Chapter 5

Evolution of Pb-Free Solders

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Additional information is available at the end of the chapter

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Abstract

This chapter discusses the evolution of lead free (Pb-free) solder, from tin-silver-copper (SAC) system with silver content of 3.0, 3.8, and 4.0 to low SAC system such as SAC0307 and SAC105 and the emerge of high reliability Pb-free solder. The discussion covers the reason and the driving force of industries implementing this change. The solder composition has evolved further recently to fulfill high reliability requirement of certain sectors such as automotive, aerospace, and military which are preparing to go green in soldering technology. This kind of high reliability solder involves additional microalloying of tin (Sn)-based solder in making it to be more robust. In this chapter, the author will introduce the techniques used by solder makers and researchers in enhancing the Pb-free solder strength in the recent evolution. Recently, attention has been drawn to low temperature joining technology again such as silver sintered joint and liquid-phase diffusion bonding material used in high power density and high junction temperature-integrated circuits. Pb-free joining material is required to replace the high Pb solder, which is still commonly used in such high-power devices.

Keywords: Pb-free solders, particle strengthening, Ag3Sn coarsening, solid solution strengthening, high temperature die attach material, silver (Ag) sintering, liquid-phase diffusion bonding (LPDB)

1. Introduction

The adoption of Restriction of Hazardous Substances Directive 2002/95/EC (RoHS 1) in 2003 was one of the driving forces mandating the electronic industries to look for alternatives to replace the tin-lead eutectic alloy (SnPb-6337), which had been used for decades. RoHS 1 has limited the content of Pb to be less than 1000 ppm by weight in each homogenous material, which is including the soldering material. The SnPb-6337 contains 37% of Pb, which is an element with known harmful effect to human health and the environment. Thus, SnPb-6337 has to be replaced in order to meet the RoHS compliance. Pb is just one of the six banned substances under RoHS 1 [1]. The banned list of RoHS has expanded to 10 under Directive (EU) 2015/863 (RoHS 2), which was published in 2015. The full list of banned substances in RoHS 2 is shown in **Table 1**. PBB and PBDE are mainly used as frame retardant in plastics and hexavalent chromium is used in chrome plating, chromate coatings and primers, and in chromic acid. DEHP, BBP, DBP, and DIBP are phthalates, which are being used as plasticizers. These substances are rare in solder materials. Out of the 10 substances listed in RoHS 2, only Pb is the most concerned substance for solder industry. This explains why some of us refer RoHS compliance solder as Pb-free solder. Although the RoHS compliance cannot help in reducing the electronics waste, which has increased tremendously in recent years, it helps to minimize the hazardousness of such trash to environment.

Since 2006, Pb-free soldering has been in the main stream of industries because RoHS 1 took effect on 1st July 2006. Many changes in alloy composition are adopted in order to match the requirement of solder joint with Pb-free definition. Tin Copper (SnCu), Tin Silver (SnAg), and Tin Silver Copper (SnAgCu or SAC) are the dominating Pb-free solder alloys adopted by the industries.

SAC alloy had received most publicity in the initial stage of conversion from SnPb-6337 to Pb-free solder. One of the reasons was because SAC alloy with 3.0% silver (Ag) and 0.5% copper (Cu), SAC305 was endorsed by the IPC Solder Value Product Council as the preferred option for SMT assembly. Other than SAC305, the industries had also adopted other SAC alloys with higher silver content such as Sn3.8Ag0.7Cu (SAC387) and Sn4.0Ag0.5Cu (SAC405), which are believed to be the true eutectic ternary solder alloys, which have single melting point at 217°C. SAC305 is a hypo-eutectic ternary alloy with melting range of 217–219°C. However, the high cost of Ag compels the industries to consider other alternatives such as low silver solution, SAC0307, or no silver solutions such as SnCuNi (SN100C®). A more detailed discussion on this topic will be covered in Section 2 of this chapter.

Substance	RoHS limit
Lead (Pb)	1000 ppm/0.1%
Mercury (Hg)	1000 ppm/0.1%
Cadmium (Cd)	100 ppm/0.01%
Hexavalent chromium (Cr^{6+})	1000 ppm/0.1%
Polybrominated biphenyls (PBB)	1000 ppm/0.1%
Polybrominated diphenyl ether (PBDE)	1000 ppm/0.1%
Bis(2-ethylhexyl) phthalate (DEHP)	1000 ppm/0.1%
Butyl benzyl phthalate (BBP)	1000 ppm/0.1%
Dibutyl phthalate (DBP)	1000 ppm/0.1%
Diisobutyl phthalate (DIBP)	1000 ppm/0.1%

Table 1. Ten substances which are banned in Restriction of Hazardous Substances Directive 2015/863 (RoHS 2).

The requirement of solder joint performance is getting stringent in order to support the modern electronification. It is especially for automotive industry. In a modern car system, the usage of advanced electronic components is getting common, for example, in logic control, switches, and sensors. The adoption of electronic components has significantly boosted the speed and accuracy of these systems. The electronification of car system such as advanced driver assistance systems (ADAS) has given another level of driving experience to consumer. On the other hand, the incorporation of multimedia system in car system, which is to increase the comfort level of driver has further increased the usage of electronic components in a car. It explains the growth of auto electronics has surpassed other industries in recent years [2]. Due to the harsh use environment where the under-hood temperature is much higher than other applications, the requirement on the solder joint performance is higher. Moreover, these systems are considered as life-critical system, which has increased the challenges in selecting an appropriate solder alloy. Due to this kind of new requirements, solder manufacturers and researchers are striking to invent new alloy, which can support this platform. It also implies that the conventional Pb-free solder alloys such as SnCu, SAC, and low SAC are showing limitations in fulfilling the demand of such applications. The various strengthening mechanisms in Sn-based solder alloy which have been deployed by the industries will be discussed in Section 3 of this chapter.

Besides in-car system, the effort of popularization of electric vehicles has further promoted the usage of electronic components in automotive industry. In view, the fact that this kind of system involves high current and high temperature, conventional SAC Pb-free alloys cannot fulfill the basic requirement. This is the reason why the exemption for RoHS compliance has been further extended to 2021 for Pb use in high-melting temperature type solders (i.e., Pb-based solder alloys containing 85% by weight or more Pb, Category 7a). Nowadays, most of the electronic devices for such application are still adopting high Pb solder as the die attach material. There are various options available in replacing high Pb solder at die attach process. But, there are still gaps to be filled up before such new materials can be fully commercialized and mass adoption of such new materials in current production.

Internet of things (IoT) has caught high attention from industries. Many industry players believe that the IoT will boost the growth of electronic component to another level, the era of IoT. The IoT has reshuffled the business process of many big organizations in preparing themselves to ride on this wave. To interpret the IoT in a simpler way, it is an application which allows the wide use of sensor in our daily life. In IoT, there is also a platform, which can connect all the relevant sensors for data analyzing and actuation. The objective of IoT is to realize a smarter world. According to *Business Insider*, there are 1.9 billion interconnected devices in 2014, with an expected 9 billion by 2018. By then, the number of IoT devices will surpass the summation of mobile phone, tablet, and PCs, which are the current major consumer market. With such high quantity of IoT device, the usage of solder as interconnect is also prospective. The selection of solder alloy to fulfill the requirement of this sector will focus in meeting the specific criteria for manufacturing, reliability, toxicity, cost, and availability.

