Environmental Influence on Sn Whisker Growth

Aleksandra Dimitrovska and Radovan Kovacevic

***Abstract*—This paper considers the influence of 1) humidity and 2) acidic humidity on the growth of Sn whiskers. Sn whisker morphology was observed over a six-month period. The results show that the electroplated surfaces exposed to pure humidity are populated with Sn whiskers dimensionally smaller than surfaces exposed to acidic humidity. Variables analyzed include surface condition, Cu–Sn inter-metallic formation at the film/substrate interface by X-ray Diffraction (XRD), and film thickness.**

***Index Terms*—Cu_6Sn_5 intermetallic compounds (IMCs), oxidation, Sn electroplating, Sn whisker growth, X-ray Diffraction (XRD).**

I. Introduction

FOR many years tin–lead (Sn–Pb) alloy was the main alloy for coating electronic components [1]. However, the recent legislation established in Europe on July 1, 2006, required significant Pb content reductions from electronic hardware due to its toxic nature [1], [2]. The popular coating alternative to the Sn–Pb alloy finish was pure Sn finish [1]–[3]. Unfortunately, pure or high tin (Sn) tends to easily form electrically conductive Sn whiskers that can cause failures in electronic components [1]–[4]. The unpredictable behavior of Sn whiskers has triggered many researchers in the past several decades to study the complex nature of their growth.

The research community has agreed on some of the fundamental issues related to the understanding Sn whisker growths, such as follows.

1) Sn whiskers are usually single crystals.
2) Whiskers are a very significant reliability problem.
3) Oxide formation is associated with volumetric expansion of surface layers of the metal. This could conceivably cause change of mechanical stress in the surface.[5]
4) Compressive stress is the primary driving force for Sn whisker growth [1]–[9].

Sn has a high affinity for oxygen as soon as it is exposed to any oxidizing environment [1], [5]. Oxygen is believed to diffuse preferentially along the grain boundaries of the Sn film [10]. Inside the grain boundaries, the oxides act as impurities and produce pinned grain boundaries [10]–[12]. The pinned grain boundaries along with the tin/oxygen reaction produce a positive volume change leading to an increase in compressive stress which in turn causes Sn whisker formation [9], [10], [13]–[15]. Humidity accelerates oxide formation and therefore, accelerates whisker formation [1]–[3], [7], [16]–[18].

In this paper, two groups of tin electroplated brass samples (group one with 2-μm and group two with 5-μm coating thickness) were stored in high humidity conditions with and without acidity for up to six months. Results showed that the more extreme oxidizing environment (acidic humidity made by mixing water with sulfuric acid) had a retarding effect on whisker growth and whisker incubation times (i.e., the time required for whisker growth to initiate) in comparison to non-acidic humidity environments.

II. Experimental Procedure

Flat, rectangular-shaped Copper Development Association nomenclature (CDA) 360 brass coupons with the dimensions of 5.08 cm $\times$ 2.54 cm $\times$ 0.1 cm and an area of approximately 13 cm^2 were used as substrates. The coupons were cut on an abrasive water-jet machine, wet-polished with #1000 silicon carbide (SiC) paper, wet-polished with sodium bicarbonate to remove any residual grit, rinsed with distilled water, and treated with 10% concentrated sulfuric acid prior to plating. Each coupon was taped on its back side with clear platers tape so that the plating was applied to one side only.

The electroplating station was equipped with a high power (HP 6235) supply connected in series to a digital volt–ohm meter (VOM) to precisely measure the applied cell current. A dc motor with an attached impeller was used to provide fluid agitation in the chemical bath during plating. All coupons were plated in 250 mL pure bright Sn bath (with approximately 0.5-μm grain size) at room temperature, with a Sn anode of 99.9% metal purity, and current set to 0.5 A according to the operating requirements set by the manufacturer.

The deposition layer thickness was controlled by plating time and the current density [19]. Following the plating procedure, each sample was post-treated in a distilled water bath and neutralized in potassium hydroxide (KOH). Each plated sample was dried with an air fan and placed inside an environmental chamber. Samples with two different coating thicknesses (2 μm and 5 μm, respectively) were observed for a total aging period of six months at ambient temperature under two environmental conditions.

1) A closed plastic container filled with 1150 mL of regular tap water.
2) A closed plastic container filled with 1150 mL of regular tap water plus 15 drops of 100% sulfuric acid (H_2SO_4).

