

Influence of 0.1%Al on the Properties of the SAC405 Lead-free Solder Alloy

Robert Augustin, Roman Koleňák, Maroš Martinkovič, Martin Provazník

Abstract - The work presented herein deals with the study of the lead-free solder Sn-4.0Ag-0.5Cu (SAC405) alloyed with 0.1% Al. Both β -Sn and Ag₃Sn were observed in the solder alloy microstructure as well as the Cu-Al (77% Cu-21% Al) intermetallic compound. Whole Al from the Sn-4.0Ag-0.5Cu-0.1%Al solder alloy was found in the Cu-Al intermetallic compound. The melting interval of the solder increased from 217-219 °C to 220-223 °C. The addition of 0.1% Al had a slightly negative effect on the wettability and spreadability of the solder on the Cu substrate. The presence of Al also affected the thickness of the intermetallic compounds formed on the solder-Cu boundary. The shear strength of the Sn-4.2Ag-0.5Cu-0.1Al solder was lower in comparison with the Sn-4.0Ag-0.5Cu solder.

Index Terms - soldering, Sn-Ag-Cu-Al, IMC, shear strength, spreadability, wettability

I. INTRODUCTION

REDUCING the concentration of Ag in Sn-Ag-Cu solder alloys has been shown to be advantageous for mobile devices. However, compared with solders containing Ag \geq 3wt% (for example SAC305 and SAC405, etc.), those with a low content of Ag are characterised by an increased melting point, a deterioration in thermal resistance and the increased occurrence of defects during the reflow process [1]. The alloys with a reduced Ag content contain micro-alloys and/or alloying elements with a concentration of around 0.1%. Such alloying elements may modify specific properties such as oxidation resistance and/or mechanical reliability [2]. One of the key drawbacks of the close-to-eutectic SAC solders used for BGA components is poor resistance against mechanical shocks (mechanical shock performance), mainly on Ni/Au surfaces. A high Ag content (3-4%) increases the toughness and strength of close-to-eutectic alloys, which affects their mechanical properties.

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R. Augustin is with the Slovak University of Technology, Faculty of Materials Science and Technology, J. Bottu 23, 917 24 Trnava, Slovak Republic, (corresponding author: e-mail: robert.augustin@stuba.sk).

R. Koleňák is with the Slovak University of Technology, Faculty of Materials Science and Technology, J. Bottu 23, 917 24 Trnava, Slovak Republic, (e-mail: roman.kolenak@stuba.sk).

M. Martinkovič is with the Slovak University of Technology, Faculty of Materials Science and Technology, J. Bottu 23, 917 24 Trnava, Slovak Republic, (e-mail: maros.martinkovic@stuba.sk).

M. Provazník is with the Slovak University of Technology, Faculty of Materials Science and Technology, J. Bottu 23, 917 24 Trnava, Slovak Republic, (e-mail: martin.provaznik@stuba.sk).

Almost 85% of suppliers have used SAC405 or SAC305 alloys on Ni/Au surfaces, which is worrying due to the reasons mentioned regarding the unacceptably high susceptibility to brittle fractures. However, the majority of suppliers would not recommend this combination of materials for use in mobile equipment where the risk of brittle fracture seems to be most serious [2].

Intermetallic compounds (IMC) on solder-parent metal boundaries and their thickness are the main factors affecting the strength and reliability of soldered joints. A favourable effect of a small amount of Al was also found during development of the Sn-9%Zn-xAl solder. The addition of minimum amount of Al to the Sn-9%Zn solder resulted in a reduction in oxides on the solder's surface. Wettability was improved and toughness increased without any decrease in strength. Both Al and Zn were concentrated on the Sn grain boundaries, which, in the opinion of the authors, resulted in strengthening of the bond between the boundaries of the Sn grains [3], [4].

In the case of the experimental solder Sn-2%Ag-(0.05 to 0.1%Al), a refinement in the grain and increased toughness were both observed [5].

Regarding the mentioned properties of close-to-eutectic SAC alloys with a high Ag content, Sn-3.1%Ag-0.41%Cu-0.1%Al, Sn-2.86%Ag-0.38%Cu-0.25%Al and Sn-2.53%Ag-0.33%Cu-0.45%Al soldering alloys were studied. The Cu-Al phases observed in the microstructure were identified as being γ_2 . After annealing at 150 °C for 1000 hours, the Cu₆Sn₅ phases were only observed in the alloy with a content of 0.45% Al [6].

