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Solderability of Sn-0.7Cu/Si_3N_4 lead-free composite solder on Cu-substrate

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Abstract

Reinforcing high performance ceramic particulates is an effective approach to improve solderability of lead-free Sn-0.7Cu solder. Various weight percentage compositions (0.5, 1.0, and 1.5) of Silicon Nitride (Si_3N_4) reinforced in Sn-0.7Cu solder were developed using powder metallurgy (PM) routes to investigate their solderability properties on copper (Cu) substrate. The solderability performances of the new composite solder will be determined and analyzed based on their contact angles on Cu substrate, including interface intermetallic compound (IMC) layer thickness and IMC phases formed for different Si_3N_4 ratios. Results also show an improvement in solderability of the Sn-0.7Cu/Si_3N_4 composite lead-free solder with optimum wettability achieved by 1.0 wt.% Si_3N_4. The minimal average decrease in IMC layer thickness and the formation of the different shaped of scallops figuring the IMC layer were observed. X-ray diffraction (XRD) also revealed the decreasing peak intensity of Cu_6Sn_5 phases with Si_3N_4. Overall, the entire range of composition of Si_3N_4 into Sn-0.7Cu monolithic solder use in this study indicated an enhancement of solderability performances on Cu-substrates.

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Keywords: Lead-free; Composite solder; Silicon Nitride; Powder metallurgy; Wettability; Intermetallic compound

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1. Introduction

Nowadays, the use of lead-free solders in electronic packaging industries is no longer an exceptional topic. Previously, the highly demanded solder alloys were the eutectic and near eutectic alloy of Sn-Pb solders. The excellent properties given by Pb-contained solders were not doubted until it was realized that lead (Pb) is a hazardous element because of its toxicity. As people became more concerned about how the growing electronic products can harm their life and living environment, Pb-solders services were restricted by governmental and legislative bodies such as WEEE and RoHS [1-3].

Many lead-free solders have been developed, including the potential eutectic alloy of Sn-0.7Cu, which recently gained researchers' attention because of its availability and low production cost as a matrix-based alloy for composite solder. Satyanarayan and K.N. Prabhu [4] summarize their reviews of recent developments in Sn-0.7Cu related to wetting characteristics. Guang Zheng et al. [5] emphasized the recent advances of Sn-Cu solders with alloying elements compared to the monolithic solders. The issues outlined that the reinforcement additions only involve the intermetallic particles, either by adding secondary (Cu_3Sn and Cu_6Sn_5) or converting elemental particles (like Ni and Zn). Reinforcing material can also come from materials that are non-reactive with Sn-Cu, like ceramic particulates, which X.L Zhong et al. [6] recently investigated to develop such composite solders by reinforcing various volume percentages of Al_2O_3 nanoparticulates into the monolithic Sn-0.7Cu solder using PM techniques. However, only mechanical performances have been investigated. Ceramics as a reinforcement material has also been reincorporated into other lead-free solders using PM techniques that simultaneously result in enhanced solderability [13] and mechanical [14] properties on their monolithic solders.

Solderability performance of a solder material can be defined by their degree and rate of wetting on metal substrates [7-8]. The effects of different percentages of various ratios of alloying elements with silver (Ag) particles reinforcing additions into the Sn-0.7Cu on a contact angle formation have been investigated on the Cu-substrate with NC flux [9-10]. These studies revealed different amounts of reinforcement addition have shown the distinct effect on the wettability of Sn-0.7Cu, as the increasing amount of reinforcement particles will only improve the wettability until the optimum ratio is reached. Higher percentage ratios after optimum ratio addition will further deteriorate wettability of the composite solder, which can be worse than the monolithic solder. A ceramic reinforcement on the Sn-Ag-Cu solder of substrate has been developed by S.M.L. Nai et al. [11], resulting in the enhancement of wettability below 3.0 vol.% TiB_2additions. The wetting of a solder material on a substrate is actually achieved by the formation of reaction bonding between the molten metal-matrix alloy of the solder reactors with the solid substrate material element forming the secondary phase of IMC on the interface. The IMC formations at the interface of the tin-base solder alloys and Cu substrate were investigated by J. Madeni et al. [12], which resulted in IMC phase formation consisting of Cu_3Sn and Cu_5Sn_6. Although the formation of IMCs promotes the bonding joint contact between the solder and substrate, their excessive presence can reduce the joint reliability because they are usually brittle in nature [4-5].

