# Effects of Nano-Tio2 Particles Additions on Microstructure Development And Hardness of Sn3.5Ag0.5Cu Composite Solder

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**ABSTRACT**

The effects of nano-TiO particle additives on the microstructure and microhardness of the 2 Sn3.5Ag0.5Cu composite solder were studied. Results show that alloying with nano-TiO 2 particles dramatically reduced the formation of primary β-Sn phase, the average size of Ag3Sn phase, and the spacing lamellae in the Sn3.5Ag0.5Cu composite solder. This is attributed to the adsorption of nano-TiO2 particles with high surface free energy on the grain surface during solidification. Microhardness improved with the addition of nano-TiO 2 particles, which refinded Ag Sn INCs. The refined IMCs acted as a strengthening phase in the 3 solder matrix and enhanced the Vicker's microhardness of the Sn3.5Ag0.5Cu composite solders, which corresponds well with the prediction of the classic dispersion strengthening theory.

**Keywords:** Nano-TiO2 particles; Composite solder; Microstructure; Microhardness.

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## 1. Introduction

Although traditional Sn-Pb solder has been widely used, many alternatives to lead-free solders are being developed because of environmental concerns about lead. Currently, "green" electronic products and systems that do not contain toxic materials such as Pb are required [1]. Among the lead-free solders, Sn-Ag-Cu has been recognized as the most promising candidate to replace eutectic Sn-Pb solder [2-5]. In the development of lead-free solders to be used in the electronic packaging industry, several challenges must be met. The trend towards miniaturization and enhancement of functional density requires much smaller solder joints and fine-pitch interconnections for microelectronic packaging in electronic devices. Hence, ball grid array (BGA) and flip chip (FC) technologies are widely used in these portable devices because of their high density input/output (I/O) connections in a limited space, and the increase in I/O density has lowered the conventional pitches to very fine sizes (20μm) [6]. In order to development new solders with a low melting point, higher strength, better microstructure properties, and high creep resistance are necessary.

In early research to comprehensively improve the properties of solder alloy using composite technology, Lin et al. [7-9] added nano-sized $TiO_2$ powders into conventional Sn37Pb solder. The micro hardness measurements and microstructure observations revealed that the addition of titanium dioxide nano particles enhanced the strength of the conventional solder. Tsao and Chang added $TiO_2$ nano particles to Sn3.5Ag0.25Cu lead-free solder alloy [10]. Mechanical property measurements indicated significant increases in micro hardness, 0.2% offset yield strength (0.2%YS), and ultimate tensile strength (UTS). However, the ductility decreased with increasing amounts of $TiO_2$ nano particles. Tsao et al. [11] added nano-powders of $Al_2O_3$ to lead-free Sn3.5Ag0.5Cu solder alloys. The refinement of $Ag_3Sn$ IMCs grains improved the micro hardness of composite solder. Recently, Nai et al. [12] have developed a Sn–Ag–Cu composite containing carbon nano-tubes (CNT) that exhibits improved strength.

In this study, small amounts of nano-$TiO_2$ were added to Sn3.5Ag0.5Cu solder to try to improve the microstructure and mechanical properties of the solder. Specifically, Sn3.5Ag0.5Cu solders were doped with 0, 0.5, or 1 wt.% $TiO_2$ 20nm nano particles. The microstructure and micro hardness effects of the nano particles on mechanical properties of the solder alloy will be discussed.

## 2. Experimental

Lead-free solder, Sn3.5Ag0.5Cu eutectic alloy (SAC), was prepared from Sn, Ag, and Cu ingots of 99.99% purity. The Sn3.5Ag0.5Cu lead-free composite solders were prepared by mechanically dispersing 0.5 and 1 wt.% of nano-TiO particles into the lead-free 2 Sn3.5Ag0.5Cu eutectic solder with subsequent remelting in a vacuum furnace at 650oC for 2.5 hours and casting in a mold. The solder was melted in a crucible and chill cast in a copper mold to form square ingots of 8 × 10 × 20 mm. The average size of the nominally spherical nano-$TiO_2$ particles was 20 nm in diameter (Nanostructured & Amorphous materials, USA).

All seven specimens were etched in a solution of 5 vol.% $HNO_3$ + 95 vol.% $C_2H_5OH$ for 2 min. The microstructure of the samples was observed with optical microscopy and scanning electron microscopy.

Hardness tests were determined on a Vickers scale using an automatic digital microhardness tester with a 10 gf indenting load and a load dwell time of 15 s. The experiments were carried out at room temperature, 25 oC.

## 3. Results and discussion

Figure 1a is a SEM image showing the original microstructure of the Sn3.5Ag0.5Cu solder under the as-cast condition. In Fig.1a, the grey regions are representative of dendrite β-Sn grains with an average size of 25.7μm, a needle-like $Ag_3Sn$, and a eutectic phase. The eutectic phase contained both β-Sn and the needle-like $Ag_3Sn$ phase. The needle-like $Ag_3Sn$ grains were 4.1 μm long and 0.79 μm wide. The $Ag_3Sn$ phase, located between the average spacing (L), was about 1.3 μm. However, no large particles of $Ag_3Sn$ plate were observed in the lead-free Sn3.5Ag0.5Cu solder.