The surface of each electroplated sample was analyzed by a scanning electron microscope (SEM) operated at 5 kV and

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30 pA. The cross-sections were prepared using a dual-beam focused ion beam (FIB). The samples were milled at a 52○ tilt angle with a 30-kV gallium (Ga) ion beam operating at a current of 30 pA. Initial trench milling of the sample was done at 20 nA and the final face milling at 1–3 nA. Extra FIB images were taken with the Ga ion beam at a current of 11 pA. All samples were examined at the coupon center over an area of 20 μm $\times$ 20 μm. The metal composition of each sample was determined with an SEM using energy-dispersive spectroscopy (EDS). All measurements were performed with an accelerating voltage of 15 kV, a probe current of 1150 pA, and a 30 s acquisition time. Last, the intensity of intermetallic formation present at the film/substrate interface was evaluated using X-ray diffraction (XRD) equipment capable of depth-controlled phase identification. XRD uses Cu K α radiation source with known X-ray wavelength $(\mathrm{lambda}(\lambda) = 1.54\ \mathrm{Aa})$, scan step set to 0.02°, scan speed set to 4 degrees/minute and the low Bragg angle theta (θ) set in a range from 30 to 70 degrees [20]. The detection consists of a computer-controlled scintillation counter or a fast semiconductor-based position sensitive detector. The amount of inter-metallic formation is detected for each angle position of 2θ degrees using Jade v7.5 software with search/match option.

III. Results and Discussions

A. *Influence of Environmental Conditions on Samples with 2-μm Sn Film*

In this paper, brass substrates with 2 μm of electrodeposited bright Sn coating were exposed to the oxidizing environments. After six months the electroplated surface for samples exposed to pure humidity (condition one) had visible wetting spots [Fig. 1(a)] and significant amounts of oxides covered the entire plated surface [Fig. 1(a) and (b)]. The surface oxides have also inhibited the outer surface of the formed hillocks growing from the electroplated Sn coating [Fig. 1(b)]. In addition to the formed hillocks, the growth of long filament-like whiskers was also detected on the surface [Fig. 1(c) and (d)]. Tin easily forms tin-oxides with oxygen but it is interesting to note that there is no presence of visible oxides along the body of the extruded Sn whiskers. It seems that the formed oxides have enhanced the development of hillocks and whiskers on the Sn surface.

Special attention was also given to the morphology of Sn whiskers. A variety of protrusion shapes and dimensions were noticed on the surfaces for those samples exposed to pure humidity. For example, some Sn whiskers were straight, with lengths up to 97 μm and a uniform diameter of 4 μm [Fig. 1(c)]. Yet another whisker type had a bent shape, longest length of 14.14 μm and a nonuniform diameter in a range from 1.5 μm to 4 μm along the body of the same whisker [Fig. 1(d)]. Further study may be needed to exactly define the factors that cause the development of these differently shaped Sn whiskers.

Extreme surface corrosion was observed on tin film surfaces exposed to acidic humidity for six months [Fig. 2(a)]. Fig. 2(a) shows a plated surface entirely covered by a mixture of sulfur rich salts, Sn particles, and Sn oxides. Due to the bad surface conditions, it was extremely difficult to accurately analyze the samples for Sn whiskers growth. However, whiskers still found

