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WHISKER FORMATION ON GALVANIC TIN SURFACE LAYER

TWORZENIE WHISKERÓW NA POWIERZCHNIOWEJ WARSTWIE CYNY WYTWORZONEJ GALWANICZNIE

The present work reports the effect of substrate composition, thickness of the tin electroplate and its morphology on pressure-induced tin whisker formation. Pure tin deposits of different thickness were obtained on a copper and brass substrates using methane sulfonic industrial bath. The deposits were compressed by a steel bearing ball forming imprint on the surface. The microstructure of tin whiskers obtained at the boundary of each imprint, their length and number were studied using both light and scanning electron microscopy. It was shown that the most intensive formation and growth of whiskers was observed in the first two hours. In general, brass substrate was shown to be more prone to whisker formation than copper independently of the tin coating thickness. The results have been compared with industrial bright tin finish on control unit socket leads and proposals have been made as to modification of the production process in order to minimize the risk of whiskering.

Keywords: Tin whiskers, galvanic tin layer, mechanical stress, X-ray Fluorescence Spectrometry, Scanning Electron Microscopy

1. Introduction

The research of lead-free coatings and connections has been proceeding since 1946 to the present day [1-2]. It has been known for decades that on the surface of some low melting metals including tin, cadmium and zinc, even at room temperature whisker formation is observed due to diffusion. At elevated temperatures whiskers can be formed on the aluminum surface as well. The whiskers formed on the tin surface are single crystals of several micrometers in diameter and up to several millimeters long. Tin whiskers have excellent electrical conductivity, which is able to cause short circuit in small electrical devices. Earlier, this problem was solved by lead alloying (Arnold, 1956) [3], but nowadays the use of lead is prohibited by the RoHS Directive. There are many documented cases in which tin whiskers have resulted in the failure of electronic equipment: pacemaker failure (1986) in health-industry, F-15 radar failure (1986), auxiliary engine of a missile in the armaments industry, satellites were destroyed (Solidaridad 1) in space industry [4].

Whisker growth is influenced by many factors such as substrate material [5], residual stress in finish [6], grain size of finish [7] and so on. The most compelling theory for tin whisker growth is that it occurs due to a compressive stress [8]. Sources of stress in tin include plating residual stress, mechanical loading [9], scratches in the plating surface, plating surface oxidation, intermetallic formation, and mismatches in the coefficient of thermal expansion between the plating and the underlying substrate [10-11]. It is already known that at elevated temperatures Cu-Sn intermetallic compounds are formed at the deposit-substrate interface, which causes additional compressive stresses in the Sn layer, which are accordingly relieved by growth of Sn whiskers.

In the case of connectors with pure tin or tin-based alloy coatings, pressure between the connector elements can produce pressure-induced tin whiskers. The nature of pressure-induced whiskers differs from that of spontaneous whiskers [12]. The former grow rapidly at room temperature, Cu-Sn intermetallic compound is not required for the growth. Mitigation practices such as increase of coating thickness, Ni, Ag barrier, reflow, heat treatment after plating yet cannot eliminate whiskers effectively to date [13-14], many questions remain. In this work a systematic study was conducted on relationship between mechanical compressive stress applied to the tin plating, substrate composition, Sn layer structure and thickness, and whisker formation intensity without formation of intermetallic compound.

2. Experimental

2.1. Tin electroplating procedure

Substrate materials used in this study were pure copper and brass sheets with 70% Cu (Eurocircuits Ltd., Eger) and...
size of 100×80×1 mm. As a preparation, after rinsing with distilled water the samples were degreased in acetone solution at 30°C for 25 min on an ultrasonic bath. After that etching with 2% HNO₃ solution was performed for 1 min in order to remove any oxide from the surface. These sheets were electroplated using a commercial aqueous electroplating bath Restin BMAT PC of the following composition: Sn (II) 20 g/l, methane sulfonic acid 200 g/l, primary (10 vol.%) and secondary (0.6 vol.%). The main function of the additives is providing fine grain structure and smooth dense deposit. Another purpose of the additives is to protect the dissolved Sn²⁺ ions from oxidation to Sn⁴⁺ during electroplating. The electroplating was performed for 3 and 10 minutes and a current intensity of 1 A in a specially shaped container “Hull cell” having the cathode at a pre-defined angle to the anode (Fig. 1). It allowed producing a range of current densities and Sn deposit thicknesses.

