Properties and Microstructures of Sn-Ag-Cu-X Lead-Free Solder Joints in Electronic Packaging

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SnAgCu solder alloys were considered as one of the most popular lead-free solders because of its good reliability and mechanical properties. However, there are also many problems that need to be solved for the SnAgCu solders, such as high melting point and poor wettability. In order to overcome these shortcomings, and further enhance the properties of SnAgCu solders, many researchers choose to add a series of alloying elements (In, Ti, Fe, Zn, Bi, Ni, Sb, Ga, Al, and rare earth) and nanoparticles to the SnAgCu solders. In this paper, the work of SnAgCu lead-free solders containing alloying elements and nanoparticles was reviewed, and the effects of alloying elements and nanoparticles on the melting temperature, wettability, mechanical properties, hardness properties, microstructures, intermetallic compounds, and whiskers were discussed.

1. Introduction

Tin-lead (SnPb) solders have been widely used in electronic packaging. However, due to the increasing environmental and human health concerns over the toxicity of lead, governments of many countries have established laws to prohibit the use of Pb from electronic application. Therefore, investigation of lead-free solder has become an important research topic in the field of electronic packaging.

In recent years, to replace the conventional Sn-Pb solder alloys, several types of Sn-based lead-free solders such as SnAg, SnCu, SnZn, SnBi, SnIn, and SnAgCu have been developed. Among series of lead-free solders, SnAgCu has been proposed as the most promising lead-free solder for replacement of traditional tin-lead solder owing to its good reliability, excellent creep resistance, and thermal fatigue characteristics [1–3]. However, there are still many unresolved issues. For example, SnAgCu solder has a high melting point, poor wettability, coarser microstructures, and so forth. In order to further enhance the properties of lead-free solder, two methods are taken. The first method is to add alloying elements to the SnAgCu solder, such as Ga element which can improve the wettability. And the addition of rare earth elements can enhance the comprehensive performance. Another method is to add micro- or nanoparticles. It mainly comprises of metal particles, compound particles, ceramic particles, the carbon nanotubes, and the polymer particles. With the changes of added particles in its type and size, the properties of SnAgCu solder are different. Not only can adding metal particles change the microstructure of the solder, but also there will be a new phase in the solder matrix, while adding compound particles or ceramic particles cannot form a new phase.

In this review, we summarize the development of SnAgCu solder alloys and analyze the effects of adding the fourth elements on the melting temperature, wettability, mechanical properties, hardness properties, microstructures, and intermetallic compounds (IMC). At the same time, we will also discuss the Sn whisker, and some suggestions have been put forward which maybe solve this issue.

2. Melting Temperature

Melting temperature is an important factor for the development of new lead-free solders. A promising solder alloy should have a low melting temperature and a narrow melting range [4]. As we all know, the eutectic SnPb has a melting point of 183°C, while the SnAgCu solder melting point is
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217°C, 34°C higher than that of the eutectic SnPb. Such high melting temperature will increase the reflowing temperature and lead to thermal damage of the polymer substrate [5]. Meanwhile, it also enhances the dissolution rate and solubility of Cu in the molten solder, thus improving the rate of formation of IMCs. This is the reason that the IMCs layer of SnAgCu thicker than Sn-Pb. Hence, some researchers expect to add the fourth elements to decrease the melting temperature of SnAgCu solders.

Trace amount of indium (In) added to the SnAgCu lead-free solder can change the melting behavior obviously. It was shown in the literature [6] that adding 3.0 wt.% of In to the solidus and liquidus temperatures decreased 21.7 and 11.5°C, respectively, as compared with 219.4 and 241.7°C for the Sn0.3Ag0.7Cu solder. But the In is very expensive, the addition of In can increase the cost of lead-free solders. Chuang et al. [7] proposed that the effect of Ti on the melting point of Sn3.5Ag0.5Cu (SAC) solder alloy. With the addition of Ti element, the melting temperatures change slightly. The liquidus temperatures are 220.95, 220.86, and 219.47°C for the SAC-Ti solder alloys with Ti contents of 0.25, 0.5, and 1.0 wt.%, respectively. Moreover, the melting range is decreased from 4.66 to 2.88°C. Generally speaking, the narrow melting range of the solder means excellent thermal properties. It is mainly attributed to the narrow melting range explaining that solders exist as part liquid for a very short time during solidification and can form reliable joints during the reflow process. Figure 1 represents the differential scanning calorimetry (DSC) curve of SnAgCu bearing different manganese (Mn) and titanium (Ti). It is indicated that Sn3.0Ag0.5Cu solder has only one endothermic peak, yet it has two peaks for the Sn1.0Ag0.5Cu (SAC) solder. Meanwhile, worthy of notice is that the degree of undercooling for eutectic Sn was significantly affected by the addition of trace alloying elements (Mn and Ti) into SAC solder alloy. The SAC-0.5Ti sample showed an extremely suppressed undercooling of only 4°C [8]. The addition of Fe into SnAgCu solder did not change much of the melting temperature [9]. The DSC results demonstrated a single peak of Sn3.6Ag0.9Cu solder. However, there are two obvious endothermic peaks (220°C and 235°C) that appear for the SnAgCu-0.2Fe solder alloy. This shows that melting occurred over a range of temperatures. It may be ascribed to the peaks overlapped; the first peak may indicate that the solder was partially fused. The addition of Fe most likely resulted in shifting of the melting point from the eutectic point to near the eutectic point, and the melting point of the solder is in the range of 222.87 to 230°C, which is higher than the SnAgCu solder melting point (217°C). When adding 0.6 wt.% Fe, only a single endothermic peak at 221.35°C was found, showing that it has a eutectic composition. El-Daly et al. [10] studied the DSC profiles of Sn1.0Ag0.3Cu solder. The DSC revealed two endothermic peaks between 220.1°C and 227.2°C. The two peaks indicated two steps in the melting process of SnAgCu solder. Based on the ternary SnAgCu phase diagram [11], the two steps were owed to the melting of ternary eutectic Sn + Ag + Cu phase and primary Sn phase. However, for SnAgCu solder containing Zn, only one endothermic peak appears in the DSC curve, and the melting temperatures were 222.8 and 220.8°C for the SAC-2.0Zn and SAC-3.0Zn, respectively. The addition of Bi decreases the melting point of Sn3.8Ag0.7Cu (SAC) solder [12]. It is found that the solidus temperatures of SAC-2.0Bi and SAC-4.0Bi were 213.08 and 206.40°C, respectively. However, when adding too much Bi, solder joint peeling will appear. DSC scan of low-Ag Sn0.5Ag0.7Cu (SAC) solder bearing Ni and the results showed that the addition of Ni had little effect on the melting temperature [13]. The peak temperatures of SAC, SAC-0.05Ni, and SAC-0.1Ni solders were 221.1, 222.9, and 223.4°C. Moreover, the values of melting range were 12.6, 11.9, and 12.8°C for the SAC, SAC-0.05Ni, and SAC-0.1Ni, respectively. It is very close to 11.5°C for the SnPb solder [14]. It was also reported in the literature [15].
It is well known that the addition of a small amount of RE elements in the metals can greatly enhance their properties [16]. However, it does not significantly alter the melting point. The DSC curves of Sn3.9Ag0.7Cu and Sn3.9Ag0.7Cu0.5RE solders were studied by Dudek and Chawla [17]; all solders show a single endothermic peak between 217°C and 219°C, showing the onset of melting for the SnAgCu solder. It is revealed that the addition of RE elements into Sn3.9Ag0.7Cu solder did not affect the melting characteristics. Moreover, it is also found that the addition of La exhibits minimal impact, while the addition of Ce and Y increases the onset temperature by approximately 2°C.