With the addition of 0.5 wt.% nano- $TiO_2$ particles to the eutectic solder, the size of the dendrite β-Sn grains decreased obviously, as shown in Fig.1b. The average grain size was around 8.6 μm. When the amount of nano-$TiO_2$ particles was increased to 1 wt.%, the average β-Sn grain size decreased to 10.0 μm, as shown in Fig.1c. According to the XRD analysis, the sn3.5Ag0.5Cu composite solder with the addition of 1 wt.% nano-$TiO_2$ particles was found to exhibit a small intensity $TiO_2$ peak. This indicated that the nano-$TiO_2$ particles were successfully blended with the Sn3.5Ag0.5Cu solder.

From Fig.1b-1c, it can be seen that the sizes of $Ag_3Sn$ IMCs in the Sn3.5Ag0.5Cu composite solders were influenced by the addition of the nano-$TiO_2$ particles. In order to precisely determine the influence of nano-structured nano-$TiO_2$ particles on the morphology of $Ag_3Sn$ IMCs, the size of the $Ag_3Sn$ IMCs and the spacing between the $Ag_3Sn$ IMCs in the fabricated solder specimens were analyzed in 30 randomly chosen locations and the average values calculated based on these data. These data are listed in Table 1. As can be seen in Figure 2, the nano-$TiO_2$ particles affected both the $Ag_3Sn$ average sizes and the spacing sizes between them in the Sn3.5Ag0.5Cu composite solder. As compared to Sn3.5Ag0.5Cu solder, the average size of $Ag_3Sn$ particles and the spacing between them in the Sn3.5Ag0.5Cu composite solder decreased with the increasing amount of nano-$TiO_2$ particles [10-11, 14].

When 1 wt. % nano-$TiO_2$ particles was added, the superfine spherical nano-$Ag_3Sn$ was about 0.25μm in length and 0.24μm in diameter, and there were no large block-like $Ag_3Sn$ or $Cu_6Sn_5$ particles in the structure. This phenomenon has also been found previously in Sn-Ag-RE solder [15]. Wu et al. investigated the microstructural evolution of near equilibrium solidified Sn-Ag solders doped with rare earth elements. They pointed out that the evolution of the microstructure matched the theory of adsorption of surface-active materials, which can be used to explain its effect on the surface energy of $Ag_3Sn$ particles. It is known that greater surface tension is correlated with faster plane growth and greater adsorption amounts of surface-active materials [16, 17]. According to the Gibbs equation [18], the theory of adsorption of surface-active material, an increase in adsorption of the nano-$TiO_2$ particles surface-active material at the $Ag_3Sn$ grain boundaries decreases its surface energy and therefore will decrease the growth velocity of $Ag_3Sn$ IMCs. For the Sn3.5Ag0.5Cu composite solders, the size of $Ag_3Sn$ IMCs were largest than the size of the nano-$TiO_2$ particles. It can thus be concluded that the nano-$TiO_2$ particles refined the $Ag_3Sn$ IMCs sizes via the absorption of nano-$TiO_2$ surface active particles, and at the same time, the β-Sn grains also become fine.

The influence of nano-$TiO_2$ particle reinforcement on microhardness is also summarized in Table 2 and shown in Fig. 3. An increase in microhardness with an increase in the weight percent of nanoparticles added into the Sn3.5Ag0.5Cu eutectic solder paste is observed. The microhardness enhancement of these solders was 20.6% to 34.8 % over that of the Sn3.5Ag0.5Cu solder. The observed increase in hardness of the composite solder is attributed to the presence of nano-$TiO_2$ particles, and the refined compounds of nano-$Ag_3Sn$ can reinforce the microstructure.

According to the dispersion strengthening theory, nano-Ag3Sn particles can increase the strength of the solder matrix. This can be attributed to (1) pinning of linear dislocations and increased dislocation densities, (2) obstacles to restrict the motion of grain boundaries, and (3) the strengthening mechanism of the matrix, finely dispersed nano-Ag3Sn phase, and nano-TiO2 particles [19]. The stress acting on the nanoparticle surfaces can be explained by the piling up of linear dislocations [20] and calculated by the following equation,

$$\tau = n \tau_0 \qquad (1)$$

where τ is the stress at particle surface, n is the number of piled-up dislocations, andô0 is the yielding stress of the alloy. In addition, the number of piled-up dislocations is calculated as follows:

$$n = \frac{\pi(1-\nu)L\tau_0}{Gb} \qquad (2)$$

where $\nu$ is the Poisson's ratio; *L* is the average spacing between the secondary particles (i.e., Ag3Sn IMCs); *b* is the Burgers vector; and *G* is the shear elastic modulus of the substrate.  Hence,

π ( 1 í ) ô 0

− L 2 (3)

τ

Gb

If we assume thatô is the fracture stress of the secondary particles (Ag3Sn IMCs) and that Poisson's ratio ($\upsilon$) is constant, the yield stress of the alloy becomes:

$$\tau_0 = \sqrt{\frac{Gb\tau}{\pi(1-\nu)L}} \qquad (4)$$

This means that with the reduction of the average spacing of the secondary particles (Ag3Sn IMCs), the strength of the composite solder increases. Shi et al. [16] proposed that the nano-sized inert reinforcement may be not very effective to enhance the mechanical strength. Thus, the amount of nano-TiO2 particles is very small and the dispersion strengthening effect is mainly contributed by the nano-Ag3Sn. In this experiment, the averaging spacing between the Ag3Sn was 1.3 μm in the Sn3.5Ag0.5Cu solder.

