

# Mechanism for the development of Sn-Cu alloy coatings produced by pulsed current electrodeposition

Wu, L, Graves, J & Cobley, A

Author post-print (accepted) deposited by Coventry University's Repository

**Original citation & hyperlink:**

Wu, L, Graves, J & Cobley, A 2018, 'Mechanism for the development of Sn-Cu alloy coatings produced by pulsed current electrodeposition' *Materials Letters*, vol 217, pp. 120-127

<https://dx.doi.org/10.1016/j.matlet.2018.01.094>

DOI 10.1016/j.matlet.2018.01.094

ISSN 0167-577X

ESSN 1873-4979

Publisher: Elsevier

**NOTICE: this is the author's version of a work that was accepted for publication in *Materials Letters*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Materials Letters*, [vol 217, pp. 120-127, (2018)] DOI: 10.1016/j.matlet.2018.01.094**

© 2018, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International

<http://creativecommons.org/licenses/by-nc-nd/4.0/>

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

# **Mechanism for the development of Sn-Cu alloy coatings produced by pulsed current electrodeposition**

Liang Wu\*, John E. Graves and Andrew J. Cobley

Centre for Manufacturing and Materials Engineering, Coventry University, Coventry,  
United Kingdom, CV1 5FB

\*Corresponding author, Email: [ac3448@coventry.ac.uk](mailto:ac3448@coventry.ac.uk)

## **ABSTRACT**

Pulsed current (PC) electrodeposition has become an essential tool for producing coatings in a wide range of industries. The pulsed current can have a significant influence on the composition, morphology and properties of electrodeposited coatings and this is particularly true when plating an alloy. In this study, the mechanism for the development of Sn-Cu alloy coatings produced by PC electrodeposition was investigated. Sn-Cu alloy coatings produced by PC electrodeposition were essentially composed of a dual layer of Sn-Cu electrodeposits and  $\text{Cu}_6\text{Sn}_5$  intermetallic compounds (IMCs). In addition, it was observed that pulsed Sn-Cu electrodeposits exhibited an increased Cu content. Experiments were carefully designed to elucidate the mechanism for this important finding and based on their results a theory is proposed which explains the increased Cu content in terms of a metal displacement reaction occurring during the 'relaxation' time of PC electrodeposition.

## **KEY WORDS**

Pulsed current techniques, Sn-Cu coatings, electrodeposition, mechanism

## **1. INTRODUCTION**

Tin is an important metal in industry as it can be alloyed with various metals (e.g. Cu, Pb, Bi, Cd, Co, Ni and Zn) to form binary alloy systems. Alloys of Sn-Cu of various compositions are of high interest due to their relatively low cost and excellent corrosion resistance and have found a range of applications in industrial sectors such as electronics, automotive and aerospace depending on their mechanical, thermal and electrical properties [1-3]. A thorough overview of electrodeposition of Sn-Cu alloy coatings can be found in a recent review paper [4]. Pulsed current (PC) electrodeposition exhibits advantages over direct current (DC) electrodeposition in the control of deposit composition, grain size, surface morphology and preferred orientation [5]. The present study was undertaken to investigate the effect of pulsed current (PC) on the characteristics of tin-rich Sn-Cu alloy electrodeposits. To the best of our knowledge, it is the first time that the mechanism of PC electrodeposition on Sn-Cu alloy coatings is thoroughly understood and reported. This mechanism is probably also applicable to electrodeposition of other metal alloys using a PC electrodeposition method.

## **2. EXPERIMENTAL**

Pure Cu panels (Yamamoto B-60-P05) of standard Hull cell size (100 mm × 75 mm × 0.3 mm) were used as cathodes, which first had a 2 μm Ni interlayer electrodeposited on it from a standard Watts bath, followed by a 10 μm Sn-Cu alloy electrodeposit from a commercial electrolyte based on fluoroboric acids. The anode materials used for electrodeposition of Ni and Sn-Cu alloy coatings were a pure Ni and a pure Sn metal panel, respectively. Prior to electrodeposition, the Cu panels were washed with detergent (Decon 90), pickled in a 30 vol. % solution of hydrochloric acid (specific gravity (SG) 1.16) for 1 min, rinsed with deionised water and dried using hot air. The anode materials

underwent the same pre-treatment process. Electrodeposition processes were carried out at various cathode current densities ranged from 5 to 50 mA/cm<sup>2</sup> for different deposition times to achieve a consistent thickness of 10 μm. PC electrodeposition was applied with a frequency of 10 Hz and a duty cycle of 10% using a benchtop pulse reverse rectifier (Plating Electronic GmbH pe86CB-20-5-25-S/GD). No agitation was applied during both direct current (DC) and pulsed current (PC) electroplating.