Recently, many researchers are also investigating the addition of nanoparticles into SnAgCu solders for providing better properties and microstructures. Xiang et al. [18] reported that the addition of Mn nanoparticles did not change significantly the melting temperature of Sn3.8Ag0.7Cu (SAC) solder alloy. The results showed that the onset melting temperatures of SAC-0.12Mn, SAC-0.18Mn, and SAC-0.47Mn composite solders were 217°C, 217.3°C and 217.5°C, respectively. Small amounts of SiC nanoparticles added to the Sn3.8Ag0.7Cu solder do not change much of the melting temperature. The well-defined endothermic peak shifts from 219.9°C to 218.9°C with the addition of 0.2 wt.% SiC [19]. Al2O3 nanoparticles have been added to the Sn3.5Ag0.5Cu solder alloy. During the heating process of the DSC analysis, the Sn3.5Ag0.5Cu solder exhibited a eutectic alloy with a melting point of 221.2°C, which has been increased slightly with the increase of the amount of nano-Al2O3 particles [20]. To identify the effects of different joint fabrication methods and the amount of TiO2 addition on the Sn3.0Ag0.5Cu (SAC) solder, DSC analysis was used. DSC analysis was used. The results showed that the melting point of SAC solder and the solder bearing 1 wt.% TiO2 nanoparticles ranged from 217°C to 217.64°C, with only a eutectic peak [21]. A similar phenomenon in other studies on the SAC composite solders was observed [22]. DSC analysis was carried out to understand the influence of ZnO nanoparticles addition to the Sn3.5Ag0.5Cu (SAC) solder on its melting temperature. From DSC results, it is indicated that the melting temperatures of plain SAC solder and SAC-0.5ZnO composite solder were about 221.18°C and 222.16°C, respectively, with only a eutectic peak [23]. The melting behavior of Sn3.0Ag0.5Cu solder reinforced with nanosized ZrO2 particles were studied by Gain and Chan [24]. The melting temperature was increased by less than 1°C when the amount of ZrO2 nanoparticles was 1 wt.%.

In summary, adding alloying elements and nanoparticle on the melting temperature has little effect. However, the new lead-free wave soldering and reflow oven that can make soldering below 250°C have been developed. Therefore, the above elements added to the SnAgCu solder can meet the requirement of the present soldering process and there is no need to make adjustment in the current reflow process. Besides, in future research, we may only need to ensure that the addition of elements can slightly influence the melting of SnAgCu solders.

3. Wettability

Wettability of solder can be defined as the ability of the molten solder to spread over on a substrate during the reflow process [25]. For the reflow process, the heating temperature at a certain condition, only a good wettability to the surface of the base material to form good wet spreading joints, namely which is to form solder joints. And the solder joints bear the entire electronic device the role of mechanical support and electrical connections; thus the solder joints directly determine the performance of electronic products. For traditional SnPb solder, due to the existence of Pb, the solder alloy owns better wettability. But for lead-free solders, the wettability may be dropped obviously due to the replacement of Pb. In order to improve the wettability of solder, the addition of alloying element is a hot research investigator. Generally, there are many methods to measure the wettability, but the wetting balance method and spreading method are considered the relatively versatile methods.

The addition of a small amount of In into SnAgCu solder was investigated by Moser et al. [26]. The wetting angle was decreased from 37° to 22° with the addition of 75 at.% of In. The wetting balance tests were conducted in air to show the wettability of Sn3.6Ag0.9Cu-xFe by Fallahi et al. [9]. It is found that the addition of 0.2 wt.% Fe increased the wetting force and reduced the wetting angle. However, the Fe was added to more than 0.6 wt.%, which resulted in a lower wettability. Zn element was incorporated into Sn3.8Ag0.7Cu solders by Zhang et al. [27]. The wettability of SnAgCu solders can be improved with the addition of Zn. When the content of Zn was up to 0.8%, Sn3.8Ag0.7Cu solder got the smallest angle. However, with the addition of 3%Zn, wetting angle was the largest. This can be attributed to the Zn is easily oxidized; the formation of oxide residue during soldering may worsen the wettability of SnAgCu solder. The addition of trace amount of Bi into SnAgCu solders can change the wetting behavior. Rizvi et al. [28] demonstrated by experiment that the effect of 1.0 wt.% Bi on the wetting behavior of Sn2.8Ag0.5Cu solder compared with Sn-37Pb alloy. It is indicated that the wetting behavior of Sn2.8Ag0.5Cu1.0Bi solder is less than that of the tradition SnPb solder for all flux types and solder bath temperatures. However, due to a high soldering temperature promote the diffusion process, thus reducing the wetting angle and improving of the wetting behavior. Moreover, the wetting behavior of Sn2.8Ag0.5Cu1.0Bi solder on Ni substrate was lower than that on Cu substrate. Researchers attribute to Ni atoms diffused into the solder through the intermetallic compounds (IMCs) much slower than did the Cu atoms. Moser et al. [29] have also investigated the effect of Bi on the SnAgCu solder under Ar-H2 protective atmosphere and found that the Ar-H2 atmosphere can better decrease the surface tension and improve the wettability. It is due to inert gas may protect the solder decreases the chance of liquid solder in contact with oxygen. Sn0.5Ag0.7Cu solder bearing Ga element was researched by Luo et al. [30]. The results show that the wetting time and wetting forces vary as a function of Ga when the Ga was added to the Sn0.5Ag0.7Cu solder up to 0.5%, resulting in a decrease in the values of mean wetting
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50
40
30
20
10
0
Wetting angle (∘)
Wetting force (mN)

Figure 2: Wetting angle and force of Sn3.5Ag0.7Cu-xRE [35].

