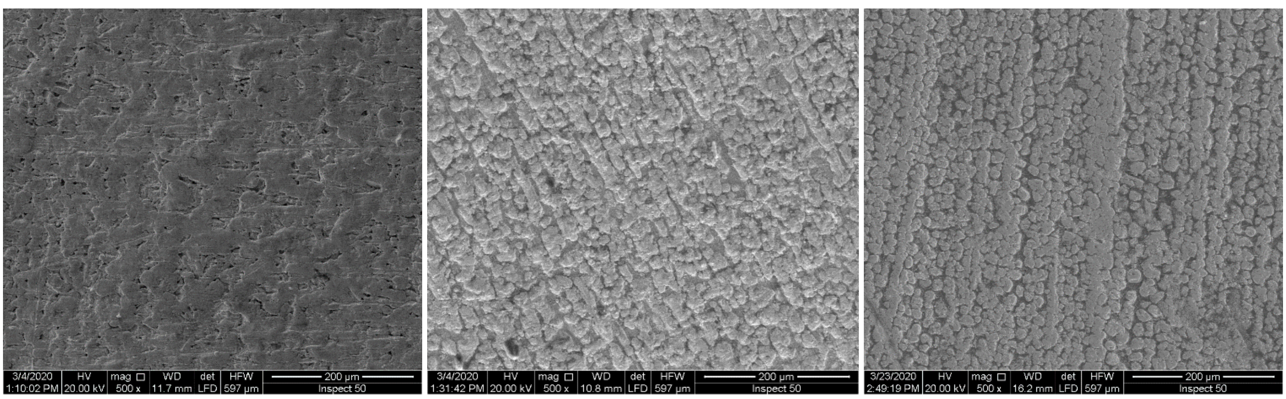
(b)

Figure 1. Photographs of lead-plated copper using lead acetate at 70˚C for 1 h (a) and lead-tin plated copper using lead acetate and stannous chlorideat 70˚C for 1 h (b).

manner (**Figure 2(b)**). The cross section of the coating shows relatively high average thickness of 24.70 μm, however, many cracks are seen (**Figure 3(b)**). The lead coating formed using lead oxide as a source of lead shows non smooth surface with a cluster-like shape. The granules are more distant relative to those obtained using bath 3 (**Figure 2(c)**). The cross section of the coating shows regular morphology with few cracks. The coating thickness is quite low with an average of 4.27 μm (**Figure 3(c)**).

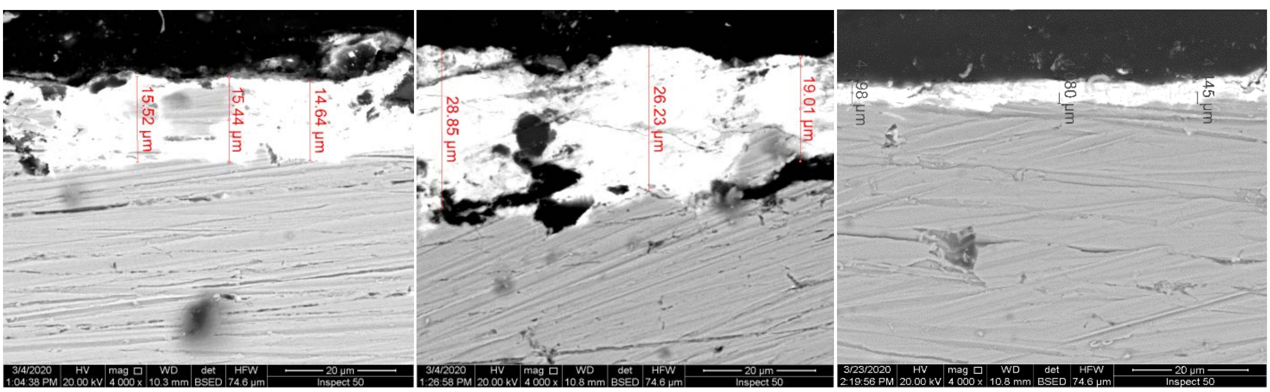
EDS analysis of the formed lead-coating using lead acetate as a source of lead denotes 89.5% Pb, 0.24% Cu and the remaining 10% O as shown in **Figure 4(a)**. This indicates the complete coverage of the copper sample with lead and the presence of oxygen indicated of the formation of stable lead oxide which protects copper from oxidation. On contrary, the formed lead-coating using lead nitrate as a source of lead denotes 45.13% Pb and 54.87% Cu as shown in **Figure 4(b)**. These observations are in conformity with the SEM obtained morphology.