Previous literature has revealed that the addition of reinforcement particulates into lead-free solder mostly increased solder joints' wettability performance. Therefore, the current study aimed at fabricating a new composite solder made from the inexpensive base material of lead-free solder with a limited amount of high-performance ceramic reinforcement additions that suit the solderability of the new lead-free composite solder on the Cu-substrate. Following the potential of utilization of ceramic particulates into the low-cost Sn-0.7Cu lead-free solder, this research reincorporates the pricey but high mechanical performance ceramic of Si_3N_4 into the monolithic solder using PM routes. This research focuses on solderability performances as the first priority of solder material is to have great or acceptable wetting characteristics on conventional substrates before considering their mechanical performance.

2. Experiment Details

2.1. Materials and processing

In this study, tin (Sn) and copper (Cu) powders with an average particle size of <45 μm were used for the base matrix material; the Si_3N_4 powder has an average particle size of <20 μm. All raw materials were bought from Sigma-Aldrich. The Cu-substrate was used for the solder joints' formation and for fluxing material as a NC flux paste bought from Qualitek, Singapore. For the fabrication of the Sn-0.7Cu/Si_3N_4 composite solder, varying volume percentages of Si_3N_4 particulates were incorporated into the 99.3Sn-0.7Cu solder matrix using the PM route. The solder materials of composite solder were fabricated with 0.5 wt%, 1.0 wt,% and 1.5 wt% of Si_3N_4 reinforcement and then homogeneously mixed with the Sn-0.7Cu base matrix powder in an airtight container using a roller blender rotated at a speed of 200 rpm for 15 hours. The monolithic solder of 99.3Sn-0.7/Cu was prepared using a similar method. Each of the solder mixtures was uniaxially compacted in a 2-mm diameter mold, and the compacted billets were sintered in an inert argon atmosphere at 175°C for 2 hours in a horizontal tube furnace (VT furnace).

2.2. Solderability Studies

The composite solder samples were placed on a Cu-substrate with a NC paste flux and reflowed in a F4N reflow oven according to the reflow profile proposed by the flux supplier (Qualitek). The samples were cross-sectioned, and the contact angle image was obtained using an optical microscope (OM) image. The contact angle of the solder sample was then measured using Image-J software. IMC formation analyses of the metallographically polished samples of the reflowed samples were carried out using Scanning Electron Microscope (SEM JEOL-JSM 6460 LA) in order to investigate thickness of the interfacial IMC layer. The IMC form at the Cu-substrate layer of the cross-sectioned samples was measured using Image-J analyzer software with an image obtained from SEM. An OM (OM OLYMPUS BX41M) was used to observe the morphology of IMC formation. X-ray diffraction (XRD) identified that IMC phases exist in the composite solder and their intensity in different additions of Si_3N_4 particulates. XRD was carried out on the cross-sectioned samples using an automated Shimadzu XRD-2000 diffractometer using Cu Kα radiation with a wavelength (λ) of 0.15406 as an X-ray source. A plot of intensity versus 2θ (θ represents Bragg angle) was obtained, resulting in peaks at different Bragg angles, from which interplanar spacings, *d*, were calculated. These values of *d* were subsequently compared and matched with standard values for different elements and compounds.

