Comparing the solderability of different SAC0307 composite solder pastes

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Abstract— In the present study, the effect of four oxide ceramics (TiO_2, ZnO, ZrO_2, and CuO) as reinforcements were investigated on the soldering parameters of the SAC0307 solder alloy. The oxide ceramics were used in nano-powder format. Composite solder pastes were composed by the standard ball milling process of the nano-particles into the SAC0307 solder paste in 0.25wt% weight fraction. The wettability, shear strength, and microstructure of the composite solder joints were studied and compared. The ceramic nano-particles did not have a major effect on the wettability of the solder. Shear strength increases were observed at the composite joints, except in the case of ZnO. Generally, Sn grain refinement was found in the Sn-matrix which could be the reason for the shear strength increase.

Keywords— composite solder alloy; oxide ceramics; nano-particles; shear strength; reflow soldering.

I. INTRODUCTION

The transition to lead-free soldering technology resulted in the change of classical SnPb to SnAgCu alloys. Recently, the so-called low Ag content ones got the most research attention, like Sn99Ag0.3Cu0.7 (SAC0307) and Sn98.5Ag1Cu0.5 (SAC105). The low Ag content is advantageous from the point of the alloys' price as well as from the point of decreased Ag_3Sn formation in the solder bulk, which can cause mechanical problems [1]. Further mechanical improvement of the solder joints can be achieved with the application of ceramic reinforcements in the solder alloys. The reinforcements are usually nano-particles (NPs) (mostly nano-powders, sometimes nano-fibers) and applied in 0.1–1 wt%. A wide range of oxide ceramics was tried in composite solder joints: Al_2O_3, SiC, ZnO, TiO_2, ZrO_2, Si_3Ni_4, La_2O_3, etc [2].

The ceramic NPs are non-soluble in Sn, so they are dispersed at the grain boundaries in the solder matrix (at the intermetallic (IMC) and Sn and grains). During the solidification of the solder alloy, NPs act as incubation "seeds" for grain formation, which results in considerable grain refinement in composite solder joints as well as blocks the dislocation movements [3]. The previously discussed effects of the NPs usually improve the basic mechanical parameters (microhardness, tensile and yield strength) of the composite solder alloys [4]. However, the optimization of the composite solder pastes for industrial use is still a complex challenge.

For our study, we selected four oxide ceramics: TiO_2, ZnO, ZrO_2, and CuO. TiO_2 is the most researched material in composite soldering. It adapts very well to the soldering environment, not sensitive neither to the applied weight fraction (between 0.1–1 wt%) nor to the primary particle size (between 20–200 nm). Below 0.5 wt%, TiO_2 can even imporve the wetting ability of the composite solder alloys [5], which is not typical with other ceramics. According to the latest results, TiO_2 can bond to Sn atoms, which could improve the reliability of the composite solder joints in a corrosive environment [6]. However, it can increase the liquidus temperature of the composite solder alloy even with 6°C [7], which is not advantageous in the case of low Ag content solder alloy with already higher liquidus temperatures (around 227°C).

From the melting temperature point, ZnO could be the best candidate, El-Daly et al. [8] found that ZnO increased the liquidus temperature only with 1-2K. Furthermore, adding ZnO NPs increased the creep resistance and the ultimate tensile strength of the composite solder joints [9]. Unfortunately, ZnO is much more sensitive to applied weight fraction than TiO_2. It was reported by several studies that over 0.5 wt%, ZnO NPs prone to agglomerate at the grain boundaries, which could ruin the structural integrity of the solder bulk [10]. In addition, ZnO is a hydrophobic material that fastly dries out the flux from the solder paste, which decreases the wettability and increases the void formation [11].

ZrO_2 is a much less researched oxide ceramic in composite soldering than TiO_2 or ZnO. Gain et al. [12] reported that ZrO_2 NPs increased the shear strength of Sn96.5Ag3Cu0.5 solder joints by a second-phase dispersion strengthening mechanism. Rajendran et al. [13] studied the reliability of Sn96.5Ag3Cu0.5 (SAC305) solder with ZrO_2 NPs during isothermal aging. They observed that the ZrO_2 NPs at the IMC layer region suppressed the diffusion of Cu into the solder bulk so, slowed the growth of the IMC layer in the solid phase. Furthermore, they observed an increase in shear strength as well. Gain et al. [14] found the same, namely that the growth rate of IMC layer in SAC305 composite solder joints is lower.