Scanning electron microscope (SEM) analysis, using a Carl Zeis (Leo) 1530 VP field emission gun scanning electron microscope (FEGSEM), was carried out to investigate the surface morphology of electroplated Sn-Cu alloy coatings. Energy dispersive x-ray (EDX) analysis of the chemical composition of electroplated Sn-Cu coatings was carried out using an Oxford Instruments X-Max 80 mm<sup>2</sup> EDX detector equipped in the FEGSEM. The cross-sectional microstructure of the Sn-Cu alloy electrodeposits were investigated using a FEI Nova 600 Nanolab dual beam focused ion beam (FIB).

### **3. RESULTS AND DISCUSSIONS**

SEM analysis of the surface morphology of Sn-Cu alloy coatings produced by DC electrodeposition is shown in Figure 1. The surface of the samples electrodeposited at 5 mA/cm<sup>2</sup> was populated with irregularly raised features (Figure 1a). EDX analysis showed that these raised features were predominantly composed of Sn (~ 91 wt.%), while a higher Cu content (~ 54 wt.%) was detected from adjacent lower surfaces. The average Cu content over the entire coating electrodeposited at this current density was over 50 wt.%. An increase in current density resulted in an increased number of raised features present on the surface, which gradually developed to cover the entire coating surface (Figure 1b). When the current density was above 30 mA/cm<sup>2</sup>, the initial deposit surface was completely covered by the raised Sn-rich features (Figure 1d). EDX analysis showed that

the electrodeposits having this surface morphology contained a high Sn content (> 95 wt.%). As the current density was further increased, the surface morphology remained very similar and the deposit surface became smoother and more compact (Figure 1 e and f). Based on these observations, it is thought that when a very low current density was applied, Cu (the more noble metal) was first electrodeposited on the cathode surface to form an initial layer of pure Cu. As the reduction potential of the Sn (the less noble metal) was obtained, Sn started to co-electrodeposit with Cu as an alloy. A further increase in the current density enhanced the electrodeposition of Sn and resulted in the development of Sn-rich grains (the raised features) from the Cu-rich coatings, which continued to grow to form a complete coverage.

For PC electrodeposited samples, it was found that the surface morphology remained very similar under the same current density, which suggested that pulsed current had little effect on the surface morphology. Deposition current density was the predominant factor that influenced the surface morphology of the electrodeposited Sn-Cu alloy coatings.

EDX analysis (shown in Figure 2) suggested that the Cu content in the Sn-Cu alloy coatings was inversely proportional to the electrodeposition current density, irrespective of electrodeposition conditions. An increase in current density resulted in a dramatic reduction in the Cu content. More importantly, it was found that a higher Cu content was obtained for PC electrodeposited samples over all the current densities. To understand the role of PC electrodeposition in the chemical composition of the Sn-Cu alloy coatings, immersion tests with the help of EDX and FIB analysis have been used in the current study. Sample I was prepared using DC electrodeposition at a current density of 40 mA/cm<sup>2</sup> for 5 min and the resultant Cu content in the alloy coatings was 1.7 wt.%. Sample II was PC electrodeposited at 10 Hz and 10% duty cycle for 5 min under the same

electrodeposition conditions. The obtained Cu content (2.0 wt.%) of the PC electrodeposited sample was 0.3 wt.% higher than that of Sample I. Since the duty cycle used is 10%, Sample II was in essence subjected to 0.5 min of electrodeposition ( $T_{on}$ ) and 4.5 min of ‘relaxation’ ( $T_{off}$ ). Sample III was firstly DC electrodeposited at 40 mA/cm<sup>2</sup> for 0.5 min, which was the same electrodeposition time as that of Sample II. EDX analysis straight after electrodeposition showed that Sample III exhibited a Cu concentration of 1.5 wt.%. Sample III was subsequently immersed in the Sn-Cu electrolyte for 1 h with no current applied. It is interesting to find that the resultant Cu content of Sample III after immersion was dramatically increased to 45 wt.%. Sample IV went through the same process as Sample III, except that the immersion time was increased from 1 to 24 h, after which the Cu content was increased to 48 wt.%.

