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RESEARCH ARTICLE

Determining whiskering properties of tin-copper alloy solder-dipped platings

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Abstract

This paper reports the effect of humidity on whisker formation in pure tin and tin-copper alloy platings. Samples with copper substrates were plated with 10 µm pure tin or tin-copper alloys (with up to 5% Cu content). The samples were stored in high humidity (105 C/100% RH) for over 2000 hours to examine the effect of humidity in whisker growth on different tin-copper alloys. Results indicate differences in whisker growth depending on the copper content. The series of tests show the significance of humidity and melting temperature of the plating alloy for whisker formation.

Keywords

tin whisker · surface finishes · SEM

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1 Introduction

As of July 1, 2006, European legislation severely restricted the use of lead in electronic components [1]. As a result, lead containing metallizations were converted to lead-free alternatives, and tin electroplating became the most popular solution because of its good wettability, low cost, and ease of storage. However, it soon became obvious that these platings easily form whiskers. Using tin-lead alloys to prevent whiskering had been an industry accepted solution for over 50 years, but the absence of lead has resulted in a reliability issue: the formation of conductive tin whiskers that grow across component leads can cause current leakage or short circuits, and ultimately the failure of electronic circuits [2]. It is theorized that tin whisker growth is caused by the development of compressive mechanical stresses, such as residual stresses caused by electroplating; stresses caused by the diffusion of different metals or the growth of oxide on the tin surface; and thermally or mechanically induced stresses. In the presence of compressive stress the whiskers are extruded as a stress release mechanism [3]-[4].

Alloying different elements to tin changes the whiskering ability of the plating depending on the alloying element. Tin platings containing more than 3% lead mitigate the formation of tin whiskers [5], [6]. There has been some research on the effects of copper on whiskering in tin-copper alloy platings [7]-[9], but these studies examined only alloys with a smaller percentage of copper (up to 3,7% Cu) on mainly electroplated platings. In addition, the aging of the platings has not been tested in high humidity conditions; hence the effects of oxidation on the alloys have not been tested. The aim of this research is to examine this oxidizing effect tin-copper alloys on a larger range of copper content (0 – 5% Cu).

2 Experimental

Samples were created by dipping pure copper wires into different melted alloys. Six types of alloys were first created and melted separately in a melting pot in 450° C. These alloys were: 100Sn, 99Sn1Cu, 98Sn2Cu, 97Sn3Cu, 96Sn4Cu, and 95Sn5Cu. The developed platings on the wires were 10μm thick. During the dipping it was important to create a smooth even surface. Because 100Sn has approximately 150°C lower melting point than 95Sn5Cu, if the temperature is too low, the plating on the alloys with high Cu content can solidify during the dipping procedure creating whisker-like copper crystal spikes. These crystals are created because the copper solidifies inside the alloy while the tin is still in a liquid form. It is important to recognize that these formations have nothing to do with whiskers, and are necessary to avoid at the creation of the samples.

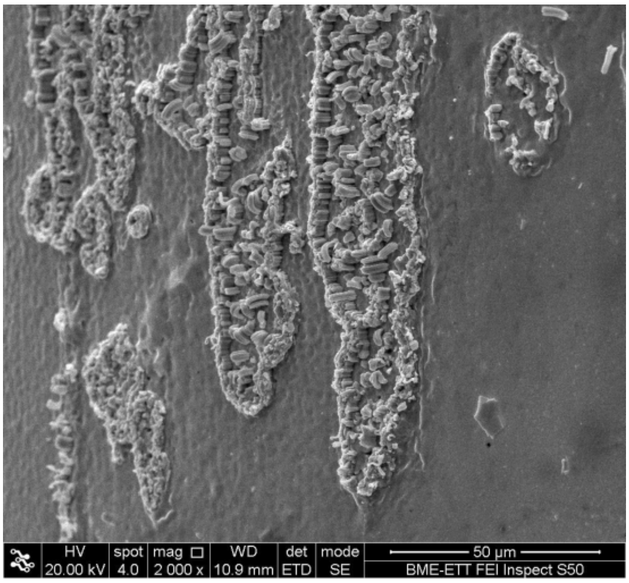

Fig. 1. Whisker development on the corrosion spots in the 96Sn4Cu samples at 1200 hours

The created samples were aged in 105°C/100%RH condition in order to observe their whiskering and corroding properties. The samples have been aged for a total of 1600 hours. They were initially checked every 400 hours with a Scanning Electron Microscope (SEM). No precautions were taken to limit condensation of vapor on the samples as our aim was to observe the effect of corrosion on whiskering.