Rare earth (RE) elements have been called the “vitamin” of metals, which means that a small amount of RE elements can obviously enhance the properties of metals [33]. In a series of performance of lead-free solder, the wettability of adding rare earth elements is the most obvious improvement. Yu et al. [34] has investigated the effect of RE elements (Ce and La) on the SnAgCu solder, where the soldering temperature was 250°C and RMA flux was used. It is found that the wetting angle of Sn2.5Ag0.7Cu is higher than Sn3.5Ag0.5Cu because of the higher melting point of Sn2.5Ag0.7Cu. And when RE is less than 0.1 wt.%, the wetting angle of Sn3.5Ag0.7Cu decreased with RE increases. Whereas the content is higher than 0.1 wt.%, the wetting angle will increase. Similar result was found by Law et al. [35]. Figure 2 shows that the wetting angle was decreased with the addition of RE elements. However, an excessive amount of RE element addition, the wetting angle will increase. The heavy rare earth element Y can improve the wettability of Sn3.8Ag0.7Cu solder, and the spreading areas increased and the contact angles decreased as the content of Y increased. When adding 0.15 wt.% Y, the spreading areas and the wetting angles reached the peak, but when Y exceeded 0.15 wt.%, the wettability of the composite solder decreased obviously [36]. Trace rare earth element Er was incorporated into Sn3.8Ag0.7Cu solder which can change the wetting behavior [37]. When the content of Er is less than 0.25 wt.%, the spreading areas will increase with the addition of Er element. However, as the content of Er element continues to increase up to 1.0 wt.%, the spreading areas will decrease. The wetting behavior of SnAgCu solder is improved with the addition of Pr element. Gao et al. [38, 39] found that trace amount of Pr and Nd addition could remarkably improve the wetting behavior of Sn3.8Ag0.7Cu solder, where the optimal wetting behavior was achieved as the RE content is about 0.05 wt.% because of the lower surface tension caused by RE elements. The addition of Yb into SnAgCu was investigated by Zhang et al. [40]. As a result, the contact angles decreased as the content of Yb increased. When the addition of Yb was 0.05%, the contact angle can decrease to the peak value, but as the Yb content exceeded 0.05%, the contact angles increased obviously. Due to the higher affinity Sn of rare earths in the solder alloys. Firstly, the Sn tend to react with Yb to form Sn-Yb particles, and the reaction is easy to go on when the Sn-Yb particles adhere to the substrate to nucleate, particularly for the nucleation of particles at the triple point in Figure 3; when the particles exist at the triple point, the balance among the gas, solid, and liquid will be broken. Effects of addition of rare earth element Ce, atmosphere, and temperature on the wetting behavior of SnAgCu-xCe solders were studied by Wang et al. [41]. The results indicate that with the addition of Ce, the wetting behavior of Sn3.8Ag0.7Cu solder is improved obviously. With the addition of 0.03% to 0.05%, the wetting time is about 0.7 s at 250°C, which is very close to the Sn-Pb solder. Moreover, in N2 atmosphere, the wetting behavior of SnAgCu solder is extremely improved. Due to the oxidation of molten solder and substrate is inhibited in N2 atmosphere. Furthermore, Zhao et al. [42] also found that the spreading area was increased with the increasing of the content of Ce. When the Ce addition is 0.1%, the Sn3.0Ag2.8Cu-Ce has the maximum spreading area of 242.80 mm². However, as the content of Ce is over 0.1%, the spreading areas will decrease. In a word, the addition of rare earth elements can change the wetting behavior; there are two reasons leading to the result: in one aspect, rare earth is a surface-active element that can reduce the surface tension of liquid solder. In the other aspect, rare earth is liable to oxidation; thus the formation of excessive amount of oxide residue during soldering may deteriorate the wettability of the solder, thereby affecting the spreading properties [43].

Currently, with the advancement of nanotechnology through the years, more and more researchers try to add nanoparticles to improve the comprehensive performance of Sn-Ag-Cu lead-free solders.

The addition of Mn nanoparticles into SnAgCu solder worsens the wetting behavior. With the addition of 0.47 wt.% of Mn nanoparticles, the wetting angle of SnAgCu solder was increased. The melting point of the nanoparticles decreased, and the spreading areas will decrease with the addition of Mn element. However, as the content of Mn element continues to increase up to 1.0 wt.%, the spreading areas will increase. The wetting behavior of SnAgCu solder is improved with the addition of Mg element. Gao et al. [38, 39] found that trace amount of Mg addition could remarkably improve the wetting behavior of Sn3.8Ag0.7Cu solder, where the optimal wetting behavior was achieved as the Mg content is about 0.05 wt.% because of the lower surface tension caused by Mg elements. The addition of Mg into SnAgCu was investigated by Zhang et al. [40]. As a result, the contact angles decreased as the content of Mg increased. When the addition of Mg was 0.05%, the contact angle can decrease to the peak value, but as the Mg content exceeded 0.05%, the contact angles increased obviously. Due to the higher affinity Sn of Mg in the solder alloys. Firstly, the Sn tend to react with Mg to form Sn-Mg particles, and the reaction is easy to go on when the Sn-Mg particles adhere to the substrate to nucleate, particularly for the nucleation of particles at the triple point in Figure 3; when the particles exist at the triple point, the balance among the gas, solid, and liquid will be broken. Effects of addition of rare earth element Mg, atmosphere, and temperature on the wetting behavior of SnAgCu-xMg solders were studied by Wang et al. [41]. The results indicate that with the addition of Mg, the wetting behavior of Sn3.8Ag0.7Cu solder is improved obviously. With the addition of 0.03% to 0.05%, the wetting time is about 0.7 s at 250°C, which is very close to the Sn-Pb solder. Moreover, in N2 atmosphere, the wetting behavior of SnAgCu solder is extremely improved. Due to the oxidation of molten solder and substrate is inhibited in N2 atmosphere. Furthermore, Zhao et al. [42] also found that the spreading area was increased with the increasing of the content of Mg. When the Mg addition is 0.1%, the Sn3.0Ag2.8Cu-Mg has the maximum spreading area of 242.80 mm². However, as the content of Mg is over 0.1%, the spreading areas will decrease. In a word, the addition of rare earth elements can change the wetting behavior; there are two reasons leading to the result: in one aspect, rare earth is a surface-active element that can reduce the surface tension of liquid solder. In the other aspect, rare earth is liable to oxidation; thus the formation of excessive amount of oxide residue during soldering may deteriorate the wettability of the solder, thereby affecting the spreading properties [43].