2.2. Estimation of tin deposit thickness

The freshly deposited Sn layers were examined by Helmut Fisher GmbH + Co. KG X-ray Fluorescence (XRF) Spectrometer at 50 kV in order to estimate Sn layer thickness [15]. The X-ray fluorescence spectra were collected by a silicon PIN detector of high-energy resolution (<200 eV). Samples were measured for 60 s using the utmost collimator (0.6 mm diameter). WinFTM (Windows-based) v.6.20 software has been used including fundamental parameter method for computation. The XRF results on relationship between current density produced during Sn electrodeposition and Sn deposit thickness on the copper or brass substrates are presented in Fig. 2.

2.3. Pressure-induced tin whisker formation

A special setup has been developed that allowed studying mechanical stress on the formation and growth of tin whiskers (Fig. 3). The device produces mechanical stress to be measured on the surface by loading it with force F via a steel bearing ball with a radius of 1.5 mm [16]. Under ambient conditions, the tinned samples were fixed on a stage and compressed by a ball forming imprint on the surface of the sample. Imprints were produced applying 2 and 24 hour exposure time and pressure of 3000 MPa at different Sn deposit thickness. Independently, imprints with 24 h exposure were prepared on a bright Sn finish of industrial sample (motor control unit sockets made of tin coated copper with 2 µm Sn layer).

Fig. 1. Schematic presentation of the Hull cell (solution volume used – 267 ml) placed in a water bath for temperature control

Fig. 2. Dependencies of tin deposit thickness on the current density after 3 and 10 minutes of electrodeposition

Fig. 3. Scheme of experimental setup for the preparation of an imprint on a tinned sample surface (a) and possible mechanism of whisker formation in the mechanically deformed region (b)
2.4. Estimation of length and number of whiskers

The microstructure of tin whiskers obtained, their length and number at the boundary of each imprint were studied using Zeiss EVO MA and Axio Imager Correlative Light Electron Microscopy system. First, the coordinates of imprints were saved by the optical microscope software. In the second step, the sample stage together with the sample were placed in the scanning electron microscope (SEM), and the imprints were found automatically by using the previously identified coordinates. After that the whiskers formed at the interface between deformed and non-deformed surfaces were observed by SEM.

3. Results and discussion

3.1. Effect of mechanical stress and its exposure time on whisker formation

The as-plated surface consists of protruding 0.5-1 µm sized surface grains of roundish shape at 0.14 A/dm² (Fig. 4a) transforming into needle-like 2-3 µm sized grain structure at 4.57 A/dm² (Fig. 4b) independently of the electrolysis duration. The cross-section of tin deposit is characterized by fine and equiaxed, non-columnar structure, which can be useful in whisker mitigation since it can better distribute the residual stress among the grains.

It is recommended in literature that the tin-plating thickness for electronic components should be at least 8 µm to reduce the propensity for tin whisker growth and/or provide a greater incubation time [17]. It was of interest to investigate pressure-induced whisker formation in the tin coating thickness range from 1 to 8 µm. The experimental results showed that mechanical stress induced the formation of whiskers Figs. 5a-b, while their growth depended on the duration of contact with the bearing ball.

After compression re-crystallization in the mechanically deformed region gives rise to a number of new grain boundaries (Fig. 3b). The new grain boundaries are along the horizontal directions and provide faster diffusion routes of atoms, to which effect whiskers are formed at the boundary between the deformed and non-deformed surface. Longer curved whiskers can be found at the region closer to the indentation site, while those formed several grains away from the indent are shorter. The electronic industry would especially like to prevent the formation of the longer curved whiskers due to their higher possibility of causing short circuits.

It has been shown that in the case of copper substrate the total number of whiskers after 24 hours of exposure was 10 times on average as high as that after 2 hours. Considering the brass substrate here, 4-5 times more whiskers formed after 24 hours of exposure than in the case of 2 hours. These
data confirm that the most intensive formation and growth of whiskers is observed in the first hours of contact with the bearing ball. The length of whiskers formed on the imprints was also measured. Generally, it can be stated that the longer was the exposure time, the greater was the average length of the whiskers formed. In the case of 2 hour exposure time the average length was 1 micrometer, while in the case of 24 hours it was 7 micrometers. Above this exposure time no significant growth was observed.

3.2. Effect of tin deposit thickness and substrate composition on whisker formation

It is also believed [5] that the presence of Zn in the brass substrates suppresses the formation of Cu-Sn intermetallic compounds, thereby reducing the risk of growth of long whiskers. In current experiments the intermetallic layer was undetectable (according to SEM cross-sectional analysis) because the deposit was obtained at room temperature. Fig. 6 features dependencies of the average whisker length on tin deposit thickness after 24 hours of contact with the bearing ball for both copper and brass substrates.

