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Pulse Electrodeposition of Lead-Free Tin-Based Composites for Microelectronic Packaging

Ashutosh Sharma, Siddhartha Das and Karabi Das

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Abstract

This chapter provides a detailed overview of the various Sn-based composites solders reinforced with ceramic nanoparticles. These solders are lead free in nature and are produced by various process like powder metallurgy, ball milling, casting as well as simple and economic pulse co-electrodeposition technique. In this chapter, various electrodeposited composite solders, their synthesis, characterization, and evaluation of various properties for microelectronic packaging applications, such as microstructure, microhardness, density and porosity, wear and friction, electrochemical corrosion, melting point, electrical resistivity, and residual stress of the monolithic Sn-based and (nano)composite solders have been presented and discussed. This chapter is divided into the following sections: such as introduction to microelectronic packaging, synthesis routes for solders and composites, various nanoreinforcement, and the mechanism of incorporation in solder matrix, the pulse co-electrodeposition technique, the various factors affecting composite deposition, and the improved properties of composite solders over monolithic solders for microelectronic packaging applications are also summarized here.

Keywords: Composite, lead free, plating, double layer, zeta potential

1. Introduction

1.1. Microelectronic packaging

Microelectronic packaging is a multidisciplinary branch of materials engineering that deals with the study of various interconnecting materials, electronic components packaging from chip level to final board level, for example, computers, cellphones, notebooks, laptops, and iPads. It also includes a method of joining various components to the respective substrates, as well as reducing their weight/volume for faster processing, multifunctionality, and portability.

In olden times, various wires and cables are used to connect the different components into an electric box. With the passage of time, printed circuit boards (PCB), or printed wire boards (PWB) invented near 1950s as a great revolution among electronics industries. Moreover, the invention of transistors and integrated circuits (ICs), analog-to-digital electronics in 1947 made luxurious life style of the common public. This technology of interconnecting various IC's and other electronic component devices like transistors, capacitors, inductors, and resistors within circuits over a PCB substrate to form a compact electronic device is known as microelectronic packaging.[1, 2] The common packages in a personal computer are shown below (Fig. 1).

Figure 1. Micropackaging assemblies inside a personal computer.

1.2. Microelectronic packaging materials

Since the civilization, the most commonly used solder is lead–tin (Sn–Pb) solder in electronic packaging. However, the toxicity of Pb is a serious concern among the electronic manufacturers. Pb containing solders are in use so far due to their indispensable properties. The effect of Pb contamination on human beings is a serious threat nowadays. Therefore, Pb and its compounds in electronic devices are now being restricted on account of the bans and regulation imposed by European organizations such as restriction of hazardous substances and waste electrical and electronic equipments.[3–5] It is also to be noted that, though Pb is cost effective, available in abundance, and provides no undesirable reaction with the substrate, yet it shows some technical problems like inferior bonding strength which is important for microjoining.[1–6] Therefore, composites solders are now being regarded as an alternative to conventional Sn–Pb solders and developed to resolve these concerns.

1.3. Lead free packaging materials

Large number of Pb-free solder alloys have been developed and studied where Sn is the major fraction. The most popular Pb-free alloy system candidates are narrated in detail in a review

paper in Ref. [7]. In the present state, the advanced solders that have been developed so far are mostly Sn coupled with other elements like Cu, Ag, Zn, Bi, Sb, Ni.[8–14] Among all the binary eutectic Pb-free alloys, Sn–Ag, Sn–Zn, and Sn–Cu are considered to be the potential candidates to replace Sn–Pb. For ternary alloys, the most commonly used system is Sn–Ag–Cu which is proved the most effective due to its lower melting temperature and superior mechanical properties compared to the other combinations.[15] However, there exist some issues of reliability such as the formation of brittle/needle type intermetallics of Ag_3Sn and Cu_6Sn_5 in ternary alloys which damages the mechanical and soldering properties.[5, 16] These Sn-rich alloys are sensitive to tin whisker growth if prolonged for a long time which is known to cause short circuiting in electronic devices. The major driving force for tin whisker growth is known to be the internal residual stresses due to the inherent compounds like Cu_6Sn_5, Cu_3Sn with time.[5]