Figure 5 shows the SEM of lead-tin coating using lead acetate as a source of lead and stannous chloride as a source of tin gives a compact coating layer free of cracks. The SEM cross section of the coating shows regular morphology with an average thickness 13.06 μm as shown in **Figure 6**.



(a) (b) (c)

Figure 2. SEM of lead-plated copper at 70˚C for 1 h and different lead sources: (a) lead acetate, (b) lead nitrate and (c) lead oxide.



(a) (b) (c)

Figure 3. SEM cross section of the lead-plated copper at 70˚C for 1 h and different lead sources: (a) lead acetate, (b) lead nitrate and (c) lead oxide.

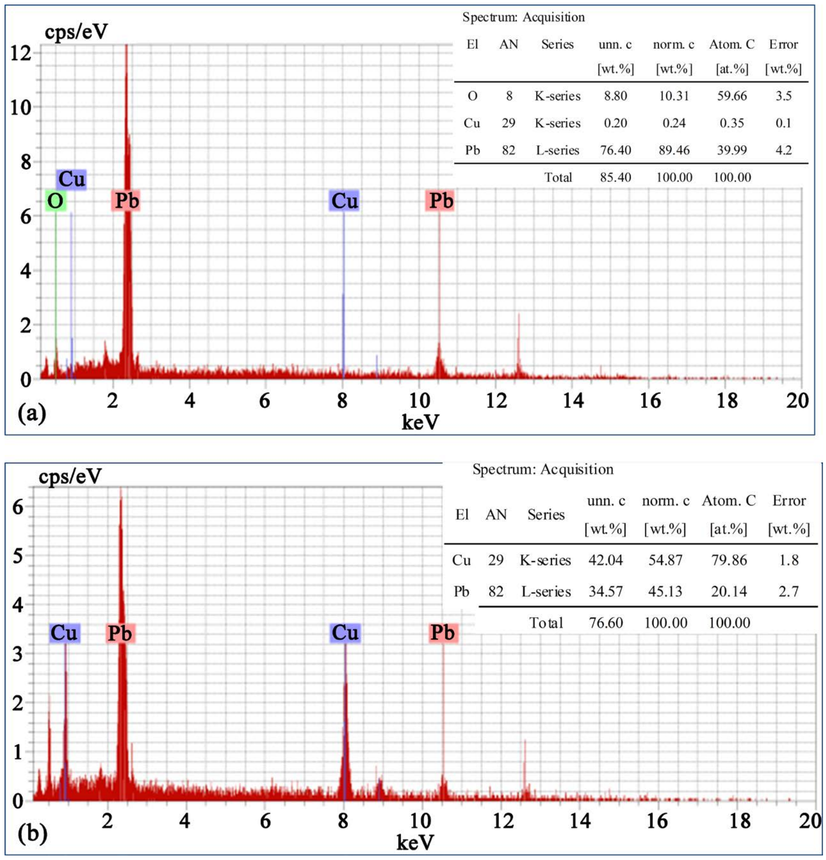


Figure 4. EDS of the lead-plated copper at 70˚C for 1 h using lead acetate (a) and lead nitrate (b).