In view of prospective growth of electronic component and new solder joint requirement, solder manufacturers and researchers are working together in developing new alloy or modifying existing alloys to close the gap between the user and supplier of solder material. In the chapters that follow the evolution of Pb-free alloy and the techniques used in enhancing solder alloy strength are discussed.

2. Evolution from high silver to low silver solder

In 2000s, SAC system had been identified as replacement for Sn-Pb eutectic solders in fulfilling the RoHS compliance. Different countries or organizations had chosen different SAC composition as their preferred solder composition. They are Sn3.0Ag0.5Cu, SAC305 (Japan), Sn3.5Ag0.9Cu, SAC3509 (European Union), and Sn3.9Ag0.6Cu, SAC3906 (USA) [3].

In 2000, it was the era of consumer product, which had incorporated many electronic components in its system such as personal computer, television, radio, rice cooker, and window-mounted air conditioner. These products were mostly using through-hole components and/or big surface mount technology (SMT) components. It implies that the consumption of solder per unit device was huge during that period of time. It explains the reason of mass adoption of SAC305 instead of other Pb-free solutions. It is because the lower silver content of SAC305 as compared to other SAC alloys mentioned in former paragraph. Silver is a precious metal and its inclusion in solder alloy does increase the cost of solder significantly. For example, to produce 1 kg of SAC305, 1 ounce of silver needs to be added. It depends on the market price of silver, assuming USD20 per ounce, the cost of silver in 1 kg of SAC305 is almost 50% of the selling price of 1 kg of SAC305 solder bar. When the silver price surges, for example, in April 2011, when the silver price was USD 40 per ounce, the cost of silver of a SAC305 solder bar was more than 50% of its selling price. For those compositions with higher silver content, the ratio of silver cost against solder bar selling price is usually more than 50% depending on the tin price. It becomes a big burden to solder users. Solder bar is mainly used in wave soldering process. It was a very common process in printed circuit board assembly (PCBA) for those consumer products mentioned above. During the peak of this era, the consumption of solder bar could exceed 2000 kg per month for a single customer who has more than 10 wave soldering lines in production. Another reason of mass adoption of SAC305 instead of other higher Ag bearing SAC alloy is more a political reason. During that time, Japanese consumer product was very popular and common. *National* brand electric rice cooker should be one of the must have electrical appliances in every home. SAC305 was the Japan Electronics and Information Technology Industries Association, JEITA recommended Pb-free alloy too.

Nevertheless, the industries were looking for alternatives for SAC305 very quickly after its introduction to industries, even though with its acceptance as Pb-free alloy in replacing SnPb-6337 solder. In general, there are two major reasons in justifying this direction, cost and drop impact resistance of SAC305 alloy. The users were looking for alternative to mitigate the high cost of SAC305 as mentioned above. This was the time when low SAC alloy started to join the supply chain of solder. **Table 2** lists some of the low SAC alloys available in market offered by different solder suppliers. The introduction of these low SAC alloys was as soon as 2 years after the mass adoption of SAC305 alloy as Pb-free solder in the industries. Nevertheless,

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SAC305 is still the major adopted alloy in the industries after 10 years of RoHS enactment. It is worth to note that Nihon Superior has introduced Ag-free Pb-free solution since 1999. It has become a main solution in soldering especially in wave soldering and Pb-free hot air solder leveling (HASL) process.

With lower silver content in SAC alloy, some users were hoping the hot tear or shrinkage cavity could be mitigated. This phenomenon which was first believed as a process defect was found when users migrating from SnPb-6337 to SAC305. To date, many users are still confused by this phenomenon even though IPC has classified it as an acceptable phenomenon. **Figure 1** shows the comparison of few low SAC alloys and a eutectic Tin Copper Nickel alloy.

Besides the appearance of solder whose difference is easily noticeable, the users were also concerned about the reliability of low SAC especially the intermetallic compound (IMC) formed in between the solder and soldering pad. **Figures 2** and **3** show the IMC of SAC 305, low SAC, SAC1205, and Ag-free Pb-free solder (SnCuNi) on Copper (Cu) pad and Nickel Gold (NiAu) pad, respectively. Both SAC alloys regardless of Ag content were showing columnar growth of IMC and the IMC continued to grow during the heat treatment at 125°C for 500 h. The SnCuNi IMC appeared to be flat and stable even after the heat treatment. Besides the columnar IMC, crack was observed at the Cu pad after heat treatment within the IMC of SAC305 but not at the SAC1205 and SnCuNi alloys. This observation matched the explanation proposed by Nogita et al. in his journal [4]. The Ni addition in Pb-free alloy has successfully suppressed the polymorphic transformation of Cu_6Sn_5, which is the culprit of this IMC crack. There is transformation of hexagonal to monoclinic Cu_6Sn_5 and vice versa at temperature of 186°C due to the allotropic attribute of Cu_6Sn_5. This transformation involves volume change of the Cu_6Sn_5 IMC, which causes high stress at this layer. The stress has exceeded the strength of this IMC and caused the crack within this layer. Micro crack might have formed within the SAC305 IMC during the solidification process of joint formation and the cracks propagated during the heat treatment due to IMC growth. This has explained why the crack still formed even though the heat treatment temperature was just 125°C, which was far below the polymorphic transformation temperature.

Solder manufacturer	**Alloy composition**	**Solidus (°C)**	**Liquidus (°C)**	**Debut (year)**
Alpha Assembly Solutions	Sn0.8Ag0.7Cu	216	225	2007–2010
	Sn0.3Ag0.7Cu	217	228	2007–2010
Senju Metal Industry	Sn0.3Ag0.7Cu	217	227	2007–2010
	Sn1.0Ag0.7Cu	217	224	2007–2010
Indium Corporation	Sn1.0Ag0.5Cu	217	225	2007–2010
	Sn0.3Ag0.7Cu	217	227	2007–2010
Nippon Micrometal Corporation	Sn1.2Ag0.5Cu0.05Ni	217	227	2000s
Nihon Superior	Sn0.7Cu0.05Ni0.01Ge	227	227	1999

Table 2. List of low SAC solder and no Ag solder as alternatives of SAC305.