FIB analysis was carried out to investigate the cross-sectional microstructure of these samples. It is apparent that there is no major difference between the microstructure of Sample I and Sample II (shown in Figure 3a and b). Both of the DC and PC electrodeposited samples were composed of columnar grains of approximately 1  $\mu$ m in width with vertical grain boundaries. More importantly, it was found that white features were present along the grain boundaries. EDX analysis of the cross-section showed a high Cu content ( $\sim$  36.7 wt%) in the white features, whilst no Cu was detected from the adjacent grains. These results suggested that the white features were in essence Cu<sub>6</sub>Sn<sub>5</sub> intermetallic compounds (IMCs) and is consistent with previous studies that propose that, for Sn-rich Sn-Cu alloy electrodeposits, Cu is present in the form of Cu<sub>6</sub>Sn<sub>5</sub> IMCs precipitated in the grain boundaries [6].

More importantly, it was found that the cross-sectional microstructure of Sample III was significantly different (shown in Figure 3c). A thin layer ( $\sim$  300 nm) was formed on the

top surface with the presence of a few holes in the Sn-Cu layer. EDX analysis of the newly formed layer showed a Cu content of 35.4 wt.% and the rest was Sn, which is similar to that of Cu<sub>6</sub>Sn<sub>5</sub> IMCs found in Sample I and II. Hence, it is proposed that the newly formed layer was in essence Cu<sub>6</sub>Sn<sub>5</sub> IMCs. Based on these observations, it is conjectured that when the Sn-rich Sn-Cu alloy samples were immersed in the electrolyte with no current applied, since Sn is more reactive than Cu, a metal displacement reaction can spontaneously occur between Sn and Cu, based on the equation below:



In other words, Sn atoms in the Sn-Cu coatings are exchanged with the Cu ions in the electrolyte and the Cu ions are reduced and form what is commonly termed an immersion deposit of Cu. Since Sn and Cu react with each other very quickly, more Sn atoms in the Sn-Cu coatings migrate to the surface to react with the reduced Cu atoms and form the Cu<sub>6</sub>Sn<sub>5</sub> IMCs. Accordingly, a new layer of Cu<sub>6</sub>Sn<sub>5</sub> IMCs is formed on the top surface and holes are present in the Sn-Cu coatings due to Sn atom depletion. This assumption is strengthened by the further analysis of Sample IV, which exhibited a similar microstructure as Sample III, with the presence of a much thicker (~ 2.5 μm) Cu<sub>6</sub>Sn<sub>5</sub> IMCs layer and larger holes in the Sn-Cu coatings (shown in Figure 3d). An increase in the ‘relaxation’ time provided longer period for the occurrence of metal displacement reaction and hence resulted in a thicker Cu<sub>6</sub>Sn<sub>5</sub> IMCs layer.

Based on all these observations, the mechanism for the development of Sn-Cu alloy coatings produced by PC electroplating is understood. A layer of Sn-Cu alloy coatings was first electrodeposited on the cathode surface during the T<sub>on</sub> time of PC electrodeposition. When the current was switched off (i.e. the ‘relaxation’ time of PC electrodeposition), a metal displacement reaction between Sn and Cu occurred and Cu

ions in the electrolyte were reduced on the deposit surface to form a layer of  $\text{Cu}_6\text{Sn}_5$  IMCs on the electrodeposited Sn-Cu alloy coatings. The Sn-Cu alloy coatings produced by PC electrodeposition were in essential composed of a dual layer of Sn-Cu electrodeposits and  $\text{Cu}_6\text{Sn}_5$  IMCs. The increased Cu content for PC electroplated samples was attributed to the occurrence of metal displacement reaction during the 'relaxation' time.

#### 4. CONCLUSIONS

Cu content in the Sn-Cu alloy coatings was inversely proportional to electrodeposition current density.

PC electrodeposition was more favourable for the co-electrodeposition of Cu, compared with DC electrodeposition.

The Sn-Cu alloy coatings produced by PC electrodeposition were **in essential** composed of a dual layer of Sn-Cu electrodeposits and  $\text{Cu}_6\text{Sn}_5$  IMCs.

A mechanism for the increased Cu content for PC electrodeposited samples has been elucidated and was attributed to **the occurrence of a metal displacement reaction** between Sn and Cu occurring during the 'relaxation' time.

#### 5. REFERENCES

- [1] Tin and Tin Alloys, Total Materia,  
<http://www.totalmateria.com/page.aspx?ID=CheckArticle&site=ktn&NM=26>,  
2001, (accessed 01 Decemebr 2017)
- [2] C.T.J. Low, F.C. Walsh, Normal and Anomalous Electrodeposition of Tin-Copper Coatings from a Methanesulfonic Acid Bath containing a Perfluorinated Cationic Surfactant, Transactions of the Institute of Metal Finishing, 86, (2008), 315-325.

