# Tin Whisker Susceptibility of SAC0307-ZnO Composite Solder Joints

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**Abstract:** In the present study, tin (Sn) whisker growth has been observed from SAC0307-ZnO composite solder joints. The commercial SAC0307 solder alloy was reinforced by ZnO nano-particles, which resulted in composite solder joints. The ZnO nano-particles were mixed into the solder paste in a 0.25 wt% volume fraction, using the ball milling process. Solder joints were prepared from the composite solder alloy and from the reference SAC0307, on Ag surface finish by conventional SMT. The solder joints were exposed to an accelerated lifetime test (85 °C/85 RH% THB, 3000 hours) to enhance the Sn whisker growth. Corrosion spots were observed after 1000 hours of aging, and the first whiskers appeared after 1500 hours of aging on the reference SAC0307 solder joints. In the case of the ZnO composite solder joints, non of the previous phenomena were observed during 3000 hours of THB aging. Furthermore the mechanical strength of the solder joints was investigated, but it was found that the ZnO nano-particle could not increase the mechanical properties of the composite solder joints considerably.

#### **1. INTRODUCTION**

The lead-free soldering technology for reducing and non-using the Pb in solder pastes, usually applies SnAgCu solder alloys. Especially, Sn95.5Ag4Cu0.5 (SAC405) and Sn96.5Ag3Cu0.5 (SAC305) such as high silver (Ag) content solder alloys[1]. These high silver content alloys have good properties in solderability, bonding strength, and thermal fatigue. But Ag increases the price of the solder pastes and it can results shrinkage defects due to the Ag<sub>3</sub>Sn intermetallic compound (IMC) islands forms during the solidification process of the solder process[2].

In the past 10 years, the microelectronics industry aimed to decrease the Ag content of the traditional lead-free solder alloys (like Sn96.5Ag3Cu0.5, SAC305), which caused the widespread of the low-silver content solder alloys, like the Sn99Ag0.3Cu0.7 (SAC0307) [3].

Unfortunately, the decrease of the Ag content increased the Sn content up to 99 wt%, and this made the alloys more prone to Sn whisker development. Sn whiskers are spontaneously growing on the surface of the typically high tin content soldering materials (like solder joints or surface finishes). The whisker was observed in 1948 by the BELL telephone company. The driving force results whisker growth is always a mechanical stress between/on the  $\beta$ -Sn grains. It could come as a direct mechanical load, as a thermo-mechanical effect, as a residual stress, or as a volumetric changes in the solder joint by oxidation or intermetallic formation. Tin whiskers can also grow because of corrosion of the surface and spread to the inside of the solder joint. The density of Sn oxides (SnO or SnO<sub>2</sub>) is lower than Sn, so their formation causes compressive stress on the  $\beta$ -Sn grains and causes whisker development [4, 5]. The dimensions of the Sn whiskers vary from 0.5 to 3000 µm, so they can cause short circuits in the fine pitch microelectronics applications and means a serious reliability risk.

The most novel research direction to improve the properties of solder joints used in microelectronics is the addition of ceramic nano-particles (NPs) as reinforcements [6]. This method results in the so-called "composite" solder joints. A wide range of ceramics (main oxide ceramics) was already applied, like Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>Ni<sub>4</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, SiC. They usually cause considerable grain refinement and disperse of dissolved intermetallics in the joint, which improve its mechanical quality [7].

In the case of SnAgCu solders, the application of ceramic NPs was reported to result in a lower IMC layer thickness [8]. Since the addition of ceramic NPs modifies the grain structure of the solder joints, it is assumed that they could influence the Sn whisker susceptibility of the composite solder joints.

The ZnO has similar properties with other oxide ceramic nano-particle alloys in solder material. The ZnO micro or nano-particles added to SnAgCu based solder alloys have suppressed the IMC layer growth at the soldersubstrate interface [9-10]. It was shown in solder alloys that ZnO nano-particles decrease the diffusion coefficient, and this suppresses the formation and growth of the IMC layer. The IMC layer grown is suppressed during aging [11] and affects solder joint strength. So, ZnO NPs are considered as a positive effect for long-time durability and reliability.