The application of CuO ceramic in composite soldering is an untouched area, but it could be promising since in other applications, CuO shows similar properties as TiO_2. Ismail [15] put 1wt% CuO and TiO_2 NPs into Sn90Zn10 solder alloy and found that both composite solder joints presented very similar microstructural and mechanical properties. Bahadur and Sunkara [16] increased the wear resistance of polyphenylene sulfide (PPS) by applying TiO_2 and CuO as fillers.

In this study, the effects of four oxide ceramics, TiO_2, ZnO, ZrO_2, and CuO, have been investigated on the wetting and shear properties of SAC0307 alloy. Furthermore, the microstructures of the composite solder joints were compared.

II. MATERIALS AND METHODS

TiO_2, ZnO, ZrO_2, and CuO NPs (produced by Sigma Aldrich) in 0.25wt% were put into SAC0307 solder paste (produced by Alpha). The primary particle sizes of the NPs were the following: 21nm - TiO_2, <50nm - ZnO, <100nm ZrO_2, and <50nm CuO. The NPs were homogeneously mixed into the SAC0307 solder paste by a YX paste mixer with 400rpm for 12 mins. 4 different composite solder pastes and the reference SAC0307 were investigated (Table 1).

TABLE I. SOLDER ALLOYS

Name	Composition
SAC	SAC0307
SAC-TiO_2	SAC0307-TiO_2 (0.25wt%)
SAC-ZnO	SAC0307-ZnO (0.25wt%)
SAC-ZrO_2	SAC0307-ZrO_2 (0.25wt%)
SAC-CuO	SAC0307-CuO (0.25wt%)

The first investigation was the spreading test to study the wetting properties of the solder alloys (Tab. 1). Test surfaces (50x50mm) were prepared on FR4 substrates with Cu wiring with imm-Ag surface finishing. On each test boards four circular solder deposits were screen printed with 5mm diameter and 125 μm thickness. The solder pastes were reflowed in a vapour phase soldering (VPS) oven. A linear thermal profile was applied: preheating till 170°C from 0 to 120s, keeping a soak between 170-210°C from 120 to 280s, and ramp-up till 255°C from 280 to 360s. The wetted surface area was measured by an Olympus BX50 optical-microscope. Four test boards (with 16 solder deposites) were prepared from each sample type.

During the second experiment, solder joints were fabricated by SMT on one-layer standard FR4 PCBs with Cu wiring. Solder pads were covered by imm-Ag surface finishing. Solder pastes were printed with a 125μm thick stainless steel stencil. 0603 sized chip resistors were placed into the solder paste by manual pick & place. The test board had places for 50 chip resistors. The solder pastes were reflowed in a vapour phase soldering (VPS) oven used the linear thermal profile presented above. Fig. 1 shows a part of a test board with the chip resistors.

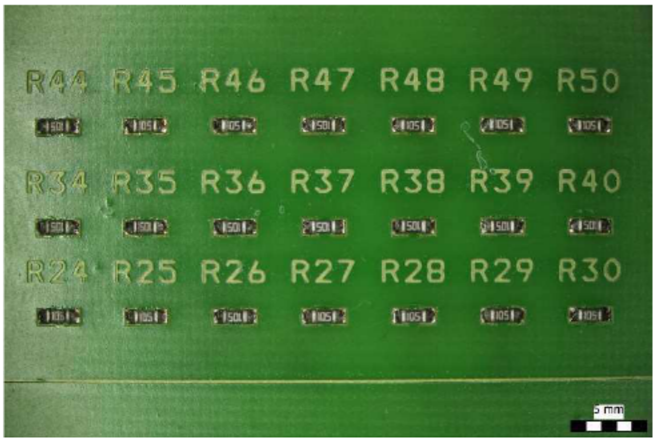

Fig 1. Test board.

A DAGE 2400 shear tester has been used to measure the shear force of the solder joints. 20 resistors were pushed off from each sample type. Metallographic cross-sections were also prepared from the solder joints to compare their microstructures. The metallogrpahic cross-sections were investigated with an FEI Inspect-S50 SEM.