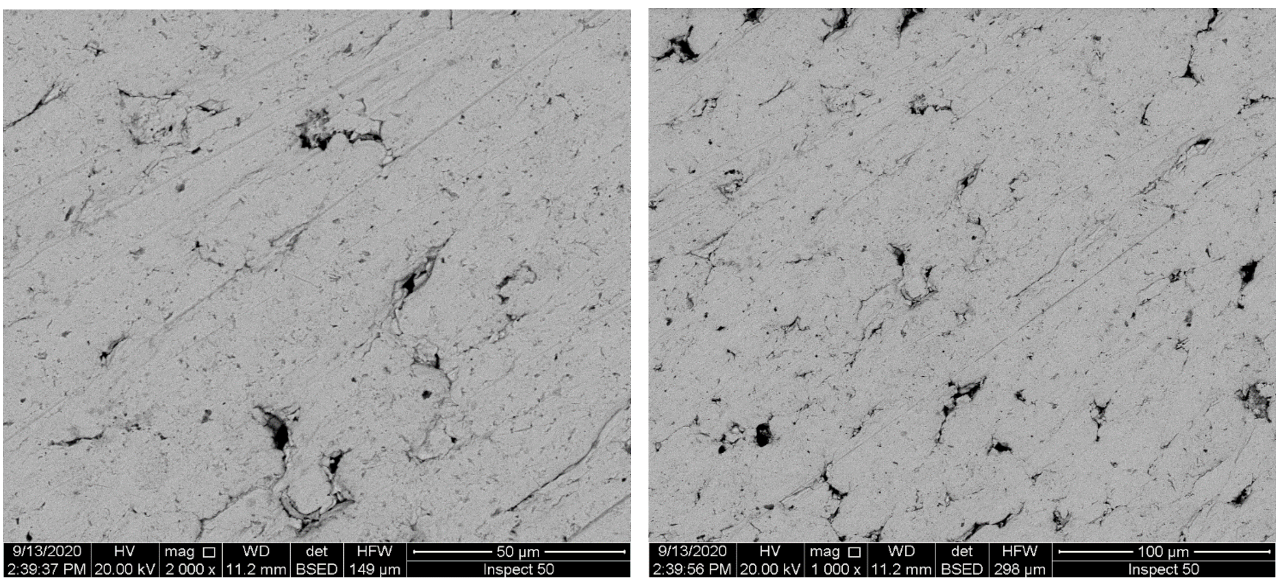


Figure 5. SEM of lead-tin plated copper at 70˚C for 1 h using lead acetate & $SnCl_2$.

EDS analysis for lead-tin plated copper formed using lead acetate as a source of lead and stannous chloride as a source of tin denotes 99.48% Pb and 0.52% Sn with no presence of copper (**Figure 7**). This indicates a complete coverage of