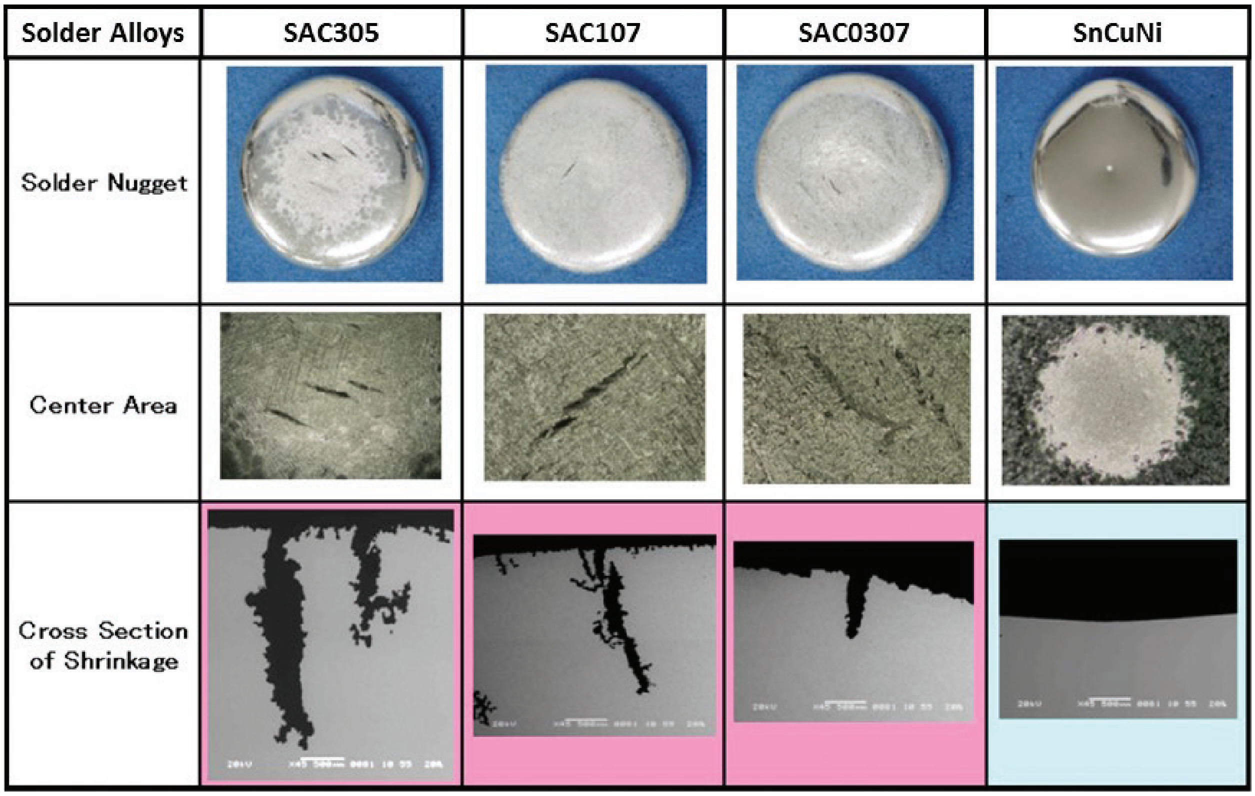

Figure 1. Appearance comparison of different SAC alloys and a eutectic SnCuNi alloy.

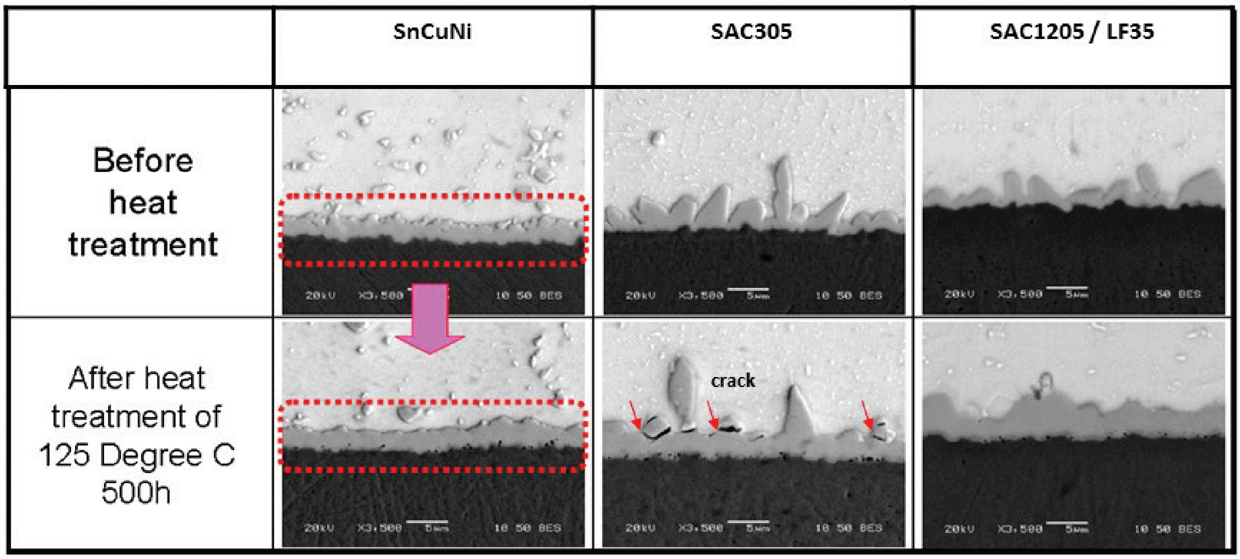

Figure 2. IMC formed on Cu pad with solder alloy of SnCuNi (SN100C®), SAC305 and SAC1205 (LF35).

Besides the cost concern mentioned earlier, another driving force which triggered the industries to consider low SAC alloy was the drop impact resistance. It is widely accepted that silver addition can effectively reduce the liquidus and increase the yield strength and modulus of SAC alloy; also because of the high strength and high modulus which make the alloy

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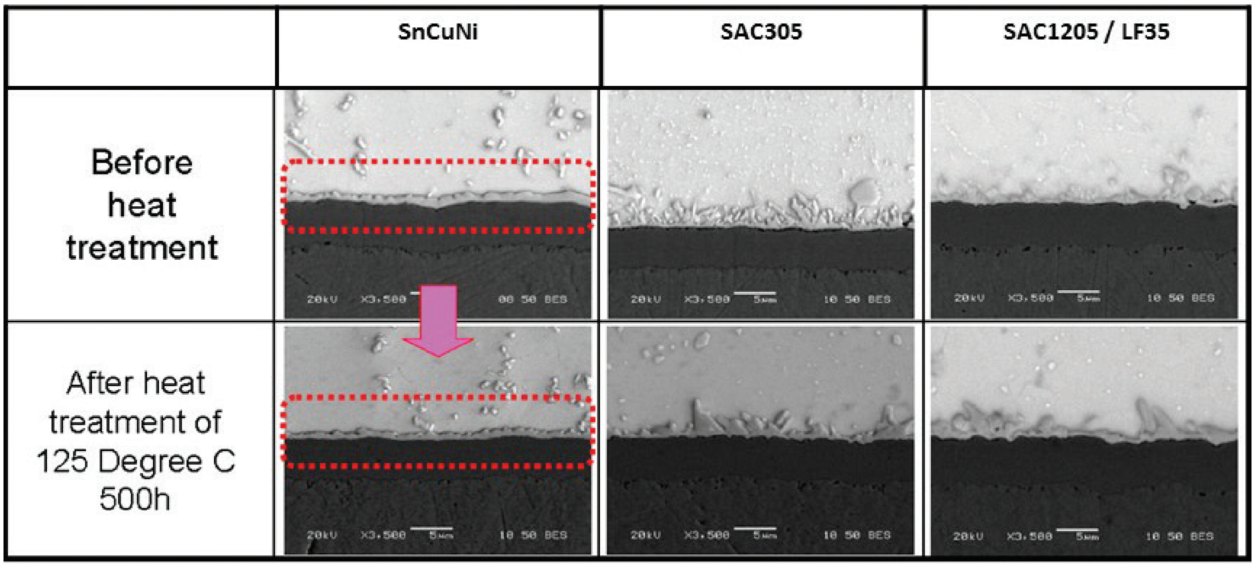