Adding Al to SAC alloys could be the most efficient way of softening (strength reduction) the alloy, and it also reduces the toughness to level comparable with the SAC105 and SAC1505 solders. The effect of Al on the properties of SAC alloys has been shown to be more significant than the effect of Ni. Adding Al to SAC alloys reduces the number of hard intermetallic Ag₃Sn and Cu₆Sn₅ particles and forms soft AlAg and AlCu particles [1].

The composite solders were prepared via the mechanical mixing of Al nano-particles (0, 0.5, 1.0 and 3.0 wt%) in a powder form into the eutectic Sn-3.5Ag-0.5Cu solder. The authors found that the thickness of the intermetallic particles on the joint boundary consistently grew with the number of reflow cycles and also the annealing time. However, after the addition of Al nano-particles a fine ternary Sn-Al-Ag intermetallic compound was formed on top of the Sn-Ni-Cu layer; furthermore, a refinement in the microstructure was also observed. The authors also stated that the addition of Al

nano-particles reduced the thickness of the intermetallic compounds, although only slightly [7].

II. MATERIALS AND EXPERIMENTAL METHODS

The experiments were performed using the solders given in Table I. As a parent material for the measurement of wettability and spreadability, a Cu plate 2 mm in thickness and with an area of 35×35 mm was used. The measurements were made with and without flux. The liquid fluxes used for the experiments are given in Table II.

TABLE I
PROPERTIES AND CHEMICAL COMPOSITION OF THE SOLDERS

Solder	Sn	SnPb37	SAC405	SAC405Al
T _r [°C]	232	183	217-219	220-223*
ρ [g.cm ³]	7.29	8.40	7.41	7.36
Sn [%]	99	63	rest	rest
Ag [%]	-	-	4.0	4.0
Cu [%]	-	-	0.5	0.5
Al [%]	-	-	-	0.1
Pb [%]	-	37	-	-

* measuring data

TABLE II:
CHARACTERISTICS OF THE FLUXES

Trade name	Mark (EN 29454-1)	Flux type	Base	Activator
Rosin	1.1.1.A	Rosin	Rosin	None
Soldaflex® 7000	3.1.1.A	Inorganic	Salts	NH ₄ Cl

The soldering temperature for each solder was 40 °C above its melting point: Sn - 272 °C, SnPb37 - 223 °C, SAC405 - 258 °C, SAC405Al - 262 °C. Weight was measured using RADWAG WPS 510/C/2 scales. The soldering temperature was measured by K (NiCr - Ni) thermocouple type. The samples were ground using SiC 600 and 1200 μm grinding disks. The final treatment consisted of polishing using 9, 6, 3 and 1 μm diamonds. The 2% Nital microstructure was used for etching. Wetting of the specimens was assessed using pictures from the scanning electron microscope (SEM) and the Stemi 2000C light microscope. Pictures of the boundary were taken by the Neophot 32 light microscope. The modified “pushing test” with the FPZ 100/1 universal testing machine and a shear strength adaptor was used for the determination of shear strength. The strain rate was 0.5 mm/1 min.

III. RESULTS AND DISCUSSION

A. Microstructure of SAC 405 and SAC 405 Al solders

The microstructure of the SAC405 (Sn-4.0Ag-0.5Cu) solder consisted of an Sn matrix where Ag₃Sn needles and Cu₆Sn₅ in the bulk form are uniformly distributed [8] - [11]. Adding 0.1% Al to the SAC405 solder changed the microstructure of the solder, as shown in Fig. 1. Similarly, the microstructure of the SAC405Al (Sn-4.0Ag-0.5Cu-0.1Al) solder consisted of an Sn matrix with Ag₃Sn needles. However, the formation of a new bulk CuAl phase was observed in this solder. The CuAl phase was non-uniformly distributed throughout the entire volume of the solder. The

composition of the CuAl phase was determined by EDX analysis, as shown in Fig. 2. The CuAl consisted of approximately of 77 wt% (60.18 atomic %) Cu and 21 wt% (39.21 atomic %) Al, as shown in Table III. It has been suggested that all Al contained within this type of solder is bound in the CuAl phase [6]. The chemical composition is assumed to consist of a mechanical mixture of ζ₂ and δ phases. The percentage of the ζ₂ phase exceeds that of the δ phase. Regarding the content of Sn in the CuAl phase, it is possible that only the ζ₂ phase was concerned.