With the addition of 0.5 wt.% nano-TiO2 particle addition, the Ag3Sn was obviously refined, with an average spacing of 0.35 μm ($LS2$).

According to Eq. 4, that is $LSAC/LS2$ = 3.71, leading to $\hat{o}\ S\ 2\ /\ \hat{o}SAC$ = 1.93. In the equation, S2 is the SAC-0.5wt. % nano-TiO2 composite solder. SAC is the Sn3.5Ag0.5Cu solder. From the experimental results in Fig.3, the ratio of the microhardness between SAC-0.5nano-TiO2 composite solder and Sn3.5Ag0.5Cu solder is $HS2/HSAC$ = 17.0/14.1 = 1.20, which is close to the above theoretical predication of dispersion strengthening theory. These resulted are shown in Table 3 and Figure 4. Hence, the experimental results of microhardness show good correlation with the composite microstructure, and that is close to the theoretical prediction from dispersion strengthening theory.

## 4. Conclusions

With the addition of nano-TiO2 particles into the lead-free Sn3.5Ag0.5Cu solder, a novel lead-free Sn3.5Ag0.5Cu composite solder was successfully blended. SEM observation of the microstructure of the Sn3.5Ag0.5Cu composite solders revealed both small β-Sn and superfine nano-Ag3Sn in the solder matrix as compared to the Sn3.5Ag0.5Cu solder. Since the adsorption of nano-TiO2 particles with high surface free energy on the grain surface during solidification decreased the size of β-Sn grains, the Ag3Sn average sizes and the spacing sizes between them in the lead-free Sn3.5Ag0.5Cu composite solder. The enhancement of micro-hardness shows good correlation with the composite microstructure, approaching the theoretical prediction from dispersion strengthening theory. In summary, the presence of these nano-TiO2 particles enhanced the mechanical properties of the Sn3.5Ag 0.5Cu composite solder alloy significantly in this research.

## Acknowledgements

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Table 1 Phase constituents, average grain size and average spacing of the composite solder.

| Sample | Addition ( Wt.%) | Ag3Sn ( μm ) | | | | β-Sn (μm) |
|---|---|---|---|---|---|---|
| | | Length | Diameter | Average size | Average spacing | |
| SAC | Nil | 4.1 | 0.79 | 2.45 | 1.3 | 25.7 |
| 1 | 0.5 | 0.32 | 0.29 | 0.31 | 0.35 | 8.6 |
| 2 | 1 | 0.25 | 0.24 | 0.25 | 0.24 | 10.0 |

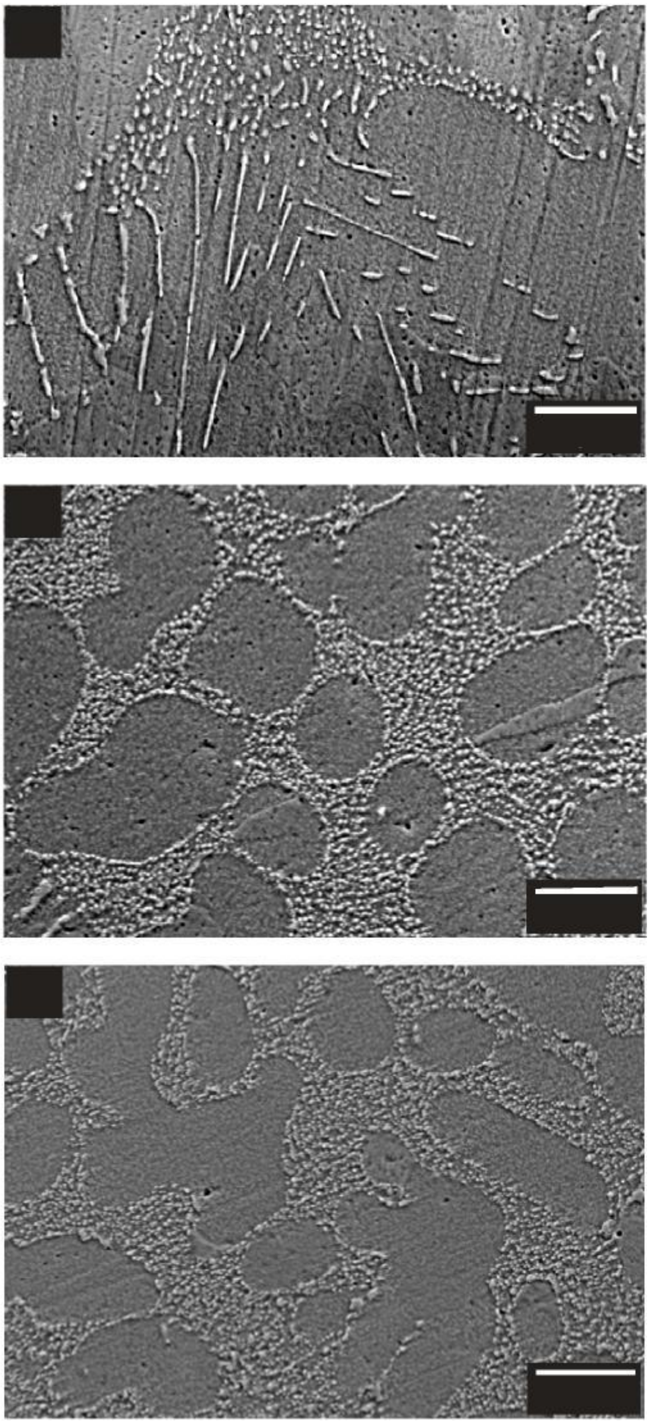
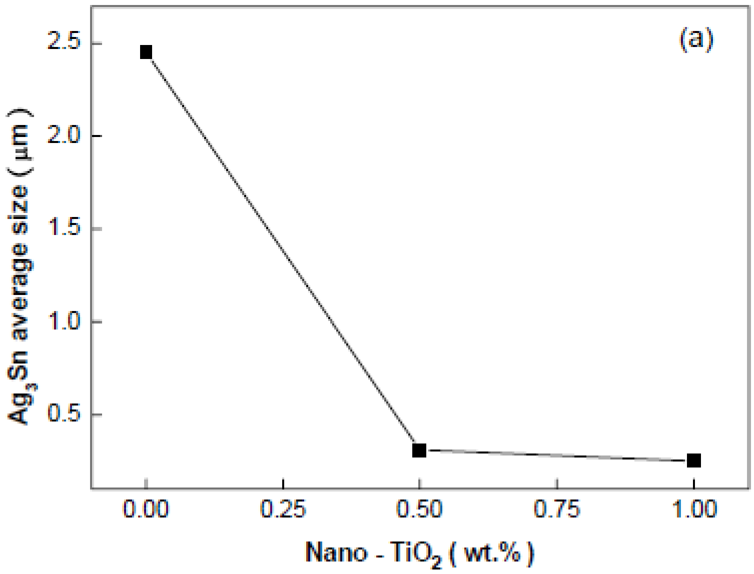


