

Soldering with SACX0307-(TiO₂/ZnO) nano-composite solder alloys

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Abstract: *In the present research, the solderability of SACX0307 nano-composite solder alloys was studied. The SACX0307 solder alloys were reinforced by ZnO or TiO₂ nanoparticles. The nanoparticles were mixed into the solder paste in different volume fractions between 0.25 and 1 wt%, using the ball milling process. Wetting and mechanical tests were performed with the nano-composite solder alloys and with the reference SACX0307 as well. It was found that the ceramic reinforcements did not have a considerable effect on the wetting of the composite solder alloys. However, the shear strength of the nano-composite solder joints increased compared to the reference SACX0307. Generally, the application of TiO₂ nanoparticles resulted in a bit better soldering properties than the ZnO nanoparticles. No straightforward correlation was found between the volume fraction of the ceramic nanoparticles and the soldering properties of the nano-composite solder alloys. Expect in the case of the ZnO nanoparticles, when the volume fraction should not exceed 0.5wt% since it can inhibit the proper reflow of the solder paste.*

1. INTRODUCTION

The integration in electronic assemblies is ever-increasing, resulting in reduced component sizes and higher power density [1]. The industry requires lead-free soldering technology solutions to provide reliable solder joints even at elevated temperatures, such as in the case of power LEDs.

Transition to the lead-free soldering technology caused the widespread use of the Sn-Ag-Cu based solder alloys, especially high silver content solder alloys such as Sn96.5Ag3Cu0.5 (SAC305) and Sn95.5Ag4Cu0.5 (SAC405) [2]. These alloys are considered good all-around performers, but the relatively high content of silver in the solder paste leads to a higher price and potential reliability issues such as shrinkage defects resulting from Ag₃Sn intermetallic compound islands in the solidification phase of the solder [3]. Since the introduction of lead-free solder pastes, researchers aim to enhance the properties of solder paste such as wettability, mechanical behaviour by maintaining the melting point and the price of the solder paste low. Alloying high silver content solders with metals such as Bi, Sb, Ni (usually below 3 wt%) lead to better performance solder pastes, such as Innolot, widely used in the automotive industry.

However, the latest research aims to lower the Ag content in the solder paste, and a promising candidate is Sn99Ag0.3Cu0.7 (SAC0307). SAC0307 is also micro-alloyed with the metals mentioned earlier but with lower alloy content (usually below <0.1 wt%), called SACX0307.

The most novel approach in enhanced reliability is the application of reinforcement materials and particles. The industry began to research composite solder paste using a wide range of ceramics in the submicron and nanoparticle size range. Ceramics particles like ZnO, TiO₂, ZrO₂, Al₂O₃, Fe₂O₃, Si₃Ni₄, SiC, La₂O₃ are used for such purposes, usually in the range of 0.05 wt% to 2 wt%. The reinforcement particles change the properties of solder alloys and solder structures, such as intermetallic layer growth rate, grain size, melting point, and melting range. However, the optimization of the composite material for a particular use is a complex problem.

The effect of TiO₂ addition on different solder alloys is investigated in several studies. In the case of Sn-Ag-Cu based solders, the addition of TiO₂ was reported to resulting in a lower intermetallic layer thickness compared to the solder alloy without doping [4-5]. TiO₂ nanoparticles among IMCs can create a more significant stress concentration and breakage of Cu₆Sn₅ during its growth phase as a potential reliability issue [4]. Grain size of Ag₃Sn IMCs and spacing between them decreased, and enhanced microhardness was also reported [7]. In the case of SnAg_{3.5}Zn_{0.5} solder, the addition of TiO₂ and Al₂O₃ elevated the melting point of the composite solder and decreased the melting range [8]. The addition of TiO₂ (up to 1 wt%) in SnZn_{6.5} solder alloy resulted in higher creep resistance and increased melting temperature, and refined grain sizes of primary β-Sn [9]. In SnCu_{0.7}Ni_{0.05} solder alloy, the shear strength was shown to increase significantly due to the addition of TiO₂; the microhardness also increased in the composite material, and the failure mode of the shear tests shifted to a more ductile failure mode instead of brittle [10-11]. The electrical properties are also affected by the doping materials. Liu et al. showed a sharp increase in the resistance of the solder over 0.6 wt% of TiO₂ in Sn-xTiO₂ alloy.

