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IMPACT OF THE GNS PARTICLES ON MICROSTRUCTURE AND THERMAL PROPERTIES OF THE Sn-0.7Cu SOLDER ALLOYS

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Abstract

Development of various types the so-called "environmentally friendly" solders has been extensively investigated worldwide as an alternative to the lead-based solders. This study investigated the impact of graphene nanoparticles on microstructure and thermal properties of the lead-free solders. The nanocomposite solders were produced using the powder metallurgy method. The graphene nanoparticles were used as the reinforcement in the form of graphene nanosheets (GNS). The microstructural analysis showed that the GNS particles were homogeneously distributed along the grain boundaries, resulting in a refined β-Sn structure. At room temperature, density was measured using the Archimedes method, while the thermal diffusivity was determined using the flash method. The thermal conductivity of the Sn-0.7Cu nanocomposite solders was calculated using a fundamental equation. Increasing the GNS content up to 0.08 wt% in the Sn-0.7Cu solder matrix led to a slight decrease in density of the nanocomposite solders compared to the base solder, while the highest thermal conductivity was achieved with a 0.05 wt% GNS addition, reaching 44.74 $Wm^{-1} K^{-1}$.

***Keywords**: lead-free solder alloys, powder metallurgy, graphene nanosheets*

1. INTRODUCTION

Microjoining of the engineered materials is one of the most important areas in the manufacturing and industrial sectors. Thanks to their excellent mechanical properties and outstanding electrical and thermal conductivity, the solder materials play an important role in achieving a reliable solder joint. The Sn-Pb solders have been popular for many years in the microelectronic applications [1]. Due to the presence of toxic lead in these solders, which poses a risk to the human health and environment, it is necessary to eliminate lead from the solder alloys. Several countries have started implementing the safety measures, including setting regulations to restrict or prohibit the use of lead in electronics. The European Union (EU) adopted two directives: WEEE (Waste Electrical and Electronic Equipment) and RoHS (Restriction of the Use of Certain Hazardous Substances) [2, 3].

Development of the lead-free solder alloys has been a major challenge for many researchers. Today, the most commonly used solders are from the Sn-Cu, Sn-Ag, and Sn-Ag-Cu systems. These solder alloys are also used as a matrix to obtain the composite solder materials [4]. Composite solder materials are the reinforced solder alloys. The powder metallurgy (PM) technique is the most commonly employed method for producing the nanocomposite solders. Various reinforcing particles can be added, such as SiC, Al_2O_3, TiO_2, ZrO_2, SnO_2, ZnO, Si_3N_4, and TiB_2, to improve the properties of composite solder materials. Certain researchers use the nanomaterials as reinforcement, based on various allotropic forms of carbon. Graphite is the first known allotropic modification of carbon. It has a layered structure, where one layer represents a modification known as graphene. Graphene is the first natural two-dimensional (2D) atomic crystal with a thickness of one atom. It is the strongest and thinnest two-dimensional material studied, due to its dense network of the sp^2 bonding. It has remarkable thermal properties and thermal conductivity which is twenty times higher than copper at room temperature [5]. The graphene nanosheets (GNSs) are most frequently used for production the nanomaterials. They represent a one-dimensional (1D) nanomaterial created by etching or shaping graphene in one direction [6]. The addition of reinforcement particles such as the graphene nanosheets (GNS), single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and fullerenes (FNs), is another area of interest [7].

The unique structural, electrical, optical, and magnetic properties of these materials have attracted the attention of many researchers [8]. Liu et al. observed that adding the GNS particles into the Sn-Ag-Cu solders reduced the grain growth, resulting in a finer microstructure [9]. Wang and colleagues concluded that adding the reinforcement particles of less than 0.5 wt% to the Sn-based solder alloys effectively refines the intermetallic compounds, thereby improving the performance of solder alloys [10]. Sun et al. determined that introducing the GNS into the Sn-0.7Cu solder matrix enhances the thermal conductivity, with the maximum improvement occurring in the GNS content of 0.16 wt% [11]. Huang and his colleagues used the PM method to produce the SAC305-0.1% GNS composite solders and found that adding the graphene nanoparticles efficiently inhibits the formation of intermetallic compound (IMC) layers. The GNS particles act as a diffusion barrier between copper and tin atoms, restricting their diffusion and limiting development of the IMC [12].