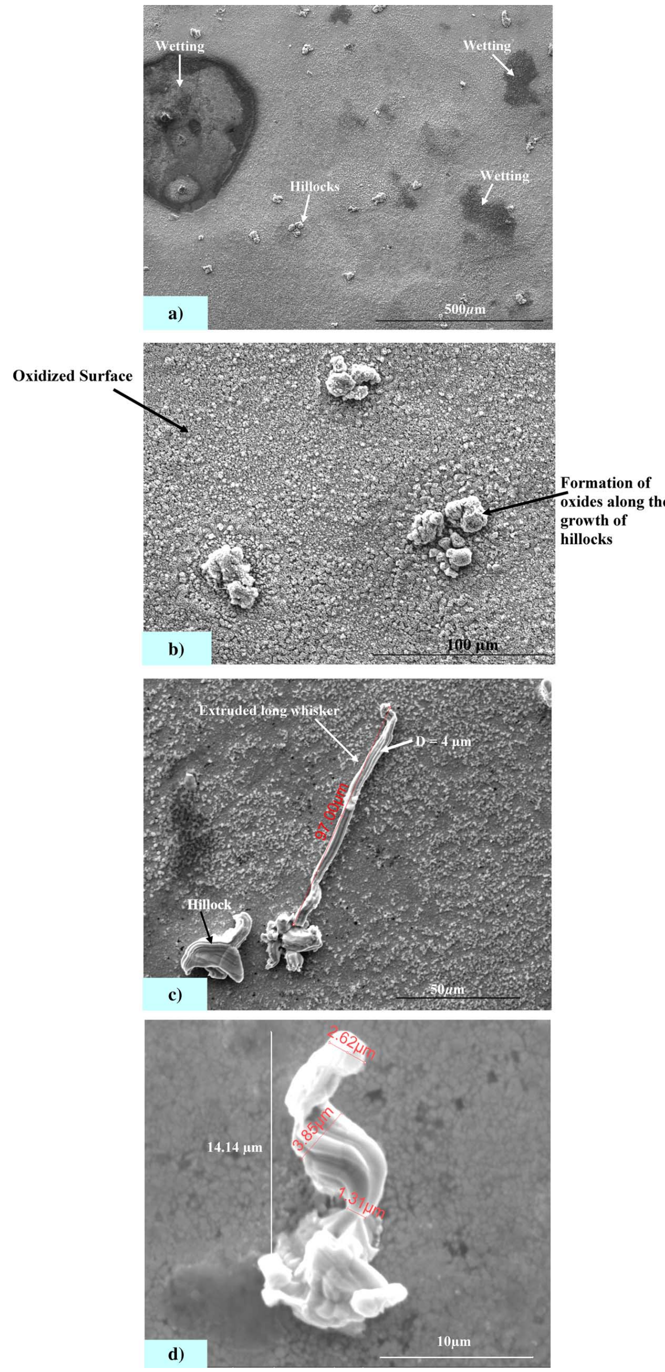

Fig. 1. SEM scans of the top surface of sample with 2-μm film exposed to pure humidity for six months (continues). (a) Top surface showing wetting spots and hillocks. (b) Higher magnification of the top surface showing significant amount of oxidation. (c) Growth of straight Sn whisker with a length of 97 μm. (d) Growth of Sn whisker with a twisted shape and length of 14.14 μm.

their way to grow straight up through the corrosion products on the film surface [Fig. 2(b)]. The whiskers for the samples with 2-μm Sn film exposed to acidic humidity were straight with a maximum length of about 38 μm and a uniform diameter of 4.51 μm [Fig. 2(b)]. The whiskers formed on these coupons exposed to acidic humidity, are almost half in length than those grown from the electroplated surfaces of the coupons exposed to pure humidity [Fig. 1(c) and 1(d)].

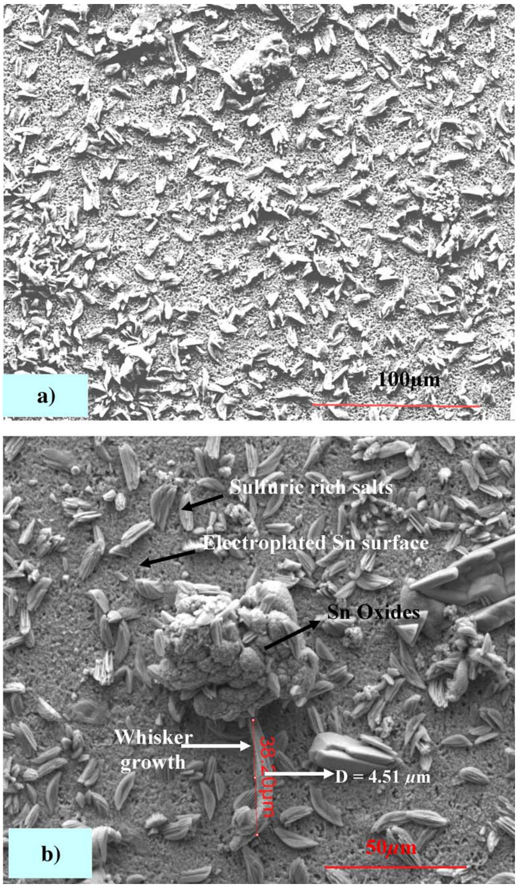

Fig. 2. SEM scans of the top surface of sample with 2 μm film exposed to acidic humidity. (a) Overview of the top surface after six months (lower magnification). (b) Overview of the top surface after six months (higher magnification).