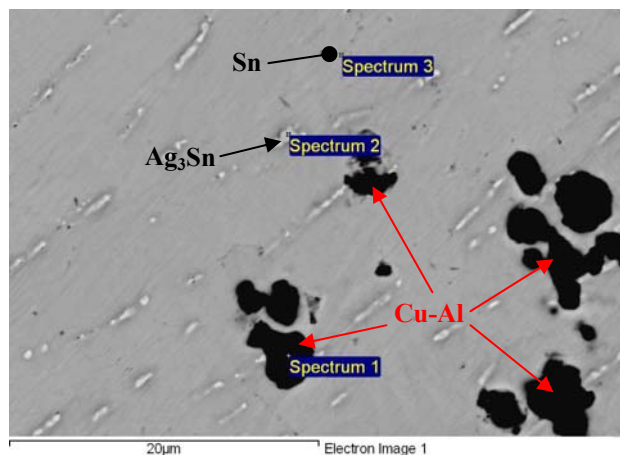


Fig. 1. Microstructure of SAC405Al (Sn-4.0Ag-0.5Cu-0.1Al) solder (SEM, BSE regime)

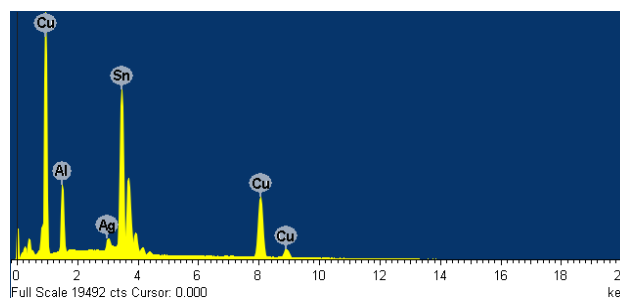


Fig. 2. The EDX graph of CuAl created in SAC405Al microstructure (Spectrum 1)

TABLE III
RESULTS OF EDX ANALYSIS

Spectrum	Al	Cu	Ag	Sn	Total
Spectrum 1	21.25	76.82		1.45	100.27
Spectrum 2			49.63	64.76	117.53
Spectrum 3				106.72	110.24

B. Melting interval

The melting interval of the solders was determined using DSC analysis, as shown in Fig. 3. The SnAg4Cu0.5 solder was found to have a melting interval of 217-219 °C. By adding Al to the solder the melting interval was slightly increased to 220-223 °C.

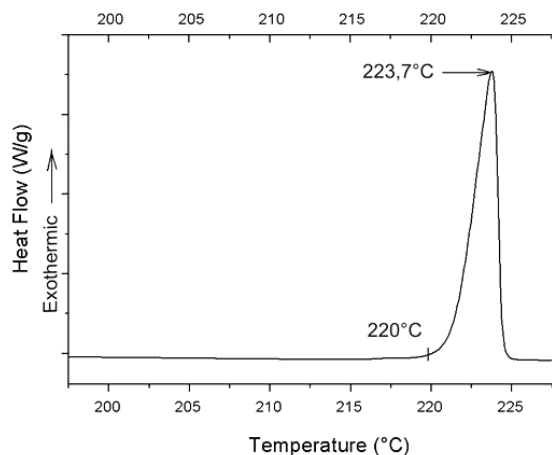


Fig. 3. DSC curve of SAC405Al (Sn-4.0Ag-0.5Cu-0.1Al) solder

C. Solder - parent material boundary.

After determining the melting intervals the solder deposits on the Cu substrate were fabricated. In the case of SAC405 and SAC405Al solders a diffusion layer was observed on the solder-Cu boundary. It was obvious that the layer of intermetallic compounds (IMC) was thinner on SAC 405 Al, as shown in Fig. 4 and 5.

