Effect on the wettability, hardness and shear strength properties of 3%-nano Titanium Oxide (TiO₂) added Sn-3.8Ag-0.7Cu (SAC)/Copper (Cu) solder joint

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Abstract. Demand towards smaller electronic devices prompts the electronic interconnection to have less density and minimal weight percentage and such of this concern tips to applications of nanoparticles incorporation to the solder alloy. In this work, the effect of titanium dioxide (TiO₂) nanoparticles (<100nm) additions on the performance of wettability micro hardness, and shear strength of the Sn-3.8Ag-0.7Cu (SAC) solder alloy soldered on the Copper (Cu) substrate was investigated. The SAC added 3% TiO₂ nanoparticles had a slight decrease in the micro hardness compared to the plain SAC in this study but the value still surpasses many other common solder alloy's hardness value. The wettability test was conducted by taking account the contact angle achieved by soldering the SAC added 3% TiO₂ solder alloy to the Cu substrate and contact angle produced was less than 40°. As for the shear strength, there was a clear increment of 13% in the shear strength compared to the plain SAC solder alloy. Quite observant, the additions of TiO₂ nanoparticles displayed significant influence on these properties that contributes to excellent performance. Much detailed discussion are elaborated in the content below aiding with results and theory behind the result achieved.

1. Introduction and Literature

Lead free solders are the current affection in the electronic industry as many governed body have banned the usage of Plumbum (Pb). Solder alloys are known as the medium that holds the integrity of an interconnection in ana electronic deivce, thus, its properties mainly mechanical strength are much debated. Various lead free solder alloys such as SnCu [1], SnAg [2], SnZn [3], SnBi [4], SnAgZn [5], SnAgCu [6] are researched and the outcome based on the results are profound. Nevertheless, some major drawbacks are also being listed upon testing these solder alloys, namely the poor wetting (SnZn) [7], thick intermetallic (IMC) layers (SnCu, SnAg) [8], low shear strength (SnAgZn, SnAg) [9], prone to corrosion (SnZnAg, SnZn) [10] and many more.

Adding to that, the shrinking in sizes of the electronic chips and devices demands less mass and density consumption of a solder alloy. This then creates a concern as only by additions of elements, the mechanical strength of any solder alloys can be enhanced, but at the same time, it will be consuming quite a sum of mass. Such trend prompts the elements to be added to be in smaller

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particles dimensions to enhance the mechanical strength and also avoid increase in mass consumption [11]. Nanoparticles additions are the solution for this issue and its effect to the prior solder alloys should be beneficial and not deteriorating the initial properties, which did occur in some studies. Nanoparticles additions can be divide in to two types, i) metal nanoparticles (Ag, Cu, Ni, In and etc) and ii) oxide/ceramic nanoparticles (TiO_2, SiC, $SrTiO_3$ and etc.), with all these depending on the outcome of the applications [12]. These nanoparticles can influence by effecting the solubility of the solder alloy and taking part in the diffusion process or contrast to that, being a discrete particles and influence in increasing the mechanical strength. It is crucial to provide and understand the influences of these nanoparticles to a solder alloy to allow application in the electronic industry.

The SnAgCu solder is widely debated by its enhancement in the advantage of having a low melting temperature (217°C) [13], near to the soldering temperature (230-250°C) [14], and possessing a comparable mechanical strength, yet some concerns arises on the thick intermetallic layer produced by this solder over sometime that degrades its initial high strength [15]. Sn and Cu elements in this solder alloy have high affinity among them and with the availability of Cu in the substrate creates an opportunity for the Sn to react and produce thick IMC layer (Cu_6Sn_5) between the solder and substrate [16]. It then worsen as this layer reacts with Cu and creates another layer between the Cu_6Sn_5 and the substrate, the Cu_3Sn layer [17]. A schematic diagram in Figure 1 shows the prior and after reflow reaction of the above explanation. This paper involves the additions of nanoparticles in the SnAgCu solder system and investigate the influence of the nanoparticles to the solder alloy.
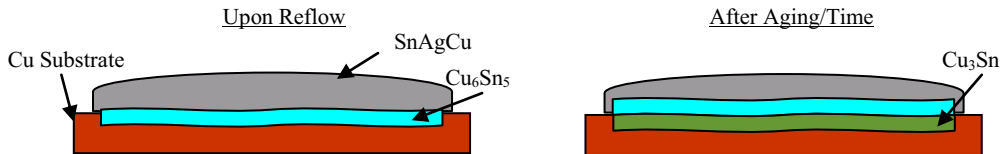
Figure 1. Intermetallic layer formation between solder and substrate (upon reflow and after aging).