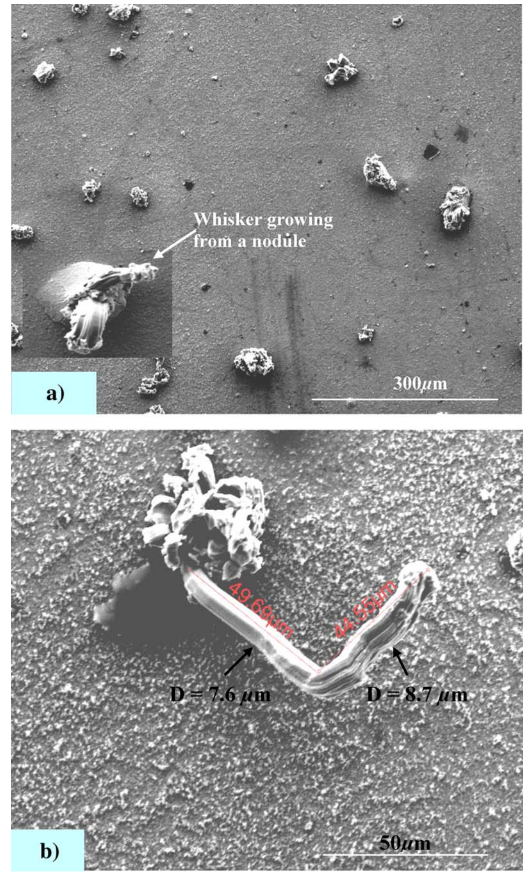

Fig. 3. SEM of the top surface of sample with 5-μm film exposed to pure humidity for six months. (a) Overview of the electroplated surface populated with nodules. (b) Whisker growing with bent shape and nonuniform diameter.

IV. Influence of Environmental Conditions on Samples With 5-μm Sn Film

Literature reports that increasing film thickness delays the onset of whisker formation [1], [16]. The goal of this study was to observe humidity effects on 5-μm Sn coatings. Coupons with 5-μm electrodeposited tin were exposed to the same previously mentioned environmental conditions for the period of six months. As expected, whiskers and hillocks were detected growing from the electroplated surfaces [Fig. 3(a) and (b)]. The longest tin whisker was 94.24 μm and had a nonuniform diameter between 7 and 9 μm, and the bending has occurred at approximately 50 μm [Fig. 3(b)]. It should be noted that whiskers grown from the 5 μm tin platings were about twice as large in diameter as those formed from the 2 μm tin films. Also noted, the density of nodules and whiskers for the 5-μm tin films was less than that for the 2-μm films.

Those 5-μm films, exposed to acidic humidity, showed the most unique whisker formation behavior. After six months, the surfaces were visibly oxidized, corrosion free, and there were large number of nodules [Fig. 4(a)]. Cracking was observed at the tip of each nodule [Fig. 4(a) and (b)]. FIB cross section of the nodules showed nonuniform Cu_6Sn_5 IMCs at the coating/substrate interface and significant voiding in the surface regions of the nodule [Fig. 4(b)]. From observations, it seems that this voiding is unique to the nodule since extensive presence of voids was not detected at regions where nodules were not formed. The authors believe that the nodule formation was initiated by continuous surface swelling due to self diffusion of Sn and possibly formation of tin oxides inside the tin film. Fig. 5(a) shows whiskers grow straight up from the cracks at the tip of the nodule. A relatively few "nodule" whiskers grew to 18 μm in length with diameters of around 2.5 μm [Fig. 5(b)]. Whiskers grown from the 5-μm-thick tin films exposed to acidic humidity had 2 to 4 times smaller dimensions than whiskers from all the other experiments presented in this study.

This study has shown that acidic humidities drastically increase the incubation period for tin whiskers formation. Other studies have also reported that acidic humidity has a retarding effect on whisker formation and growth while pure humidities have an accelerating effect [5].