Figure 3: Schematic of Yb effect on wetting angle [40].
increased from 10.71° to 25.6° and the spreading rate of the solder was also reduced from 88.9% to 77.4%. It is caused by the increased viscosity for the addition of nanoparticles during soldering [18]. Tay et al. [44] found that the addition of Ni nanoparticles alters the wettability of Sn3.8Ag0.7Cu solder alloy. Results showed that the addition of Ni nanoparticles into SnAgCu solder leads to the wetting angle increasing from 19.3° to 29.9°. For Sn3.8Ag0.7Cu solder bearing Co nanoparticles, the effect of Co nanoparticles on wettability was found by Yoon et al. [45]. With the Co nanoparticles addition, concentration increasing, the wetting angle increased, and the spreading rate decreased. Similar effects were reported by Haseeb et al. [46, 47]. Al2O3 nanoparticles can significantly change the wetting behavior of Sn3.5Ag0.5Cu solder. The wetting angle of SnAgCu solder was decreased with the addition of Al2O3 nanoparticles; a minimum angle of 28.9° can be found with 0.5% nano-Al2O3 particles addition [20]. Li et al. [48] produced Sn3.0Ag0.5Cu solder by mechanically mixing TiO2 nanoparticles and pointed out that trace amount of TiO2 nanoparticles can effectively affect the wetting behavior of Sn3.0Ag0.5Cu solder. It is clear that the wetting time can be decreased by 53.7% and the wetting force can be increased by 37.6% with the addition of 0.25%TiO2 particles. Liu et al. [49] studied the addition of graphene nanosheets (GNSs) into Sn3.0Ag0.5Cu solder using the powder metallurgy. The results show in SAC-xGNS solder that, with GNSs addition content increasing, the contact angle was decreased. When the content of GNSs was 0.1%, the contact angle can be decreased by 15.5%. Nai et al. [50] investigated the effect of nonreactive and noncoarsening foreign enhancements on the wettability of SnAgCu solder. It is found that the wetting angles were reduced by 15.7% and 19.8% with the addition of 0.04% and 0.07% of carbon nanotubes (CNTs). Han et al. [51] also found that the addition of trace amount of Ni-coated carbon nanotubes (Ni-CNTs) did significantly improve the wettability of SnAgCu solder.

In conclusion, the addition of nanoparticles did not significantly affect the wettability of SnAgCu solders and may even deteriorate the wetting angles. However, according to Kripesh et al. [52], the wetting quality is considered as “very good” when the value is 0° < θ < 20°. For the value 20° < θ < 40°, it is considered as “good and acceptable.” The wetting behavior is “bad” when θ > 40°. Therefore, with the addition of nanoparticles, the wetting angle of SnAgCu composite solder is in the acceptable range. Moreover, different researchers obtained different result. It may be attributed to solder composition, soldering temperature, processing atmosphere, flux type, substrate metallurgy, and so on.

4. Mechanical Properties

The mechanical property is an important index to evaluate solder properties. It plays a vital role in the reliability of solder joints.

The effect of In element on the tensile strength of low-Ag Sn0.3Ag0.7Cu solder was studied by Kanlayasiri et al. [6]. With the 3.0 wt.% In added, the tensile strength of SnAgCu increases approximately by 79%. The addition of Ti can remarkably increase the mechanical properties of SnAgCu solder. However, with the addition of Ti being over 1.0 wt.%, the mechanical properties of Sn3.5Ag0.5Cu were decreased due to the appearance of coarse Ti3Sn2 in the eutectic colonies [7]. Fe element can increase the shear strength of SnAgCu solder. Fallahi et al. [9] found that the shear strength of Sn3.6Ag0.9Cu solder was 29 Mpa; with the addition of Fe being 0.2 wt.% and 0.6 wt.%, the shear strength was raised up to 40 Mpa and 53 Mpa. When 0.8 wt.% of Zn was added to the Sn3.8Ag0.7Cu solder, the tensile force of SnAgCu solder joint can be improved by 10%. With further increase of Zn content, the tensile force decreases evidently. It is attributed to the fact that Zn has stronger affinity for oxygen, and an excessive amount of Zn addition will form superfluous Zn-oxides. Therefore, the mechanical properties of SnAgCu-xZn solder joints were decreased [27]. The similar strengthening effect of Zn on the tensile strength of SnAgCu was also found by Song et al. [53]. Bi element can also improve the mechanical properties of SnAgCu solder. When the addition of Bi was 2.0 wt.%, an improvement of 47% of the ultimate tensile strength (UTS) was achieved. When the addition of Bi was 4.0 wt.%, the UTS was almost 2 times that of SnAgCu solder [12]. Ni can enhance the mechanical properties of Sn2.0Ag0.5Cu solder, which was studied by El-Daly and El-Taher [54]. It is found that the ultimate tensile strength (UTS) and yield strength (YS) both increased with the increasing amount of Ni. The tensile strength of SnAgCu solder joint bearing Sb was investigated by Li et al. [55], as shown in Table 1. Results showed that the addition of Sb can obviously improve the tensile strength of SnAgCu solder alloys and joints during the ageing time. The reason could be attributed to solid solution hardening and particle hardening. Luo et al. [30] reported that the shear strength of Sn0.5Ag0.7Cu solder joint can be improved with the addition of Ga. When the addition of Ga was up to 0.5 wt.%, shear strength gives a 17.9% increase.

Adding an appropriate amount of rare earth elements mainly containing Ce and La elements can remarkably increase the mechanical properties of SnAgCu solder [34], as shown in Figure 4. Moreover, with the increasing of Ag, the tensile strength is also improved. The strength of Sn3.8Ag0.7Cu solder joint was improved with Y addition. However, when the Y content exceeds 0.15 wt.%, the strength of joint has a dramatical decrease [36]. With the addition of Er, the shear strength of Sn3.8Ag0.7Cu solder was improved significantly. When the Er addition is up to 0.1 wt.%, given a 18% increase compared with SnAgCu solder [37]. The mechanical properties of Sn3.8Ag0.7Cu solder joint bearing

| Ageing time (h) | SAC UTS (MPa) | SAC-0.8Sb UTS (MPa) | SAC-2.0Sb UTS (MPa) |
|----------------|--------------|---------------------|---------------------|
| 0              | 46.63        | 52.38               | 44.55               |
| 200            | 39.73        | 47.62               | 45.97               |
| 400            | 34.82        | 43.71               | 39.80               |
| 600            | 33.09        | 45.29               | 36.05               |

Table 1: Tensile strength of Sn3.5Ag0.7Cu-xSb [55].
The measurement of hardness, especially Vickers microhardness, is a usual method to characterize the mechanical properties of solder. The microhardness of the solder is often connected with how the metallic material resists wearing or abrasion. It also determines the applicability under various circumstances [64].