2. Synthesis of nanocomposites solders

Although enormous amount of research activities are being done all around the world for a better lead-free solder alloy, no solder alloy is able to completely replace the conventional Sn–Pb solder in terms of performance, economy, availability, solderability, simplicity, mechanical strength, and substrate reaction.[4, 17]

In current research scenario, the development of solder alloys reinforced with nanoceramic particles is being paid more attention toward designing a lead-free solder. Such reinforced solder alloys are generally termed as nanocomposite solders. Nanocomposite solders have shown excellent solderability and reliability. Most of the solder matrix composites are reinforced with ceramic particles like ZrO_2, Al_2O_3, TiO_2, SiC, Cu_2O, SnO_2, La_2O_3.[7, 18, 19, 21–25] The reinforcing particles suppress growth of intermetallic compounds (IMC) and provide uniform stress distribution in the matrix.[8, 18, 19] This method of nanotechnology would provide high strength and reliable solders for microelectronic packaging devices.[18, 20]

Various processing routes like melting and casting, powder metallurgy, high-energy ball milling/mechanical alloying, physical vapor deposition, sol–gel, plasma sprayed deposition, chemical methods, and electroplating have been employed to produce solder materials.[9–10, 26–31] Powder metallurgy and mixing methods have been often used to fabricate the lead-free solders reinforced with nanoparticles: Cu, SiC, ZrO_2, Al_2O_3, SnO_2, Y_2O_3, TiB_2, carbon nanotube (CNT), rare earth.[9, 21–22, 25, 32–36] There is also a limit on the amount of nanoreinforcement addition in the solder matrix; otherwise, it will deteriorate the solderability and strength. In literature, there is a limited research on solders produced by electrodeposition with a few studies on Sn–CNT and Sn–Bi–SiC solders.[37, 38] Electrodeposition has been already shown to improve reliability of microelectronic devices in 3D Through Silicon Via interconnection packaging.[39, 40] Recently, Sharma *et al*. developed CeO_2 nanoparticle reinforced Sn–Ag alloy by pulse co-electrodeposition technique and found a great enhancement in strength, microstructure, and successfully manipulated the residual stress to mitigate of dangerous tin whiskers.[41]

3. Pulse co- electrodeposition of Sn based composites

Initially, the pulse electrodeposition was used for decorative and jewellery applications to improve the surface appearance and shine, wear and friction, fretting corrosion resistance.[42] Recently, more attention has been paid to incorporate different nanoparticles to obtain much improved properties. There are various processing parameters in electrodeposition that affect the particle incorporation in composite deposits, such as (1) particle type, size, and shape; (2) bath pH, constituents, additives, and aging; (3) deposition variables, such as particle concentration in bath, current density, agitation, pulsing methods, and temperature.[42–44]

Composite system	Methodology	Improved properties	Reference
Sn-reinforced with CNT	Electrodeposition	Improved shear properties	[37]
Sn-Pb reinforced with Cu and TiO$_2$ nanoparticles	Blending and solidification	Improved microhardness	[47]
Sn-Cu reinforced withAl$_2$O$_3$ nanoparticles	Powder Metallurgy	Improved mechanical performance	[21]
Sn-Cu reinforced with Si$_3$N$_4$	Powder Metallurgy	Improved wetting	[48]
Sn-Bi reinforced with SiC nanoparticles	Electro Deposition	Improved shear properties	[38]
Sn-Bi reinforced with Yttrium oxide nanoparticles	Powder Metallurgy	Improved shear strength	[33]
Sn-Ag reinforced with ZrO$_2$ nanoparticles	Casting and solidification	Improved mechanical performance	[22]
Sn-Ag reinforced with SnO$_2$ nanoparticles	Powder Metallurgy	Improved mechanical performance	[25]
Sn-Ag reinforced with Cu$_6$Sn$_5$, Ni$_3$Sn$_4$, FeSn$_2$ nanoparticles	In situ methods	Creep resistant	[46]
Sn-Ag reinforced with CeO$_2$ nanoparticles	Pulse electroplating	Whisker resistant	[41]
Sn-Ag-Cu reinforced with SiC nanoparticles	Mixing and solidifying	Improved mechanical performance	[22]
Sn-Ag-Cu reinforced with Multiwalled CNT	Powder Metallurgy	Improved mechanical performance	[34]
Sn-Ag-Cu reinforced with TiO$_2$ nanoparticles	Melting route	Improved mechanical performance	[23]
Sn-Ag-Cu reinforced with TiB$_2$ nanoparticles	Powder Metallurgy	Improved mechanical performance	[49]