III. RESULTS AND DISCUSSION

Typical examples of the spreading tests are presented in Fig. 2. Generally, the wettability of the composite solder alloys decreased a bit compared to the ref. SAC. In the case of the reference SAC0307 alloy, the wetted area usually even increased a bit (with 5-6%) over 5mm (Fig. 2a), while in the case of the composite alloys usually decreased below 5mm (Fig. 2 b-d). However, the decrease was marginal, between 1-2%. No difference was observed according to the type of the applied NPs. It can be stated that the addition of the NPs in 0.25wt% did not have a significant effect of the wettability of the composite solder alloy.

Fig. 3 shows the shear force statistics of the different solder alloys in a box plot diagram. The dashed line marks the average (mean) shear force of the reference SAC0307 solder joints, the squares mark the averages, and the lines mark the medians. The deviations of the results were generally high in all cases. However, it is clearly visible that the TiO_2, ZrO_2, and CuO NPs slightly increased the average shear force of the composite joints compared to the ref. SAC, with 10%, 13%, and 9%, respectively.

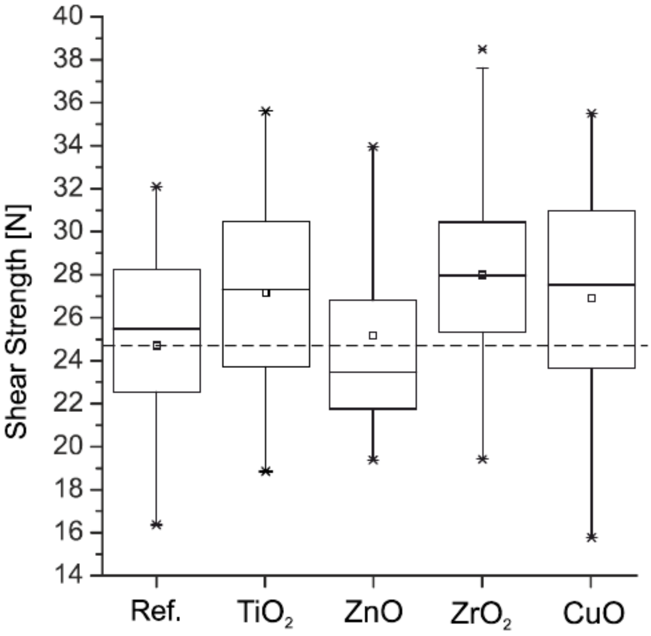

Fig. 3 Shear strength statistics of the solder alloys.

In the case of the ZnO NPs the average shear force of the composite solder joints did not change, but the median decreased. It was observed only in the case of ZnO samples. If the median is smaller than the average, it means that the distribution of the data is skewed to the left, which means that the values below the average were in the majority of the data set. In the case of TiO_2 and ZrO_2 the median was almost identical with the average. In the case of ref. SAC and CuO solder joints, the median was a bit higher than the average. It means that the distribution of the data skewed to the right, namely that the values above the average were in the majority in the data set. From the point of the shear strength, the higher mean (the lastly discussed occasion) is favorable. It needs to be highlighted that the "unknown" CuO NPs performed as well in the shear strength tests as the TiO_2 and ZrO_2 NPs.