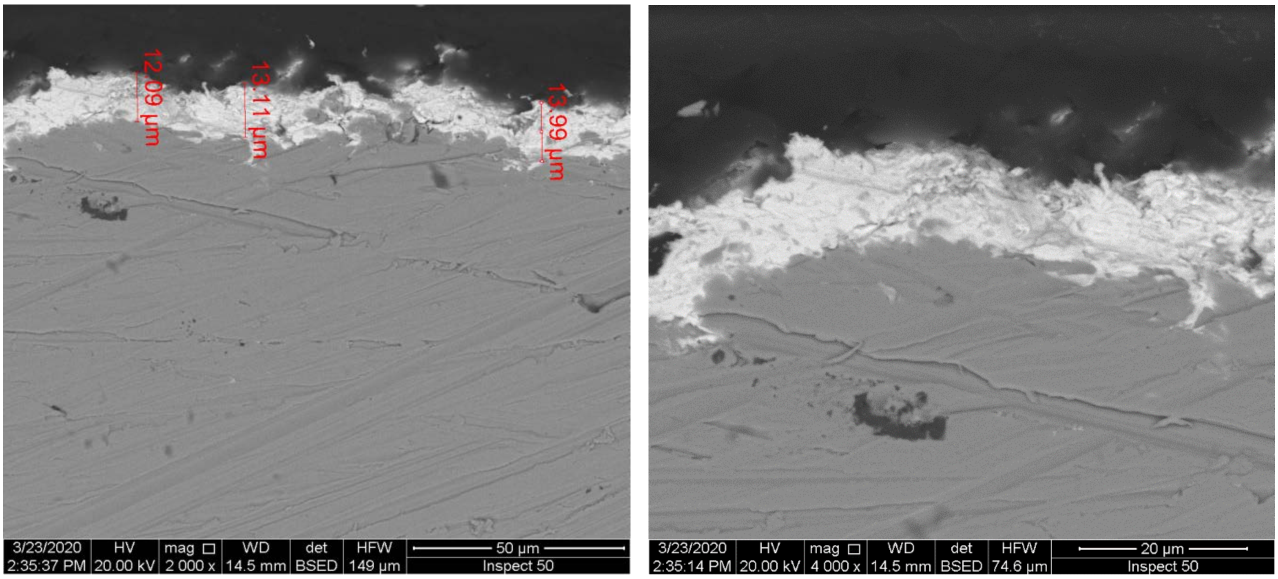


Figure 6. SEM cross section of lead-tin plated copper at 70˚C for 1 h using lead acetate & $SnCl_2$.

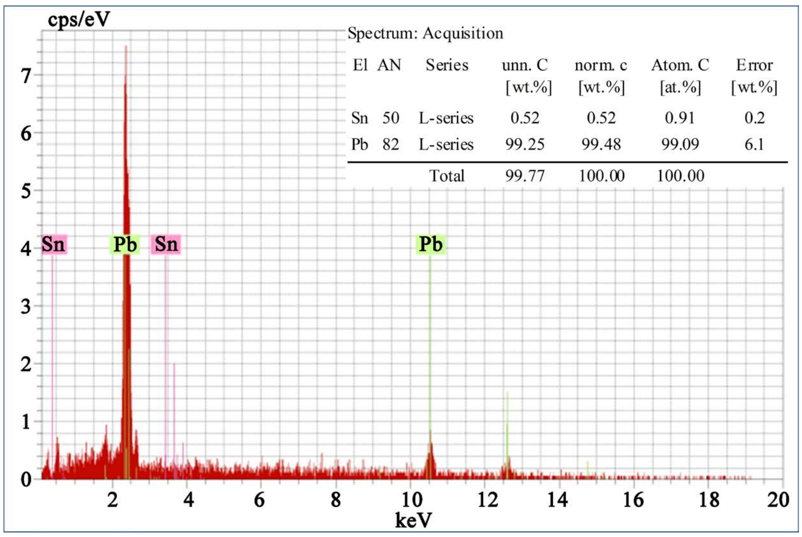


Figure 7. EDS of lead-tin plated copper at 70˚C for 1 h using lead acetate & $SnCl_2$.

copper with lead-tin alloy and very compact coating layer with no cracks. It is expected that the thickness of coating will increase with the increase of the percent of tin, *i.e.* the amount of $SnCl_2$ in the bath and also good stirring condition.

The corrosion behavior of uncoated copper and lead, lead-tin coated samples were investigated in 3.5% NaCl solution using electrochemical impedance spectroscopy (EIS) technique. The EIS experiments of samples treated in 6% NaCl hot water (90˚C) for 6 hours were also performed to address the effect of high temperature on the corrosion behavior of the coated samples in comparison to the blank. EIS results were presented using Nyquist, Bode and Phase angle plots. Figure 8(a) shows Nyquist plot of non-heat treated samples while Table 2 shows the analysis results of Nyquist plots. Blank sample shows higher polarization