Table 1. Nanocomposite solder produced by various routes

The different nanocomposite solders produced in literature are shown in Table 1. The composite approach has been developed mainly to improve the strength and reliability of solder joints. Nano-sized reinforcement particles in conventional solder matrices due to their effectiveness in improving the reliability by spreading the stress uniformly in the matrix.[19, 45, 46]

In this chapter, an effort has been made to discuss the strength related concerns by incorporating the reinforcement nanoparticles within the solder matrix using co-electrodeposition process.

3.1. The co-electrodeposition mechanisms

Guglielmi demonstrated the mechanism of codeposition for the first time in 1972. The mechanism provides a fundamental insight of codeposition theory.[50] According to this model the entrapment of particles is based on various adsorption processes. This is a mathematical formulation of the influence of particle content and current density on the particle codeposition rate into the metal matrix excluding particle characteristics and hydrodynamic conditions.

3.1.1. Guglielmi model

The first step involves the loose adsorption of the particles onto the electrode surface. This is a physical adsorption process. However, in the second step, the particles are attracted towards the electrode under electric field and causes a stronger adsorption of particles onto the electrode, as shown in Fig. 2.
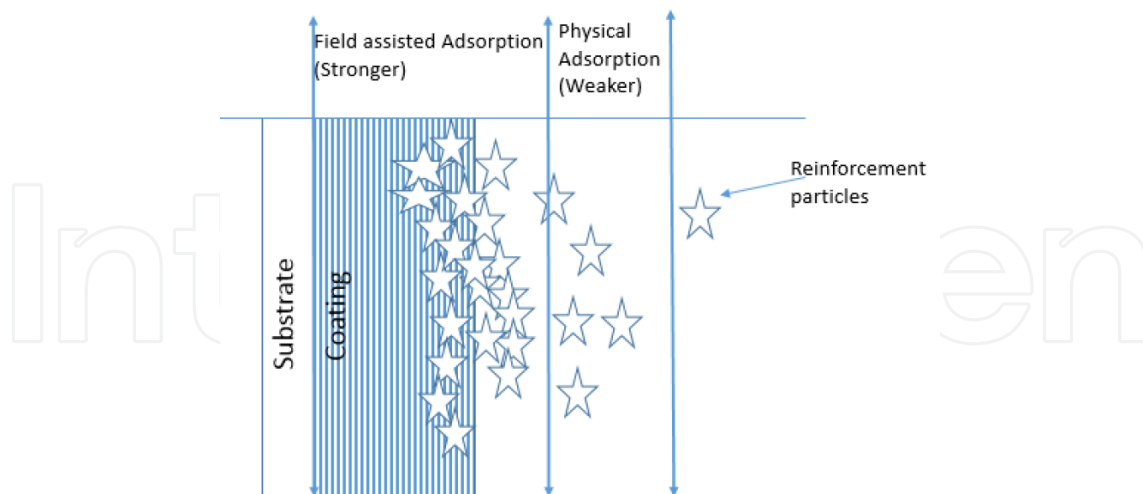

Figure 2. Codeposition mechanism into a metal matrix.[50, 51]

As a result of strong adsorption, the particles are incorporated in the deposit and form a composite layer. This model is the simplest and is adopted for various composite systems, however, it does not account for hydrodynamic effects, particle size, type and shape in detail.