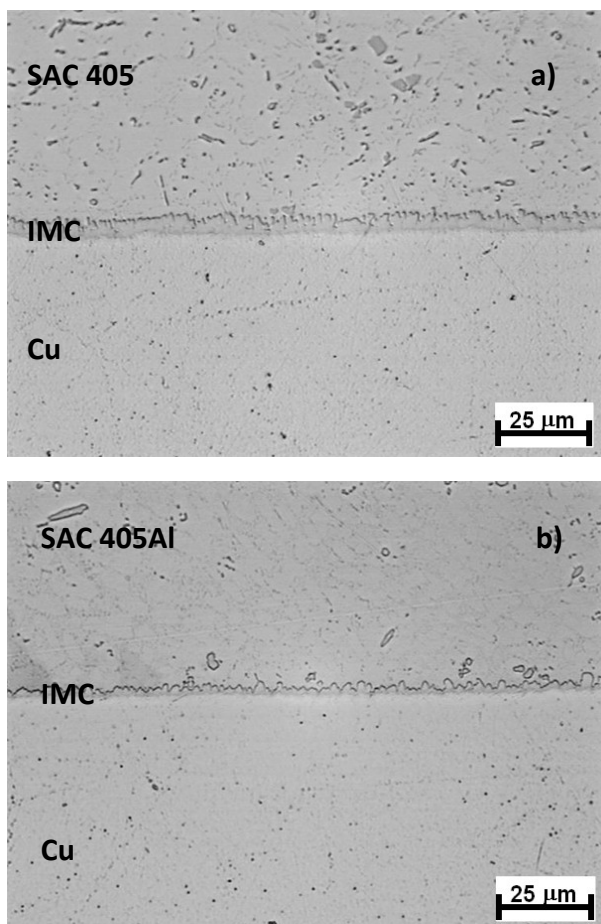


Fig. 4. IMC layer thicknesses on Cu-solder boundary:
a) SAC405 at 260°C/5 min. b) SAC405Al at 260°C/5 min. magnified 426x

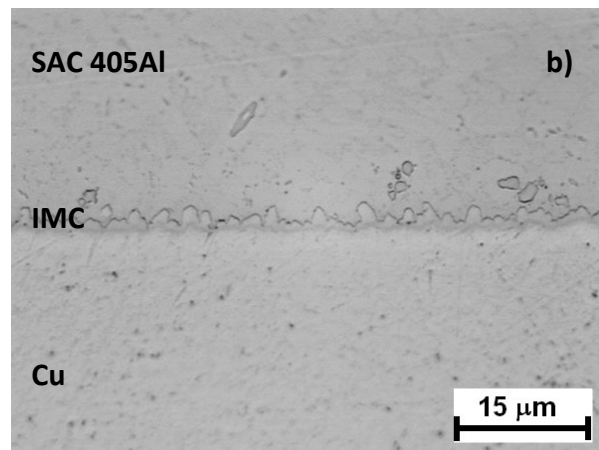
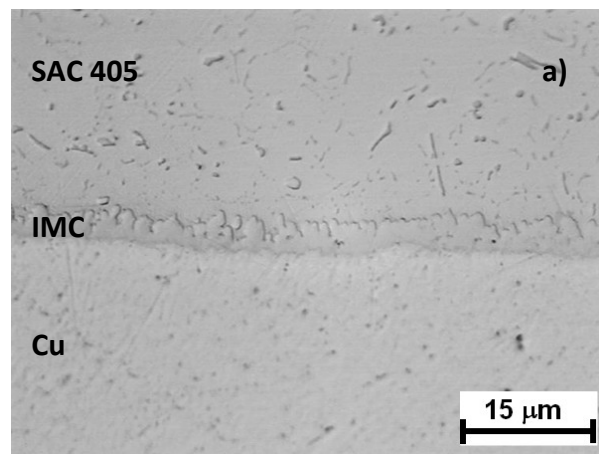


Fig. 5. IMC layer thickness on Cu-solder boundary:
a) SAC405 at 260°C/5 min. b) SAC405Al at 260°C/5 min. magnified 855x

The EDX line analysis of the SAC 405Al-Cu boundary is shown in Fig. 6. The results, which are shown in Fig. 7, do not prove the presence of Al at the SAC 405Al-Cu boundary in the form of a layer. This means that Al did not directly contribute to reducing the IMC thickness. The density of Cu (8960 kg.m^{-3}) is almost three times higher than that of Al (2699 kg.m^{-3}). Therefore, Al contained in solder may considerably affect the microstructure of the solder and thus also its properties at the solder-Cu boundary, despite its low concentration (0.1%).