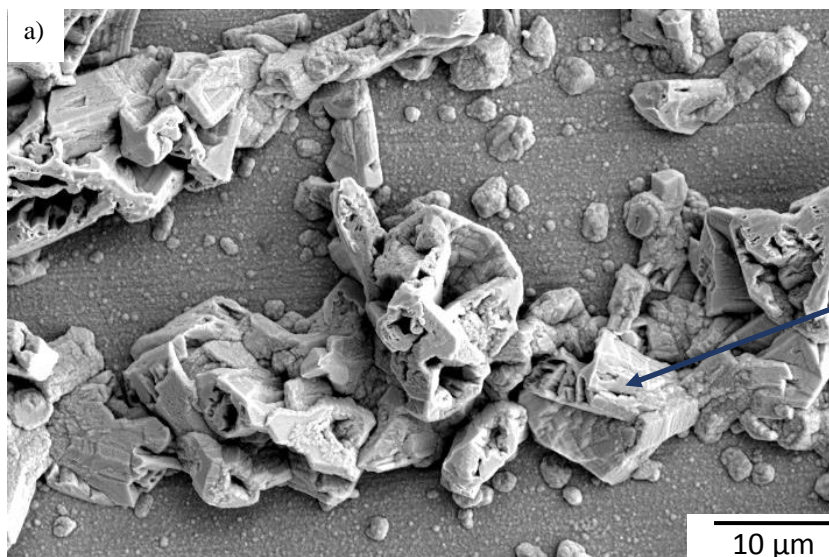


- [3] C.T.J. Low, E.P.L. Roberts, F.C. Walsh, Numerical Simulation of the Current, Potential and Concentration Distributions along a Rotating Cylinder Hull Cell Cathode, *Electrochimica Acta*, 52, (2007), 3831-3840.
- [4] F.C. Walsh, C.T.J. Low, A Review of Developments in the Electrodeposition of Tin-Copper Alloys, *Surface & Coatings Technology*, 304, (2016), 246-262.
- [5] M.S. Chandrasekar, M. Pushpavanam, Pulse and pulse reverse plating- Conceptual, advantages and applications, *Electrochim. Acta.*, 53, (2008), 3313–3322.
- [6] K.W. Moon, M.E. Williams, C.E. Johnson, G.R. Stafford, C.A. Handwerker, W.J. Boettinger, The Formation of Whiskers on Electroplated Tin Containing Copper, in: *Proc. 4th Pacific Rim Inter. Conf. Adv. Mater. Process.*, Gaithersburg, USA, 2001: pp. 1115–1118.

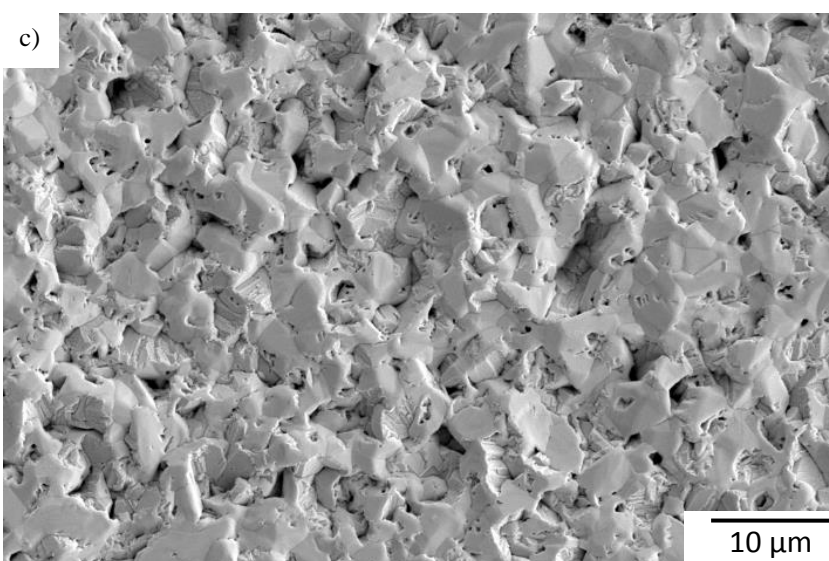
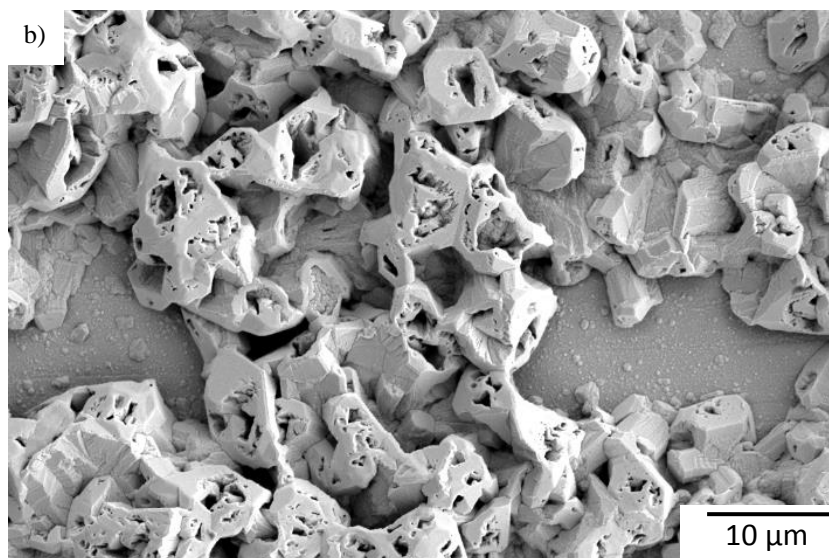
## **ACKNOWLEDGEMENTS**