Figure 3. IMC formed on NiAu pad with solder alloy of SnCuNi (SN100C®), SAC305, and SAC1205 (LF35).

readily transfer the stress to the solder joining interface which is the region of IMC [5]. Due to this mechanism, most of the failures found in drop impact resistance test with conventional SAC alloys mostly locate at the IMC region, and most of these failures are early failures. By reducing the Ag content of SAC alloy, the modulus of alloy decreases. It has significantly increased the resistance to the drop impact. The urge of looking for an alloy with high drop impact resistance increased further due to the popularity of portable devices in mid-2000 to late-2000. During that period of time, portable music player such as MP3 player and iPod and handheld game console were very common. The robustness against drop shock was crucial to keep a reasonable reliability of such devices. For example, during the initial implementation of Pb-free soldering, most of the solder ball used in ball grid array, BGA package is SAC305 composition. Many mobile integrated circuits, ICs had migrated to LF35 or SAC1205 BGA solder ball in order to increase the drop test performance of the ICs. However, by only lowering the Ag content of SAC alloy did not give a total solution to meet the expectation of users. Many other microalloying had been deployed by solder manufacturers in order to increase the alloy performance of low SAC alloy such as adding Nickel, Ni, Zinc, Zn and Manganese, Mn into the alloy system. As shown in **Figure 2**, the addition of Ni into LF35 composition has suppressed the polymorphic transformation of Cu_6Sn_5 during the solidification. It cannot be achieved by only reducing the Ag content of SAC alloy.

The acceptance of low SAC or SnCuNi as Pb-free solution is also encouraged by the readiness of other material to Pb-free soldering process. One of the major challenges in adopting low SAC or SnCuNi alloy is the high melting point of this alloy. It has approximately 44 and 10°C higher melting point comparing to eutectic SnPb alloy and SAC alloy, respectively. However, the market is now more ready for this Pb-free soldering. The reflow and wave soldering machines are having higher heat capacity to accommodate the high melting point of Pb-free solder, PCB, and electronic components are using higher glass transition (Tg) temperature materials and soldering flux can survive longer in high-temperature reflow. All these improvements have enabled the adoption of low SAC and SnCuNi alloy in soldering. This has also explained the market share of this low SAC and SnCuNi alloys is expanding in recent years. SN100C® has become one of the preferred choices in Pb-free wave soldering process.

In short, there are two driving forces, which have triggered the proliferation of low SAC and SnCuNi alloys for electronic industries. Someone has named the low SAC as second generation of Pb-free alloy. **Figure 4** summarized the evolution of this Pb-free alloy from conventional SAC to low SAC alloy for electronic industries. This transition is very important to support the IoT era. One of the characteristics of IoT is huge in quantity. The high usage of electronic components in IoT era also prompts the usage of solder. The type of solder for this era must be able to fulfill the specific requirement in manufacturability, reliability, toxicity, cost, and availability. The second generation Pb-free alloy should be a better choice for the IoT era.

The following section discusses the development of Pb-free alloy into third generation alloy for high reliability application.

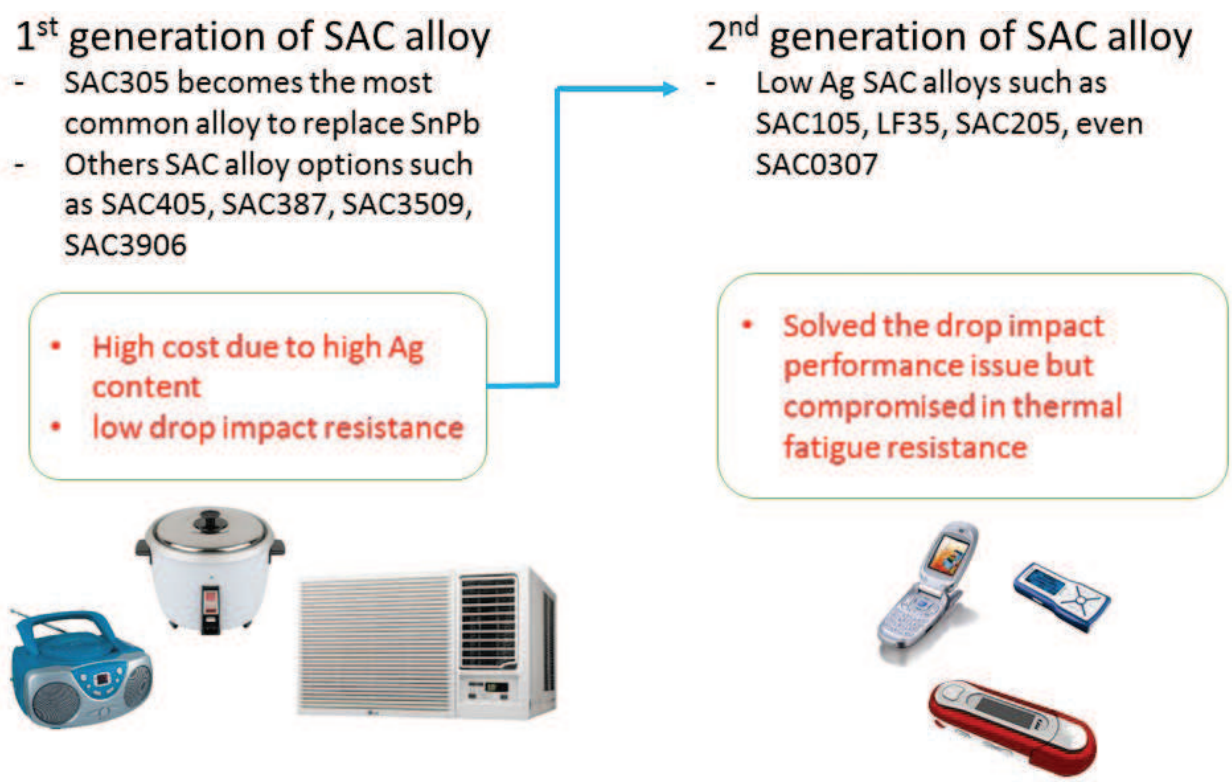

Figure 4. Evolution of SAC alloys in Pb-free solution from first generation to second generation.