2. Materials and Experimental Procedure

The preparation of bare Sn-3.8Ag-0.7Cu (SAC) solder alloys were based on the weight percentage of 95.5% Tin (Sn) Alfa Aesar , 3.8% Argentum (Ag) and 0.7% Copper (Cu) and all the materials are readily available and purchased from Alfa Aesar Inc. with 99.9% purity. An overall weight of 20g of SAC was used and this small amount of weight composition is selected to replicate the usage of small consumption of solder paste used in the electronic industries. These elements were then melted using an induction furnace for $1^{1/2}$ hour at a constant temperature of 1100°C to ensure a homogeneous mixture of all elements. The TiO_2 nanoparticles (size < 50nm, Alfa Aesar Inc) of 3% addition from the overall weight of the solder alloy (20g) gives a total mass of the nanoparticles of 0.6 gram and the nanoparticles were was mechanical mix in the SAC solder alloy and melted in the furnace at 1100°C for hour to allow the mixing of the nanoparticles in the solder alloy. To ensure all nanoparticles are properly mixed, the SAC added with the TiO_2 (SAC + 3% TiO_2) was re-melted using a hot plate with stirring for 30 minutes. The SAC + 3% TiO_2 solder alloy were then compacted into billets form, (5mm × 1mm) for experiment purposes. The billets were polished and etched in Nital for 60 seconds to avoid debris before tests and produce clean surface finish. Wettability test was done by measuring the contact angle (calculated using the VIS Pro software) between the SAC + 3% TiO_2 and Cu substrate (10×10mm), upon soldering at 250°C for 30s. The hardness of the SAC + 3% TiO_2 solder alloy was based on the Vickers microhardness test with 1kgf load dented to the solder billet. Shear test meanwhile, was tested using the Universal Tensile Machine (Instron) with application of single shear lap method with the SAC solder billets soldered on the Cu substrate (30mm × 10mm × 0.5mm) at 250°C. Cross section sample was analysed using the Scanning Electron Calorimetry (SEM) to investigate the interfacial property between the solder and substrate.

3. Results and Discussion

3.1 Wettability of SAC + 3% TiO$_2$/Cu.

The wetting characteristics of the SAC + 3% TiO$_2$ solder alloy was studied using the contact angle parameter. Wetting behavior could also be studied by applying the surface tension equation (1) that shall give the wetting force [18] to evaluate the wetting characteristic but this aspect is widely discussed in literatures and was not included in this study.

$$\gamma_{sv} = \gamma_{ls} + \gamma_{lv} \cos \theta \tag{1}$$

γ_{sv} = surface tension of solid, γ_{ls} = interfacial energy,
γ_{lv} = surface tension of liquid, θ = contact angle