Figure 1 SEM micrographs of as-cast solders: (a) SAC, (b) SAC-0.5TiO2 and(c) SAC-1TiO2.



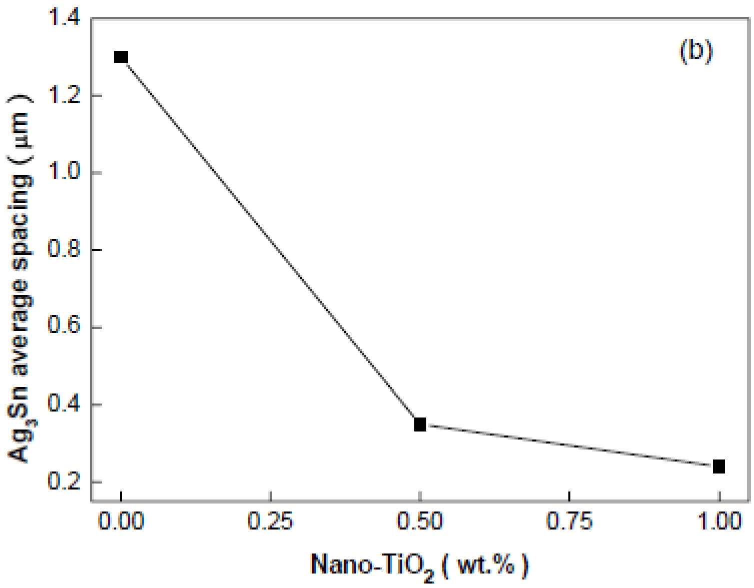




Figure 2 Comparison of $Ag_3Sn$ IMC average sizes (a) and the spacing sizes between $Ag_3Sn$ IMC in the SAC composite solder (b).

Table 2 Microhardness measurements of the Sn3.5Ag0.5Cu composite solders.

| Sample # | Addition (Wt.%) | Microhardness indention results ( Hv ) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Trial 1 | Trial 2 | Trial 3 | Trial 4 | Trial 5 | Average |
| SAC | Nil | 14.2 | 14.0 | 14.7 | 13.8 | 14.3 | 14.1 |
| 1 | 0.5 | 17.5 | 17.2 | 16.7 | 16.8 | 16.9 | 17.0 |
| 2 | 1 | 18.6 | 18.7 | 19.6 | 19.4 | 18.7 | 19.0 |