The authors would like to thank **the European Union’s Horizon 2020 Research and Innovation programme** for funding this research as part of the BeLEADFREE project.

**FIGURES**



Sn: 91.3%  
Cu: 5.8%  
C: 2.1%  
O: 0.8%



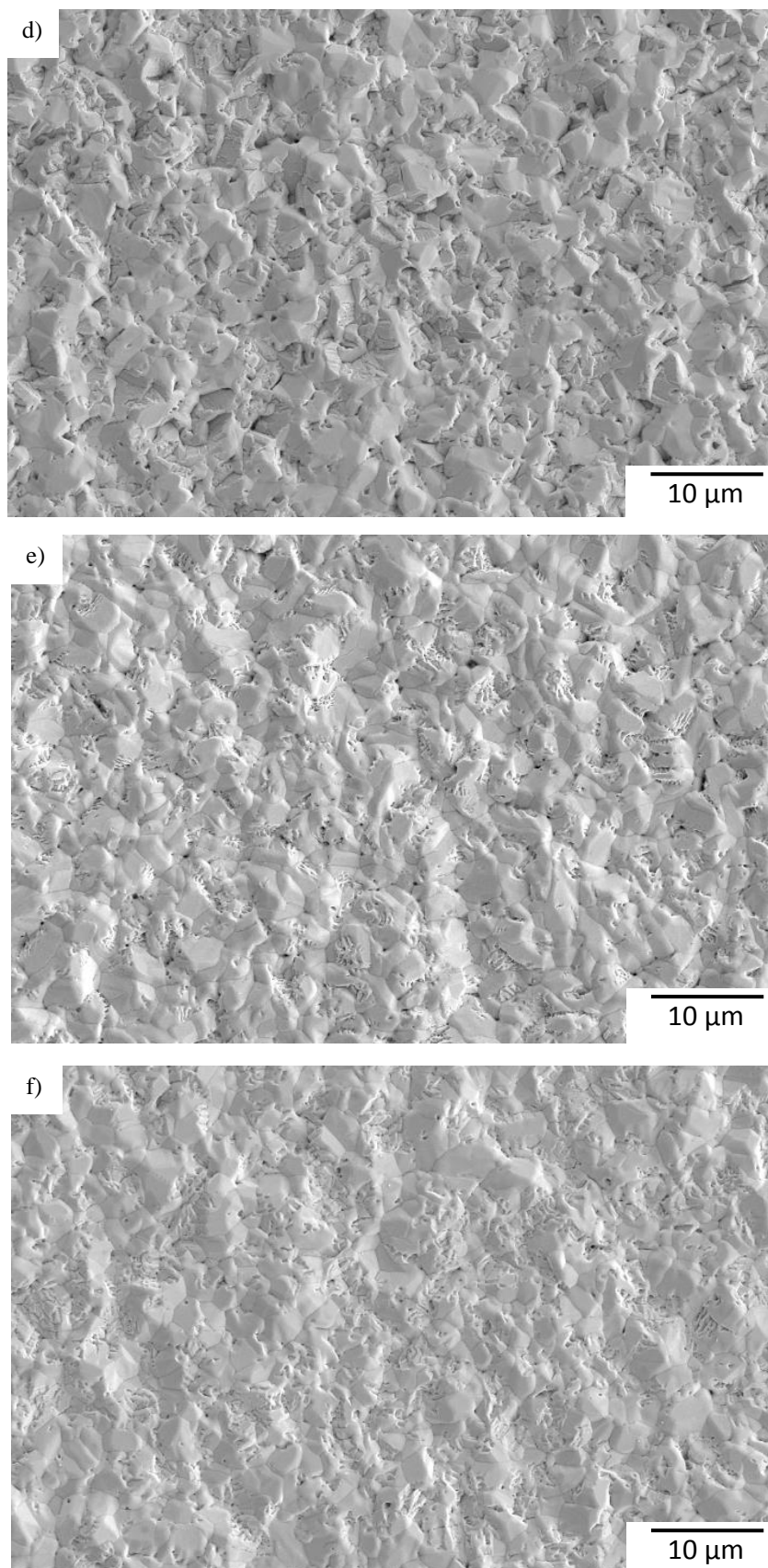


Figure 1 FEGSEM images showing the surface morphology of Sn-Cu alloy coatings electrodeposited at different current densities: a)  $5 \text{ mA/cm}^2$ , b)  $10 \text{ mA/cm}^2$ , c)  $20 \text{ mA/cm}^2$ , d)  $30 \text{ mA/cm}^2$ , e)  $40 \text{ mA/cm}^2$ , f)  $50 \text{ mA/cm}^2$