It is defined that a smaller contact angle produces better joint and strength [9, 19] and researches recommends contact angles less than 50° is advantageous [14]. The results of the contact angle for the SAC + 3% TiO$_2$ solder alloy was an average of 32.7° and is considered beneficial taking account the proposed sufficient contact angle of below 50° by [14]. Being compared with other literatures, Sn3.8Ag0.7Cu (24.81°), Sn3.5Ag0.5Cu (33°), Sn6Zn4Bi (35°), Sn40Pb (8), Sn3.5Ag (38), Sn58Bi(35°), Sn2.5Ag0.7Cu0.1(Ce,La) + 0.1%Ni (35°), Sn3.5Ag4Ti (Ce,Ga) + Al$_2$O$_3$ (51°), Sn0.7Cu0.2Ni + 0.3%In (59°) and Sn0.7Cu + 0.2%S (35°) [7, 14, 18, 20-24], this solder tops in providing lower contact angle compared to other plain and nanoparticles added solder alloys. Yet, comparing with the plain SAC and the traditional SnPb solder alloy, the contact angle of latter was lower compared to SAC + 3% TiO$_2$ in this study. Point has to be taken in to account that these bare solder alloys (SAC and SnPb) are not added with nanoparticles. Additions of nanoparticles will slightly increase the viscosity of the solder alloy that increases the contact angle. It is a typical characteristics of the nanoparticles to move to the leading edge of the molten solder during soldering, as they do not take part in the diffusion process [25], and at an instant of 250°C of soldering temperature, the heat would have no influence to melt the TiO$_2$ (T$_M$ = 1843°C). This was similarly reported by [26]. This means that the nanoparticles behaves as discrete particles and moves to the site which has higher energy [20, 21], at the edge of the molten solder alloy during soldering. Though, a proper mixing would allow proper separation of nanoparticles evenly throughout the molten solder rather than occurrence of agglomeration that will cause catastrophic effect on wettability because the agglomerated nanoparticles will pin the leading edge and contributes to an ineffective wetting (large contact angle). This was the comment made by [22] upon addition of high amount of Al$_2$O$_3$ (> 3%) nanoparticles to the Sn3.5Ag that later decreased the joint strength as a cause of large contact angle (crack initiator). This aspect was considered in this research and a minimal of 3% additions was chosen to be added in SAC. This was also aided with proper mixing of the nanoparticles and contributes to a lesser increase (about 8%) in the contact angle compared with the plain SAC. As aforementioned, producing contact angle below 50° reflects better joint between solder and substrate and was the outcome for this SAC + 3% TiO$_2$ solder joint.

3.2 Microhardness and Shear Strength of the SAC + 3% TiO$_2$ solder.

The Vickers hardness of the SAC + 3% TiO$_2$ solder alloy produced an average of 25.9Hv which is considered high compared to other solder alloys in recent available literatures, Sn58Bi (27.5Hv) [27], Sn0.7Cu0.05Ni (9.82Hv) [28], Sn0.3Ag0.7Cu (8.7Hv) [29], Sn-9Zn-In (15Hv) [30], Sn0.3Ag0.7Cu + 1% CNT (9.05Hv) [29], Sn3.5Ag (14.8Hv), Sn3.5Ag0.7Cu (15.8Hv), and Sn3.5Ag0.7Cu + 0.5TiO$_2$ (17.6Hv) [31]. There was a clear increase in the hardness values of the SAC + 3% TiO$_2$ solder alloy. Firstly, the increase is due to the nanoparticles in the solder alloy acting as site for heterogeneous nucleation because they do not take part in the diffusion process [25, 29]. This will increases the eutectic area of the solder alloy, and eutectic areas are known to have higher surface are per unit volume, contributing to the increase in load to penetrate through this phases [18]. According to energy absorption theory [32], the molten solder alloy of SAC being exposed with more nanoparticles (TiO$_2$) will tend to extract the nanoparticles to the grain boundary (high energy site) and this will decrease the

growth kinetic of atoms in the molten solder alloy, and as consequent, reduces the grains sizes [10]. Smaller grains are known to have higher surface area to withstand stress exposed. Similar statements were provided by [24]. The TiO_2 nanoparticles at this instant likewise behaves as a solid solution that adds up as another barrier for the stress to overcome, thus increasing the stress to deform the structure and increases the hardness [33]. The concern here is that to limit the additions of the nanoparticles (3% of TiO_2), where an over additions might have no positive grain refinement effect in the molten solder alloy because a content of high amount of these nanoparticles will attract to each other as a cause of Van Der Waals force between them [9].