A doping material usually affects the melting point, viscosity, and printability of solder pastes. Using differential scanning calorimetry to find ZnO effect on the melting point of SnCu solder alloy, ZnO addition to SnCu solder alloy was shown to slightly increase the liquidus-solidus point of the composite solder alloy [12]. The creep resistance and life of the solder joints were also reported to be improved after ZnO NPs addition into SnZn6.5 alloy [13].

Kanlayasiri et al. showed that the cold slump properties of SnAg0.3Cu0.7 were decreased with ZnO addition (up to 1 wt%). The maximum hot slump (at 150 °C) resulted at 0.25 wt%. On a Cu substrate, solder paste printability is decreased with higher ZnO NPs concentration [14]. In the case of Sn99Ag0.3Cu0.7 (SAC0307) solder paste, reflow is suppressed when ZnO NPs wt% is over the 0.5 wt% [15].

Our research aimed to study the effect of ZnO NPs on the Sn whisker growth from low-Ag content SAC0307 solder alloys reinforced by 0.25 wt% ZnO NPs (having 100nm primary particle size). Furthermore, the mechanical strengths of solder alloys have been investigated as an important quality/reliability parameter.

## 2. MATERIALS AND METHODS

The whisker growth and mechanical strength of SAC0307 composite solder alloy reinforced by ZnO nanoparticles were studied. The ZnO NPs with primary particle size 100nm were added into SAC0307 solder paste in 0.25 wt%. The ZnO NPs had decreased the reflow of solder paste when over 0.5 wt% in SAC0307 [15], therefore, ZnO NPs were used only in 0.25 wt%. In order to ensure the homogeneous mixing of the ZnO NPs into the solder paste, a ball milling process was used. It took for 10 min with 300 rpm by a planetary ball mill. Table 1 shows the investigated sample types.

Sample name	Composition	
REF	SACX0307	
ZnO	SACX0307-ZnO (0.25 wt%)	

Table 1. Solder alloys.		
mple name	Composition	
EF	SACX0307	
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Solder joints were prepared from the composite solder alloy and from the reference SAC0307 as well, on Ag surface finish by conventional SMT. The solder pastes were stencil printed, 0603 sized chip resistors were placed into the paste, and the whole structure was reflowed in an IR reflow oven with a linear thermal profile. A linear type thermal profile took in an air atmosphere: pre-heating 180–190 °C for 180 s, ramp-up 245–255 °C for 60 s, and cooling back to room temperature. After soldering, the flux was removed by a metal brush. The solder joints were exposed to an accelerated lifetime test (85 °C/85 RH% THB, 3000 h) to enhance the Sn whisker growth.

The samples were checked at every 500 hours of the THB test by Scanning Electron Microscopy (SEM), FEI Inspect S50, to observe the corroded areas and the whisker grow on the solder joints. The mechanical strength of the solder joints was measured every 1000 hours. The test method was the standardized shear stress measurement using a DAGE 2400 tester. Means and deviations of the shear strengths were calculated by ten resistors test results at each time and solder type.

#### 3. RESULTS AND DISCUSSION

In the function of the time, corroded areas were appeared on the sample due to the highly corrosive test environment. When observing the sample by SEM, the corroded area was changed from brighter gray to the dark gray color. Because oxide change the volume and molecules structure of Sn then back ground scattering is changed at corroded area. This changing is visible Fig. 1 and 2. Fig.1 and 2 are SEM micrographs of the REF and ZnO samples between 500h and 3000h THB test. (In Fig. 1, the peeling dark gray layer on the solder joint is the flux residue, which was removed later.) On the surface of the REF samples (Fig. 1), corrosion spots appeared between 1000-1500h aging (Fig. 1,c red circle). The corroded area. It van be compared in Fig. 1 and Fig. 2, how ZnO NPs were effective to prevent corrosion of on the solder joints.