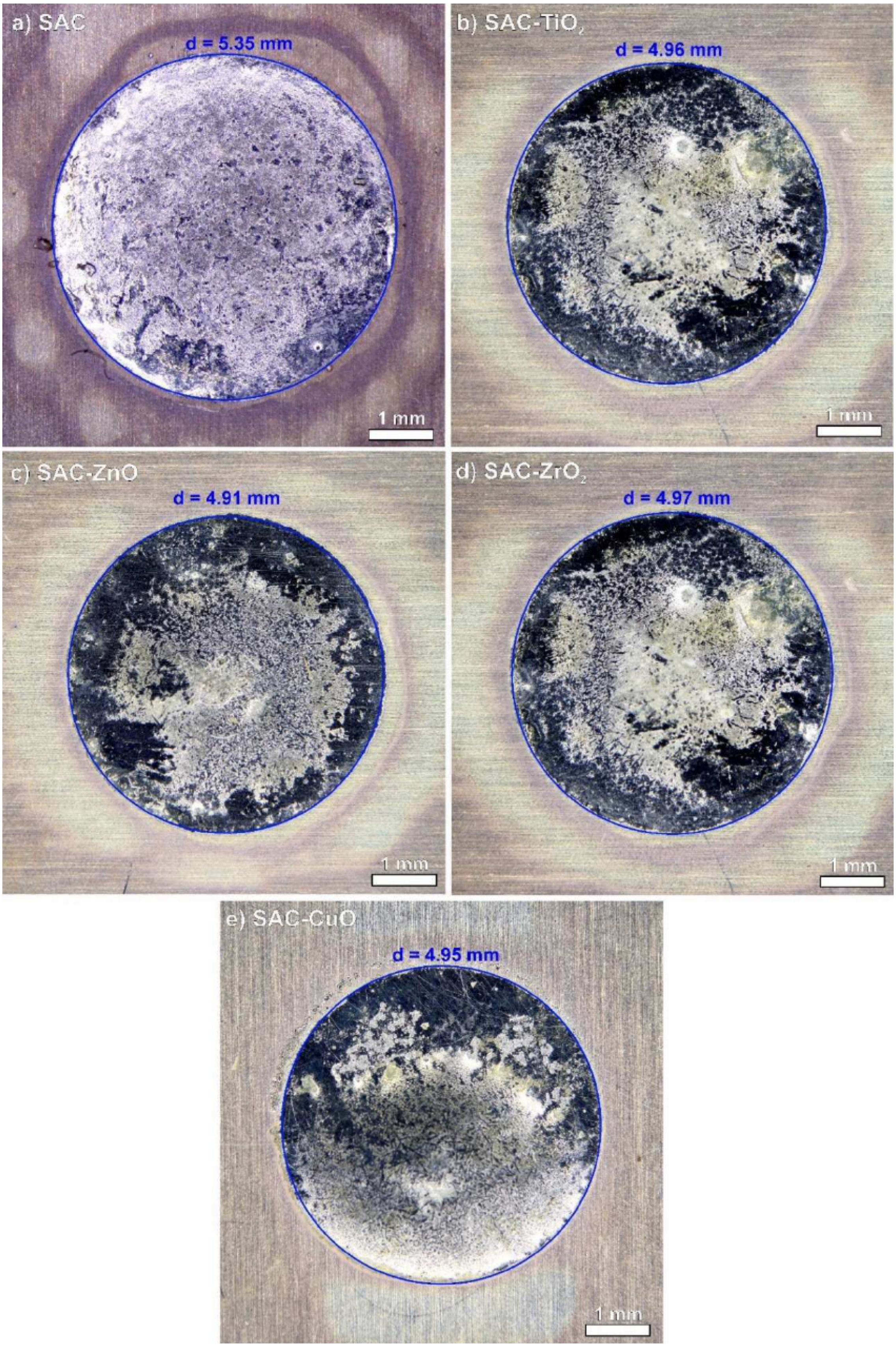

Fig. 2 Example results of the spreading test.

Metallographic cross-sections were fabricated from ref. SAC, SAC-TiO$_2$, and SAC-ZnO solder joints to study the microstructural differences. The cross-sections were observed with SEM. Example results done by backscattered electron detector (BSE) can be seen in Fig. 4. The addition of the oxide ceramic NPs resulted in considerable microstructural changes in the composite joints (Fig. 4b and c) compared to the ref. SAC (Fig. 4a). General microstructural refinement occurred in the composite joints. The different phases (Sn and different

IMCs) in the Sn-matrix can be easily distinguished due to the elemental contrast of the BSE micrographs.

The Cu_6Sn_5 layer thickness in the composite joints decreased by 20-40% compared to the reference SAC. The size of the dispersed Cu_6Sn_5 and Ag_3Sn IMCs in the solder bulk also decreased considerably. In the reference SAC sample (Fig. 4a), even 5-10 ı m long Cu_6Sn_5 IMC grains can be found, while in the composite joints (Fig. 4b and c) the size of the same particles are 1-2 ı m. In the case of the Ag_3Sn IMC grains, next to the size decrease, the most visible change was the lack of their agglomeration (Fig. 4b and c), which was typical in the reference joints (Fig. 4a).