3.1.2. Celis model

Guglielmi model triggered the development of other codeposition theories by Celis, and his co-workers. They predicted the co-deposited particles content in the matrix. According to the Celis model the inert particles approach towards the cathode in a specific sequence: (1) the adsorption of ionic cloud surrounding the particle surface, (2) the force of convection currents in electrolyte also supports the particles incorporation partly, (3) the diffusion kinetics of particles across the electric double layer, (4) the adsorption of the inert particles and the absorption of ionic cloud onto the cathode, and (5) the decrease in adsorbed ionic content and their embedment in the metal coating (Fig. 3).
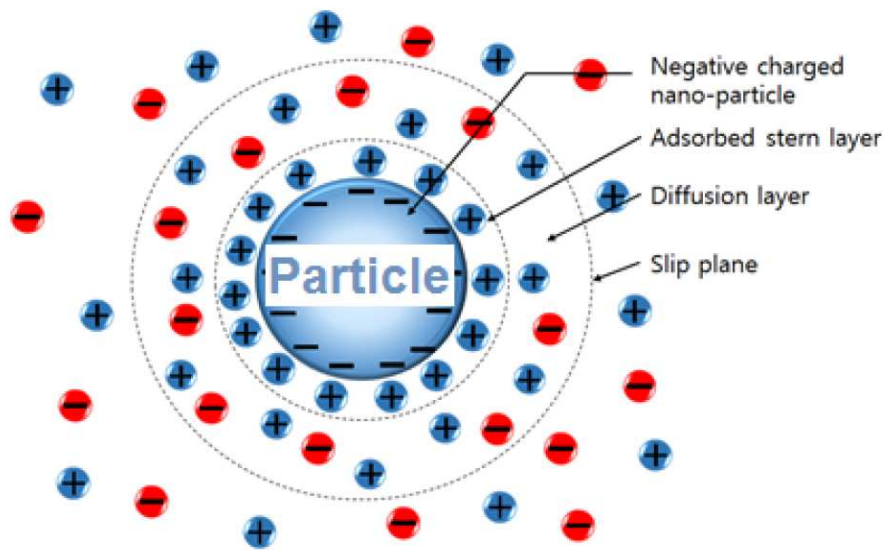

Figure 3. Electric double layer around the ceramic particle showing the ionic concentration and generated potential difference as a function of the distance from the charged particle suspended in electrolyte.[51]

There are various other codeposition models such as for non-Brownian motion of particles in the bath.[52, 53] Although the various developed codeposition models are important tools in the nanocomposite fabrication yet. these models are not perfect for the understanding the influences of process parameters on the codeposition rate in the metal matrix without any experimental data.

4. Factors affecting composite co-electroplating

4.1. Deposition current density

The deposition rate in electrodeposition process plays a vital role in the fabrication of nano-composites. The number density of particles approaching the cathode surface depends on the applied electric potential, and the thickness of the growing metal is determined by the deposition current density. The rate determining step in the co-electrodeposition is when the

strong adsorption of particles on the cathode surface occurs. A strong adsorption of particles is always difficult and is improved by applying current or feeding the corresponding overpotential in the electrolyte. As a consequence, the particle incorporation in the coating increases continuously. However, at a sufficiently high current density, the codeposition rate of the coating decreases drastically. This may be caused by the limited supply of the metal ions toward cathode leading to the decrease in the particle amount.[54] The embedded particle density as a function of current density has been studied for different particle concentrations in the bath in Ref. [55]. It has been reported that at lower current densities (0.5 A dm-2), the embedded particle density is poor due to a weaker adsorption of nanoparticles on the cathode. In few reports, there is a negligible effect of current density on the particle density in the matrix. [42, 56] In other cases, various optimum particle concentrations have been detected in the current density versus particle concentration graph.[51, 57–59] It is also noteworthy point that the current density not only influences the codeposition rate, but the particles present in the electrolyte also modify the current density and hence the morphology of the deposits.[60, 61]

4.2. Zeta potential

The zeta potential is a parameter used to measure surface charge of the particle in the solution, and it indicates the stability of the colloidal suspensions. A higher zeta potential means a lower degree of particle agglomeration in the electrolyte.[62] From electrodeposition point of view, the stability of the nanoparticles is an important factor for a better embedded particle density in the matrix. It has been found that for the nickel matrix composites, when the electrostatic repulsion within the dispersed particles increases, particle agglomeration decreases, and the embedded particle density increases uniformly in the nickel matrix.[62] Uniform dispersion of nanoparticles shows higher attraction toward cathode and thus produces strong adsorption. [63] The zeta potential depends on the various factors, i.e., size of particles (nano or micro), addition of surfactants, electrolyte composition, the particle shape, the bath pH, and the energy of hydration.[64–66] Bund and Thiemig reported that negatively charged particles are highly attracted when there is an excess plus charge on the electrical double layer. This observation works for various composite systems. However, in case of electrophoresis, the negatively charged particles have been successfully deposited into the nickel matrix.[68] This might be correlated to not only the zeta potential but the absolute value of the zeta potential too in addition.