Cu content/wt.%

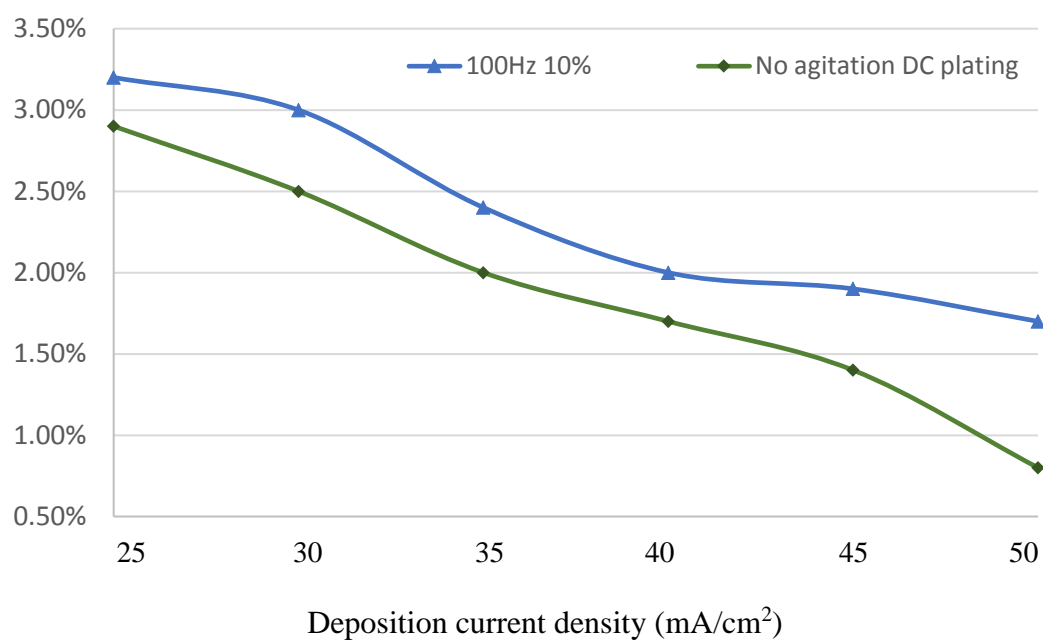
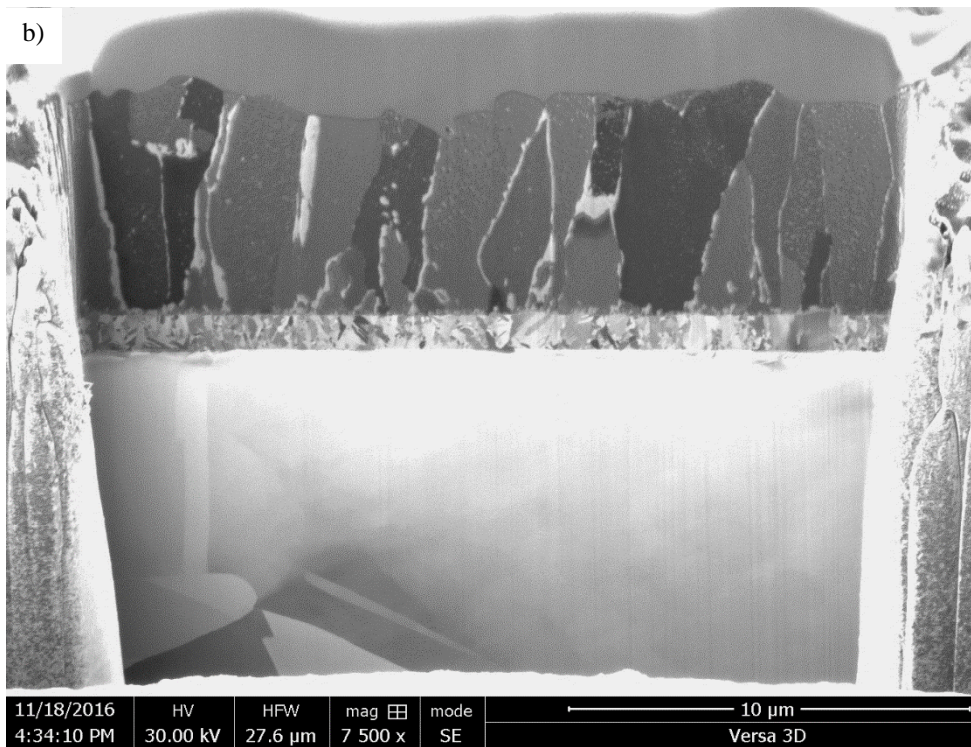
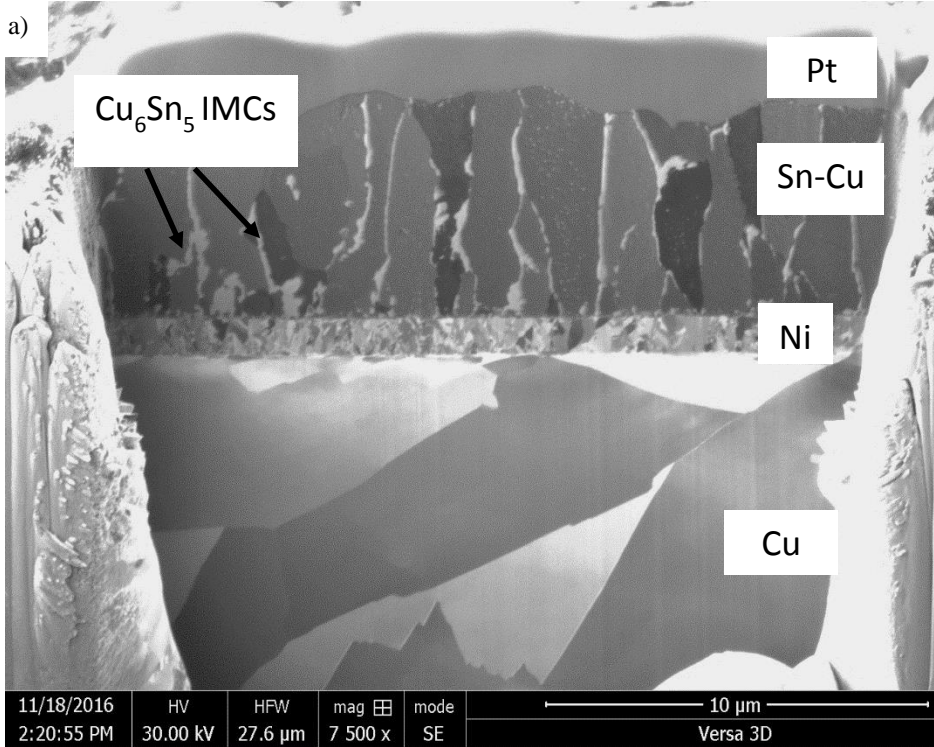


Figure 2 EDX analysis showing the effect of pulse current electrodeposition on the Cu content in the electroplated Sn-Cu alloy coatings



