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DEVELOPMENT OF LEAD-FREE NANOCOMPOSITE SOLDERS USING OXIDE BASED REINFORCEMENT

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ABSTRACT

In this study, Sn.3.5Ag/SnO_2 nanocomposite solders are developed. Composites with 0.7 and 1.0 volume percentage of tin oxide were synthesized through powder metallurgy route incorporating microwave assisted rapid sintering technique followed by hot extrusion. The extruded specimens were examined in terms of their physical and tensile properties. Tensile characterization studies revealed that 0.2% yield strength and ultimate tensile strength were increased significantly by addition of 0.7 volume percent of nano SnO_2 particles. An attempt is made to correlate mechanical properties of Sn-3.5Ag with the presence of SnO_2 particles at the nanometer length scale.

INTRODUCTION

Tin-lead (Sn-Pb) solders have been widely utilized in the electronics industry in the past few decades due to their unique properties of low melting point, wetting characteristics and mechanical properties [1, 2]. However, in recent years, increasing environmental and health concerns over the use of toxic Pb, coupled with strict legislations on the ban of Pb usage in consumer electronics had been the driving force in the development of new lead-free solder alloys. Among the lead-free solders being developed, Sn-3.5Ag is one of the most promising lead-free alloys because it possesses excellent mechanical properties and improved high temperature resistance compared to Pb–Sn solder [2-4].

Exiting literature shows that the composite approach is effective in providing solders and solder joints with improved mechanical behavior [5-11]. The reinforcement particles used in the composite materials usually included micro-/nano-size metallic, intermetallic, or oxide particles [5-11]. In this study, tin oxide (SnO_2) particulates at the nanometer length scale were used. Key advantages of using SnO_2 as reinforcing particulates include: (i) close density to Sn-3.5Ag , ρ (Sn-3.5Ag) =7.360 g/cm^3 and ρ (SnO_2) = 6.95 g/cm^3, (ii) high hardness when compared to Sn-3.5Ag matrix, (iii) low cost when compared to nano-size reinforcements used by other investigators such as TiO_2, CNTs and ZrO_2 particulates stabilized with 8 mol.% of Y_2O_3 particulates [7, 9-12] and (iv) being a n-type semiconductor.

The processing technique of composite materials also plays a crucial role on the end properties of the materials [13, 14]. Powder metallurgy (PM) is one of the common manufacturing techniques used in the synthesis of metal matrix composites. In the PM method, sintering plays a crucial part in realizing the end properties of the materials whereby densification and the formation of bonds (to minimize level of porosity) takes place. Investigations have shown that microwaves can be utilized to sinter both monolithic and composite powder compacts much more rapidly than conventional sintering, resulting in better microstructural and mechanical properties [15-17]. Furthermore, use of microwaves can result in impressive energy saving upto 90% and even higher in some cases. Hence, in this study microwave sintering was used.

To accomplish the low-cost low-temperature fluxless bonding, an approach of solid-state bonding (such as thermal compression, thermosonic and ultrasonic bonding) is adopted whereby solders do not go through a conventional melting and solidification. The properties of the original solder are mostly retained particularly in ultrasonic (US) bonding [18, 19]. Kim et al. [19] has reported that using a Sn-3.5Ag solder interlayer, Si-dice and printed circuit board substrates were bonded by US. Therefore, the properties of nanocomposite solders synthesized by PM technique can successfully be retained by using these bonding techniques.

Accordingly, in the present study, Sn-3.5Ag solder and nano-size SnO_2 were used as matrix and reinforcement, respectively. Particular emphasis was placed to investigate the effect of increasing SnO_2 nanopowder addition on the microstructural and mechanical properties of a Sn-3.5Ag solder.

EXPERIMENTAL METHODOLOGY

Sn-3.5Ag powder with a size range of 25-45 µm obtained from Qualitek^R, USA, was used as the matrix material. SnO_2 nanopowder of 99.5% purity with a size range of 60-80 nm obtained from NanoAmor (Nanostructured & Amorphous Materials, Inc.), USA, was used as the reinforcement.

Pure Sn-3.5Ag powder and SnO_2 nanopowder were weighed carefully and blended in a RETSCH PM-400 mechanical alloying machine using a speed of 200 rpm for 1 hour. No balls or process control agent was used during blending step. The blended powders were uniaxially compacted using a pressure of 510 MPa to billets (40 mm height with 35 mm diameter). Compacted billets were then sintered using microwave assisted sintering technique for 6 minutes and 45 seconds to reach the temperature of 221ºC under ambient condition in a 900 W, 2.45 GHz SHARP microwave oven. SiC is used as the microwave susceptor material [15-17]. This hybrid heating method results in a more uniform temperature gradient within the billet and circumvents the disadvantages of heating using either conventional heating or microwaves only. The sintered billets were then extruded at 221ºC using an extrusion ratio of 26.5:1 on a 150 ton hydraulic press, to produce an extruded rod with a final diameter of 7 mm. The preforms were also soaked at 221 ºC for 5 minutes in a constant temperature furnace before extrusion.