3. High reliability alloy is required

As discussed in Section 2, there is an evolution of Pb-free solder from conventional high Ag bearing SAC alloy to low SAC alloys because of cost and drop impact resistance. This is

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the transition of first-generation SAC alloys to second-generation SAC alloys. However, the lower Ag content has compromised in thermal fatigue performance. It is because the strength enhancement of SAC alloy is through the dispersion of very small Ag_3Sn IMC within the tin matrix. This fine Ag_3Sn IMC has the effect in inhibiting the dislocation movement of the tin matrix. This mechanism makes the SAC alloy to have higher modulus as compared to the SnPb-6337. The more Ag content will increase the amount of fine Ag_3Sn IMC, but it also increases the possibility of large size Ag_3Sn platelet growth. This large Ag_3Sn platelet can be the stress concentration point and crack will initiate from this point. In extreme case, the large Ag_3Sn plate can even protrude out the solder surface and deform the small solder joint [5]. Therefore, the large Ag_3Sn platelet is not a desirable morphology in a solder joint. However, the lower Ag content in low SAC alloys has tremendous reduction in amount of Ag_3Sn IMC. Although there is another IMC, which is the Cu_6Sn_5 within the bulk solder, this IMC is much fewer compared to Ag_3Sn IMC of conventional SAC alloys. Moreover, a portion of the Cu of bulk solder will be extracted in forming the IMC at Cu pad. This further reduces the amount of Cu_6Sn_5 within the bulk solder. Thus, the main strength of the SAC alloy is still the dispersion of fine Ag_3Sn within the tin matrix.

The compromise in thermal fatigue performance of SAC alloy has been further complicated by the phenomenon of Ag_3Sn IMC coarsening. The Ag_3Sn coarsening is a process of Ostwald ripening. This is an evolutional process of an inhomogeneous structure where the small particle is growing and drawing the adjacent particle to form a bigger particle over time. This is a spontaneous process because big particle is more energetically stable than small particle. It is because the internal pressure is reversely proportional to the radius of a particle. Hence, the small particles have higher surface energy. The small particles will try to achieve a higher energetic stability by growing to bigger size. This is coarsening. Besides that, the Ostwald ripening is a thermodynamically driven process. If the environment temperature is high, the process of coarsening will increase. This Ag_3Sn coarsening has significant impact to the strength of SAC alloy. As discussed earlier, the strength of SAC alloy is the dispersion of fine Ag_3Sn IMC. **Figure 5** shows an example of the Ag_3Sn coarsening within SAC305 alloy after exposed to high temperature, 125°C for 6 months.

In the coarsening process, two changes will be observed: 1. The amount of Ag_3Sn in the tin matrix, and 2. The distance between Ag_3Sn IMCs. When the amount of Ag_3Sn shrinks and the distance between Ag_3Sn gets wider, its ability in inhibiting the dislocation movement reduces. This is a degradation process of SAC alloys. In fact, we can easily demonstrate this mechanism by exposing SAC alloy to high temperature environment over a period of time. The tensile strength of SAC alloy reduces after the thermal aging. **Figure 6** shows an example of this degradation in SAC305 alloy. This is an experimental data of the comparison of tensile strength of tensile test specimen made of SAC305 alloy with and without exposure to isothermal aging (150°C for 500 h).

3.1. High reliability solder alloy for PCBA

The degradation of SAC alloys over time is worrying because it is a challenge for reliability engineer to predict the life of a solder joint. It is especially critical on those life-critical system

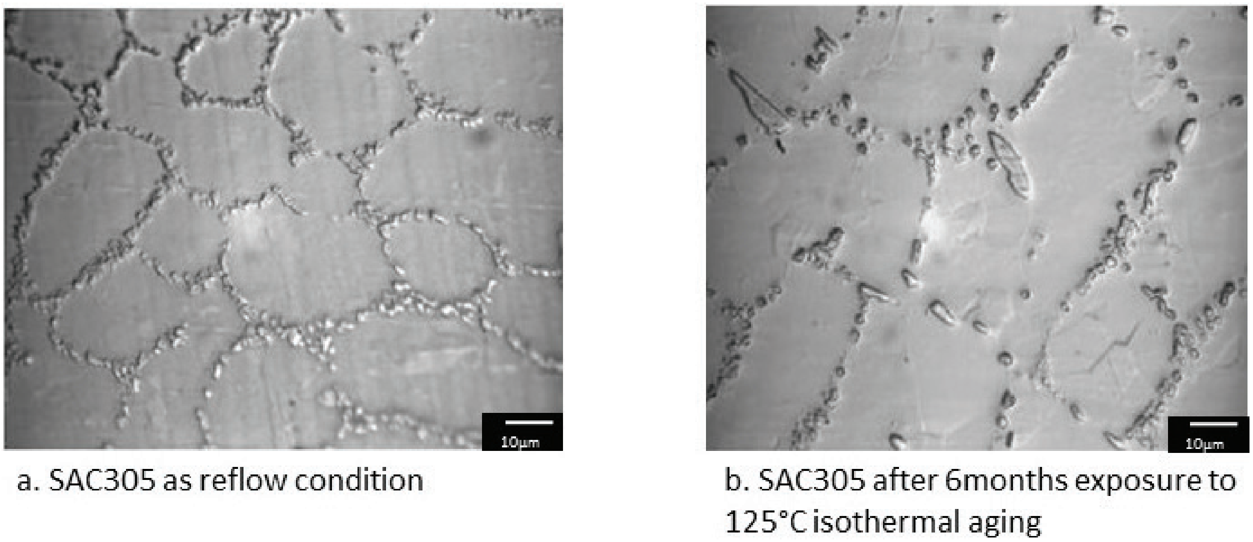

Figure 5. Ag_3Sn coarsening in high temperature storage test.

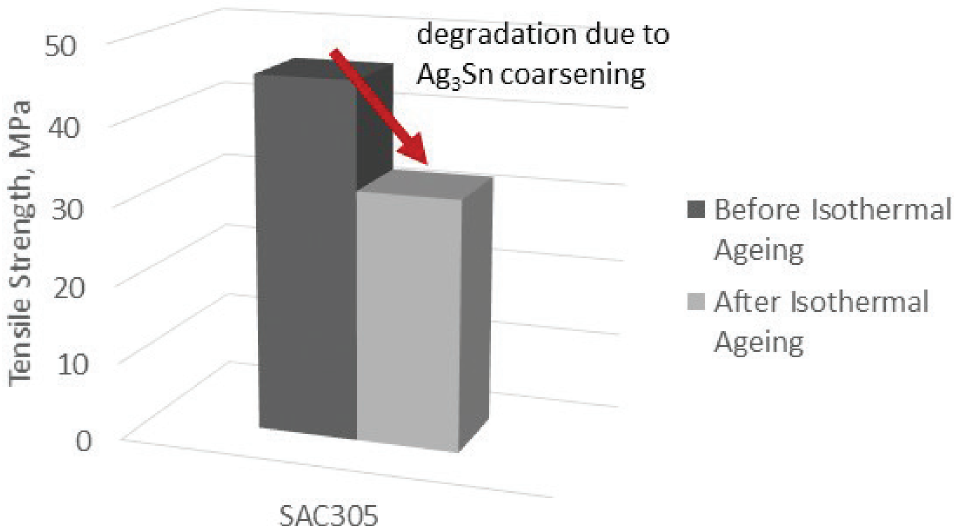

Figure 6. Tensile strength of SAC305 before and after isothermal aging at 150°C for 500 h.

such as the electronic system in a car or air plane. As mentioned in Section 1, the growth of auto electronics industry is very aggressive recently. This industry demands high reliability and zero defect electronic components. There are some original equipment manufacturer (OEM) parts that have long guaranteed product life ranging from 10 to 15 years. This is the reason why in some of the automotive applications, the SnPb-6337 is still being used. Since Pb-free soldering is getting pervasive even in these kind of high-end applications and SAC305 is still the most common Pb-free alloy, which apparently cannot fulfill the high reliability requirement of such applications, great driving force arises to drive solder manufacturer and researchers to identify new solution of Pb-free alloy.