The main focus of this research is to understand how small additions of the GNS particles affect the microstructure and thermal properties of the nanocomposite solders. In this study, the graphene-reinforced composite solders were produced using the PM technique. The obtained results for the nanocomposite solders were compared with those of the base Sn-0.7Cu solder.

2. EXPERIMENTAL

Powders of two metals, Sn (99.90%) and Cu (99.96%), with particle sizes ranging from 25 to 45 μm, along with the GNS particles (average diameter 3-6 μm, thickness 3-5 nm), were utilized to obtain the Sn-0.7Cu-xGNS composite solders. Using the PM technique, the nanocomposite solders were synthesized with different contents of the GNS particles (0%, 0.02%, 0.05%, and 0.08%) in a Sn–0.7Cu solder matrix. Initially, the Sn powder was alloyed with Cu powder to create the Sn–0.7Cu base solder powder. The GNS reinforcement particles were added to the base solder powder and stirred for 30 hours. The composite powder was compacted under a pressure of 300 MPa, and the obtained green compacts were sintered in a furnace at 180°C for 3 hours in an argon atmosphere.

The microstructural changes in the sintered nanocomposite solders were studied using the metallographically prepared, polished, and etched samples to identify and analyze the morphological characteristics of grains, pores, and intermetallic compounds. Microstructure analysis was performed with the optical microscope 'Reichert MeF2' at 1000x magnification. The etchant solution was prepared mixing 2 vol.% HCl, 3 vol.% HNO3, and 95 vol.% methanol.

The thermal diffusivity of the nanocomposite solders was measured at room temperature using the Discovery Xenon Flash (DXF-500) device, while the density was determined using the Archimedes method. Samples were shaped into round discs with a diameter of 12.6 mm and thickness of 2.5 mm. Measurements were conducted in an inert protective atmosphere. The thermal conductivity of the analyzed sample was calculated using the following fundamental equation (2):

$$\lambda = \alpha \times \rho \times Cp \qquad (2)$$

where λ is thermal conductivity ($Wm^{-1}K^{-1}$), α is thermal diffusivity (m^2s^{-1}), ρ is density (gcm^{-3}) and Cp is specific heat capacity ($Jg^{-1}K^{-1}$).

3. RESULTS AND DISCUSSION

Figure 1 shows the microstructures of the Sn-0.7Cu-xGNS nanocomposite solders. During the sintering process, the minimal diffusion on the particle surfaces was observed. This diffusion was sufficient for compacting the powders but was not intense enough to cause the formation of eutectic phase, as also confirmed in the study by Huang et al [12].

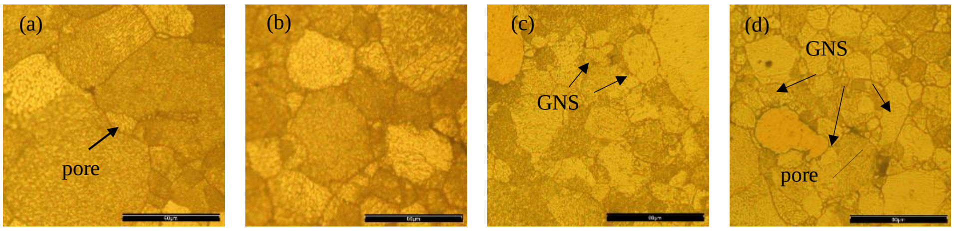

Figure 1. *OM microphotographs of the solder alloys at 1000x magnification; (a) Sn-0.7Cu; (b) Sn-0.7Cu-0.02% GNS; (C) Sn-0.7Cu-0.05% GNS; (d) Sn-0.7Cu-0.08% GNS*

The microstructure of the base Sn-0.7Cu solder is shown in Figure 1a. All other microphotographs present the microstructures of solders containing the GNS particles. At an addition of 0.02 wt% GNS (Figure 1b), the presence of GNS particles in the nanocomposite solder is barely noticeable. However, with higher additions of 0.05 wt% GNS (Figure 1c) and 0.08 wt% GNS (Figure 1d), their presence becomes more evident. The reinforced GNS particles are distributed along the grain boundaries, and pores are visible in the microstructures. In the study by Yang et al., it was observed that as the weight content of the GNS particles exceeds 0.08 %, these reinforcement particles tend to agglomerate along the grain boundaries [13].