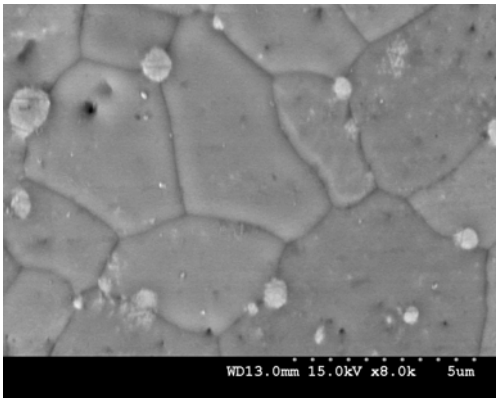
Microstructural analysis of the metallographically polished samples was carried out using HITACHI S4300 field emission scanning electron microscope (FESEM) to investigate: (i) morphological characteristics of pores, (ii) presence and distribution of nano-size reinforcements, and (iii) presence and distribution of intermetallic compounds (IMCs). The Scion image analysis system was used to quantify the microstructural features.

The tensile properties of the extruded samples were determined in accordance with ASTM test method E8M-01. The tensile tests were conducted on round tension test specimens of 5 mm diameter and 25 mm gauge length using an automated servohydraulic testing machine (MTS 810) with a crosshead speed set at 0.254 mm/min.

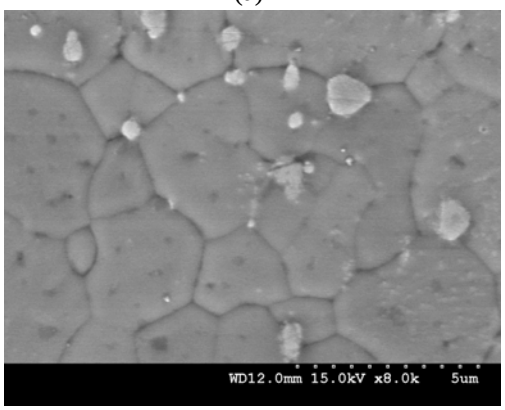
RESULTS AND DISCUSSION

Monolithic Sn-3.5Ag and Sn-3.5Ag/SnO_2 nanocomposites were successfully synthesized using PM technique incorporating microwave assisted rapid sintering. The results of macrostructural characterization on all the sintered performs revealed absence of sintering defects like circumferential or radial cracks. Following extrusion, the samples also did not reveal presence of any macro defects. The outer surfaces were smooth and free of circumferential cracks. This indicates suitability of hybrid microwave sintering which ensures reduced sintering time without affecting the end properties of monolithic and composite samples. Other advantages such as lower energy requirement and cost savings make microwave sintering an extremely attractive option for the synthesis of materials.

Microstructural characterization results revealed fairly uniform distribution of Ag_3Sn intermetallic phase (see Fig. 1) and nano-size SnO_2 reinforcement particles in the solder matrix (see Fig. 2).



(a)



(b)

FIGURE 1. MICROGRAPHS SHOWING THE DISTRIBUTION OF Ag_3Sn INTERMETALLICS IN (a) Sn-3.5Ag AND (b) Sn-3.5Ag/SnO_2 SAMPLES.

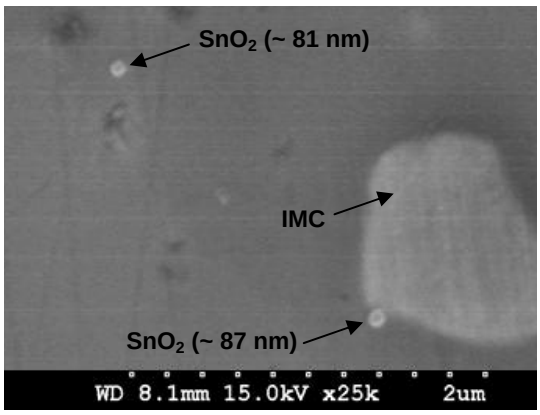


FIGURE 2. REPRESENTATIVE MICROGRAPH SHOWING PRESENCE OF NANO-SIZE SnO_2 PARTICULATES IN Sn-3.5Ag/SnO_2 SAMPLES.

Theoretically, when secondary process with a large enough deformation is introduced, homogenous distribution of reinforcement can be achieved regardless of the size difference between matrix powder and reinforcement particulates [20]. Hence, reasonably uniform distribution of SnO_2 particulates confirms the efficiency of blending and extrusion parameters used in this study (see Fig. 2). It may be noted that one of the essential factor for the extent of strengthening that can be realized in composite materials is the uniform distribution of SnO_2 reinforcement in the matrix [21].

Table 1 shows the results of porosity level and pores aspect ratio of the monolithic and nanocomposite solders. With the addition of 0.7 vol. % of SnO_2 particulates, there is no change in the level of porosity as compared to that of monolithic solder. However, as the amount of reinforcement increased to 1.0 vol. %, the average porosity level increased by ~ 50%. With increasing addition of reinforcements, the pores aspect ratio also increased. This indicates that the presence of more reinforcement particulates leads to higher irregularity of the pores. These results are consistent with the findings on nanocomposites by other researchers [22, 23].

TABLE 1. RESULTS OF POROSITY AND PORES ASPECT RATIO.

