Corrosion properties of tin–copper alloy coatings in aspect of tin whisker growth

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ABSTRACT

The appearance of corrosion at elevated temperature and humidity conditions could also be responsible for the growth of tin whiskers. In this paper the relation between the corrosion of different tin–copper alloys (0–5 wt.% Cu) and whisker growth was investigated. The alloys, applied as surface coating on copper base, were stored at an elevated temperature and humidity condition (85 °C/85% RH). It was observed that the tin–copper alloys show differences in the tendencies of the whisker growth. Polarisation measurements were performed to find a relation between whiskering behaviour and corrosion resistance of the alloys. The corrosion behaviour of the layers was also studied by cross-sectioning with a focused ion beam. The series of tests have shown that the whisker appearance probability of different alloys is affected by three different factors: corrosion resistance of the surface finishing, expansion rate of the corrosion product and recrystallization speed of the metal/alloy.

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1. Introduction

Using tin–lead alloys to prevent tin whiskering had been an industry accepted solution for over 50 years, as it is a well-known fact that pure tin coatings easily form whiskers. However, recently the absence of lead has resulted in the re-appearance of this reliability issue. Tin whisker growth is caused by the development of compressive mechanical stresses within the tin layer, such as residual stresses caused by electroplating; stresses caused by the diffusion of different metals; the growth of oxides and thermally or mechanically induced stresses. Whiskers are extruded as a stress release mechanism in the presence of compressive stress [1–5]. Tin whiskers can develop on the original coating and even on various solder alloys [6–8]. Alloying tin with a second metal changes the whiskering properties of the coating. Tin–lead alloys (>3% Pb) [9] mitigate tin whisker formation; bismuth suppresses whisker growth in tin–bismuth alloy finishes when added to tin in amounts of 2–4 wt.% [10].

Other materials can change the whiskering properties of the tin alloy layer in the opposite way. Tin copper alloys are known to enhance whisker growth [11], and they are widely used in the electronics industry as a coating material for component leads. Boettinger et al. [12] proved by using deflection measurements on plated cantilever beams, that the co-deposition of tin with other

materials in the amount of a few mass percent alters the compressive stress compared to pure tin. They claimed that larger compressive stress is generated in the electrodeposit with copper addition to the electrolyte and smaller compressive stress is generated in the deposit with lead addition to the electrolyte. In tin–copper alloy films, beside the coating layer/copper interface, the added copper forms Cu_6Sn_5 within the grains. Williams et al. [13] noted that the addition of copper to the plating electrolyte allows Cu_6Sn_5 intermetallic precipitates to form in the tin grain interiors and along the tin grain boundaries. This feature increases the compressive stress compared to pure tin. Additionally, the intermetallic precipitates pin the tin grain boundaries, which inhibits the relaxation of compressive stress in the Sn–Cu deposit and promotes whisker growth rather than conical hillock formation. Increasing copper concentration in the layer generates increasing compressive stress in the Sn–Cu film [14]. Sarobol et al. [15] introduced a defect phase diagram that shows in a systematic way how Cu and Pb additions change the coating layer characteristics and create surface defects. For the tin–copper alloy films, an increasing Cu concentration up to 0.5 wt.% showed an increase in defect density; the defect morphology changed from small compact hillocks to hillocks with large initial vertical growth and whiskers. Compared with pure tin films, the Sn–Cu–Pb alloyed coatings showed a decreasing defect density with increasing lead (Pb) concentration. In this case, the defect morphology changed from hillocks with large initial vertical growth to medium hillocks with gradual broadening and large hillocks with gradual broadening [15]. According to Boettinger et al. [12] Cu addition does not alter the

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columnar grain structure found in pure tin deposits, whereas the lead addition causes an equi-axed grain structure to develop. In their experiments aging tin–lead alloy coatings provided no whisker or hillock growth. Compared to the pure tin and tin–copper alloy coatings, the tin–lead coatings have much more grain boundaries parallel to the top surface. Co-deposition of lead is known to significantly reduce any crystallographic texture in the tin by preventing columnar growth [16].

Compressive stress in the tin layer is a necessary condition to initiate the tin whisker growth. Without a surface oxide (SnO_x) layer however, the internal compressive stress in the tin will be relieved uniformly over the entire tin surface and inhibit growth. With a SnO_x layer, the internal compressive stress in the tin layer can be relieved at certain weak spots of the SnO_x layer, at which the tin whiskers can initiate and grow [17]. After a tin layer is plated to the copper base and an oxide film (SnO_x) is formed on the surface, an internal compressive stress state in the tin layer is observed. If the oxide film has a small opening (weak spot), the internal compressive stress inside the tin layer will tend to drive the tin material out of the opening [17].

In addition several studies have shown that whisker growth at elevated temperature and humidity conditions can be induced by the oxidation or corrosion of the tin finish [18,19]. Oberndorff et al. [20] tested matte tin plated leadframe packages in high humidity inducing severe oxidation and corrosion. They observed a high molar volume of tin oxide which resulted in whisker growth. Su et al. [21] performed a statistical study of the whisker population and growth. They stated that between 60 °C/85% relative humidity (RH) and 60 °C/93% RH condition the latter had a higher whisker population per component and a longer maximum whisker length, due to corrosion developed stresses. Osenbach et al. [22] studied tin plated samples tested in similar conditions and found that on regions of the tin layer where water condensation was present, the entire thickness of the layer was corroded and the corrosion product was highly crystalline SnO_2. Tin has two main oxides: stannic oxide (SnO_2) and stannous oxide (SnO). The existence of these two oxides reflects the dual valency of tin (oxidation states of 2+ and 4+, respectively). SnO is not as well characterised as SnO_2 [23]. The crystal structure of stannous oxide (SnO) is a tetragonal unit cell with the litharge structure, isostructural to PbO [24]. The density is 6.45 g/cm³. It possesses the same rutile structure as many other metal oxides, e.g. TiO_2. The crystal structure of stannic oxide (SnO_2) is a tetragonal unit cell [25] and the density is 6.95 g/cm³.