The effect of ZnO addition has a similar effect to some extent. In the case of SnAgCu-based solder alloys, the addition of ZnO micro- and nanoparticles resulted in a thinner IMC layer at the solder-substrate interface [12-13]. The wettability was also increased slightly over 0.5 wt% addition [13]. It was shown that ZnO nanoparticles could decrease the diffusion coefficient of the IMC layer and constrain the formation and growth of IMCs; the growth of the IMC layer remains restrained during aging [14], which is considered as a positive effect from the aspect of long-time reliability. Based on differential scanning calorimetry, it was shown that ZnO addition in the case of SnCu solder alloy also slightly increased the melting point of the composite [15]. The creep life and creep resistance of the solder was also reported to be improved by ZnO addition into SnZn_{6.5} alloy [16].

The doping material also alters the viscosity and printability of the solder paste. Kanlayasiri et al. showed that the cold slump properties of SnAg_{0.3}Cu_{0.7} with xZnO composite solder decreased with increased addition (up to 1 wt%) of nano-ZnO. However, the maximum hot slump (at 150 °C) resulted at 0.25 wt%. Printability of the solder paste on a Cu substrate decreased with higher nano-ZnO concentration [17].

Gain et al. showed that on a Ni/Au plated copper surface, the addition of ZrO₂ nanoparticles into SAC305 alloy resulted in a lower initial thickness of (CuNi)₆Sn₅ intermetallic layer thickness and increased slower after several reflow cycles. The shear strength of the solder was also increased due to the ZrO₂ nanoparticles [18]. The addition of 0.5 wt% of Fe₂NiO₄, Fe₂O₃, NiO, ITO, carbon nanostructure (diamond) to SAC305 was shown to result in elevated hardness (enhancement of 44.1-77.5%) but also in higher wetting angle and lower spreading rate [19].

Most of the researches have proceeded on bulk solder material; reflow soldered onto a substrate without the addition of through-hole or surface-mounted components. The behaviour of the composite solder alloys can behave differently in case of the presence of a component [20]. The novel approach of our research is the usage of surface mounted components to investigate the composite solder material in an actual assembly as a solder joint, not as a bulk material. For reflow soldering, a low-Ag content SACX0307 is being used, with ZnO or TiO₂ nanoparticle addition.

2. MATERIALS AND METHODS

The wettability and shear strength of SACX0307 nano-composite solder alloys were studied. ZnO and TiO₂ nanoparticles were used with 100nm primary particle size, in the range of 0.25 to 1 wt%. The investigated composite solder alloys can be seen in Table 1. Previous works used different ceramic contents between 0.05 and 1wt%, so our aim was to study the effect of the ceramic content on the wettability of the solder alloy and on the shear strength of the composite solder joints. The nano-particles were mixed into the solder paste homogeneously using the ball milling process, which was carried out for 10 min at 300 rpm using a planetary ball mill.

Table 1. Investigated solder alloys.

Sample name	Composition
REF	SACX0307
ST1	SACX0307-TiO ₂ (1 wt%)
ST2	SACX0307-TiO ₂ (0.5 wt%)
ST3	SACX0307-TiO ₂ (0.25 wt%)
SZ1	SACX0307-ZnO (1 wt%)
SZ2	SACX0307-ZnO (0.5 wt%)
SZ3	SACX0307-ZnO (0.25 wt%)

Initially, standard spreading tests were performed to investigate the wettability of the different composite solders on FR4 substrate with Ag surface finishing. During the spreading test, round-shaped solder drops were deposited onto a continuous surface finish. After the reflow process, the wetted area was measured, and the surface quality of the solder spread was evaluated. The printed deposits were 5 mm in diameter, and the tests were repeated 16 times for each type of sample.

Solder joints were fabricated with size 0603 chip resistors on the same substrate using classical SMT. First, the solder paste was printed onto the substrates' contact pads using stencil printing with a 125 μm thick stencil. The components were then placed onto the solder paste, and the solder paste was reflowed in an IR batch reflow oven. A linear type thermal profile was used: pre-heating to 180–190 °C in 180s, ramp-up to 245–255 °C in 60s, and cooling down to 150 °C in 100s. The soldering took place in an air atmosphere. The shear strength of the chip resistors was measured using a DAGE 2400 tester. Twenty resistors were tested at each solder type, and the means and deviations of the strengths were calculated.