Besides the Ag_3Sn coarsening, the homologous temperature of solder system becomes greater due to higher application environment temperature. In order to keep the strength especially in fatigue, solder with lower homologous temperature is needed. The under-hood electronic components are a good example of this case. It has further justified the need of new alloy to support future electronics reliability needs.

There are consortiums and nonprofit organizations such as Universal's Advanced Research in Electronics Assembly (AREA) Consortium and International Electronics Manufacturing Initiative (iNEMI) gathering the experts of solder to jointly identify new Pb-free alloy in solving the issues mentioned above [6]. This new alloys are named as third generation of Pb-free alloy, which has superior performance in both thermal fatigue resistance and drop impact resistance to fulfill the high demand of solder joint reliability. **Figure 7** summarizes the evolution from first generation to third generation of Pb-free alloys.

Apparently, more strengthening of Pb-free alloys is required in order to improve the strength. As discussed earlier, SAC alloys are using particle strengthening technique in enhancing the alloy strength. The main enhancement is coming from the dispersion of Ag_3Sn IMC in tin matrix. Definitely, more Ag can be added to make the alloy modulus higher, but it will increase the possibility of Ag_3Sn platelets formation. Besides that, the high Ag-bearing Pb-free alloy has lower drop impact resistance. High Ag content in the alloy system will add more burden to the material cost too. Therefore, other approach is needed.

Solid solution strengthening is one of the options in strengthening the Pb-free alloy. In fact, solid solution strengthening had been widely applied during the SnPb soldering era where the Pb is added into Sn to improve the alloy characteristics. Somehow, this technique was not

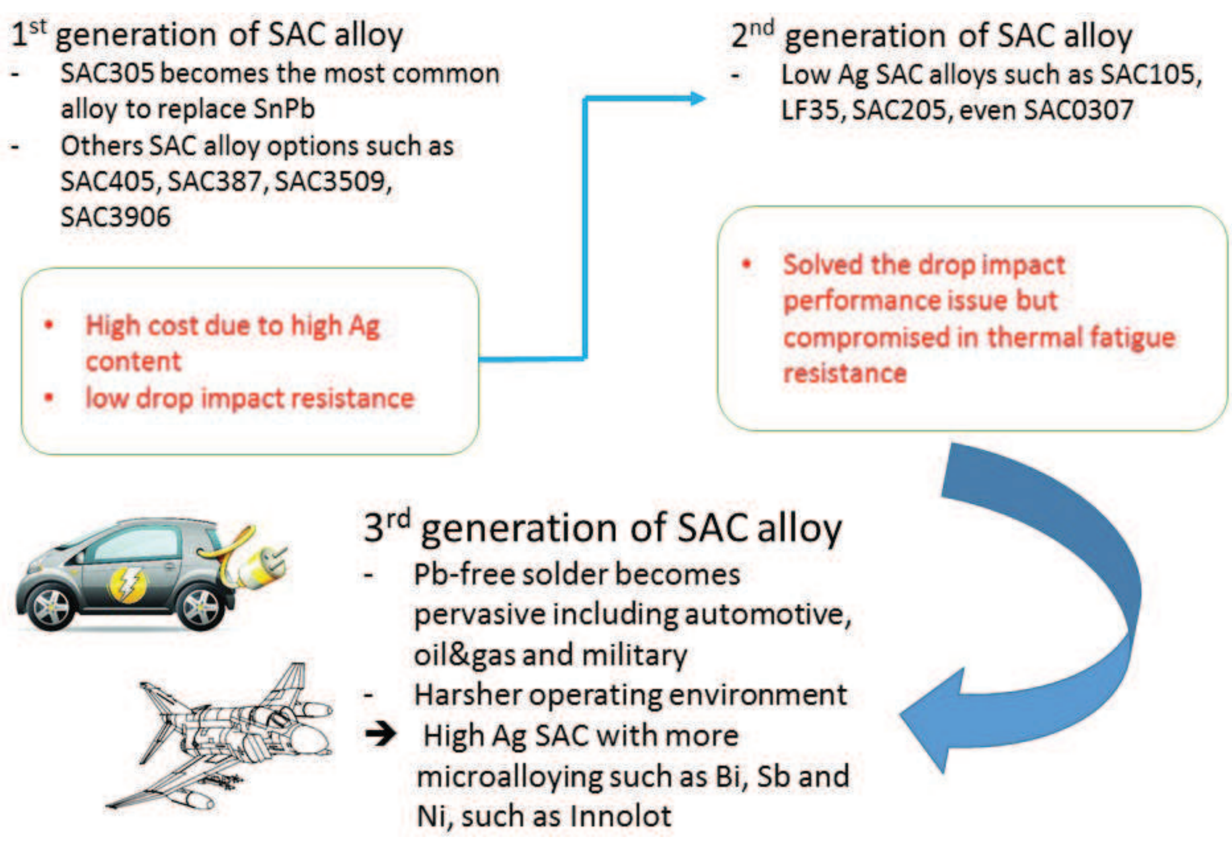

Figure 7. The evolution of Pb-free alloys from first generation to third generation, high reliability alloy for harsh use condition.

common during the conversion from SnPb to Pb-free soldering. In Pb-free alloys, the Cu and Ag are added to tin, separately or together, to make the most widely used SAC alloys, which have almost no solubility in the β-tin matrix. The Cu and Ag appear in the microstructure only as the intermetallic compounds, Ag_3Sn and Cu_6Sn_5 as discussed earlier. Surely, Pb cannot be considered again as solute in solid solution strengthening because of the RoHS compliance. Other solutes should be considered to achieve this objective, for example, Bismuth, Bi; Indium, In; and Antimony, Sb. These three substances are the most common and possible candidates selected by the solder manufacturers and researchers in enhancing the strength of Sn-based Pb-free alloy. Bi and In can decrease the liquidus of Sn-based alloy but Sb can increase the liquidus. It depends on the requirement of end application. If a solder alloy with lower homologous temperature is needed, microalloying with Bi or In may not be appropriate. However, Sb is a banned or restricted used substance in some applications such as mobile and consumer industries. It has limited the use of this substance for microalloying to improve the solder strength.