V. XRD Analysis of Cu–Sn Intermetallic Compounds Formed in the Sn Film for Each Case

It is commonly accepted that compressive stresses developed from Cu_6Sn_5 formation at the coating/substrate interface, are the main cause for the growth of Sn whiskers in tin films on copper substrates [1], [4], [10], [16], [21]. Since the morphology and the amount of whiskers formation varied from case to case in this study, it is important to determine if the intensity and the orientation of Cu_6Sn_5 IMCs present in the tin film also varied between the various cases. XRD analysis was performed for each studied case. For reference, XRD distribution curves were added for three other cases:

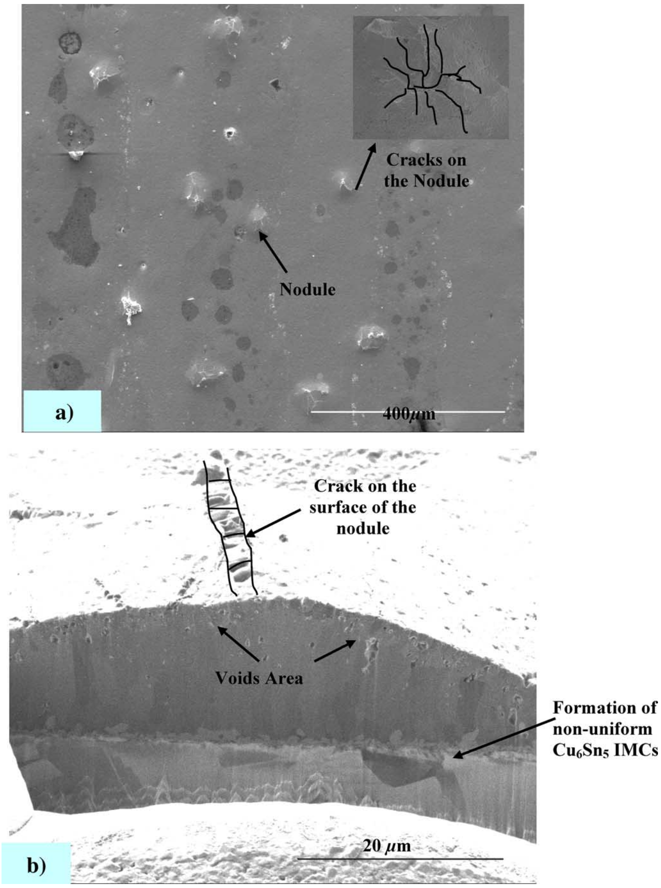

Fig. 4. Evaluation of sample with 5-μm film exposed to acidic humidity for six months. (a) SEM scan of the electroplated surface populated with nodules. (b) FIB cross section of a nodule showing voids in the film.

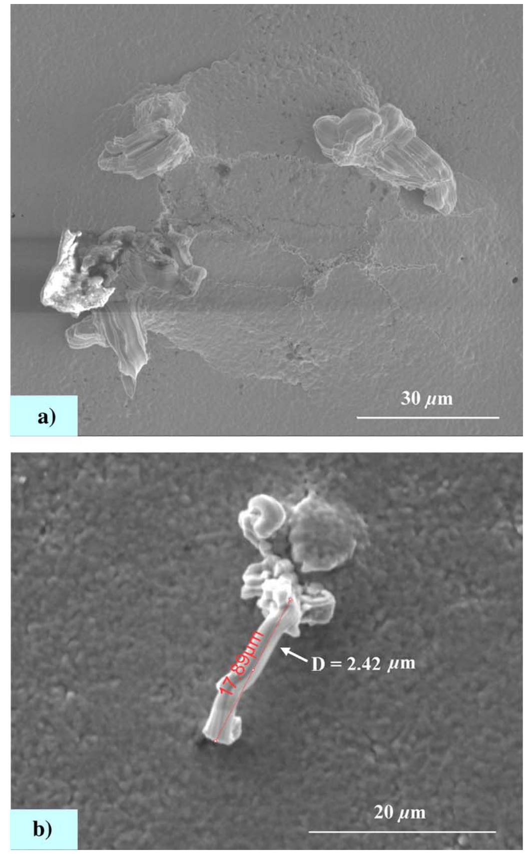

Fig. 5. SEM scans of top surface of sample with 5-μm film exposed to acidic humidity. (a) Whiskers grown from the cracks of the nodule. (b) Extruded whisker grown from the electroplated surface.

1) sample plated with 2-μm bright Sn;
2) sample plated with 5-μm bright Sn;
3) sample plated with 5-μm matte Sn.