3. RESULTS AND DISCUSSION

The wetting behavior depended on the added ceramics. Fig. 1 shows typical examples of the wetting property of the TiO₂ composite solder pastes. TiO₂ addition did not show a considerable effect on the wetting properties compared to the reference SACX0307. Oppositely, in the case of the ZnO nanoparticles (Fig. 2) the wetting property of composite solder pastes decreased compared to the reference SACX0307, and it highly depended on the volume fraction of the ZnO nanoparticles.

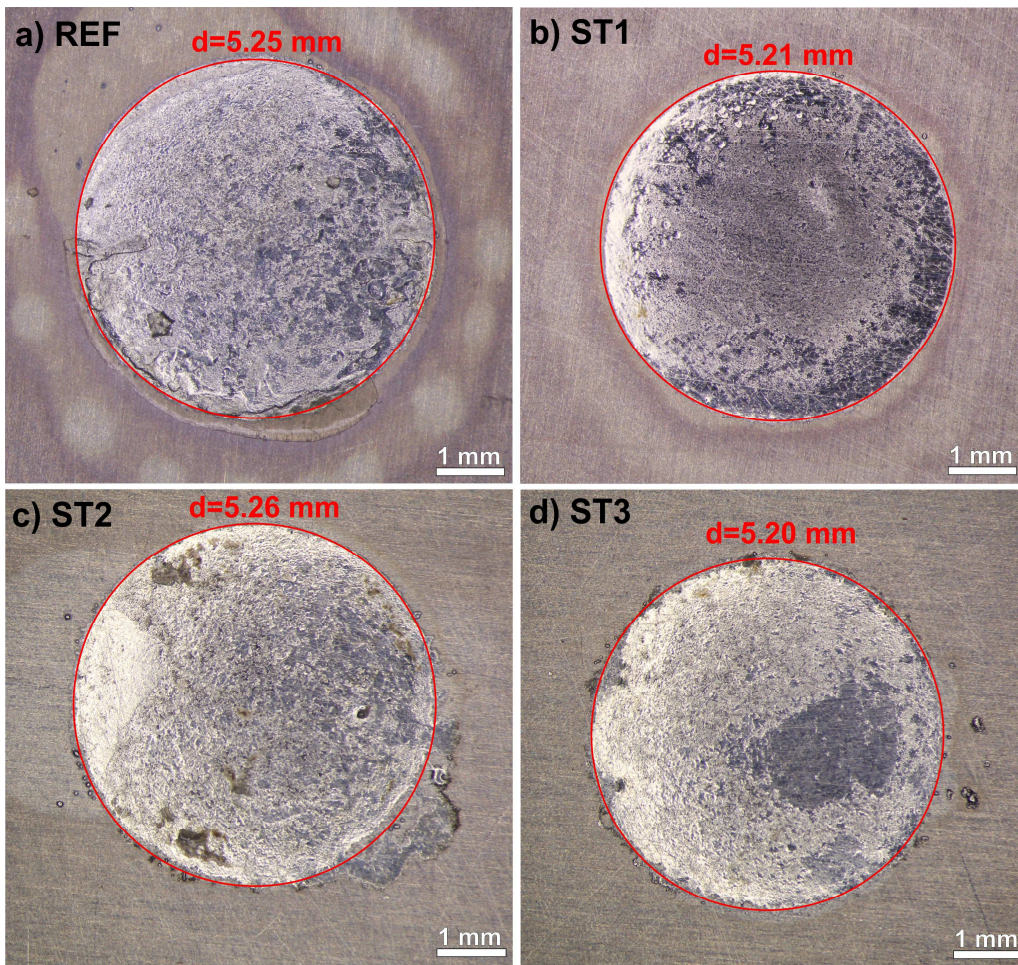


Fig. 1. Spreading results of SACX0307-TiO₂ composite solder pastes.