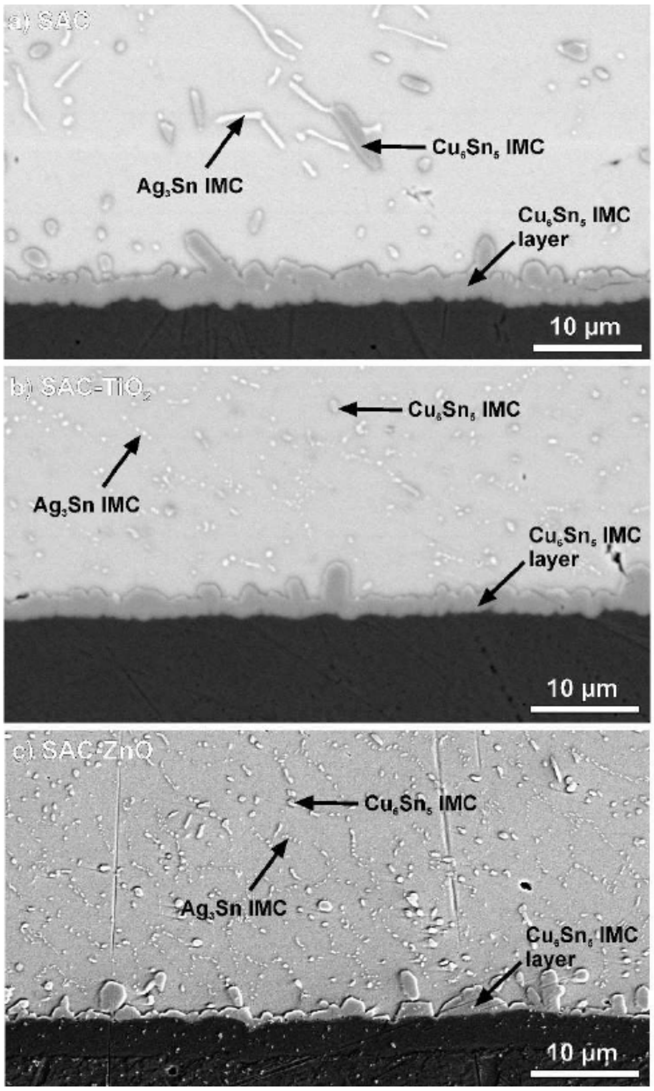

Fig. 4 SEM-BSE micrograph about the microstructure of the solder joints: a) SAC; b) SAC-TiO_2; c) SAC-ZnO.

The finer Ag_3Sn network in the composite joints indicated the Sn grain refinement as well. The Ag_3Sn IMCs are always stuck between the Sn grains, so they are good indicators for calculating the Sn grain size in the solder bulk. According to the Ag_3Sn networks, Sn grains with 20-25ı m size are visible in the reference SAC solder joint (Fig. 4a), which grain size decreased to 4-6ı m in the composite joints (Fig. 4b and c).

IV. CONCLUSIONS

The effect of TiO_2, ZnO, ZrO_2, and CuO oxide ceramics as reinforcements were investigated on the soldering parameters of the SAC0307 solder alloy. The main conclusions are the followings:

¿ The oxide ceramics slightly decreased the wettability of composite solder alloys. Considerable differences were not observed between the different ceramics.

¿ The increased shear strength of the composite joints showed that the second phase dispersion strengthening mechanism worked in the case of TiO_2, ZrO_2, and CuO NPs.

¿ ZnO NPs did not reach mechanical improvements, which is interesting since the microstructural refinement occurred in these composite solder joints as well. However, the SAC-ZnO solders performed the worst spreading/wetting, which could have a negative effect on the mechanical improvements.

¿ The unknown CuO NPs performed very similar and positive results as TiO_2 NPs, so it is suggested for application in soldering technology just like ZrO_2 NPs. According to our results, ZnO NPs are not favorable for soldering.

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REFERENCES

[1] O Krammer, T Garami, B Horv®th, T Hurtony, B Medgyes, L Jakab, Investigating the thermomechanical properties and intermetallic layer formation of Bi micro-alloyed low-Ag content solders, J. Alloys Compnd. 634 (2015) pp. 156-162.