3. Result and Discussion

3.1. Wettability Measurement

Solder wettability was determined with respect for the contact angle (θ°) to the Cu-substrate as shown in Fig. 1; the smaller the contact angle, the better the wettability of the interconnections. An acceptable range of contact angle should be below 45˚. The addition of 0.5 wt.% and 1.0 wt.% of Si_3N_4 particulates decreased the respective contact angle, thereby indicating improvement in the wetting property as shown in Fig. 2. The optimum value of the contact angle (14.25˚) is achieved at 1.0 wt.% of Si_3N_4. The addition of a higher ratio of 1.5 wt.% of Si_3N_4 particulates shows a higher contact angle beyond the optimum value (18.30˚). However, the contact angle of all composite solders developed in this study remains lower than the monolithic solder. In this study, the Sn-0.7Cu/Si_3N_4 composite solder has shown similar wettability performance with Sn-0.7Cu nano-sized Ag reinforcement [9], but with micron-sized Si_3N_4 particulates as both had reached an optimum value at a low ratio of reinforcement. A similar graphical relationship in the wettability test result of the Sn-Ag-Cu/TiB_2 lead-free ceramic composite solders on Cu-substrate was identified by S.M.L. Nai et al. [11]. It was claimed that TiB_2 has improved the Sn-Ag-Cu monolithic by 22.2%, with an optimum value obtained at 1.5 vol.% reinforcement ratio; in this study, Si_3N_4 enhanced the Sn-0.7Cu solder wettability at a higher percentage (53.09%, 14.25˚) in a lower ratio of reinforcement (1.0 wt.%).

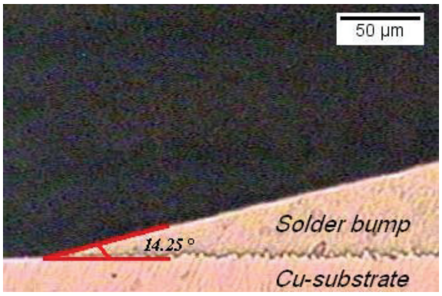

Fig. 1: Representative image of the measurement of contact angle for Sn-0.7Cu/1.0Si_3N_4 composite solder sample.

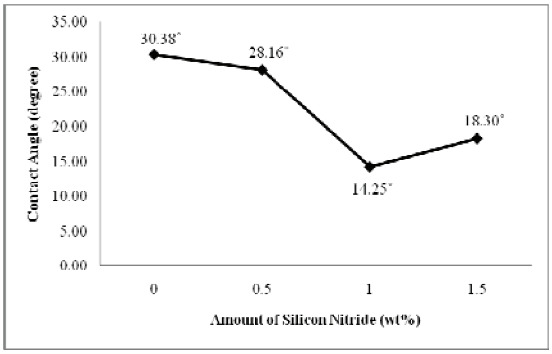

Fig. 2: Graphical relationship between weight percentage of Si_3N_4 addition in Sn-0.7Cu solder matrix and contact angle.

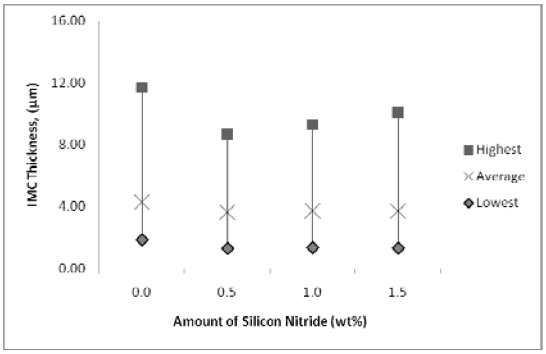

Fig. 3: Result of the overall thickness measurement (highest, average, and lowest) taken from the IMC layer with respect to increasing weight percentage of Si_3N_4 addition.

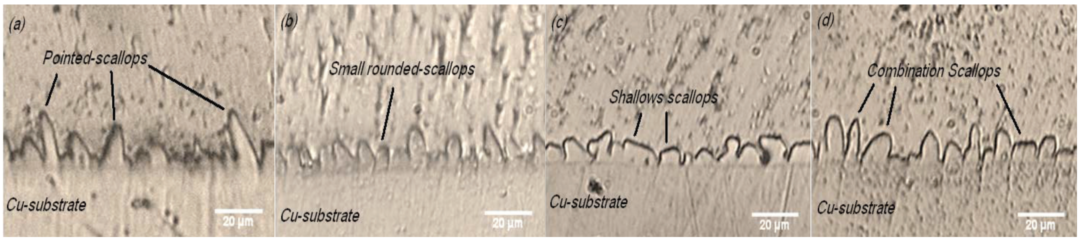

Fig. 4: OM images (50x magnifications) of the IMC layer formation of composite solder sample with different (a) 0 wt.%; (b) 0.5 wt.%; (c) 1.0 wt.% and (d) 1.5 wt.% composition of Si_3N_4.