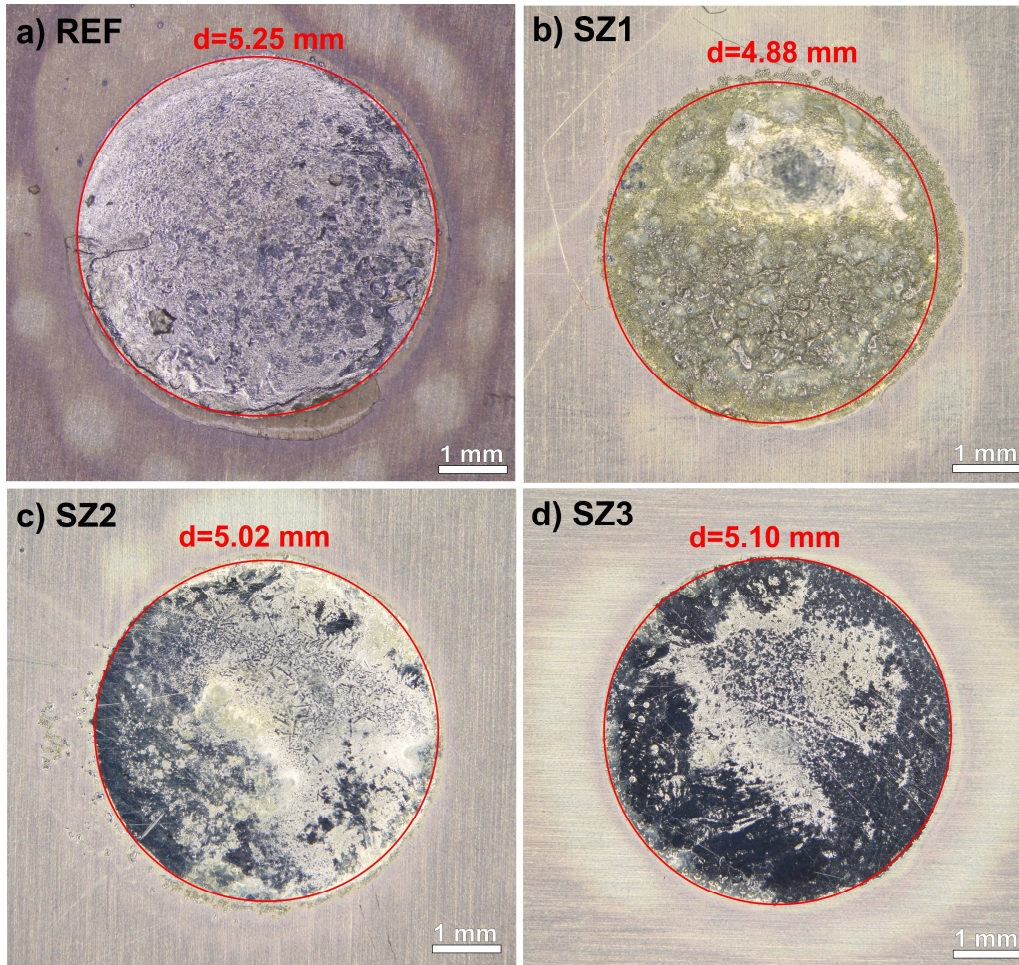


Fig. 2. Spreading results of SACX0307-ZnO composite solder pastes.

In the case of sample SZ1 (1 wt% ZnO) the wetting was unacceptable. The solder could not reflow into a continuous surface (Fig. 2a), and significant dewetting occurred since the 5mm diameter of the solder spot always decreased. At lower volume fractions (0.25 and 0.5 wt%) proper wetting was observed (Fig. 2c and d).

For a more accurate comparison, the statistics of the wetted areas were calculated and showed in box plots (Fig. 3), where the small squares represent the average, the horizontal lines indicate the median, the borders of the boxes indicate the $\pm\sigma$ standard deviation and the crosses mark the min-max values. Minor grew of the average wetted area was found with the application of TiO₂ nanoparticles. In the case of ZnO nanoparticles, the average wetted areas did not change. The results of 1 wt% volume fraction ZnO were not evaluated due to the unacceptable wetting. The 0.5wt% nanoparticle content resulted in the best wetting at both composite solder alloy types.

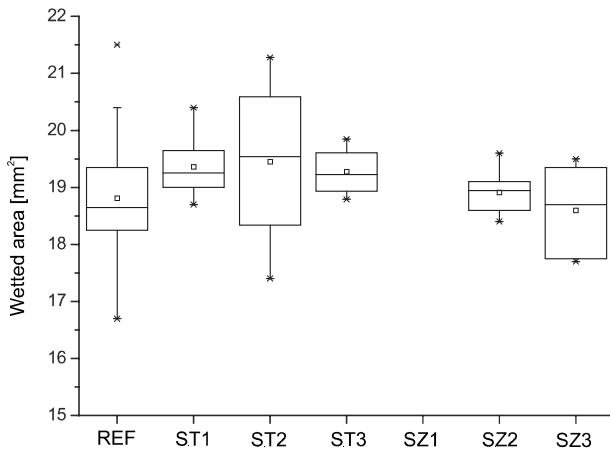


Fig. 3. Box plots of the wetted areas in the case of the different composite solder pastes.