4.3. Bath temperature and pH

Generally, effect of temperature is always to increase the metal grain growth rate. There are different results of the effect of temperature on various codeposition systems. For example, the nickel matrix composite reinforced with Al_2O_3 shows no increment of the volume fraction of particles with temperature.[60, 69] On the contrary, the Ni–Co alloy matrix composite shows a significant increment in the reinforced TiO_2 as a function of temperature up to 45 °C.[70] Similar behavior was shown by the nickel matrix composite reinforced with SiC at 50 °C. [71] Several reports are also available that show a linear decrease in the mass fraction of copper matrix composites as described in Ref. [42].

The bath pH is directly related to the surface charge density of the nanoparticles in the electrolyte. The surface charge density is generally related to the parameter termed as zeta potential. Zeta potential is a measure of the colloidal stability. The nickel matrix reinforced with the Al_2O_3 shows no effect on incorporation rate when bath pH >2. When the bath pH is increased beyond 2, the incorporation rate declines.[60] This result is consistent with those of Verelst and his co-workers.[69] Similarly, Wang et al. observed that nickel matrix reinforced with SiC nanoparticles shows an improvement in particles incorporation rate beyond a bath pH of 5.[72] Park and his co-workers also investigated the effect of pH on nickel matrix composites reinforced with SiO2 and TiO2 nanoparticles. They found that the dispersion of SiO_2 is better at alkaline pH (~ 8) values rather than in acidic pH values. Moreover, for the dispersion of TiO_2, the acidic pH (~3.5) provided better results.[73] The particle content in the composite also behaved in the similar way. They correlated this to the fact that SiO_2 has a negative zeta potential from pH 2–11. It is not clear if these effects are accompanied by a decrease of particle content below pH 2, because the SiC content of the deposits is not investigated. However, in the case of Ni–TiO_2, the TiO_2 particles experience a point of zero charge around pH<5 in the plating bath and particle content increases.

4.4. Bath agitation

Electrolyte agitation is always required to avoid the settling of the particles in electrolyte and to improve their movement toward the cathode. Vaezi and his co-workers observed that increasing the stirring rate up to 120 rpm increases the amount of SiC nanoparticles in the matrix but falls at a higher stirring rate. At a higher stirring rate, the flow is turbulent and not only the metal ions but the SiC particles are washed away on the cathode surface quickly.[74] A similar trend was observed by Baghery *et al*.[75] in the electrodeposition of Ni–TiO_2 nanocomposite. Sen. *et al*.[76] also studied the effect of stirring rate on the microstructure of Ni–CeO_2 nanocomposite and found that fraction of CeO_2 particles increases up to stirring rate of 450 rpm, whereas at higher stirring rates the incorporation of CeO_2 decreases. The coelectrodeposition of ultrafine WC into Ni matrix on a rotating disk electrode with various rotation velocities in the range of 200–1200 rpm under pulse and direct current (DC) conditions is performed in Ref. [77]. This study also verified the fact that the increase in rotation speed has a beneficial effect up to a certain limit. In some studies, the ultrasound waves have been utilized in an attempt to avoid the formation of agglomerated nanoparticles in the plating bath due to the generation of large pressure causing breakdown of agglomerates. Kuo *et al*.[63] reported that the diameter of the agglomerated alumina particles may be refined by ultrasound energy, but the result of particle incorporation is not reasonable.

4.5. Particle concentration and size

Generally, the smaller particles possess higher van der Waals force of attraction or repulsion. It has been reported that the volume fraction of nanoparticles in nickel matrix increases with increasing particle concentration in the electrolyte.[60] The dependence of particle content in the deposit and consequently on the microstructure and surface properties has been studied by many authors.[78–80] In all studies, the volume fraction of the incorporated particles in the coatings with increase in the particle concentration in the plating bath up to an optimum value

and decreases again. The particle shape affects the adsorption of the particles on the cathode by varying the charge on the particle surface and the suspension stability. Regarding the effect of particle size on codeposition, different results have been reported. Such as for Ni–Co/SiC[80], an increase in the fraction of embedded particles was reported for micron-sized SiC compared to nano-SiC, while a negligible influence of particle size is observed for Ni–A1$_2$O$_3$ composite.[69] It can be explained as when two particles come closer, agglomeration occurs as the force of attraction exceeds the force of repulsion between them. The magnitude of the net forces thus produced depends on the bath parameters and the processing conditions of the system.[41]