Material	Designation	Porosity[1] (%)	Pores aspect ratio[2]
Sn-3.5Ag	SA	0.6 ± 0.05	1.3 ± 0.24
Sn-3.5Ag/0.7SnO_2	SA/0.7SnO_2	0.6 ± 0.20	1.6 ± 0.32
Sn-3.5Ag/1.0SnO_2	SA/1.0SnO_2	0.9 ± 0.12	2.7 ± 0.34

[1] Scion Image software was used to determine the porosity level.
[2] Around sixty pores were quantified in each case.

The results of ambient temperature tensile testing (see Table 2) revealed that strength improvement of Sn-3.5Ag matrix can be realized when 0.7 vol. % of SnO_2 particulates was incorporated. The statistical t-test was carried out and the results exhibited a substantial difference in the tensile properties. SA/0.7SnO_2 samples showed 18% and 32% higher 0.2% YS and UTS, respectively over monolithic samples. The improvement in 0.2% YS and UTS is even more significant (up to ~ 105% and ~ 115%, respectively) when compared with published Sn96.5/Ag3.5 and Sn63/Pb37 values by Qualitek^R (see Table 2).

The strength of a reinforced matrix can be defined by equation (1) [15]:

$$\sigma_{my} = \sigma_{mo} + \Delta\sigma \tag{1}$$

where σ_{my} and σ_{mo} are the yield strength of the reinforced and unreinforced matrix, respectively. $\Delta\sigma$ represents the total increment in yield stress of the reinforced Sn-3.5Ag matrix and is estimated by equation (2) [24]:

$$\Delta\sigma = \sqrt{\left(\Delta\sigma_{Orowan}\right)^2 + \left(\Delta\sigma_{CTE}\right)^2 + \left(\Delta\sigma_{EM}\right)^2} \tag{2}$$

The improvement in material's strength in the case of SA/0.7SnO_2 can be mainly attributed to: (i) Orowan strengthening mechanism ($\Delta\sigma_{Orowan}$) due to presence of nano-size SnO_2 particulates in the solder matrix, (ii) increase in dislocation density due to coefficient of thermal expansion (CTE) mismatch ($\Delta\sigma_{CTE}$) between Sn-3.5Ag and SnO_2 particulates (3.76×10^{-6}/ ºC and 26.4×10^{-6}/ ºC for SnO_2 [25] and Sn-3.5Ag, respectively) and (iii) elastic modulus (EM) mismatch ($\Delta\sigma_{EM}$) between matrix and reinforcement (233 GPa for SnO_2 [25] compared with 10 GPa for Sn-3.5Ag).

TABLE 2. RESULTS OF TENSILE TEST.

Material	0.2% YS[1] (MPa)	UTS[1] (MPa)	Total FS[1] (%)
SA	38 ± 1	44 ± 0	46 ± 1
SA/0.7Sn O_2	45 ± 1	58 ± 2	24 ± 1
SA/1.0Sn O_2	40 ± 4	44 ± 5	21 ± 1
Sn96.5/Ag3.5[2]	22	27	24
Sn63/Pb37[2]	27	31	48

[1] YS: Yield Strength; UTS: Ultimate Tensile Strength; FS: Failure Strain.

[2] Company catalogue provided by Qualitek[R], USA, 2006.

However, it was also noted that the results showed a decline in material's strength (SA/1.0SnO_2) when the amount of SnO_2 increased from 0.7 to 1.0 vol. %. This can be attributed to the higher porosity level (~ 0.9%) as well as higher pores' aspect ratio (~2.7) compared to SA/0.7SnO_2 (see Table 1). The higher pores aspect ratio in SA/1.0SnO_2 signifies the presence of sharp edge pores in the microstructure which justifies the lower tensile properties in this material. The ability of porosity to serve as a crack initiation site and to adversely affect strength has been established convincingly for both monolithic and composite materials [22, 26]. In a recent study, Alam et al. [22] reported that increasing pores aspect ratio in pure tin led to a decrease in material's strength. Furthermore, it has been reported by others that there is a threshold where incorporation of too much reinforcement could lead to detrimental effect on the properties of material [7]. Total failure strain (TFS) of all composite samples was found to decrease as the amount of reinforcement increased in the solder matrix (see Table 2). This can be attributed to the presence of harder reinforcing phase serving as crack nucleation sites, resulting in a decrease in TFS under tensile loading conditions. This observation is consistent with the observation made by others working on other tin-based composite systems [23, 27].

CONCLUSIONS

The following conclusions can be drawn from the experimental findings of this study:

1. Sn-3.5Ag composites containing SnO_2 particulates at nanometer length scale can be successfully synthesized using powder metallurgy technique incorporating microwave sintering technique.
2. Microstructural characterization revealed that secondary phase (Ag_3Sn) and nano-size SnO_2 particulates were uniformly dispersed throughout the matrix.
3. Tensile results revealed that the best overall mechanical properties was achieved in Sn-3.5Ag reinforced with 0.7 volume percent of SnO_2 particulates. Improvement of 18% in 0.2%YS and 32% in UTS over monolithic Sn-3.5Ag was observed.

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