During the solder tests, the solder joints were always appropriate when the wetting was acceptable. Fig 4. shows an example of a soldered component.

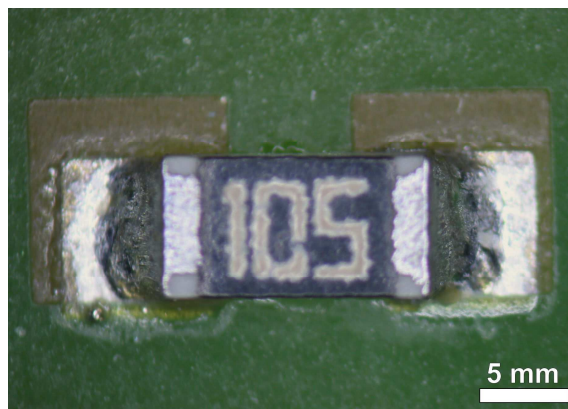


Fig. 4. A soldered 0603 resistor with SZ1 composite solder paste.

Fig. 5 shows the results of the shear tests in box plots. (The interpretation of the box plots is the same as in Fig 3.) The average shear strength of the composite solder joints increased compared to the reference SACX0307. The reference shear strength was 21.8N. It reached 24-26N in the case of TiO_2 reinforcements and 23N in the case of ZnO. A straightforward correlation between the shear strength and the volume fraction of the nanoparticles was not found. The best average shear strength (26.25N) was observed in the case of 0.25 wt% TiO_2 . As in the wetting tests, the TiO_2 performed better than the ZnO in the mechanical tests too.

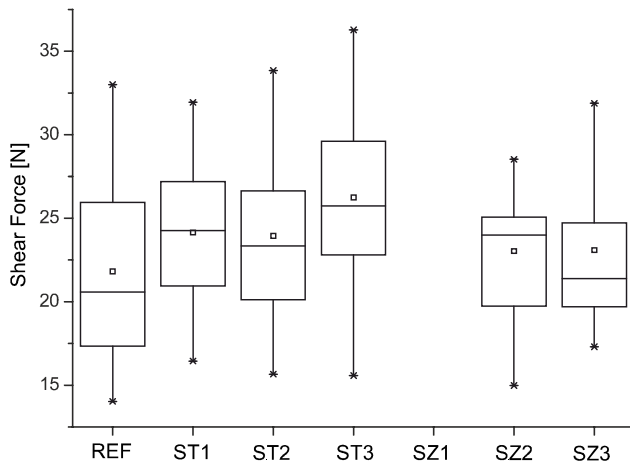


Fig. 5. Box plots of the shear forces of the composite solder joints.

The mechanical strength improvement cannot be caused by the better wetting properties since only minor wetting differences were found. In the case of ZnO nanoparticles the wetting was even weaker a bit, oppositely to [13]. The literature generally agrees that the ceramic nanoparticles refine the microstructure of the solder joints (the β -Sn grains and the IMC particles as well), which usually results in the improvement of the mechanical properties. This might happen in our case too, however further microstructural investigations are necessary.

4. CONCLUSIONS

Solder tests were performed with SACX0307 nano-composite solder alloys reinforced by ZnO or TiO₂ nanoparticles. The main conclusions are the following:

- The ceramic reinforcements have a minor effect on the wetting of the composite solder alloys, except the 1wt% ZnO, which blocked the proper wetting. The best wetting was observed in the case of 0.5wt% nanoparticle content at both composite alloy types.
- The shear strength of the composite solder joints increased compared to the reference SACX0307. Generally, the application of TiO₂ nanoparticles resulted in a bit better wetting and mechanical properties than the ZnO nanoparticles.
- No straightforward correlation was found between the volume fraction of the ceramic nanoparticles and the soldering properties of the composite solder alloys. But the volume fraction of ZnO should not exceed 0.5wt% since it can block the proper wetting.

5. ACKNOWLEDGEMENT

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