All the above were exposed to ambient air for six months. Fig. 6 compiles all the XRD results. The results showed very uniform texture distribution for each case regardless of the coating thickness and the different environment that each sample underwent. The XRD distribution curves match almost identically for all cases presented. Some difference is noticed for cases 3, 4, and 5 (all 2-μm tin samples) where the intensity of Cu_6Sn_5 IMCs is slightly more present at the range of $2\theta = 35^\circ$ to 40° and $2\theta = 54^\circ$ then in the other cases. This result confirms that thinner coating is more prone to Sn whisker growth most probably due to the increased Cu_6Sn_5 volume reaching the top surface in comparison to the 5 μm coatings. The XRD analysis also confirms that the composition type (bright/matte) of Sn film and the environmental influence do not affect the type formation of Cu_6Sn_5 IMCs. In this paper, all cases have shown different behaviors with respect to Sn whisker formation and growth when exposed to different environments, but Fig. 6 shows that all cases display almost same type of IMC formation traits.

The type of Cu_6Sn_5 IMCs in the film could be an important contributor to the growth of Sn whiskers but results have shown that they are not the main factor in the formation and the morphology of Sn whiskers.

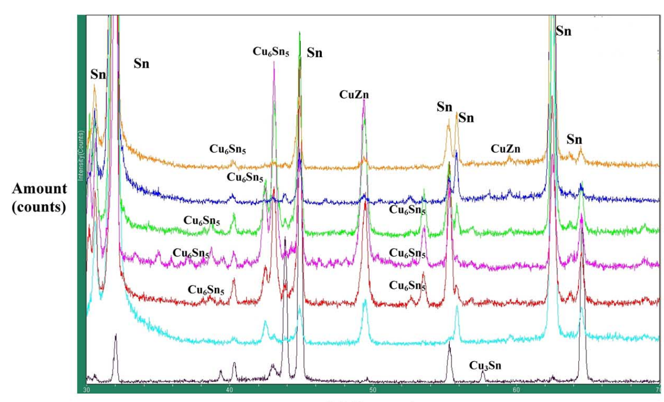

Chart Details:

1. Brass substrate with 5μm matte Sn coating exposed to ambient temperature
2. Brass substrate with 5μm bright Sn coating exposed to ambient temperature
3. Brass substrate with 2μm bright Sn coating exposed to pure humidity
4. Brass substrate with 2μm bright Sn coating exposed to acidic humidity
5. Brass substrate with 2μm bright Sn coating exposed to ambient temperature
6. Brass substrate with 5μm bright Sn coating exposed to pure humidity
7. Brass substrate with 5μm bright Sn coating exposed to acidic humidity

Fig. 6. XRD analysis of the amount of Cu_6Sn_5 IMCs present in each case after six months.

VI. Conclusion

The results discussed in this study seek to address the fundamental behavior and the morphology of Sn whiskers growth. The effect of different environments over a six-month period has been investigated comparatively for samples with various film thicknesses. Humid environments are used as accelerating factors to trigger the growth of Sn whiskers from the Sn-plated surface. Several conclusions can be made with respect to the presented results. Depending on the environment, the behavior of Sn whiskers cannot be easily predicted, and whiskers can grow in a variety of shapes and dimensions over different time span. The analysis also shows that thicker electroplated coatings have decreased Sn whiskers densities but the whiskers are larger in diameter. A pure humidity has an accelerating effect on the growth of Sn whiskers where acidic humidity has retarding effect. Cross section of the formed nodules in some samples showed extensive voiding present in the surface region of the nodule which is a unique behavior to the nodule. Several factors such as continuous self diffusion of Sn, selective oxidation, and localized condensation of the film could be considered as possible initiators for nodules to form only in particular locations of the film. Additionally, the presence of nonuniform stress gradient formed in the film could possibly cause the crack in the nodule [22]; however, further work is necessary to obtain the stress results. The authors have not seen this nodule behavior in experiments of samples with matte tin film so they believe that the nodules could be a unique trait to the bright tin film. Additional benefit in this study is that the growth of whiskers was detected at different stages of their formation, e.g., Sn whiskers grow directly from cracked nodules formed on the plated surface.

The rapid formation of nonuniformly distributed Cu_6Sn_5 inter-metallic compounds is present at the coating/substrate interface. However, the type of inter-metallic compounds is important but not the only cause for the growth of Sn whiskers. Additionally, the environmental conditions and the plating thickness have an effect on the growth of whiskers, but they do not directly affect the type formation of IMCs.

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