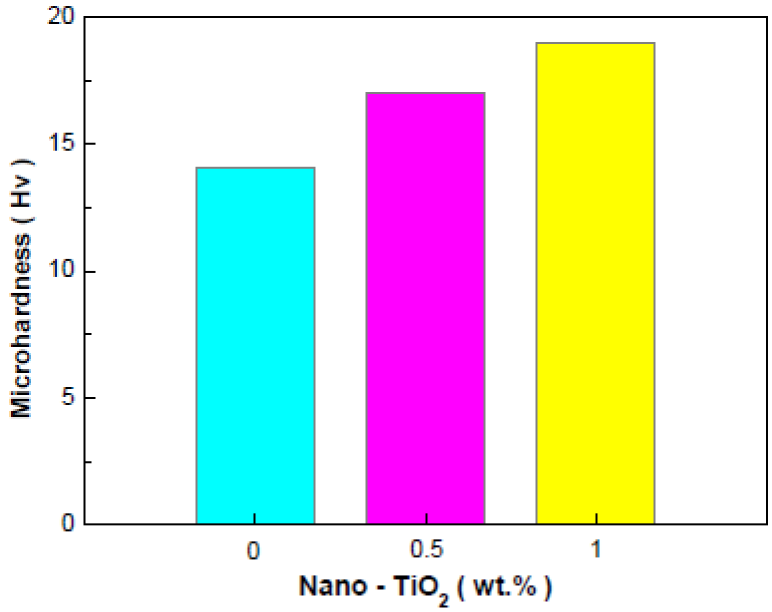



Figure 3 Influence of weight percent of nano-$TiO_2$ particles on the hardness of the Sn3.5Ag0.5Cu composite solder.

Table 3 The ratio of yield stress and the ratio of microhardness of the Sn3.5Ag0.5Cu composite solders.

| No. | Ratio spacing $Ag_3Sn$ ( $L_{SAC}$ / $L_S$ ) | Ratio yield stress ( $\tau_S / \tau_{SAC}$ ) | Ratio microhardness ( $H_S$ / $H_{SAC}$ ) |
|---|---|---|---|
| 1 | 3.71 | 1.93 | 1.20 |
| 2 | 5.41 | 2.32 | 1.35 |

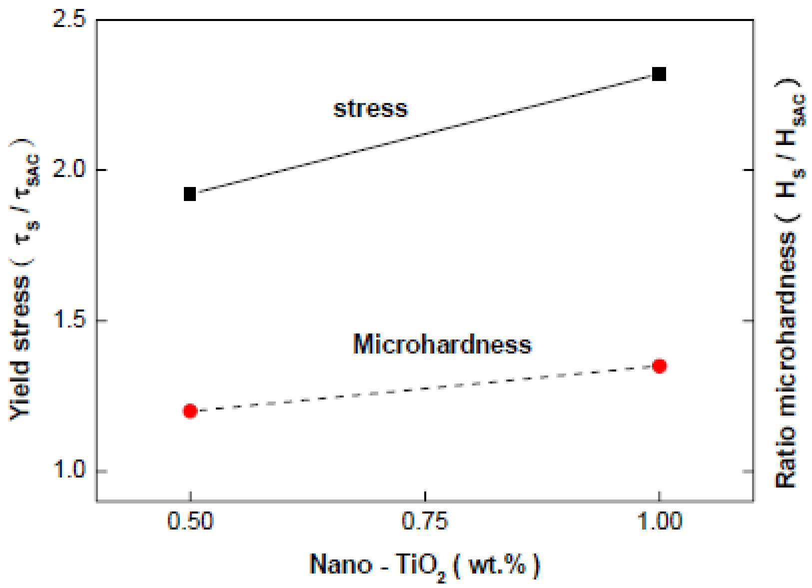



Figure 4 The ratio of yield stress and the ratio of micro-hardness of the Sn3.5Ag0.5Cu composite solder.

# Effects of Nano-TiO2 particles additions on microstructure development and hardness of Sn3.5Ag0.5Cu composite solder

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# Context

- Introduction
- Experimental
- Results and discussion
- Conclusions

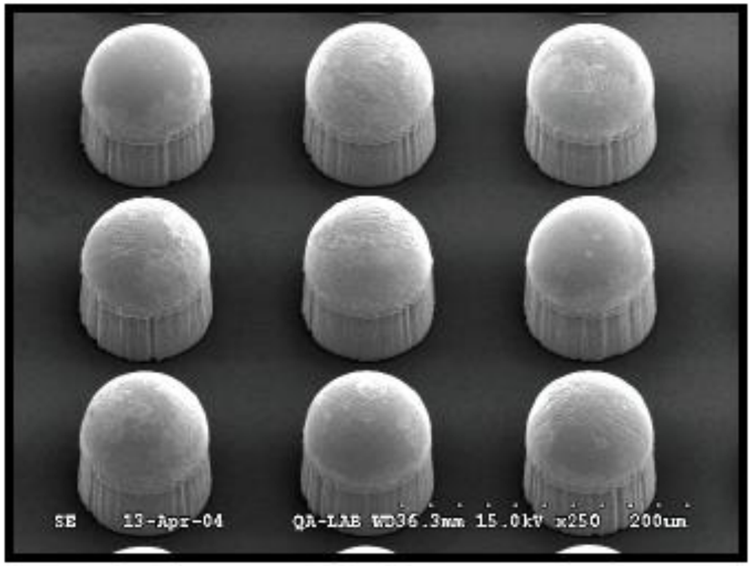
# Introduction

- Although traditional Sn-Pb solder has been widely used, many alternatives to lead-free solders are being developed because of environmental concerns about lead. Currently, “green” electronic products and systems that do not contain toxic materials such as Pb are required .