3 Results and discussion

After 2000 hours it can be clearly seen that the surface of the samples became heavily oxidized and that severe spot corrosion occurred on the samples. On these corrosion spots large amount of corrosion product has been grown. These spots formed in the areas where water has condensed on the sample surface. Development of whiskers was only found in these corroded areas, the rest of the surface stayed unharmed (Fig. 1).

The total area of the oxidation was about the same in all samples, since the level of water condensation in the humidity chamber was similar in all samples. However, the level of whiskering was different in these corroded areas. At 2000 hours the whisker density was similar in all samples with copper alloy platings (99Sn1Cu-95Sn5Cu). In these cases the corrosion spots were almost completely filled with short whiskers. On the platings with pure tin (100Sn), the corrosion spots contained only a few whiskers.

The average whisker length was calculated by lognormal distribution from 20 pieces of whiskers at each point. The length of the whisker was measured on the SEM images according to the magnitude with simple broken-line fitting. At 2000 hours, the longest whiskers (on average) were developed on the samples with 5% copper alloy plating, where the average whisker length was 6.7 μm. In case of 0%, 1%, 2%, 3% and 4% the average whisker lengths were 1.5 μm, 1.3 μm, 3.6 μm, 1.8 μm, 5.7 μm, respectively (Fig. 2). At this monitoring time point, the length of the whiskers was a function of the ratio of copper in the plating alloy.

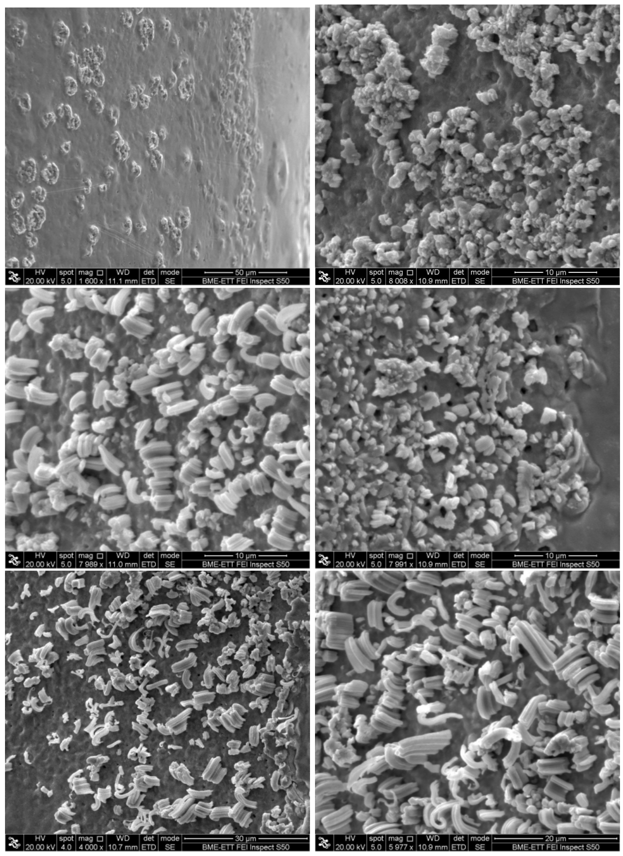

Fig. 2. Whiskering on the corrosion spots at 2000 hours on samples with the following percentage of copper: a. 0%, b. 1%, c. 2%, d. 3%, e. 4%, f. 5%.

A difference was found in the detected time point when the first whiskers have developed. On the platings with 1-4% copper content, the first whiskers were found at 800 hours. In case of samples with 5% copper content and pure tin (0%), the first whiskers appeared at 1200 hours.

In case of pure tin coated samples, whiskers were found in traces. While the corrosion spots on all other copper plating alloys were dense with whiskers, the corrosion spots on pure tin coated samples contained SnO_x corrosion product instead. It can be visually seen that the surface of the samples has a black discoloration where the corrosion spots occur. This means that the majority of the corrosion product on these spots is tin-oxide (SnO). Corrosion spots develop on the tin surface when water vapor in the air condenses as micro-water droplets and corrosive O_2 is absorbed in these surfaces.