In early period of Pb-free soldering adoption which was about 2006, there was a working group formed to develop a more robust Pb-free alloy for automotive industries. Since then, the industries understand the need of a stronger alloy for future auto electronics requirement. This working group members include Siemens, Bosch, Heraeus, Alpha Metals, Infineon, the Fraunhofer Institute, and etc. 90iSC was the outcome of this group's effort. The 90iSC is a high Ag SAC alloy with addition of Bi, Sb, and Ni. It is a very complex system in which the characteristics and reliability cannot be fully understood and assessed. Solder manufacturers such as Nihon Superior has adopted a simpler approach by just micro-alloying Bi into SnCuNi system in order to achieve a stronger alloy. It is SN100CV®. Without the Ag addition into SN100CV®, the worry of alloy degradation due to Ag_3Sn coarsening can be lifted. Many users may still be skeptical on the Pb-free alloy without Ag addition. They are worrying about the strength of this Ag-free Pb-free solder. In fact, the solid solution strengthening with Bi addition is even more effective in increasing the tensile strength of the alloy. For example, in the SN100CV®, the 1.5% Bi microalloying can significantly increase the tensile strength of the SnCuNi alloy and make it even higher strength when comparing to SAC305 which containing 3% Ag. **Figure 8** is the comparison of tensile strength of three alloys, which are SnCuNi (SN100C®), SnCuNiBi (SN100CV®), and SnAgCu (SAC305).

Besides the as-cast comparison, the three different alloys shown in **Figure 8** have been subjected to thermal aging at 150°C for 500 h. After the thermal aging, tensile strength data were collected. As expected, there is significant degradation in strength for SAC305 sample due to the Ag_3Sn coarsening. The drop in tensile strength for both SnCuNi and SnCuNiBi is minimum. **Figure 9** summarizes the comparison data after thermal aging.

However, choosing a right ratio of Bi into SnCuNi system is challenging. If too little of Bi added, the effect of solid solution strengthening is negligible. But if too much of Bi added, precipitation of Bi out of β tin will occur. **Figure 10** shows the tensile strength of different alloys before and after thermal aging at 150°C for 500 h.

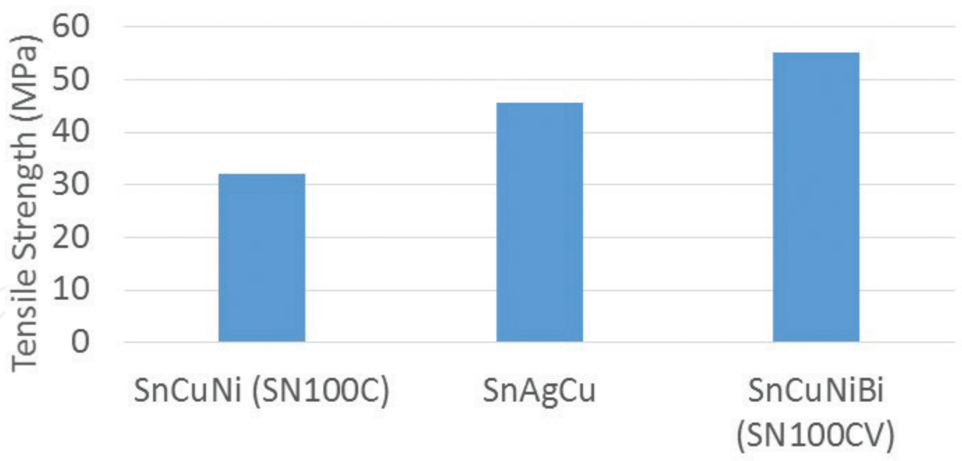

Figure 8. Tensile strength comparison for three alloys in as-cast condition.

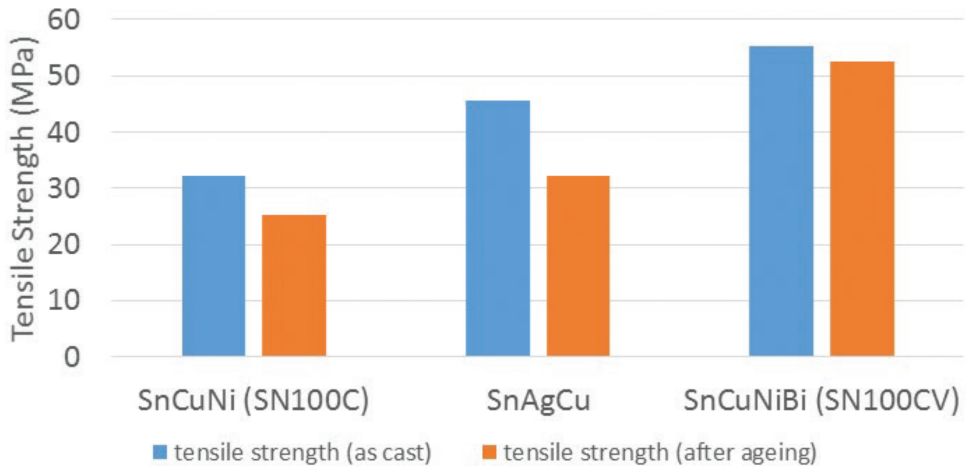

Figure 9. Tensile strength comparison for three alloys in as-cast and after thermal aging.

3.2. High reliability solder alloy for die attach

Solder usage is not limited to the interconnects between electronic components and PCB at the PCBA process. Within the electronic components such as integrated circuit (IC), solder has been used as die attach material especially in the device where there is a need of high thermal and electrical connectivity between the die backside and lead frame or substrate. This kind of IC includes the high power devices and high speed switches such as Power MOSFET, insulated-gate bipolar transistor (IGBT), high power diode and transistor, rectifier, and inverter. Due to high operating temperature of such IC, which is usually above 260°C, the industries are still exempted from RoHS compliance, and they are still using the high Pb solders such as Pb5Sn and Pb5Sn2.5Ag in die attach process. It is because the conventional Pb-free Sn-based alloys have melting point lower than 260°C. The RoHS committee allows another 5-year extension for this exemption in 2016 because of technical limitation with current technology. So far, there is still no straightforward drop-in solution in replacing the high Pb solder for such application.