[2] J. Wu, S. Xue, J. Wang, S. Liu, Y. Han, L. Wang, Recent progress of Sn¯Ag¯Cu lead-free solders bearing alloy elements and nanoparticles in electronic packaging, J Mater Sci: Mater Electron 27 (2016) pp. 12729¯12763

[3] A. Skwarek, P. Ptak, K. GÆecki, T. Hurtony, B. Ill¶s, Microstructure Influence of SACX0307-TiO2 Composite Solder Joints on Thermal Properties o Power LED Assemblies, Materials 13 (2020) 1563.

[4] Y. Tang, G. Li, Y. Pan, Effects of TiO_2 nanoparticles addition on microstructure, microhardness and tensile properties of Sn¯3.0Ag¯0.5Cu¯xTiO2 composite solder, Mater. Des. 55 (2014), pp. 574¯582.

[5] Y. Tang, Y.C. Pan, G.Y. Li, Influence of TiO2 nanoparticles on thermal property, wettability and interfacial reaction in Sn¯3.0Ag¯0.5Cu¯xTiO2 composite solder, J. Mater. Sci. Mater. Electron. 24 (2013), pp. 1587¯1594.

[6] B. Ill¶s, H. Choi, J. Byun, K. Dusek, D. Busek, A. Skwarek, Incorporation and corrosion protection mechanism of TiO2 nano-particles in SnAgCu composite alloys: experimental and density functional theory study, Ceram. Inter. (2023) in press.

[7] L. Tsao, S. Chang, Effects of Nano-TiO2 additions on thermal analysis, microstructure and tensile properties of Sn3.5Ag0.25Cu solder, Mater. Des. 31 (2010), pp. 990¯993.

[8] A.A. El-Daly, T.A. Elmosalami, W.M. Desoky, M.G. El-Shaarawy, A.M. Abdraboh, Tensile deformation behavior and melting property of nano-sized ZnO particles reinforced Sn¯3.0Ag¯0.5Cu lead-free solder, Mater. Sci. Eng. A 618 (2014), pp. 389¯397.

[9] Fawzy, A.; Fayek, S.A.; Sobhy, M.; Nassr, E.; Mousa, M.M.; Saad, G. Tensile creep characteristics of Sn¯3.5Ag¯0.5Cu (SAC355) solder reinforced with nano-metric ZnO particles, Mater. Sci. Eng. A 603 (2014), pp. 1¯10.

[10] H. Peng, G. Chen, L. Mo, Y.C. Chan, F. Wu, H. Liu, H. An investigation on the ZnO retained ratio, microstructural evolution, and mechanical properties of ZnO doped Sn3.0Ag0.5Cu composite solder joint, J. Mater. Sci.: Mater. Electron. 27 (2016), pp. 9083¯9093.

[11] A. Skwarek, O. Krammer, T. Hurtony, P. Ptak, K. GÆecki, S. Wroиski, D. Straubinger, K. Witek, B. Ill¶s, Application of ZnO nanoparticles in Sn99Ag0.3Cu0.7 based composite solder alloys, Nanomaterials 11 (2021), 1545.

[12] A.K. Gain, Y.C. Chan, W.K.C. Yung, Effect of additions of ZrO_2 nano-particles on the microstructure and shear strength of Sn-Ag-Cu solder on Au/Ni metallized Cu pads. Microelectron. Reliab. 51 (2011), pp. 2306¯2313.

[13] S.H. Rajendran, S.J. Hwang, J.P. Jung, Shear Strength and Aging Characteristics of Sn-3.0Ag-0.5Cu/Cu Solder Joint Reinforced with ZrO_2 Nanoparticles, Metals 10 (2020), 1295.

[14] A.K. Gain, Y.C. Chan, Growth mechanism of intermetallic compounds and damping properties of Sn¯Ag¯Cu-1 wt% nano-ZrO2 composite solders. Microelectron. Reliab. 54v (2014) 945-955.

[15] R.A. Ismail, An Investigation of Microstructure and Mechanical Properties of Different Nano - Particles Doped Sn-Zn Lead-Free Solder Alloys, Arab J. Nucl. Sci. Appl., 53/1 (2020), pp. 191-199.

[16] S. Bahadur, C. Sunkara, Effect of transfer film structure, composition and bonding on the tribological behavior of polyphenylene sulfide filled with nano particles of TiO2, ZnO, CuO and SiC, Wear 258 (2005), pp. 1411-1421.