Adding In element to the SnAgCu solder will affect its microhardness by changing its microstructure. When the addition of In was 3.0 wt.%, the microhardness of Sn0.3Ag0.7Cu solder was increased by 81% [6]. The addition of Ni and Zn into Sn2.0Ag0.5Cu solder was reported by El-Daly and El-Taher [54]. It is found that the microhardness of SAC-0.05Ni and SAC-0.5Zn solders was increased to 12.2 and 12.6 Hv, respectively, as compared with 11.4 Hv of Sn-Ag-Cu solder. Lin et al. [8] investigated the effects of Ti and Mn addition on hardness of Sn-Ag-Cu solder alloy, as shown in Figure 5. The experimental results indicated that the hardness values of TiSn2, and MnSn2 were 9.1 ± 0.2 and 8.9 ± 0.1 GPa. Moreover, the Young’s moduli determined from nanoindentation experiments were as follows: 151.7 ± 2 GPa for Ti5Sn3 and 143.9 ± 1 GPa for MnSn2. The intermetallic compounds induced by alloying elements were obviously harder and stiffer than Cu6Sn5 and Ag3Sn. Therefore, enhanced hardness...
of SnAgCu solder was achieved in this trial by adding Ti and Mn. The rare earth La can also influence the microhardness of Sn3.0Ag0.5Cu solder, which was investigated by Zhou et al. [65]. With the addition of La, the microhardness of β-Sn and eutectic area was enhanced from 13.8 to 16.4 Hv and from 16.8 to 18.8 Hv, respectively. With the Al and Ni nanoparticles addition, the hardness of SnAgCu solder can also be improved [66]. The addition of Cu, Ni, and Mo nanoparticles into Sn3.8Ag0.75Cu solder was studied by Mohankumar and Tay [67]. The results showed that, with Cu, Ni, and Mo addition concentration increasing, hardness was enhanced. Meanwhile, it is also found that the Mo nanoparticles increase the hardness value apparently higher than Ni and Cu. The hardness values of SnAgCu composite solders follow a trend with Mo > Ni > Cu. The amount of Al2O3 nanoparticles can enhance the microhardness of Sn3.5Ag0.5Cu solder and increase the range of from 8.5% to 52.3% [20]. The CeO2 nanoparticles can alter the microhardness value of Sn3.5Ag0.7Cu composite solders. It is found that the increase of the amount of CeO2 can increase the microhardness value [60]. The researchers attributed this to the presence of hard CeO2 nanoparticles reinforcement in the solder matrix as well as higher constraint to the localized matrix deformation. The Sn3.8Ag0.7Cu solder containing 0.05 wt.% SiC nanoparticles can increase the microhardness by 44% compare with the plain solder [19]. The microhardness of Sn3.0Ag0.5Cu bearing POSS molecules was studied by Shen et al. [68]. The microhardness increased with the increase amount of POSS molecules. Furthermore, with the addition of 5 wt.% POSS, the microhardness of SnAgCu solder was reduced, which can be attributed to the agglomeration of POSS molecules and the appearance of a coarse lath-shaped structure in solder matrix.

### 6. Microstructures

Material properties depend on the microstructure. The typical microstructures of SnAgCu lead-free solder alloys are made up of primary β-Sn grains, platelet-type Ag3Sn, and scallop-type Cu6Sn5 [69] (Figure 6). According to a dispersion strengthening mechanism, uniform microstructure has positive effects on the enhanced mechanical properties of the solder joint.

Kanlayasiri et al. [6] have found that, by the addition of In into SnAgCu solders, the Sn-rich phase and the intermetallic compounds become much finer and more uniform. Ti element can change the microstructure of Sn3.5Ag0.5Cu solder. With the addition of 1.0 wt.% Ti, the grain size of β-Sn was about 4.8 ± 1.7 μm, and the width of the eutectic area was 1.2 ± 0.4 μm, as compared with 24.8 ± 5.9 μm and 6.8 ± 2.8 μm for the Sn3.5Ag0.5Cu solder. It was attributed to the unique properties of active element Ti, which can enhance appearance of heterogeneous intermetallic compounds and a morphological change of IMC [7]. Shnawah et al. [70] compared the Sn3.0Ag0.5Cu solder with Sn1.0Ag0.5Cu solder and found that the Sn3.0Ag0.5Cu has smaller primary β-Sn dendrites and wider interdendritic regions than Sn1.0Ag0.5Cu. In addition, with the addition of Fe element, a large FeSn3 intermetallic compound was formed and caused a weak interface with the β-Sn matrix. Trace amount of Mg into SnAgCu solder will cause the eutectic phases to become coarsened, and the fraction of eutectic microstructure will decrease [32]. The addition of Al can change the microstructure of Sn1.0Ag0.5Cu solder. Results showed that the primary β-Sn dendrites were refined and the interdendritic regions were enlarged. Moreover, the formation of Ag3Sn and Cu6Sn5 intermetallic compounds was suppressed. And the Ag5Al and Al5Cu intermetallic compounds were found [71]. Zhang et al. [27] in their study on Zn-doped SnAgCu solder found that Zn can significantly refine the dendrite β-Sn and when the Zn was 0.8%, the dispersed Cu-Zn intermetallic compounds was formed. The microstructure and mechanical properties of low Ag-content Sn0.5Ag0.7Cu solder doped with Ni element have been investigated by Hammad [72]. It is found that adding 0.05Ni can refine the microstructure of Sn0.5Ag0.7Cu solder and can reduce the sizes of Sn-rich phase. Meanwhile, the Ag5Sn and (Cu, Ni)5Sn3 intermetallic compounds were uniformly distributed in the Sn matrix. However, the addition of 0.1Ni into Sn0.5Ag0.7Cu solder cause the formation of relatively high fraction of the primary β-Sn and the intermetallic compounds appeared abrasive within the matrix. El-Daly et al. [73] added Ni element to the Sn3.0Ag0.5Cu solder.
Figure 7: Sn-Nd phase [39].

alloy and observed a similar phenomenon. Chen and Li [74] reported that the addition of Sb into SnAgCu solder can obviously improve the microstructure and properties of lead-free solder. It was indicated that some of the Sb powders were fused in the β-Sn matrix (Sn-rich phase); some of them participate in the form of Ag$_3$Sn, and the rest fused in the Cu$_6$Sn$_5$ IMC layer. With the addition of Sb, both thickness and grain size of IMC were decreased. Furthermore, the results reveal that Sn$_3$Ag$_0.7$Cu with about 1.0 wt.% Sb solder system exhibited the smallest growth rate and gives the most prominent effect in retarding IMC growth and refining IMC grain size. It is due to Sb element has higher affinity to Sn, and it will reduce the activity of Sn by forming Sn-Sb compound, leading to a reduced driving force for Cu-Sn IMC formation. A heterogeneous nucleation effect for restricting the IMC growth due to Sb addition is proposed.