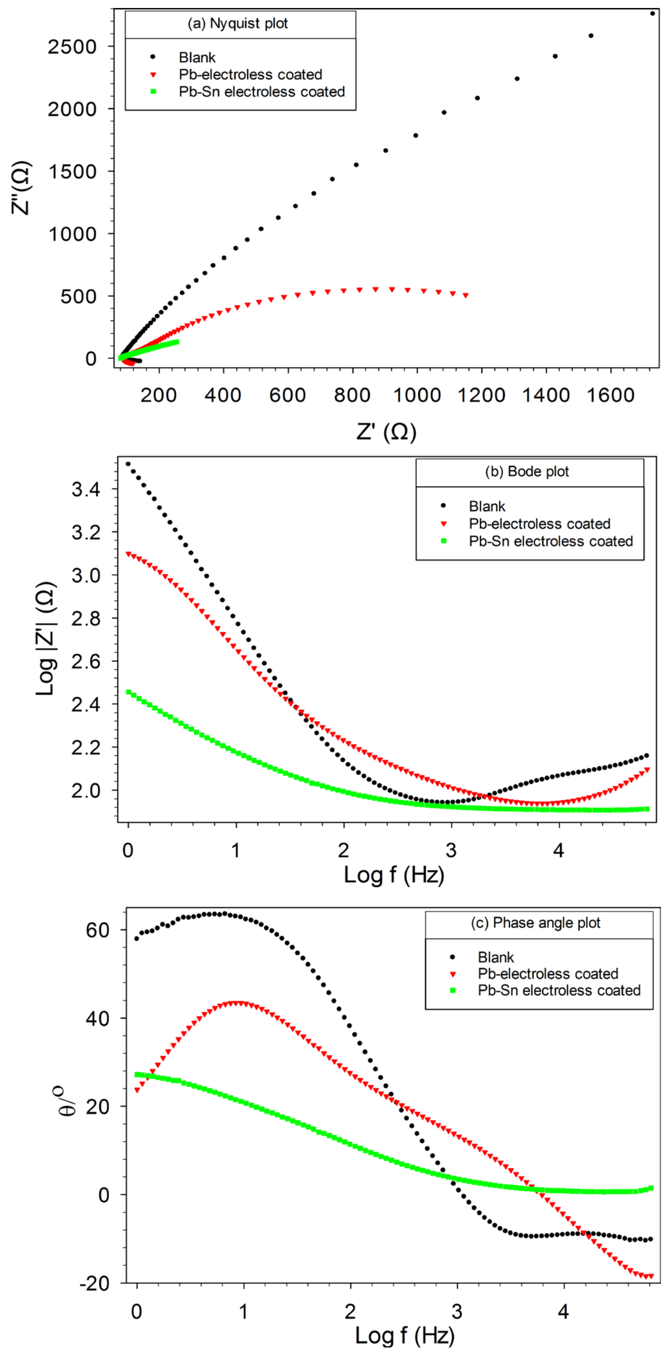


Figure 8. EIS spectra of uncoated, lead-coated (bath 1) and lead-tin coated (bath 2) copper samples in 3.5%NaCl solution (a) Nyquist plot, ((b) & (c)) Bode plot.

Table 2. Impedance parameters for blank, Pb-coated sample and Pb-Sn coated sample in 3.5% NaCl solution.

Sample	Z (Ω)	θ Degree (˚)	R_s (Ω)	R_p (Ω)
Blank	1731	63.52	80.80	14,424.9
Pb-coated sample	1150	43.44	86.75	1653.09
Pb-Sn coated sample	254	27.20	80.12	1169.49

resistance than the coated samples. In contrary lead-tin coated sample of lead acetate and stannous chloride shows the highest polarization resistance of 3363.80 Ω after treatment in hot 6% NaCl solution as shown in Figure 9(a) and Table 3. The incorporation of small percent of tin (2%) to the lead coating solution increased the polarization resistance from 685.27 Ω for lead-coating surface to 3363.80 Ω for lead-tin coated surface. The uncoated sample shows the worst behavior giving 569.12 Ω.