- The Sn-Ag-Cu has been recognized as the most promising candidate to replace eutectic Sn-Pb solder .

# Electronic devices

- miniaturization and enhancement of functional density
- smaller solder joints and fine-pitch interconnections for microelectronic packaging →Ball grid array (BGA) , Flip chip (FC) ,3D packaging



# Composite technology

- Development new solders with a low melting point, higher strength, better microstructure properties, and high creep resistance are necessary.
- Add to nano-sized $TiO_2$, $Al_2O_3$, containing carbon nanotubes (CNT)
- Significant increases UTS, YS
- Modify microstructure, refine to β-Sn grain and IMC

# This study

- small amounts of nano-$TiO_2$ were added to Sn3.5Ag0.5Cu solder to try to improve the microstructure and mechanical properties of the solder. Specifically, Sn3.5Ag0.5Cu solders were doped with 0, 0.5, or 1 wt.% $TiO_2$ 20nm nanoparticles.
- The microstructure and microhardness effects of the nanoparticles on mechanical properties of the solder alloy will be discussed.

# Experimental

Material: intermixing Sn3.5Ag0.5Cu(SAC) solder and 0, 0.5 , 1 wt.% of $TiO_2$ nanopowder

SAC + 20 nm $TiO_2$

↓

Melting ( vacuum, $650^0C$, 2.5h)

↓

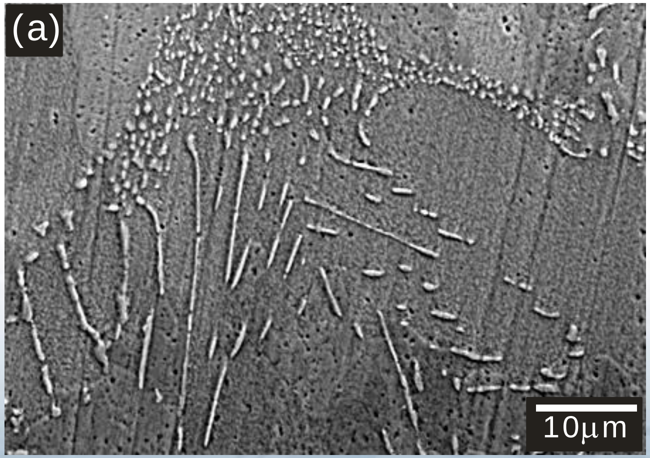
Casting to  cupper mold (8 x 10 X 20mm)

↓

Analysis (OM, SEM, Microhardness)

# Results and discussion

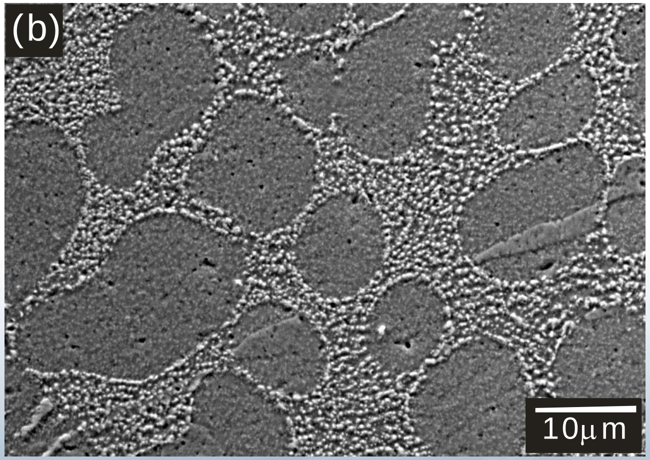
- Lead-free Sn3.5Ag0.5Cu solder was composed of dendrite β-Sn grains with an average size of 25.7μm, a needle-like Ag3Sn, and a eutectic phase.
- The needle-like Ag3Sn grains were 4.1 μm long and 0.79 μm wide.
- The Ag3Sn phase, located between the average spacing (L), was about 1.3 μm.
- no large particles of Ag3Sn plate were observed in the lead-free Sn3.5Ag0.5Cu solder.

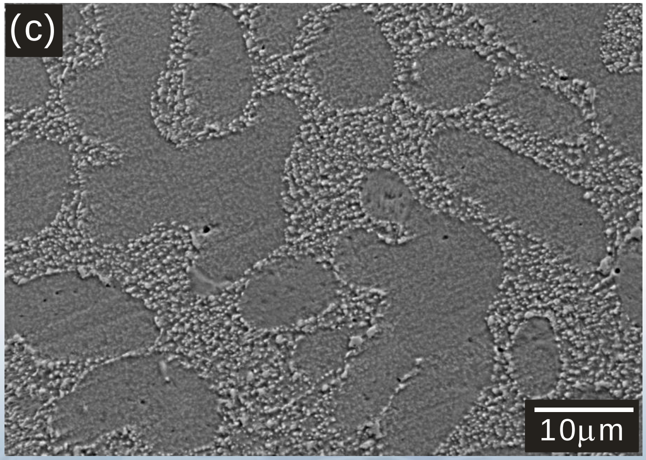



Microstructure of the Sn3.5Ag0.5Cu solder under the as-cast condition

# Composite solder

- The average β-Sn grain size was around 8.6 μm( 0.5 wt.%).
- The average grain size decreased to 10.0 μm. ( SAC 25.7 μm)