In general, trace rare earth addition had little influence on the melting temperature but can remarkably refine the microstructures of SnAgCu lead-free solders. Law et al. [35] noted that, by adding RE into Sn$_3$Ag$_0.7$Cu solder, the grain size of β-Sn phases was refined and reduced to about 5–10 μm, respectively, as compared with 10–20 μm of Sn$_3$Ag$_0.7$Cu solder. It is mainly because RE is active elements, which can accumulate the interface of intermetallic particles [75]. Therefore, the addition RE elements affect the microstructure of SnAgCu solder. Nevertheless, the addition of an excessive amount of RE elements would cause the appearance of a large number of the RE compounds, whose the shape is similar to a “snowflake” [76]. Shi et al. [37] studied the influence of rare earth Er on the microstructure and property of SnAgCu solder and found that addition of 0.25Er into Sn$_3$Ag$_0.7$Cu reduces the size of Ag$_3$Sn and Cu$_6$Sn$_5$ intermetallic compounds particles. The addition of Pr and Nd has a significant effect on the microstructure of SnAgCu solder. The β-Sn dendrites and the intermetallic compounds growth were refined. Meanwhile, with the change of rare earth content, the microstructures of Sn$_3$Ag$_0.7$Cu-xPr (Nd) solders change. The reason is attributed to Pr and Nd atoms tending to react with Sn atoms to form RESn$_3$ compound (Figure 7) and uniformly dispersed fine RESn$_3$ particles can act as heterogeneous nucleation sites for solidification. Furthermore, the Cu$_6$Sn$_5$ and Ag$_3$Sn phase growth attaches to primary RESn$_3$ phase; thus the microstructure of SnAgCu solder becomes finer. However, an excessive amount of RE added can form bulk RESn$_3$ phase and deteriorate the mechanical properties of SnAgCu solder joint [38, 39]. Zhang et al. [40] added 0.05Yb to the Sn$_3$Ag$_0.7$Cu solder and observed that the sizes of Sn and eutectic microstructures were obviously reduced to become finer particles and the eutectic phase further spread to form network areas. It is due to the absorption of Yb with a high surface free energy on the grains during solidification during solidification. However, when adding Yb to 0.1%, the microstructure will become coarser than that of Sn$_3$Ag$_0.7$Cu0.05Yb. Moreover, the Sn-Yb particles can be observed based on scanning electron microscopy (SEM) testing. Dudek and Chawla [17] investigated the microstructure and mechanical behavior effects of adding La, Ce, and Y to the Sn$_3$Ag$_0.7$Cu solder. It is found that the addition of La, Ce, and Y into SnAgCu solder can refine the microstructures and reduced the thickness of the intermetallic compounds of SnAgCu solder. With a further increasing RE content, the LaSn$_3$, CeSn$_3$, and YSn$_3$ intermetallic compounds formed.

Gain and Chan [66] found that the incorporation of Al and Ni nanoparticles suppressed the formation of Cu$_6$Sn IMC layer and refined IMC grains. The possible reason could be attributed to very fine Sn-Ni-Cu IMC and Sn-Ag-Al IMC particles, respectively, in the SnAgCu-0.5Ni solder and SnAgCu-0.5Al solder joints. Moreover, they were uniformly distributed in the β-Sn matrix. Zhang et al. [77] also have reported that the addition of Al nanoparticles into SnAgCu composite solder can decrease the average size of IMCs and the spacing between them obviously. The addition of small percentage of Fe microparticle into Sn$_3$Ag$_0.5$Cu solder alloy had a change on the microstructure of solder joint. Clearly, the microstructure was refined and the FeSn$_3$ phase was appeared. With the addition of Al$_2$O$_3$ nanoparticles can influence the microstructure of SnAgCu solder ball. Figure 8 shows that the volume fraction of the eutectic colony was broader and Ag$_3$Sn was refined [58]. It is due to the adsorption effect and high surface free energy of the Al$_2$O$_3$ nanoparticles on the grain surface during solidification process [20]. Tang et al. [59] reported that the addition of trace amount TiO$_2$ nanoparticles can influence the microstructure of Sn$_3$Ag$_0.5$Cu solder, and the size and spacing of Ag$_3$Sn decrease significantly. When the content of TiO$_2$ nanoparticles was 0.1 wt.%, the Ag$_3$Sn grains size and spacing were decreased by 57.76% and 52.31%. With a further increase of TiO$_2$ addition, the microstructure was similar to TiO$_2$-free noncomposite solder matrix. It was attributed to the agglomeration and segregation of TiO$_2$ nanoparticles in the solders, because the van der Waals forces caused TiO$_2$ nanoparticles to become entangled with each other as they approached about 0.1 wt.%; therefore, the Ag$_3$Sn grains size will not decrease more. Liu et al. [19] developed the Sn$_3$Ag$_0.7$Cu solder bearing SiC nanoparticles. It can be seen that the growth and size of the IMCs in the composite solder matrix decrease significantly. However, when the content of SiC nanoparticles was 0.2 wt.%, the IMCs size did not decrease. For the addition of SrTiO$_3$ nanoparticles into Sn$_3$Ag$_0.5$Cu solder, very fine needle-shaped Ag$_3$Sn, spherical-shape Cu$_6$Sn$_5$, and AuSn$_3$ IMCs were found in the solder matrix. The reason might be explained by the second phase reinforcement SrTiO$_3$ nanoparticles and promoted
a high nucleation rate in the eutectic during solidification [78]. Fawzy et al. [23] investigated the effect of ZnO nanoparticles on the microstructure of Sn3.5Ag0.5Cu solder. After adding ZnO nanoparticles, the volume fraction of Ag3Sn and Cu6Sn5 IMCs was suppressed; meanwhile, the β-Sn grain size was reduced by 22%. The effects of addition ZrO2 nanoparticles on the microstructure of SnAgCu solder on Au/Ni metallized Cu pads were investigated by Gain et al. [79]. A Sn-Ni-Cu IMC layer was found in both SnAgCu plain solder and SnAgCu-ZrO2 solder, and with the number of reflow cycles, the IMC layer thickness was increased. As the content of ZrO2 nanoparticles increased, AuSn4, Ag3Sn, and Cu6Sn5 IMC particles and ZrO2 nanoparticles were homogeneously distributed in the solder matrix. Therefore, adding a small amount of ZrO2 nanoparticles refined the microstructure of the composite solder. Adding POSS molecules to the Sn3.0Ag0.5Cu composite solder can decrease the grains sizes and space lengths of Ag3Sn IMCs. As the POSS content increases further, the microstructure of SnAgCu solder has no significant change [68]. The graphene nanosheets (GNSs) as the additive into SnAgCu solder can restrict the grains growth and lead to finer IMC grains. With the addition of 0.03%, 0.07%, and 0.10%GNS, the average size of the IMCs was reduced to 1.35 μm, 1.24 μm, and 1.21 μm, as compared with 1.96 μm for the Sn3Ag0.5Cu solder [49]. For SAC-SWCNT composite solders, with increasing SWCNT additive, the average size/morphology of the secondary phase was sharply reduced [63]. Due to CNT being a ceramic material, the surface diffusion of the Ag3Sn can be suppressed by the exceedingly quicker translations of ceramic materials through the temperatures that are produced while the sintering reaction takes place [80]. Han et al. [51] and Yang et al. [62] also have reported the influence of Ni-coated carbon addition on the microstructure of Sn3.5Ag0.7Cu nanocomposite solder. It is found that the morphology of Ag3Sn and Cu6Sn5 was uniformly distributed in the solder matrix.

In short, the addition of the fourth elements can significantly change the microstructure of SnAgCu solders. However, their principles are different. Some researchers by adding alloy elements produced the intermetallic compounds, which alloying elements react with Sn, thus refining the microstructure of SnAgCu solder. Other researchers choose to add some low solubility and diffusivity in Sn, such as Al2O3, TiO2, SiC, and POSS. Meanwhile, we also found that the addition of elements has a critical value. When more than a critical value will cause harm to the properties of solder joint.