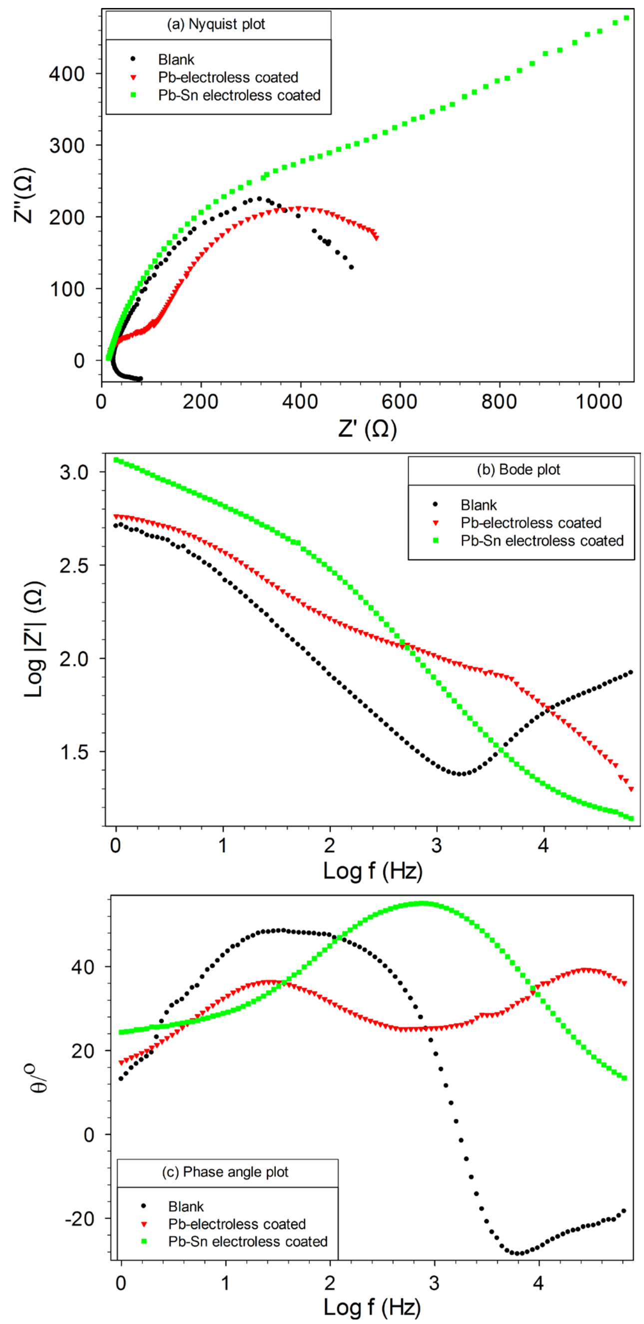


Figure 9. EIS spectra of uncoated, lead-coated (bath 1) and lead-tin coated (bath 2) copper samples in 3.5% NaCl solution (a) Nyquist plot, ((b) & (c)) Bode. Samples were treated in hot water (90˚C) for 6 h.

Bode plots (Figure 8 & Figure 9(b)) and Table 2 & Table 3 represent the same trend observed by Nyquist plots for the non-heat treated and the heat treated samples. (Figure 8 & Figure 9(c)) and Table 2 & Table 3 show the phase angle "θ" plots of the non-heat treated and the heat treated samples. Regarding the non-heat treated samples, the blank sample shows the highest phase angle of 63.52˚ compared to the lead and lead-tin coated sample values of 43.44˚ and 27.20˚, respectively. For the heat treated samples the lead-tin coated shows the highest phase angle of 55.10˚.

The EIS results predict the importance of lead and lead-tin coating in protecting copper from corrosion at high temperature. However lead-tin coating shows better resistance than lead-only coating.

Figure 10 shows X-Ray Diffraction (XRD) analysis of the formed lead and lead-tin coatings where lead acetate and stannous chloride were used as sources

Table 3. Impedance parameters for uncoated, Pb-coated and Pb-Sn coated copper samples in 6% NaCl after prolonged treatment in hot water (90˚C) for 6 h.