4.6. Bath types and surfactants

The type of plating baths also affects the co-electrodeposition process. For example, few studies have been conducted on non-aqueous plating baths and organic solvents. In some cases, water has been used partially or completely mixed with organics to avoid hydrogen embrittlement and to obtain a wider processing window.[82] Shrestha *et al*. studied the codeposition of nickel matrix composite using ethyl alcohol base in nickel bath and succeeded to achieve maximum amount of particle incorporation in the Ni matrix. They also found superior wear properties of the composite coatings prepared from ethanol electrolyte compared to those obtained from Watts's type plating bath.[83] Singh *et al*. also investigated the electrodeposition of Ni–TiC composite in acetate bath using *n*-methyl formamide as non-aqueous solvent and found better composite properties.[78]

Surfactants also enhance the rate of particle incorporation in composite electrodeposition. The choice of a given surfactant depends on their charge or polarity. Cationic surfactants are widely used for increasing the particle incorporation rate in the metal matrix. They impart positive charge to the particle surface and prevent the agglomeration in the plating bath.[84] It has been observed that the cationic adsorption is more effective if the particle size is in the nanoscale. [85] According to one report, cationic surfactants can increase the particle content up to 5 times for nickel matrix composites.[57] In another study, the content can be SiC content increased up to 50 volume percent with a fluorocarbon surfactant.[42] Similar study shows that azo-cationic surfactant improved the incorporation rate up to 62.4 volume percent.[86] However, it is always recommended to use surfactants in a minute concentration in the plating bath to avoid carbon compounds in the coating.

4.7. Plating mode

Various electrodeposition modes utilizing pulsing waveforms like pulsed current (PC), pulsed reverse current, and DC have been used to improve the embedded particles density into composite matrix.[87] The application of PC technique in nickel electroplating has been shown to improve mechanical properties, wear and friction, and more uniform distribution of the particles compared to DC technique.[77]

At a given average current density, a decrease in t_{on} time induces a fine crystallite size and increases nucleation rate have been reported.[88] In addition, a longer t_{off} promotes the grain growth and the arrival of more particles near the cathode. Therefore, pulse plating is impor-

tant for co-electrodeposition of nanocomposites. For example, in Ni–SiC deposition, the application of PC results in the production of composite coatings with higher fraction of particles, and better properties than obtained with DC plating.[89] In another technique of pulse reversing, the pulsed-reverse current (PRC) technique, a stripping time is also applied to the pulse waveform, during which the surface projections are dissolved and produce more smooth deposit.[90] The Zn matrix nanocomposite reinforced with the TiO_2 nanoparticles using the PRC technique has been shown to improve the embedded TiO_2 particle density in the matrix.[91]

5. Properties of electro-composites

The original driving force for the preparation of nanocomposite solders was to improve the mechanical, thermal, and corrosion resistance of the solder alloys to utilize them in high temperature, harsh service conditions. The properties that are improved compared to the conventional Pb–Sn solder are summarized as follows:

5.1. Density

The density of a microelectronic device is very important for developing portable electronic goods. There are various reports which show a reduction in density values in nanoparticle reinforced composites. [18, 21, 41] Zhong *et al.* reported that the Al_2O_3 reinforced Sn matrix composite is lighter compared to monolithic matrix, while Babaghorbani *et al.* found that SnO_2 reinforced Sn–3.5Ag matrix did not show any change in density. This may be due to the fact that the matrix and reinforcement have the similar values of density.[21, 25]

5.2. Electrical conductivity

The electrical conductivity of a metal matrix is a function of various factors like fraction of secondary reinforcement phase, fraction of pores, size and shape, and the metal matrix. [92, 93] Nai *et al.* observed that the dispersion of CNT in the Sn based matrix does not decrease the conductivity of the matrix.[94] They correlated this fact with the low volume fraction of pores as well as reinforcement in the solder matrix. This type of behavior has been also observed by Sharma *et al.* for Sn–CeO_2 and Sn–Ag/CeO_2 nanocomposites.[41, 95] Babaghorbani *et al.* studied the electrical properties of nanocomposite solders in detail and reported that nano-sized reinforcements is advantageous in not degrading the electrical conductivity of the device, while micron sized particles can degrade the conductivity values .[96] This further confirms the unique properties of nanocomposite solders for electromigration property microelectronic packaging devices. Recently, it has been demonstrated the nanoparticles reinforced solders can be promising candidates for preventing electromigration failure in electronic packaging devices.[97]