Fig. 1. SEM micrograph about the REF solder joints during the THB test: a) 500 h, b) 1000 h, c) 1500 h, d) 2000 h, e) 2500 h and f) 3000 h



Fig. 2. SEM micrograph about the ZnO solder joints during the THB test: a) 500 h, b) 1000 h, c) 1500 h, d) 2000 h, e) 2500 h and f) 3000 h.

On the ZnO solder joints, corrosion spots were not observed during the whole THB test (Fig.2). So, ZnO NPs had an effect on improving the corrosion behavior of Sn. Probably that is why ZnO samples did not grow Sn whisker at all during the whole THB test.

The first wiskers were observed after 1500 h of THB aging on the REF samples. For comparison of the REF and ZNO samples, Fig. 3 shows the samples with higher magnification, both samples aged 2500 h and 3000 h. Sn whiskers were found on the REF sample at the boundary of the corrosion spots. Comparing Fig.3,a and b, a few more whiskers were grown betweem 2500 and 3000h. Fig. 3,c and d about the ZnO samples in the same time frame did not show whiskers. Because ZnO NPs decreased the corrosion of Sn. In Fig. 3,a, the first whiskers are presented. Thei physical parameters of no1. were 12.43  $\mu$ m length and width is 6.60  $\mu$ m. The whisker no.2 were the bigest whisker in Fig. 3,a. It had 26.49  $\mu$ m length and 7.49 width. The whisker no.3 grew vertical side, so only its width was measurable, and it was 6.60  $\mu$ m.





Fig 4. presents the statistical results of mechanical strength results. In other researches, mixing the ceramic nano-particle into the solder paste usually considerably increased the mechanical properties of the composite solder joints[16, 17]. But in the present study, both types of solder joints provided very similar mechanical strengths during the whole study. However, generally, the addition of ZnO nano-particles slightly increased the mechanical strength of the composite solder joints.

During the first mechanical test at 0 h, REF samples had 21.81N, and ZnO had 23.08 N average shear strength. So the ZnO NPs increased only with 5.82% the shear strength compared to REF solder joint. The REF sample had average strength 20.7 N with 3.5N standard deviations after 1000h aging. The ZnO samples showed the same average shear strength (20.7N) with 6.0N standard deviation. At 2000 h, both samples performed a bit better shear strength than at 1000 and during 3000 hour. The average strength was 21.96 N and 22.96 N in the case of REF and ZnO samples, respectively. On the surface of the REF sample corrosion was observed from 1000 h aging (Fig. 1,c). But this type of spot corrosion could not spread deep inside the solder joint, remains on the surface area. Therefore, it cannot have an effect on the mechanical properties of the solder joints.



Fig. 4. Mechanical strength of REF and ZnO samples.

The ZnO NPs suppressed the whisker growth during THB aging, so increased the reliability. During the THB test, the SACX0307-ZnO solder joints were mechanically stable. So the application of ZnO NPs in the SAC0307 solder alloy resulted in a positive effect on solder joints' durability and reliability.

## 4. CONCLUSIONS

A study for Sn whisker susceptibility of SAC0307 solder alloy reinforced by 0.25 wt% ZnO NPs were performed. The main conclusions are the following:

- The ZnO NPs improved the corrosion resistance of the composite solder joints. Corroded areas were observed on the reference SAC0307 solder joints after 1000h of THB. They spread during the test on the surface area of the solder joints. The addition of ZnO NPs suppressed the corrosion, no corroded areas were observed until 3000h THB aging.
- The ZnO NPs suppressed the Sn whisker growth probably by improving the corrosion resistance of the composite solder alloy. On the reference samples, the Sn whiskers grew at the boundary of corroded areas.
- The ZnO NPs improved the reliability of the composite solder joints, so their application is favorable for the electronics industry.

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