Fig. 6. Average whisker length vs. tin deposit thickness after 24 hours of contact with the bearing ball

In general, brass was shown to be more prone to whisker formation than copper. This observation can be explained by higher hardness of brass, which does not neutralize but rather induces additional mechanical stress in the tin plating. It can be seen that in the case of brass substrates after 24 hours of exposure the whiskers are similar in average length but the highest values were observed in the range of 4-5 µm thick tin layer. The longest whiskers on the copper substrate were observed in the case of 3 µm thick tin layer.

Fig. 7 summarizes the results on the number of 5 µm and longer whiskers/imprint comparing copper and brass substrates after 24 h exposure.

It should be noted during evaluation that a number of manufacturers consider 50 micrometer long whiskers to be critical since the lifespan of contacts is longer than 1 day. In our case, for 24 hour exposure, the critical whisker length has been calculated by Eq. 2 found in literature [18]:

\[
\text{Ln}(t) = A(1 - e^{-B \cdot t})
\]

(2)

where \( \text{Ln} \) is the expected average whisker length within group (micrometer), \( A \) and \( B \) – constants (in the paper, \( A = 28 \), \( B = 2.78 \cdot 10^{-4} \)), \( t \) is the exposure time (hour). Thus, in the current experiments whiskers of 5 micrometers and longer were considered most dangerous. Hence, the data processing included estimation of number of tin whiskers above 5 micrometers long regarding to single imprint. It should be mentioned that whiskers longer than 1-2 µm were formed quite rarely. In the case of 3 min electrolysis a tendency was observed, according to which the greater is the thickness of the tin layer the bigger is the difference in number of whiskers between copper and brass substrates. The difference between two substrates varies

Fig. 7. Number of 5 µm and longer whiskers vs. tin deposit thickness after 24 hours of contact with the bearing ball

Fig. 8. Tin whiskers (a) at the boundary of the imprint obtained after 24 hours of contact with the bearing ball on the industrial sample with 2 µm thick tin layer and comparison of whiskers formed on the industrial sample and the ones galvanized in the present study – all the 3 curves belong to 2 µm thick tin layer (b)
in the range 2-15 times, except the values at 3 µm thick tin layer. Increasing the tin layer thickness, the following potential effects should be considered. The mechanical stress is better distributed on thicker layers, thus its effect will be less significant. On the other hand, more tin is available for whisker formation (if the layer thickness is doubled, that is, twice as much tin is available).

These results have been compared with industrial bright tin finish on control unit socket leads being determined as 2 µm thick layer. On average, two times as long whiskers (18 µm) were formed on the industrial sample after 24 h exposure (Fig. 8a), while their length is distributed in a wider range than that of the samples obtained in this study (Fig. 8b). The longest whisker formed on the industrial sample is about 40 micrometers.

It can be explained by smaller grain size of industrial tin finish than tin deposit obtained in the Hull cell. In case of smaller grains there are more grain boundaries for grain boundary diffusion and related growth of intermetallics and oxides; therefore, more stress is created from these sources [17]. Additionally, smaller grain sizes result in smaller grain boundary areas for the whisker grain which means it takes less stress to cause grain boundary sliding. For this reason, bright tin is more vulnerable to whiskering than matte tin (grain size >1 µm).

4. Conclusions

Mechanical stress could induce whisker formation and the rate of growth increased with an increase in the applied stress already in the first hours of exposition.

It can be stated that the longer was the exposure time, the bigger was the average length of the whiskers formed. In the case of 2 hour exposure time the average length was 1 micrometer, while in the case of 24 hours it was 7 micrometers for both substrates.

In general, brass was shown to be more prone to whisker formation than copper independently of the tin coating thickness. This observation can be explained by higher hardness of brass.

A tendency to form longer whiskers (8-10 µm on average) was observed in the case of thicker tin electroplates after 10 minutes of electrolysis, which can be explained by the larger quantity of tin available for whisker formation.

On average, two times longer whiskers (18 µm) were formed on the industrial sample with bright tin finish than on the tin electroplates with 2 µm tin layer after 24 h exposure.

The commercial bath used in the present work for tin electrodeposition can be recommended for industrial use since it guarantees tin deposit with quite fine and equiaxed, non-columnar structure, which reduces the risk of long whisker formation.

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