A thin film of moisture on a metal surface forms the electrolyte for electrochemical corrosion. Most metal corrosion occur via electrochemical reactions at the interface between the metal and an electrolyte solution. Electrochemical corrosion involves two half-cell reactions: an oxidation reaction at the anode and a reduction reaction at the cathode [10]. For tin corroding in water with a near neutral pH, these half cell reactions can be represented as:

Anode reaction: $2Sn \Rightarrow 2Sn^{2+} + 4e^-$

Cathode reaction: $O_2 + 2H_2O + 4e^- \Rightarrow 4OH^-$

Initially, the tin and tin-copper alloy coatings produced by hot-dipping are completely stress-free. The additional stress develops in the plating in time and hence whisker growth at elevated temperature and humidity can clearly be induced by the corrosion of the Sn finish [11]-[14]. Compressive stress is necessary in the tin layer for the initiation and growth of tin whiskers. Certain weak spots on the oxide layer will relieve the developed internal compressive stress inside the tin layer, which drives the tin material out of the opening so that whiskers can grow [15]. When the tin is transformed to SnO_x, the volume of the tin layer expands [14]. Therefore, a compressive stress is generated by the oxidation in the tin layer; that drives the nucleation and growth of whiskers [11],[12],[16].

In case of platings where there is copper content, the oxygen also reacts with the copper. The oxidised copper can transform into Cu_2O or CuO. The density of pure copper is 8.94 g/cm^3, and the density of Cu_2O and CuO is 6.0 and 6.31 g/cm^3, respectively. The difference in densities is due to the different crystal structure and the place of the oxygen atom between the copper atoms. Hence, in case of oxidation of copper grains in the alloy, the volume can expand up to +41% depending on the ratio of the developed copper-oxide type. The density of pure tin is 7.365 g/cm^3, and the density of SnO and SnO_2 is 6.45 and 6.95 g/cm^3, respectively. Therefore, the larger the copper content in an alloy, the more stress will develop in the layer due to the corrosion of the alloy plating.

Tin is considered a special material due to its low melting temperature (T_m = 505 K). At 286 K (0.55 × T_m), tetragonal β-tin transforms into cubic α-Sn. Recrystallization temperature is typically 0.4-0.7 of the melting temperature for metals; therefore, the recrystallization temperature of tin is very low, and recrystallization occurs even around room temperature (which is 0.58 × T_m) [17, 18]. For this reason grain growth is also carried out at low temperatures, which can happen as either normal grain growth, where the main mechanism is the disappearance of the smallest grains in the distribution, or as 'abnormal' grain growth, where the latter process involves the growth of a few grains that become much larger than the average. The main cause of whisker growth can be regarded as the abnormal grain growth, which instead of consuming the neighbour grains; grows out at the surface, due to the migration of atoms at grain boundaries by diffusion.

Pure tin has a melting point of 504K (231°C). While there is an eutectic point at 0.7% copper content where the melting point of this Sn-Cu alloy is reduced to 501K (228° C), the melting points of alloys with higher copper content rapidly rise. For this reason the melting point of 95Sn5Cu is 648K (375°C) (Fig. **??**). Because of this property, grain growth due to recrystallization may not be so efficient and develops slower, and hence the first appearance of whiskers occurs later in time. But since the high copper content has a higher corrosion rate, the additional stresses due to the tin and copper oxides accelerate the whisker growth after the first appearance.

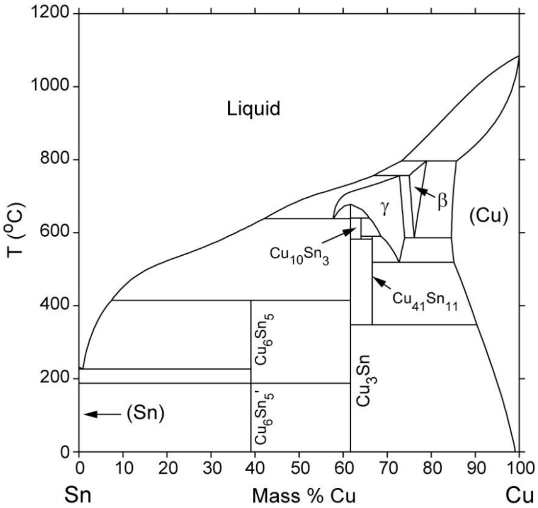

Fig. 3. Sn-Cu phase diagram

4 Conclusions

The density of corrosion spots and the total area of the oxidation were similar in all samples due to the equality of the level of water condensation in the humidity chamber. In all cases whiskers only grew in the spot corrosion areas. In average, the longest whiskers found at 2000h were developed on the samples with 5% copper alloy plating.

Due to the higher ratio of density decrease for copper-oxide compared to tin, platings with larger copper content are more vulnerable to developing stresses in the layer in high corrosion environments. However, recrystallization process may slow down due to the higher melting point of the alloy, which can delay the appearance of the whiskers.

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