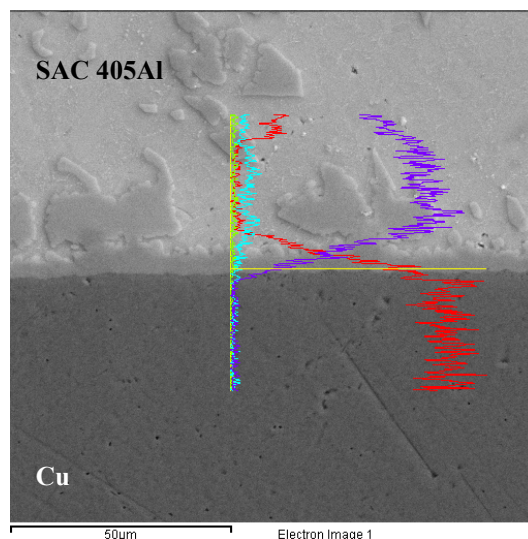


Fig. 6. EDX analysis of SAC405Al-Cu boundary at 260 °C/5 min.

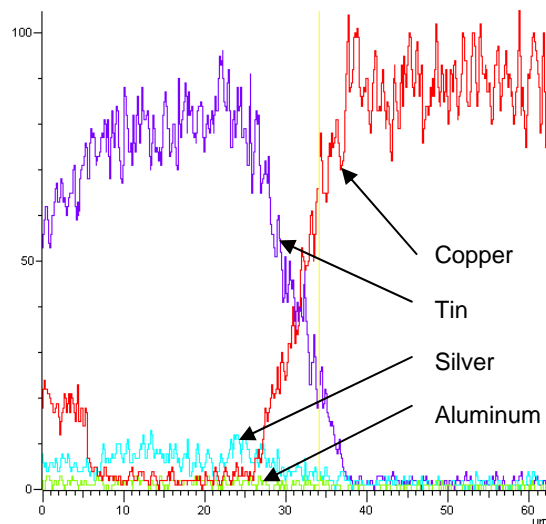


Fig. 7. Result of SAC405Al-Cu boundary EDX analysis at 260°C/5 min.

D. Spreadability, wettability and surface tension

Spreadability of the solders was measured via the following parameters: dwelling times on soldering temperature - 1 min, solder weight - 1 g, flux weight - 1 g. All solders, attained better spreadability with the use of the 3.1.1.A flux. The 3.1.1.A flux was designed for lead-free alloys. Lead-free alloys wet at a slower rate, have a greater surface tension and operate under higher temperatures compared to lead alloys. In this case, the reason could be lower spreadability when used with SnPb37. The SAC405 solder alloyed with 0.1% Al showed almost the same spreadability as the SAC 405 solder at with the 3.1.1.A flux. When used with the 1.1.1.A flux the SAC405Al solder showed considerably worse results. This was caused by the presence of Al, which acts as an impurity in soldering alloys and also reduces the amount of Cu_6Sn_5 . A lower amount of Cu_6Sn_5 could also be the reason for the higher wetting angle of SAC405Al. The resulting spreadability values are shown in Fig. 8.

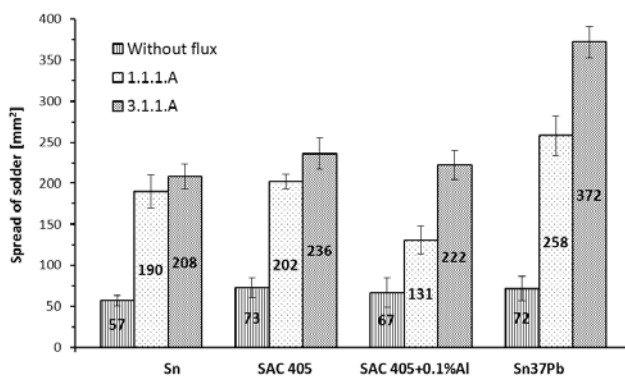


Fig. 8. Results of spreadability measurements of solders

The wettability of studied solders was assessed on a Cu plate. The soldering parameters were identical, as were the spreadability measurements. All solders wetted the Cu surface with wetting angle α of up to 30°. The studied solders showed very good ($20^\circ < \alpha < 40^\circ$) or even excellent ($0^\circ < \alpha < 20^\circ$) wettability. Similar to the spreadability testing, the best values were achieved by the SnPb37 solder. The

SAC405 solder alloyed with 0.1% Al showed an almost similar wettability to the original SAC405 solder, although always slightly worse (by about 2 - 6°). The resulting wettability values are shown in Fig. 9.