Microstructure of the Sn3.5Ag0.5Cu solder (b) 0.5 wt.%; (c) 1wt.%

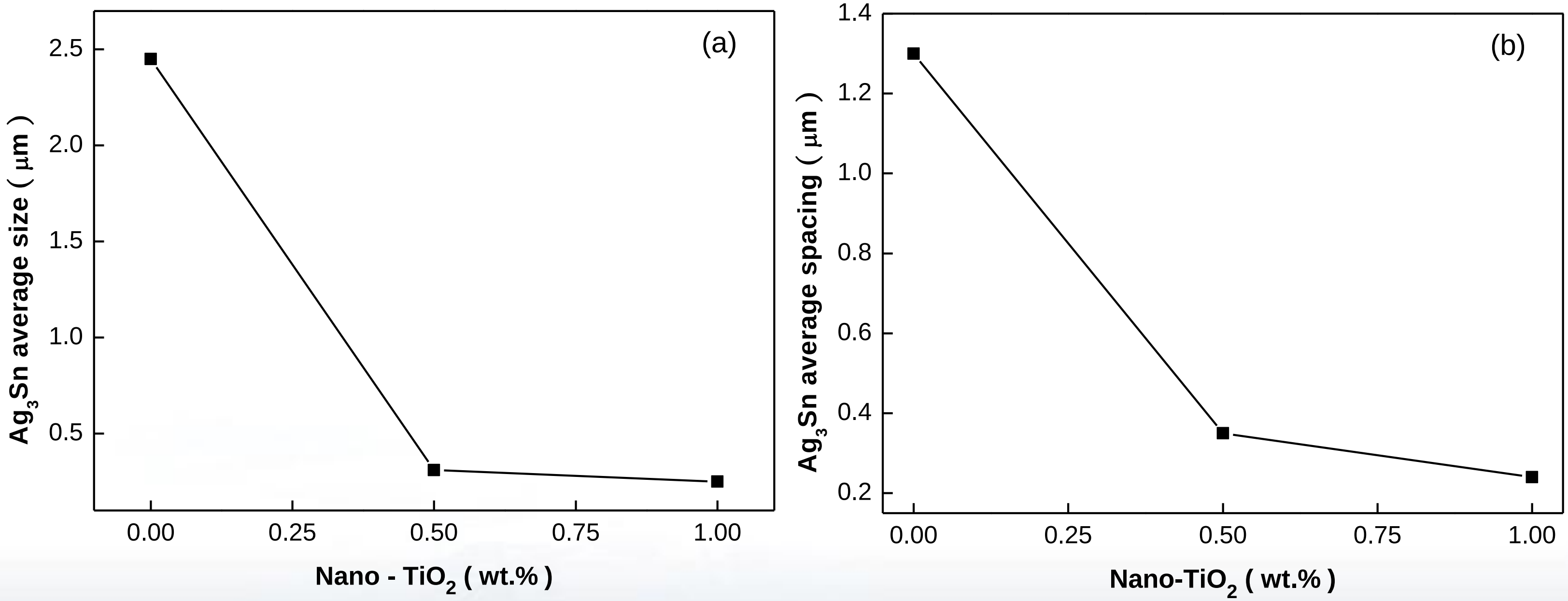
# Data analysis

- As compared to Sn3.5Ag0.5Cu solder, the average size of Ag3Sn particles and the spacing between them in the Sn3.5Ag0.5Cu composite solder decreased with the increasing amount of nano-TiO2 particles.
- This phenomenon has also been found previously in Sn-Ag-RE solder.

Phase constituents, average grain size and average spacing of the composite solder.

| Sample | Addition ( Wt.%) | $Ag_3Sn$ ( μm ) | | | | β-Sn (μm) |
|---|---|---|---|---|---|---|
| | | Length | Diameter | Average size | Average spacing | |
| SAC | Nil | 4.1 | 0.79 | 2.45 | 1.3 | 25.7 |
| 1 | 0.5 | 0.32 | 0.29 | 0.31 | 0.35 | 8.6 |
| 2 | 1 | 0.25 | 0.24 | 0.25 | 0.24 | 10.0 |

# Ag3Sn IMC data




- Comparison of Ag3Sn IMC average sizes (a) and the spacing sizes between Ag3Sn IMC in the SAC composite solder (b).

# Reason

- The evolution of the microstructure matched the theory of adsorption of surface-active materials, which can be used to explain its effect on the surface energy of $Ag_3Sn$ particles.

- Greater surface tension is correlated with faster plane growth and greater adsorption amounts of surface-active materials .

- The theory of adsorption of surface-active material, an increase in adsorption of the nano-$TiO_2$ particles surface-active material at the $Ag_3Sn$ grain boundaries decreases its surface energy and therefore will decrease the growth velocity of $Ag_3Sn$ IMCs.