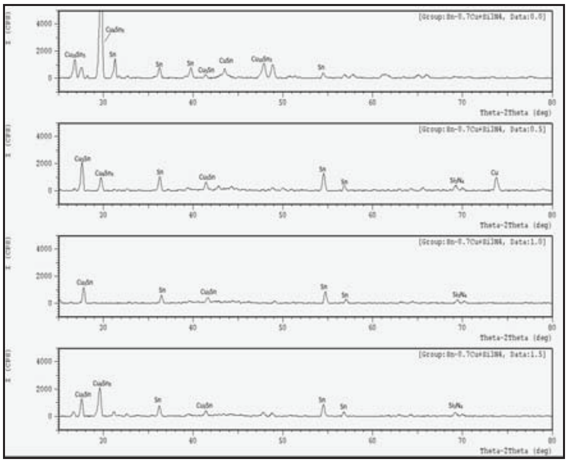

Fig. 5: XRD spectra of the monolithic and composite solders.

3.2. IMC Thickness and Characterization

The thickness of the IMC layer, which indicates the amount of reaction, defined the strength and reliability of the solder joint [13]. The distributions of the thickness data were calculated and present in the graphical form and shown (Fig. 3). Increasing the amount of Si_3N_4 from 0.5 wt.% to 1.5 wt.% resulted in a minimal reduction of the average interfacial IMC layer thickness growth during reflow. According to the graph, only an insignificant change in the average IMC layer thickness can be seen; however, the average formations of the highest peak detected from all composite solder systems are still lower than the highest peak observed in the monolithic solder. The changes of thickness may be able to be observed clearly if isothermal aging is done through all the samples. During the reflow process, the Cu atoms from the Cu-substrate can freely diffuse to the monolithic matrix solder and react to form Sn-Cu IMC. In composite solder, the existence of hard particulates of Si_3N_4 may block the diffusion of Cu and Sn from reacting to each other, thereby limiting the reaction and reducing the IMC growth. As a result, the growth of interfacial IMC layer was thus retarded. Fig. 4 shows the morphological shape of the IMC layer formed between the joints of the monolithic and composite solders. The monolithic solder sample of the IMC layer has a pointed scalloped shape with the presence of the highest thickness of IMCs, while considerably uniform thickness formation was observed in the composite solder samples as seen in Fig. 4 (b)-(d). The addition of 0.5 wt.% Si_3N_4 established the formation of small scallop,-shaped IMCs between the joints while 1.0 wt.% Si_3N_4 addition formed shallow IMCs. The 1.5 wt.% Si_3N_4 additions seem to have a combination shape of IMCs. The presence of Si_3N_4 in the monolithic changed the formation of non-uniformly pointed thick IMC layers to more rounded and even a greater thickness of scalloped IMCs on the Cu-substrate layer.

3.3. IMC Phase Identification

The X-ray diffraction analysis results corresponding to the monolithic Sn-0.7Cu and composite solders are presented in Fig. 5. The peaks corresponding to the formation of intermetallic compounds—namely Cu_3Sn and Cu_6Sn_5—are presented in this figure. It should be noted that the intermetallic compound of Cu_6Sn_5 phases decreased in composite solder samples and disappeared in the 1.0 wt.% Si_3N_4. The formation of the CuSn phase only occurred in the monolithic sample due to the high diffusivity of Cu into the solder matrix. This occurred only in the monolithic sample as more paths of diffusion could take place compared to the composite sample, which has ceramic particulates to block their ways. This result confirmed that the addition of the ceramic particulates into the monolithic solder retards the growth of the IMC phases.

4. Conclusion

A new lead-free composite solder of Sn-0.7Cu/Si_3N_4 with enhanced wettability was successfully fabricated using powder metallurgy techniques. Optimum wettability was achieved by the monolithic solder with the addition of 1.0 wt.% Si_3N_4 into the matrix solder, which reduced the contact angle to 14.25˚. A more rounded and more even thickness of pointed scalloped IMCs presented on the Cu-substrate layer with the addition of Si_3N_4. The IMC phases of Cu_6Sn_5 in composite solders were reduced. Overall, based on the results achieved, all the compositions of Si_3N_4 used in this study simultaneously showed enhanced solderability compared to the monolithic solders and can be applied to further investigate their effect ins term of mechanical performance testing.

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