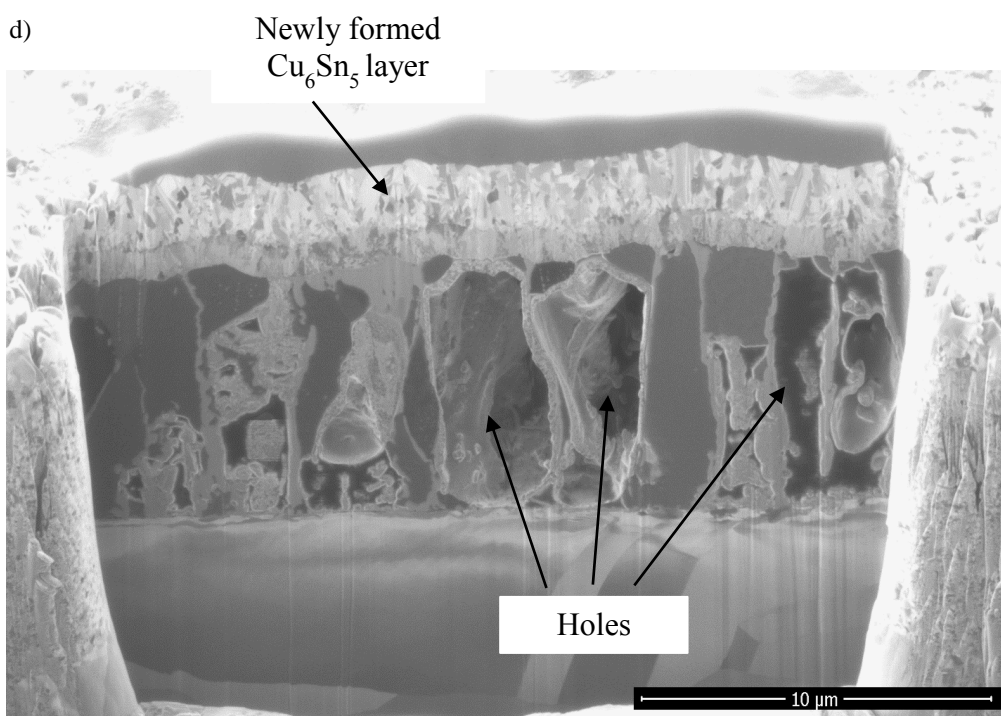
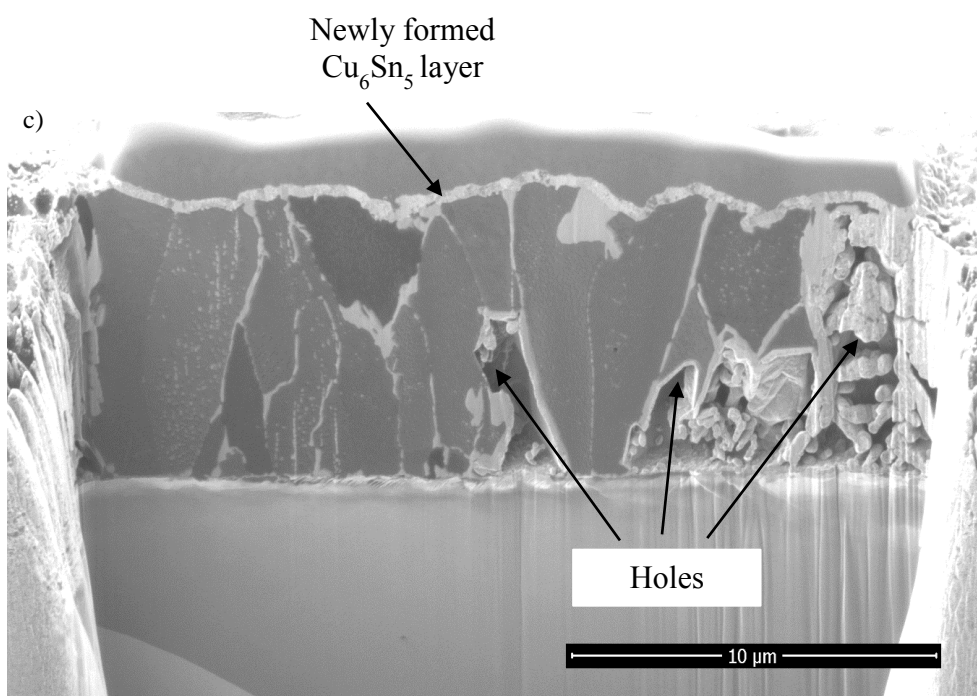


Figure 3 FIB images showing the cross-sectional microstructure of the electrodeposited Sn-Cu alloy coatings on Cu substrates: a) DC electrodeposition at a current density of  $40 \text{ mA/cm}^2$  for 5 min, b) PC electrodeposition (10 Hz and 10% duty cycle) at a current density of  $40 \text{ mA/cm}^2$  for 5 min, c) PC electrodeposition (10 Hz and 10% duty cycle) at a current density of  $40 \text{ mA/cm}^2$  for 0.5 min and then immersed in the electrolyte with no current applied for 1 h and d) PC electrodeposition (10 Hz and 10% duty cycle) at a current density of  $40 \text{ mA/cm}^2$  for 0.5 min and then immersed in the electrolyte with no current applied for 24 h