An interfacial between solder and substrate is an important factor to provide integrity between the solder and substrate [1, 15]. This provides the basis of obtaining the shear strength of a solder joint. The shear strength of the SAC + 3% TiO_2 solder joint was recorded to be 51.5MPa compared with other recent results of shear strength of other common solder alloys, SnPb (49MPa), Sn3.5Ag (25), Sn3.0Ag0.5Cu (43MPa), Sn3.8Ag0.7Cu (44.9MPa), Sn0.7Cu (27.9MPa), Sn0.7Cu + 1% Si_3N_4 (28.1MPa) and Sn3.0Ag0.5Cu + 3%ZrO_2 (44MPa) [14, 34-36]. The increase of the shear strength is directly attributed by the intermetallic (IMC) layer produced between the solder and substrate. This is where the elements from the solder and substrate comes into contact and diffusion takes place to produce the IMC layers [35]. A typical IMC layer of Cu_6Sn_5 was noticed in between the solder and substrate as observed from Figure 2. Normally, with presence of adequate Sn and Cu, this layer would grow thicker and react with Cu and produce the Cu_3Sn layer as explained in Section 1. However, there was absence of this Cu_3Sn layer in this research pointing out that further diffusion process was blocked by the TiO_2 nanoparticles. The characteristics of the TiO_2 nanoparticles to segregate along the grain boundary will block the diffusion process between solder and substrate and vice versa [37], prohibiting thick Cu_6Sn_5 IMC layer and production of Cu_3Sn layer. Aiding with this, thin IMC layer, 2.32μm in this research enhances the shear strength of the joint. This is another factor contributing to a lower contact angle produced in this research as discussed earlier. Furthermore, the presence of TiO_2 nanoparticles along the grain boundary contributes to Orowan strengthening mechanism, whereby the stress induced during loading has to break through or bypass the nanoparticles at the end of dislocation, and this phenomenon increases the stress [10]. Table 1 shows points G (solder side), H (solder and interfacial) and I (interfacial) that were taken to analyse the element existence at these areas, and it was quite obvious the TiO_2 nanoparticles preferentially accommodated at points H and I. This disables the Cu to pass through beyond point H to react with Sn and produce thicker IMC layer by rapid diffusion and verifying the earlier justification.
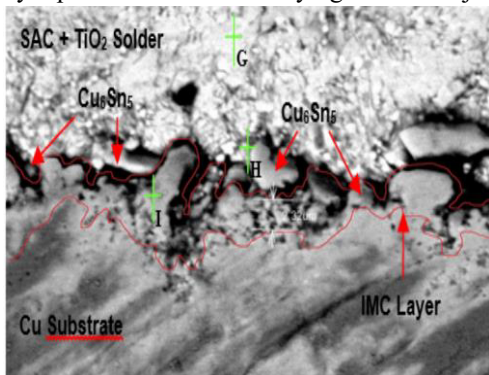
Figure 2. SEM image of SAC + 3% TiO_2/Cu joint.

Table 1. Element of SAC + 3% TiO_2/Cu joint.

Points	Elements (wt. %)					
	Sn	**Ag**	**Cu**	**Ti**	**O**	**C**
G	39.9	44.6	-	0.1	11.9	3.32
H	30.1	0.07	17.2	0.1	9.96	42.3
I	37.5	-	34.2	-	-	28.2

4. Conclusion

In this research, the outcomes were obvious to focuses on the interconnection (mechanical) of the nanoparticles added solder alloy. Key aspects of wettability, hardness and shear strength were discussed to provide the relevancy among these important parameters. As to improve the properties of

the SAC solder alloy, this research introduced the 3% TiO_2 nanoparticles to the solder alloy. The additions of the nanoparticles provides low contact angle that is desirable to be applied in the electronic industry. The surface tension was not discussed in this paper as the information are widely available yet the information (1) was provided to serve as literature aspect. Microhardness result (25.9Hv) shows an increment as the TiO_2 possesses a high resistance for deformation compared to many other researched solder alloys. The presence of TiO_2 as discrete particles at the interface between solder and the substrate was vital as they block a vast diffusion process to maintain a thin IMC layer and added with these TiO_2 nanoparticles' presence, the shearing strength was increased quite noticeably (51.5MPa). Literally, the presence of thee nanoparticles are they key of such beneficial properties enhancement, yet preparation of the nanoparticles additions should be also given key attention, as improper mixing could result in deterioration rather than improvement.

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