5.3. Melting point

There is wide distribution of results on the thermal behavior of solders.[18, 22, 23, 41, 95, 98, 99] The melting points of the nanocomposite solders generally decreases with an increase in

the fraction of the nanoparticles in the matrix. Liu *et al.* reported that Sn–Ag–Cu/nano-SiC showed a reduction in melting point compared to monolithic Sn-Ag-Cu alloy. They correlated this observation to the increase in the interface surface instabilities after the addition of SiC nanoparticles. Similarly Kumar *et al.* also observed a slight depression in the melting point in CNT reinforced solder matrix. However, Nai *et al.* did not observe any significant drop in the melting point.[98, 99] Shen *et al.* while working on ZrO_2 reinforced solder the reinforcement particles, i.e., ZrO_2 nanoparticles behave as a nucleating agents and promote the nucleation of the matrix during solidification. Therefore, more nucleating sites results in grain refinement and a drop in melting point could be noticed. [22] Recently, Sharma *et al.* have found a decreased melting point of $Sn–CeO_2$ and $Sn–Ag/CeO_2$ nanocomposites and explained this behavior to the refinement of matrix grains after addition of nanoparticles.[41, 95]

5.4. Solderability

During soldering, in order to form a proper metallurgical bond between two materials, wetting must take place. There is an increase in solder wetting onto the metallic substrates after addition of the nanoparticles in the solder matrix. The high surface energy nanoparticles decrease the surface tension and wetting angle and results in the improved solderability. However, too much addition of nanoparticles in the solder may degrade the wetting properties due to the increase in agglomeration of nanoparticles in the molten alloy.[35] Additions of metallic additives also have been shown the similar behavior where the wetting decreases due to the increase in surface tension and oxidation of the reinforcing phase.[100] Recently, Sharma *et al.* investigated the solderability of Sn–Ag–Cu alloy reinforced with La_2O_3 nanoparticles in terms of spreading ratio and wetting balance measurements. They also found that the wetting is improved up to an optimum amount of La_2O_3 nanoparticles and decreases beyond that due to the increase in surface tension and melt viscosity.[19]

5.5. Microhardness

The nanocomposite solders developed have better microhardness as required for the electronics packaging industry. It has been reported that the addition of ceramic oxides or inert nanoparticles [19, 21–23, 34–37, 41, 95] can improve the mechanical performance, tensile strength, elongation and creep properties of nanocomposite solders. Moreover, the additions of nanoparticles refine the grains of the matrix as well as are adsorbed on the intermetallic to refine them. In general, there is an enhancement at the cost of ductility of the solder which is undesirable. Recently, Sharma *et al.* have produced Sn–Ag–Cu/La_2O_3 solder with an improved tensile strength as well as ductility. They explained this due to the mechanism of slip mode transition of dislocation when interacting with the La_2O_3 nanoparticles in the solder matrix.[19]

5.6. Wear and friction behavior

In various microelectronic devices and assemblies, Sn based connectors such as press fit plugs and sockets, separable interconnects in consumer electronic appliances are gaining popularity

nowadays. Gold and silver based contacts provide optimum wear resistance in sliding contacts but they are not economical. Therefore, the sliding wear and tear are important for Sn based solders may limit their applications. [101] Tin based contacts are generally susceptible to fretting wear which is a prime concern in automobile applications.[102, 103] Sn based connectors are very ductile and more sensitive to fretting wear. Hammam *et al*. investigated the wear and frictional properties of various Sn coating prepared hot dipping, electroplating, and reflow processes. They suggested that the different processing routes for Sn deposition produce different thickness of the Sn coatings and hence the intermetallic compounds on a metallic substrates. [104] In case of nanocomposite solders, Jun *et al*. reported that tin bronze reinforced with carbon fibers improves the resistance against the fretting wear appreciably.[105] Sharma *et al*. have recently found a significant enhancement on the wear resistance of Sn and Sn–Ag matrices reinforced with CeO_2 nanoparticles.[41, 95]