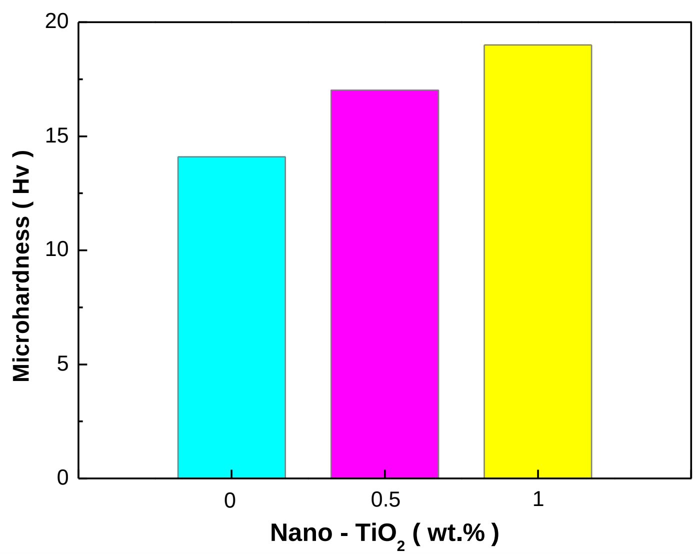
- the nano-$TiO_2$ particles refined the $Ag_3Sn$ IMCs sizes via the absorption of nano-$TiO_2$ surface active particles, and at the same time, the β-Sn grains also become fine.

# Microhardness

➢An increase in microhardness with an increase in the weight percent of nanoparticles added into the Sn3.5Ag0.5Cu eutectic solder paste is observed.

➢The microhardness enhancement of these solders was 20.6% to 34.8 % over that of the Sn3.5Ag0.5Cu solder.

➢Increase in hardness of the composite solder is attributed to the presence of nano-TiO2 particles, and the refined compounds of nano-Ag3Sn can reinforce the microstructure.




- Influence of weight percent of nano-TiO2 particles on the hardness of the Sn3.5Ag0.5Cu composite solder.

# Dispersion strengthening theory

- pinning of linear dislocations and increased dislocation densities
- obstacles to restrict the motion of grain boundaries
- the strengthening mechanism of the matrix, finely dispersed nano-Ag3Sn phase, and nano-TiO2 particles .

# Dispersion strengthening theory analysis

- Average spacing of the secondary particles & the strength of the composite solder:

$$\tau_0 = \sqrt{\frac{Gb\tau}{\pi(1-\nu)L}}$$

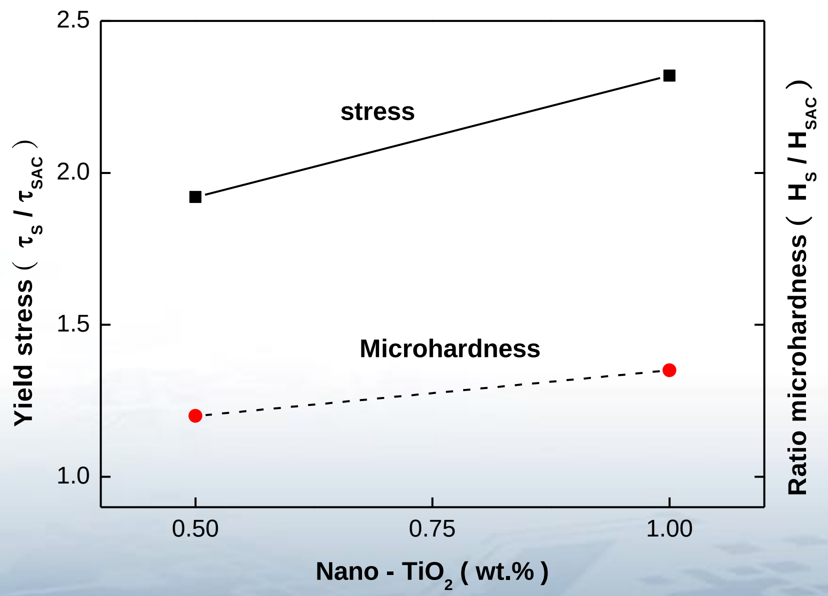
SAC-0.5wt. % nano-TiO2 composite solder :

$L_{\mathrm{SAC}}/L_{S2}$ = 3.71, leading to $\tau_{S2}/\tau_{SAC}$ = 1.93.

the ratio of the microhardness between SAC-0.5nano-TiO2 composite solder and Sn3.5Ag0.5Cu solder is *HS*2/*H*SAC = 17.0/14.1 = 1.20

# Analysis

The experimental results of microhardness show good correlation with the composite microstructure, and that is close to the theoretical prediction from dispersion strengthening theory.




The ratio of yield stress and the ratio of microhardness of the Sn3.5Ag0.5Cu composite solder.

# Conclusions

- The microstructure of the Sn3.5Ag0.5Cu composite solders revealed both small β-Sn and superfine nano-Ag3Sn in the solder matrix as compared to the Sn3.5Ag0.5Cu solder.
- The adsorption of nano-TiO2 particles with high surface free energy on the grain surface during solidification decreased the size of β-Sn grains, the Ag3Sn average sizes and the spacing sizes between them in the lead-free Sn3.5Ag0.5Cu composite solder.
- The enhancement of microhardness shows good correlation with the composite microstructure, approaching the theoretical prediction from dispersion strengthening theory .

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Thanks!
Q&A