Based on the OM results, it can be concluded that an increase in the weight content of GNS particles leads to a grain refinement due to the uniform distribution of reinforcement particles along the grain boundaries. The microstructure of the composite solders is more uniform and finer-grained than the base Sn-0.7Cu solder. Based on this observation, it can be assumed that the GNS particles act as the centers of heterogeneous nucleation, leading to the grain refinement. Furthermore, a higher GNS content increases the barrier effect, which inhibits the grain growth.

The graphene nanoparticles have a thermal conductivity of 5000 $Wm^{-1}K^{-1}$ [14], while the base Sn-0.7Cu solder alloy has a significantly lower value of 53 $Wm^{-1}K^{-1}$ [15]. Therefore, it can be assumed that adding the GNS particles would enhance the thermal conductivity. However, in composite materials, the situation is not that straightforward. The geometric orientation of the reinforcement in the matrix affects the value of the specific thermal conductivity. When the reinforced particles are oriented parallel to a direction of the heat flow, the thermal conductivity typically improves [16].

Figure 2 shows the thermal conductivity of the Sn-0.7Cu-xGNS nanocomposite solders. The results indicate that adding the reinforcement particles enhances the thermal conductivity of the nanocomposite solders.

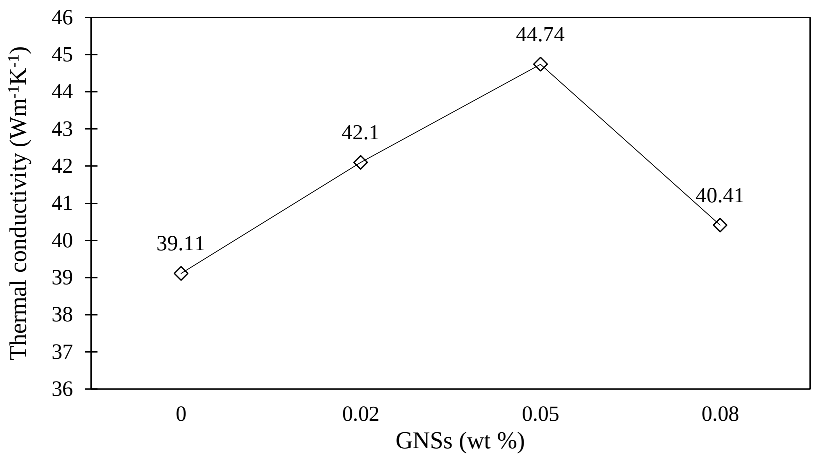

Figure 2. *Thermal conductivity of the Sn-0.7Cu-xGNSs nanocomposite solders*

The base Sn-0.7Cu solder has a thermal conductivity of 39.11 $Wm^{-1}K^{-1}$, while the solder with 0.05 wt% GNS has the highest thermal conductivity value of 44.74 $Wm^{-1}K^{-1}$. When the GNS content in the nanocomposite solder reaches 0.08 wt%, the thermal conductivity decreases to 40.41 $Wm^{-1}K^{-1}$. It is assumed that a decrease in thermal conductivity is due to the agglomeration of the GNS particles along the grain boundaries, which causes the accumulation of dislocations and distorts the matrix lattice. This increases the probability of electron scattering, reduces the number of effective electrons in crystal, increases the resistance, and decreases the thermal conductivity.

4. CONCLUSION

In this study, the Sn-0.7Cu solders with different contents of the GNS reinforcement particles were successfully synthesized using the powder metallurgy technique. The following conclusions have been drawn:

- The microstructure analysis showed that the nanocomposite solders possess a more homogeneous and finer-grained microstructure than the base Sn-0.7Cu solder alloy. As the weight content of the GNS particles increases, the grain refinement occurs due to the barrier effect of the reinforcement particles, which inhibits a grain growth.
- The thermal conductivity of the nanocomposite solders improves with the addition of GNS particles, reaching its highest value at the GNS content of 0.05 wt%. Changes in density compared to the base Sn-0.7Cu solder are minimal due to the small weight percentages of the reinforcement.

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