Sample	Z (Ω)	θ Degree (˚)	R_s (Ω)	R_p (Ω)
Blank	502.50	48.50	21.54	569.12
Pb-coated sample	552.90	39.25	50.07	685.27
Pb-Sn coated sample	1055	55.10	3.30	3363.80

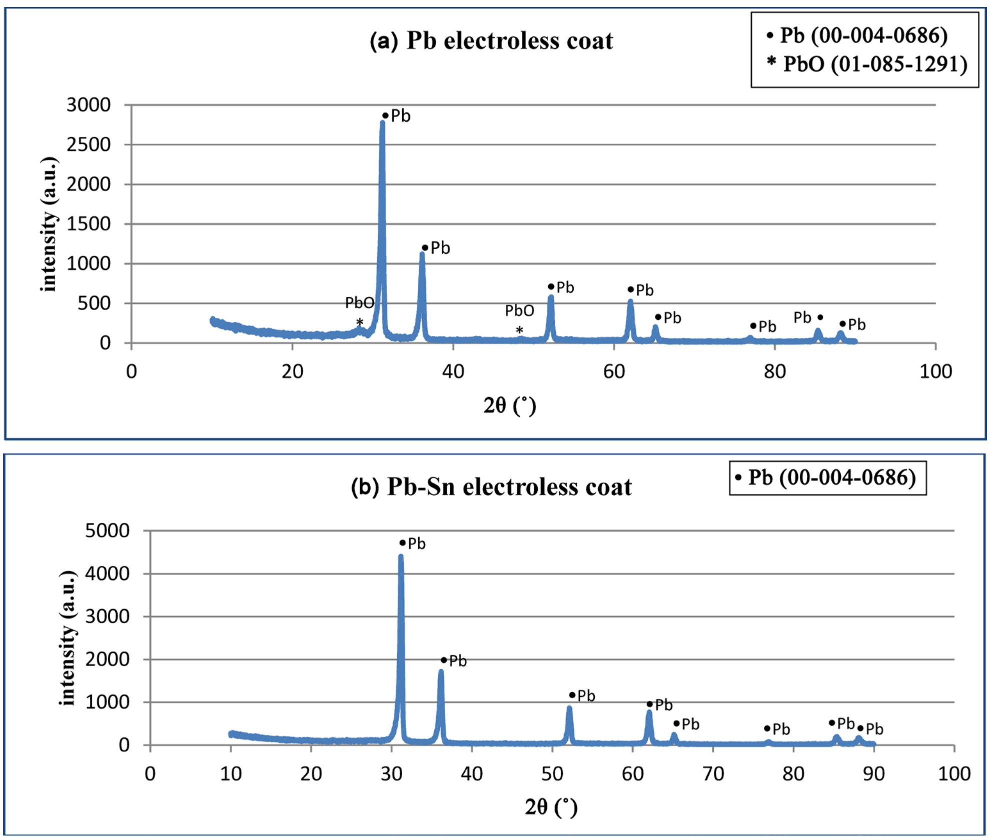


Figure 10. XRD analysis of: (a) lead-coated copper sample (bath 1) and (b) lead-tin coated copper sample (bath 2).

of lead and tin. Lead-coated sample shows peaks of Pbcubic according to card no. (00-004-0686) and PbO tetragonal according to card no. (01-085-1291), while lead-tin coated sample shows only peak of Pb cubic according to card no. (00-004-0686). XRD wasn't able to detect the presence of Sn in the lead-tin coated sample which may be attributed to the low content of Sn in the coating. It is worthy to mention that very low amount (≈0.5%) of Sn was detected in lead-tin coated sample using EDS technique. EDS is a point analysis technique so that it can detect the existing elements irrespective of its content or crystallinity.

After heat treatment of lead-tin coated sample at 100˚C for 6 hours, X-Ray Diffraction (XRD) analysis shows peaks of cubic Pb according to card No. (00-004-0686), PbO tetragonal according to card No. (00-005-0561), Pb_3O_4 tetragonal according to card No. (01-085-0859) and SnO orthorhombic according to card No. (01-077-2296) are shown in **Figure 11**. Heat treatment increases the crystallinity of the formed lead-tin coating, so that the presence of small amount of Sn in the lead-tin coating can be detected.

The present work depicts that the best lead coating morphology, compactness and thickness where obtained using the bath containing lead acetate salt as a source of lead. On the other hand the bath containing lead acetate as a source of lead and stannous chloride as a source of tin was efficient to produce lead-tin coating. The addressed electroless plating technique can be applied easily with high turn-over and can be made-up easily by the addition of the plating solution. Some parameters affecting the quality of coating are discussed below:

1) Temperature

Temperature is a very important parameter to obtain a good morphology coating [10]. Temperature is also a key role during the preparation of the coating solution bath and to avoid settlings of bath ingredients during coating process and also during storage.