7. Interfacial Reactions

Interfacial reaction is solder/substrate systems which are of particular importance to the manufacturability and reliability of electronic packaging [81]. During soldering, the solder alloys react with the substrate to form intermetallic compounds (IMCs) at the interface [82], such as Cu6Sn5, Cu3Sn, and other IMCs. Figure 9 shows the IMC layers formed between the solder and substrate after soldering [83]. It is well known that a thin IMC layer is desirable to achieve a good metallurgical bond at the interface. However, excessive IMC growth may have a detrimental effect due to the brittle nature of IMC [84]. Therefore, knowledge of the morphology, growth behavior, and properties of IMC is crucial for understanding of the reliability of the solder interconnection.

The formation of IMC is divided into two stages: one stage which is Cu6Sn5 forms first at the interface during soldering, and the other which is Cu3Sn will form between Cu6Sn5
and Cu by solid-stage reaction and the Kirkendall voids were observed in the Cu₅Sn₃ layer (Figure 10), which is attributed to the faster diffusion of Cu atoms compared to that of Sn atoms through the interface [85].

From the brief review, we will find how to suppress the growth of IMC. Some researchers study only the liquid-stage, and some study the solid-stage, while others study both.

Below, we shall review that the addition of the fourth alloys into SnAgCu lead-free solders influences the interfacial microstructure.

The effect of solid state reactions between Sn0.3Ag0.4Cu0.7In composite solder and Cu substrate was studied by Lejuste et al. [86]. The experimental results showed that two IMCs layers, Cu₅(Sn, In)₃ and Cu₅(Sn, In), were formed at the interface. Meanwhile, they found that the growth coefficients of Cu₅(Sn, In)₃ layer were similar to those of plain SnAgCu solders, while the growth coefficients of Cu₅(Sn, In) layer were found to be clearly lower than those for the SnAgCu solders. Therefore, it is indicated that the addition of In element can suppress the growth of IMC layer during thermal aging. The 0.8% Zn addition into Sn3.8Ag0.5Cu solder can retard the growth of Cu-Sn IMC in liquid/solid state reaction and analyzes the reasons resulting in this situation. It is mainly caused by an accumulation of Zn atoms at the interface [27]. Wang et al. [87] also found that the growth of IMC was significantly reduced by the 0.2% Zn addition into SnAgCu solder. The addition of 1 wt.% Bi into Sn2.8Ag0.5Cu solder was studied by Rizvi et al. [28], showing that 1 wt.% Bi addition could restrict the excessive formation of IMC during the soldering reaction and thereafter in aging condition. After a few days of aging, the morphology of the IMC layer between the SnAgCu-Bi solder and the Cu substrate transformed from the scallop type to the planar type, and the intermetallic growth rate of SnAgCu-Bi was calculated as 1.91 × 10⁻⁷ m²/s compared with 2.21 × 10⁻⁷ m²/s for the SnAgCu solder. Adding a small amount of Ni alloying to the Sn3.0Ag0.5Cu (SAC) solder can also reduce the IMC layer thickness. Comparing the SAC-Ni with the SAC, it was found that the IMC thickness of SAC-Ni composite solder exhibits a slight change after aging, whereas the IMC thickness of SAC was markedly increased by approximately 60% compared to that at the as-reflowed state [15]. Chen and Li [74] proposed that adding Sb can also restrain the IMC growth because of the formation of Sn-Sb compound. Ma et al. [88] reported that Co reinforced Sn3.0Ag0.5Cu composite solder suppressed the growth of IMC layer. It is attributed to Co particles which can attract Sn and Cu to form Co-Sn or Co-Cu IMCs during the reflow process. Afterwards, Co close to the interfacial layer can hinder Cu from being available for formation of the IMC layer and thereby reduce its growth rate. Luo et al. [30] demonstrated that a minor Ga addition has the ability to inhibit the growth of interfacial intermetallic compounds (IMC). It is found that, with the addition of 0.5% Ga, the thickness of IMC layer is 58.9% thinner than that of the plain solder/substrate IMC layer. It is explained that Ga can reduce the activity of Sn, thus depressing the growth of Cu₅Sn₃ and the excessive reaction of the interface.