The exact growth process of the whiskers due to stress from oxide growth is not yet fully understood. Currently, there is only limited research on how the humidity (and the corrosion created due to high humidity) affects the growth of tin whiskers. Additionally, there is only limited research on the effects of copper on the whiskering of tin–copper alloy coatings which has been examined only on alloys with a small percentage of copper (up to 3.7% Cu) on mainly electroplated coatings. The aim of this research is to examine the whisker growth behaviour of tin–copper (0–5 wt.%) alloy surface finishes in highly oxidising environments.

2. Material and methods

Pure copper wires were used as substrates during the whiskering tests. The surface finishes were created by dipping the copper wires into different molten alloys. Six types of alloys were applied: 100Sn (wt.%), 99Sn1Cu (wt.%), 98Sn2Cu (wt.%), 97Sn3Cu (wt.%), 96Sn4Cu (wt.%), and 95Sn5Cu (wt.%). The thickness of the developed surface finishes were between 4 and 6 μm which has been clarified with cross-sectional polishing of the samples. In order to create a smooth even surface during the dipping process, the applied pot temperature was 450 °C in all cases. Pure Sn has approximately a 150 °C lower melting point than the 95Sn5Cu alloy. If the temperature is too low during the dipping process, the alloys with high Cu content can solidify creating whisker-like copper crystal spikes. These crystals are created during cooling because the copper separates from the alloy and solidifies

inside it while the tin is still in a liquid form. It is important to recognize that these formations are not related to the whiskers, and it is necessary to avoid their formation during the preparation of the samples.

85 °C/85% RH temperature and humidity conditions were used to accelerate the appearance of the whisker for up to 2400 h in order to keep the samples in a highly corrosive environment. No precautions were taken to limit condensation of vapour on the samples as the aim was to observe the effect of corrosion on whiskering. Investigations were made by using a FEI Inspect S50 Scanning Electron Microscope (SEM) (Acc. Voltage of 20 kV) at a period of every 200 h, from then the 1200 h, from then observations were made every 400 h. The results were evaluated by the average and maximum whisker length and the average whisker density. During the statistical evaluation of the results, the axial length of a whisker is defined by JEDEC JESD201. The statistics of the whisker phenomenon follow the log-normal distribution [26]. Therefore, the average whisker length and density was calculated by lognormal distribution from 20 whisker pieces and from 20 selected areas (the area size was 2500 μm²) respectively at each time point. The cross-sections of the layers and whiskers were developed by a JEM-9320FIB Focused Ion Beam (FIB) (with a Ga Ion Source and Acc. Voltage of 30 kV) and observed by FIB Scanning Ion Microscope Image (FIB-SIM) after aging.

The polarisation measurements were made in a conventional two compartment, three-electrode electrochemical cell. The reference electrode was a saturated calomel electrode (SCE) separated from the main compartment by a bridge with a Luggin capillary tube. All potentials quoted in this paper are given with reference to this electrode. The counter electrode was a platinum wire. The test specimens for the polarisation measurements were different compared to the test set up for the whiskering. Here, the test specimens were in the form of the original alloy rods that were used for the coating the copper substrates when creating the whiskering samples. These rods were then embedded in a plastic holder with an exposed surface area of 1 cm². In order to remove the surface oxides, the electrode surface was abraded to #800 finish with emery papers and rinsed in distilled water. The test solution was distilled water with 5% Na_2SO_4. A new electrode surface and solution were used for each experiment. All experiments were carried out at 85 °C solution temperature. The reference electrode was kept at 25 °C with the help of circulating cold water around the holder. Potentiosat, SDPS-501C, Syrinx Co. was used for recording and controlling the corrosion potential (E_{corr}) and polarisation curve measurements. For E_{corr} measurements, specimens were kept at −1.5 V for 5 min, and then the potential changes were measured for the next 24 h.

3. Results and discussion

Aging at 85 °C/85% RH condition developed only few corrosion spots on the surface of the samples, these can be observed well with SEM Backscattered Electron (BSE) image mode (Fig. 1, darker spots). The observed whiskers were developed mainly by the corrosion spots. The darker area around the base of the whiskers is a corrosion spot. The surface of the whisker is free of the dark corrosion and measuring the whiskers with EDX showed that it contains more than 99% Sn. Measurement on the corroded regions show peaks of O.
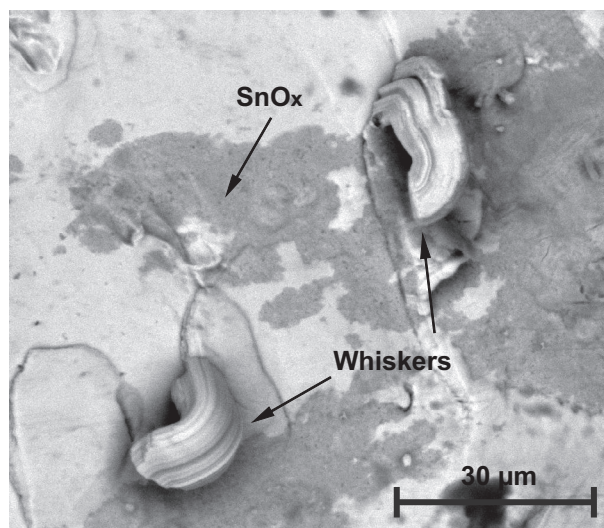

Fig. 1. Localised corrosion with whiskers, observed by SEM-BSE observed on a 96Sn4Cu sample, at 2000 h.