2) Stirring

Stirring is important during the formation of coating solutions to quickly make a completely soluble bath. Stirring with slow speed also is very useful during the coating procedure to avoid sedimentation and to distribute the lead or tin ions equally in the whole solution around the copper substrate which aid to

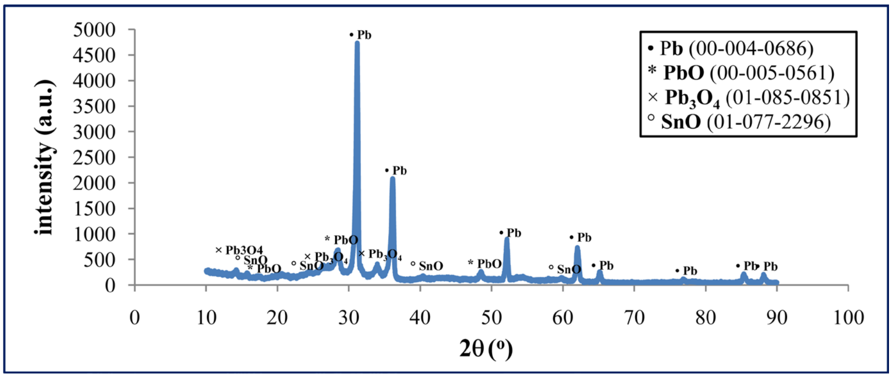


Figure 11. XRD analysis of lead-tin coated sample after heat treatment at 100˚C for 6 h.

obtain a full covered homogeneous coating.

3) Additive agents

There are some additives which are necessary to acquire a coating with the desired properties [11]. The present work involves the testing of some of these additives. After a series of experiments, it was found that the addition of gelatin (5 - 10 g/L) to the bath produces a smooth and bright coating.

4) EDTA

EDTA was found to play a good role in increasing the coating thickness. EDTA is a powerful complexing agent forming a stable complex with lead ions in the bath [12]. The masking effect of EDTA towards lead ions moderates the reduction effect of thiourea. In the absence of EDTA, thiourea reduces lead ions at a higher rate leading to lead precipitation in comparison to lead coating. **Figure 12** shows the expected masking reaction.

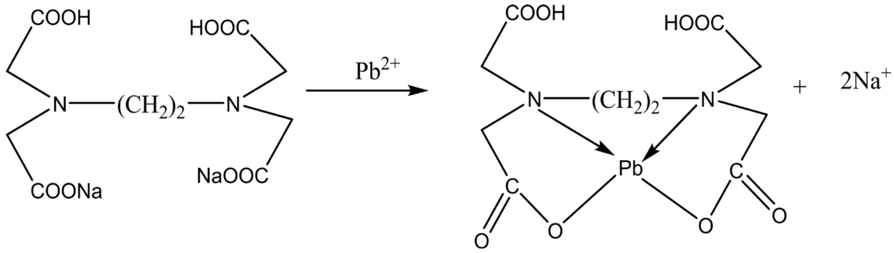


Figure 12. The reaction mechanism of EDTA with lead ions.

4. Conclusions

The present work investigates the electroless lead or lead-tin plating of copper. The following conclusions can be driven:

- The best lead coating morphology was obtained using the plating bath containing lead acetate as the source of lead, thiourea as the reducing agent. EDTA is a complexing agent to moderate the effect of thiourea. Gelatin in the bath serves to smooth the coating. The optimum bath temperature was 70˚C. 1 hour was sufficiently enough to give a well-covered coating.
- In the lead-tin electroless plating, stannous chloride was successfully added as an adequate source of tin.
- EIS results show that the lead and lead-tin coatings improve the corrosion resistance in high temperatures aqueous solutions, which indicates the importance of these coatings in protecting copper serpentines in gas heaters.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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