The addition of trace amount of RE elements (mainly Ce and La) into SnAgCu solder was investigated by Law et al. [35]. The research achievement shows that a layer of Cu₅Sn₃ was observed between the Cu₅Sn₃ IMC layer and Cu pad. At the same time, there are many Kirkendall voids between Cu₅Sn₃ IMC layer and the copper substrate. However, with the addition of RE, the growth of IML was significantly inhibited. Rare earth Y element can show an effective influence on the interfacial growth of IML in SnAgCu solder. With the addition of Y, the thickness of IML was reduced and the growth of the IML was suppressed during the high-temperature aging [36]. Gao et al. [39] note that the addition of Nd can change the growth of intermetallic layer. When the addition of Nd was 0.05%, the thickness of IML reduced by 45.8% compared with the plain solder joint. The reason may be attributed to the formation of Sn-Nd compound, thus retarding the growth of the Cu₅Sn₃ IMC during the soldering. The advantage of rare earth Yb addition into SnAgCu solder was shown by Zhang et al. [40], who found that 0.05% Yb addition into SnAgCu alloy suppressed the growth of IMC and the morphology of Cu₅Sn₃ layer can be changed to a relatively flat morphology. Small amounts of La were added to the SnAgCu lead-free solder for studying the growth of the IMC layer between the solder and the Cu substrate. Comparing the SnAgCu solder, the IMC thickness has reduced by approximately 60% with adding trace amount of rare earth La [89]. Liu et al. [90] investigated the effects of addition of Ce on the formation and growth of interfacial IMCs between the SnAgCu solder joint and Cu substrate. It is found that the thickness of interfacial IMC can be reduced during the soldering and aging with the addition of Ce into SnAgCu solder.
Adding trace amounts of Fe microparticles can restrain the growth of intermetallic compounds (IMCs). During liquid state reaction, Fe can effectively suppress the growth of Cu$_6$Sn$_5$ and Cu$_3$Sn layer. However, during the reflow process, Fe trended to retard the growth of the Cu$_3$Sn layer. Moreover, the total thickness of IMCs for the SnAgCu-Fe composite solder was similar to that for the plain SnAgCu solder [91]. Xiang et al. [18] reported the positive effect of Mn nanoparticles on the SnAgCu solder for restricting the growth of intermetallic compounds after first and six times of reflow. However, for Cu$_3$Sn thickness, the addition of Mo nanoparticles was not affecting it. The addition of Al nanoparticles can alter the growth of interfacial IMC between SnAgCu solder alloys and Cu substrate with 1 cycle and 16 cycles of reflow [57]. When the content of Al nanoparticles was 3 wt.%, the thickness of the IMC decreased from 2.8 μm to 2.4 μm with one flow cycle. After 16 reflows, the thickness of the IMC decreased from 6.7 μm to 6.1 μm. Ni nanoparticles can also influence the thickness of IMC layer. With the addition of Ni nanoparticles, the morphology of Cu$_6$Sn$_5$ changes from a scalloped structure to a planar type after reflow. In addition, the growth of (Cu, Ni)$_3$Sn$_4$ enhanced, and that of Cu$_3$Sn was suppressed [44]. Haseeb et al. [46, 92] investigated the effect of Mo and Co nanoparticles additions on the morphology of interfacial IMCs between SnAgCu solder and Cu substrate. It is found that the addition of Mo nanoparticles can decrease the thickness and diameter of Cu$_6$Sn$_5$. However, the addition of Co nanoparticles can enhance the growth of Cu$_6$Sn$_5$ and suppress the growth of Cu$_3$Sn. Due to the fact that Co nanoparticles dissolved in Cu$_6$Sn$_5$, then change the intermetallic compounds composition. Nevertheless, Mo nanoparticles remain intact without any chemical change or recognizable physical and segregate preferentially at the interfaces. Therefore, they hinder the path for diffusion and restrict the intermetallic compound growth. Chan et al. [93] developed a novel composite solder by incorporating Zn nanoparticles into Sn3.8Ag0.7Cu solder, and these Zn nanoparticles were found to have much decreased the Cu$_6$Sn$_5$ IMC thickness. When the addition of Zn nanoparticles was 0.3%, no Cu$_5$Zn$_8$ can be observed, while with the addition of 0.8% Zn nanoparticles, Cu$_5$Zn$_8$ can be observed and exhibited 1.53 μm thickness. After one reflow, Cu$_3$Sn was not noticeable. After 6 reflows, the Cu$_6$Sn$_5$ thickness was reduced with the addition of Zn. When the addition was 0.8% Zn, the thickness of Cu$_6$Sn$_5$ reduced from 4.11 μm to 0.97 μm. Meanwhile, the Cu$_5$Zn$_8$ IMC thickness was increased to 1.72 μm, and the Cu$_3$Sn was found to have a thickness of 0.56 μm. Tsao and coworkers [58] showed that small amounts of Al$_2$O$_3$ nanoparticles into SnAgCu solder suppressed the growth of the IMC thickness during the reflow cycles. Gain et al. [21] found that the addition of TiO$_2$ into SnAgCu solder reduced the IMC thickness after thermal cycling, as shown in Figure II. When ZrO$_2$ nanoparticles were added to the SnAgCu solders, it is found that the intermetallic compounds (IMCs) can be depressed [24]. Fouzder et al. [78] studied Sn3.0Ag0.5Cu composite solder with 90–110 nm SrTiO$_3$ reinforcement particles and reported significant reduction the IMC layer thickness. With the content of 0.05 wt.% SrTiO$_3$,
the IMC thickness was decreased from 6.7 \( \mu \text{m} \) to 5.8 \( \mu \text{m} \) after sixteen reflow cycles. Nai et al. [94] added carbon nanotubes (CNTs) to the Sn3.5Ag0.7Cu solder alloy. Results revealed that, with the addition of CNTs, the nanocomposite solder exhibited a lower diffusion coefficient; thus the growth of IMC layer was retarded. Han et al. [95] also reported a similar effect of Ni-CNTs on the interfacial IMC.

### 8. SN Whiskers

In past reports, the addition of rare earth (RE) elements has showed many beneficial effects. However, with further research, Pb-free solder containing rare earth encountered unexpected problems, namely, Sn whisker. For electronic device, tin whiskers formation is fatal and easily causes short circuits as well as system failures because whiskers can grow to a length exceeding several hundred microns and these tin whiskers are nearly pure single crystals with excellent electrical conductivity [96]. Figure 12 [97] shows a scanning electron image of whiskers on the legs of a lead frame, where a very long whisker can be observed to have bridged a pair of the legs.

In recent years, rare earths were wildly used in the Pb-free solders to enhance solderability. However, as a surface-active element, the reactive nature of rare earth elements with oxygen and accelerate tin whisker growth in a rare earth element-containing solder alloy [98]. Hao et al. [99] found that 1.0% Er doping could form whiskers and the morphology of the Sn whiskers changes from rod-like to thread-like with the storage temperature increases from 25°C to 150°C. Dudek and Chawla [100] also investigated the effect of 2 wt.% Ce, La, or Y additions on the whiskering behavior of Sn3.9Ag0.7Cu. It is found that oxidation of \( \text{RESn}_3 \) causes compressive stresses that ultimately result in the formation of Sn whiskers. Moreover, the size of the \( \text{RESn}_3 \) has a significant impact on oxidation and whiskering:

\[
\begin{align*}
2\text{LaSn}_3 + \frac{3}{2} \text{O}_2 & \rightarrow \text{La}_2\text{O}_3 + 6\text{Sn} \\
\text{CeSn}_3 + \text{O}_2 & \rightarrow \text{CeO}_2 + 3\text{Sn} \\
2\text{YSn}_3 + \frac{3}{2} \text{O}_2 & \rightarrow \text{Y}_2\text{O}_3 + 6\text{Sn}
\end{align*}
\]

According to the existing literature, we find that previous research added too much rare earth elements into SnAgCu solder and the minimum addition amount of the rare earth was 1%, thus providing large \( \text{RESn}_3 \) phase for whiskers growth. In order to prevent rapid whisker growth, Chuang and Lin [101] showed that 0.5% Zn addition into SnAgCu solder refined the microstructure and suppressed whisker growth. Figure 13 shows SnAgCu-Ce surface whisker.

Although the addition of alloying elements can suppress the rapid growth of tin whiskers in RE-containing solders, it does not inhibit the emergence of tin whiskers. We think whiskers formation is mainly due to an excess of rare earth elements. Therefore, researchers should control the content of rare earth. It is attributed to addition of trace amounts of rare earth elements; RE phase formation is limited, thereby having difficulty in providing the driving force for whisker growth.

### 9. Conclusions

With the addition of alloying elements and nanoparticles, the wettability, mechanical properties, and hardness properties of SnAgCu solder and solder joints were enhanced obviously. However, excessive elements can decrease these properties; for example, when adding excessive amounts of rare earth elements, the tin whiskers will appear. And with the addition of excessive amounts of nanoparticles, metal nanoparticles easily react with matrix; thus the phenomenon of grain growth occurs and affects the reliability of solder interconnections. For inert nanoparticles, for example, \( \text{Al}_2\text{O}_3 \), \( \text{ZrO}_2 \), \( \text{SiC} \), and so on, they are prone to agglomeration and cause the effect of dispersion strengthening to be lost. Therefore, selecting the appropriate additive amount is very important. In addition, the alloying elements and nanoparticles can refine the microstructure of SnAgCu solders and the retarding effect of elements on the intermetallic compounds in the solder/copper is also demonstrated.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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