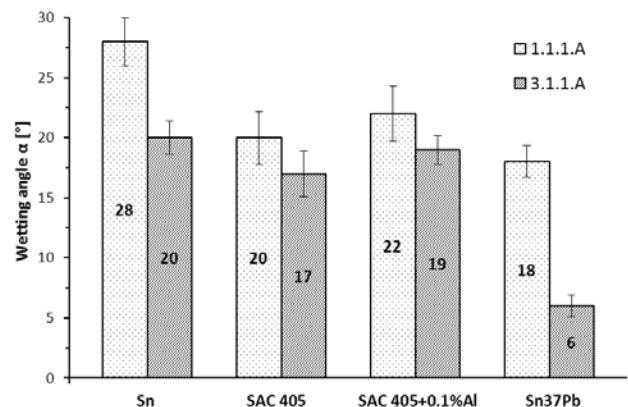


Fig. 9. The resulting wetting angles of solders and effect of flux

E. Shear strength, shear energy

Shear strengths of the solder-substrate boundary and the toughness-fracture energy were measured. The fracture energy-toughness of the bond was calculated from the area under the curve in the force F-displacement L diagram. The shear strength of the Sn-4.0Ag-0.5Cu solder was 36.5 MPa compared to 35.6 MPa for the Sn-4.0Ag-0.5Cu-0.1%Al solder. Fracture energy is composed of two components - shear energy and rupture (final failure) energy, as shown in Fig. 10.

Shear energy is related to the strain properties of the joint; the strain energy (when the joint is strained no cracks form) is thus related to cracking resistance, whereas rupture energy is related to resistance against cracking. The fracture in the S curve shape subsequently lowers the force drop gradient due to mutual wear on the S area, which increases the value of the rupture energy measured.

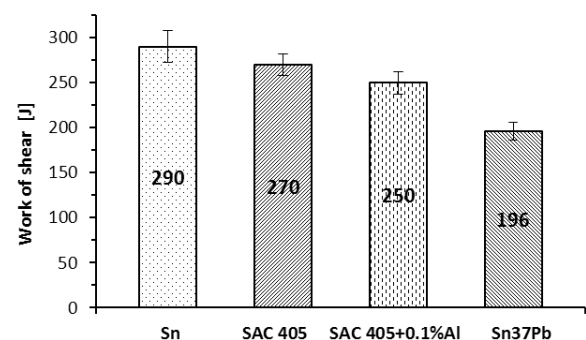


Fig. 10. Work of Shear measured on solder alloys

The measurements suggested a lower shear strength and lower shear energy of the SAC405Al solder compared with the SAC405 solder. Based on the drop in shear strength, a decrease in the yield point may be also supposed [12-14]. A high yield point reduces drop reliability [15], [16] in solders with a high Ag content ($\text{Ag} \geq 3 \text{ wt\%}$), similar to IMC thickness and Ag_3Sn morphology. This is why it is possible for the Sn-4.0Ag-0.5Cu-0.1%Al solder to show better

properties during the drop test.

IV. CONCLUSION

1. Adding 0.1% Al to the SAC405 solder resulted in the formation of a fine microstructure. In the primary Sn matrix with Ag₃Sn needles, a new bulk Cu-Al phase occurred that was non-uniformly distributed throughout the entire volume of the solder. The Cu-Al phase was composed of approximately of 77 wt% (60.18 atomic %) Cu and 21% (39.21 atomic %) Al. The solid solution of ζ_2 and δ phases was involved. The percentage of the ζ_2 phase exceeded that of the δ phase.

2. Adding Al to the solder shifted the melting interval from 217-219 °C (SAC405) to 220-223 °C (SAC405Al).

3. In the case of the SAC405Al solder, a diffusion layer was observed at the solder-Cu boundary which had a smaller width than the SAC 405 solder. The EDX analysis did not prove the presence of Al in the form of a continuous layer along the joint boundary.

4. Measurements of spreadability and wettability of the solders revealed a slight decrease in the average spreadability and wettability values of the SAC405Al solder compared with the SAC405 solder. The differences were more significant depending on the type of flux used. In order to enable a comparison, the same characteristics were also assessed on a pure Sn and Pb solder type: SnPb37.

5. The shear strength of the SAC405Al solder was slightly lower than the SAC405 solder, namely: 35.6 MPa versus 36.5 MPa. The decrease in shear strength may have resulted in a lowered yield point.

Adding 0.1% Al to the Sn-4.0Ag-0.5Cu solder resulted in a slight increase in the melting point of the alloy and also in a slight deterioration of spreadability and wettability values; the effect on the microstructure of the solder and also IMCs was more significant, as also shown by the shear strength measurements.

Based on these conclusions, the effect of the addition of 0.1% Al on the properties of soldering alloys seems to be positive and will be further investigated in our future work.

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