5.7. Electrochemical corrosion

Electrochemical behavior of Sn based coatings is important in microelectronic packaging devices. The corrosion of Sn base coatings may deteriorate the microstructural properties of the solder joints and ultimately lead to entire failure of the device. For example, in marine applications, the chlorides ions from the sea can dissolve the solder joints by forming soluble compounds.[106] There are various forms of corrosion such as pitting, crevice, and/or galvanic corrosion of solder and substrate material. Therefore the corrosion of electronic devices may impose a serious threat among microelectronics community to produce corrosion resistant solder materials. However, there is a scarcity of information of electrochemical corrosion of the solder joints.[107, 108] It has been shown that presence of Bi in Sn–Bi solder can increase the dissolution of Sn slightly in sulfuric acid solution and vigorously in nitric acid solution compared to that of pure tin.[108, 109]. It has been noticed that lead-free solders are highly corrosion resistant towards chloride ion attack compared to conventional Sn-Pb solder. [110] Recently, Sharma *et al.* proposed that use of nanoparticles is better idea to avoid the localized dissolution of Sn coatings. If the nanoparticles are added in an optimum concentration in the solder matrix, the corrosion resistance of the solder matrix can improve significantly by setting up of homogeneous corrosion instead of preferential and sudden damage. The high surface energy nanoparticles in the solder matrix reduce the corrosion potential, corrosion current, and diffusion capacitance, thus increasing passivity of the solder coating.[111]

5.8. Whisker growth mitigation

Tin whisker growth in the Sn based coatings is a serious issue in microelectronic packaging devices. The driving force of these whisker growth is the generation of compressive stresses in the coatings on storage for a long time. When plated on a metallic substrate like copper, the Cu-Sn interdiffusion across the interface may give rise to the formation of Cu6Sn5, Cu3Sn etc., IMCs and grow with time causing a volume expansion of the interface. The expansion of the interface causes the setup of compressive stress in the coatings. Recently, it has been identified by various researchers that addition of nanoparticles may suppress the growth of IMCs and restrict the formation of whiskers in the matrix. Generally, the ceramic nanoparticles are very

smaller compared to size of IMCs. Therefore they can easily attach with the growing IMC in the molten metal and restrict the growth of IMCs during solidification as predicted by the surface adsorption theory.[18, 19, 22, 41]

6. Summary

Addition of nanoparticles in the solder matrix improves the microstructural properties due to the refinement in the grain size as well as the thickness of the IMC (Cu_6Sn_5, Ag_3Sn) in the solder matrix. Wettability is improved due to the decrease in interfacial energy in presence of high surface energy nanoparticles. The higher hardness of nanosolder composites as compared to monolithic alloys can be attributed not only to the grain size and dispersion strengthening effect, but also to the refinement of the IMCs such as Cu_6Sn_5, Ag_3Sn by ceramic nanoparticles. The melting point of the solders is minimum form an optimum reinforcement amount in the matrix, which indicates its possibility to use without any change in the existing soldering procedures. There is a rise in the resistivity of the composite matrix compared to the monolithic materials. However, the resistivity of the composites falls within the usable limits as reported for other Sn and Sn–Ag-based composites, used for electrical contact applications. The nanoscale reinforcements are added in minute concentrations and do not degrade the resistivity much if their distribution is uniform and electromigration phenomena in the composite solders. The addition of reinforcement in the Sn matrix also improves the wear resistance, which ultimately increases the coating life for application. The wear resistance of the composite coatings is better than that of the monolithic materials, and it is associated with an enhancement in the microhardness of the composite. It is also observed that composite solders possess the better corrosion resistance as compared to monolithic ones. The presence of fine Ag_3Sn compounds in composite increases the passivation of the matrix which acts as a noble barrier in addition to ceramic reinforcements against corrosion propagation. It is also observed that an incorporation of CeO_2 nanoparticles in the composite matrix reduces the compressive stresses developed in the coatings. The residual stresses of monolithic materials are negative, i.e., compressive in nature. A decline in residual stress indicates that the driving force for whisker growth can be minimized by choosing an optimum concentration of ceria, and thus, the coating life can be improved.

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