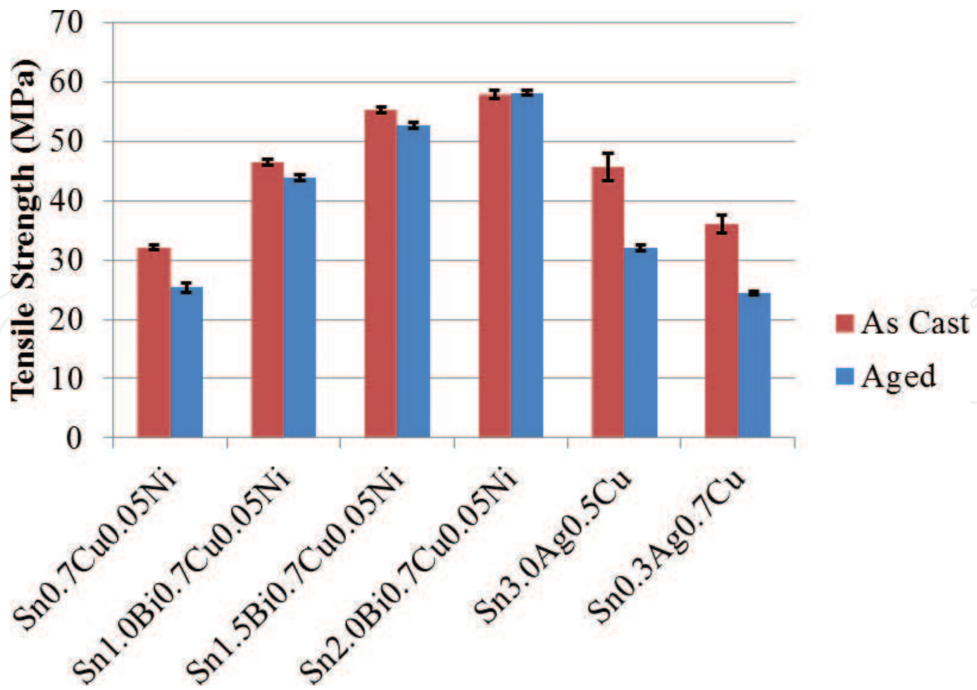

Figure 10. Tensile strength of test alloys as-cast and after thermal aging at 150°C for 500 h.

Since most of the Sn-based Pb-free alloys have solidus lower than 260°C, other Pb-free alloys such as gold tin (AuSn), bismuth silver (BiAg), and zinc aluminum (ZnAl) are being considered as candidates to replace the high Pb solder, which is the current high-temperature die attach material. However, there are some limitations in these alloys which the manufacturers need to overcome before the mass adoption is possible. The limitations include high cost (AuSn), low thermal conductivity, poor wettability (BiAg), and low workability due to brittleness (ZnAl). Indium Corporation has innovatively improved the characteristics of BiAg to make it more user-friendly product for the die attach process. To improve the wettability of BiAg, this company has introduced a solder paste consists of two types of solder powder. The first type is the major powder which is the BiAg and the minority powder which is the additive powder. The additive powder has lower melting point than BiAg and better wettability on common soldering pad. The additive powder can be the familiar SnBi eutectic, SAC alloy, or SnAg alloy. In the reflow process, the additive powder will melt first and react with soldering pad then follows by the melting of majority powder which is the BiAg. It is an irreversible process because the minority powder will be fully consumed or reacting with the majority powder during the reflow process. The joint formed using this solder paste will have similar properties as the BiAg, which is the majority part of this solder paste. More studies are required to assess the suitability of this solder paste in replacing the high Pb alloy. The solidus of BiAg is still lower than the high Pb solder. Therefore, the homologous temperature is different for these two solders.

Besides solder alloys, the industries are also working actively to develop sintering material to replace high Pb solder. The driving force to develop sintering material is not only to replace the existing high Pb solder but also to prepare a solution for future application. Based on the power IC roadmap, the IC operating temperature can go up to as high as 600°C especially for the silicon carbide (SiC) die. With such high operating temperature, it will be a challenge for conventional solder alloy. Sintering is an atomic diffusion process. Heat and pressure can be applied to accelerate this diffusion process. The atoms in the powder particles diffuse across the boundaries of the particles, fusing the particles together and creating one solid piece (bulk material). In other words, a lower process temperature than the material melting point is required to complete the sintering process. In sintering process, there is no melting involved. The joint formed after sintering will have the characteristics similar to the bulk material. Since Ag is the most common major ingredient for sintering material, the joint formed with Ag sintering material will re-melt only when the temperature exceeds the Ag melting point which is 961°C. This is the main attraction of Ag sintering material to be used in this application. In fact, the industries had explored Ag sintering material in 1980s. But, it still required high sintering temperature and pressure to complete the process during that period of time. It made the acceptance of this material low. With the recent development of nano Ag particle, the sintering process can be completed within an acceptable sintering temperature range. Nihon Superior has developed a Ag sintering paste, Alconano®, which has demonstrated good quality of silver joint at die attach layer with sintering temperature as low as 200°C. This is only possible because of the nano size Ag particles which have high surface energy. The challenge of manufacturing Ag sintering paste is not only in producing the Ag particles, but also in the development of right passivation system to keep the particles in good condition until the sintering process starts. Alconano® has utilized alcohol as the passivation system, which forms alkoxides with silver atoms on the surface of the nanoparticle. The advantage of these chemicals in this application is that the oxygen-silver bond, which is strong enough to stabilize the nanoparticle during manufacturing processes and subsequent storage and handling, is weak enough that it can be broken at a relatively low temperature to expose the active surface of the nanoparticle so that it can bond to adjacent particles. Another advantage of using alcohol as the passivation system is it leaves no harmful residue behind after the sintering process. The residue is free from sulfur and nitrogen compounds that can interfere with the performance of the sintered silver and contribute to corrosion problems in service. The challenge of mass adoption of Ag sintering paste does not limit to paste manufacturing only. Application of this paste at die attach process is also challenging. Many engineering works are required in developing an appropriate set of process parameter. Sintered Ag joint is a porous layer. In fact, this porosity is necessary to make the Ag be a reasonable die attach joint. Bulk Ag joint without any porosity could be too rigid to support the IC architecture. In such case, die crack will be the most prominent defect in the field. Getting a right properties of this Ag joint should be a joint effort between the user and supplier. One of the wonder of this Ag sintering paste is the porosity can be adjusted via sintering process. By varying the pressure and temperature during sintering, different range of porosity can be achieved. **Figure 11** shows an example of Ag sintered joint of Alconano® with porosity less than 10%. This joints were formed with pressurized sintering parameters: 10MPa, 300°C and 5 min sintering time. The consistency of porosity percentage is satisfying. Besides satisfying the processibility, the reliability of joint made of this Ag sintering material must be on par or even better than the performance of high Pb solder. There are two main characteristics of such die attach material, which the users are emphasizing. They are thermal conductivity and electrical conductivity of the joint. Based on a recent industry wide survey on Pb-free high-temperature die attach material, thermal conductivity stands out to be the most required property for this material [7]. It is crucial to keep high thermal conductivity throughout the entire product life. In some cases, the joint has degraded thermal conductivity due to the thermal fatigue crack within the joint especially in hot and cycling atmosphere. Therefore, in developing the Alconano®, Nihon Superior has compared the performance of Alconano® versus the high Pb solder and conventional SAC solder after exposure to thermal cycling reliability testing, −40°C/+200°C with dwell time of 30 min. The comparison results are shown in **Figure 12**.

Pb-free liquid-phase diffusion bonding (LPDB) material is another emerging material, which can potentially be used as high-temperature Pb-free die attach material. The bonding process of this LPDB is very similar to the modified BiAg paste mentioned above. Similar to the modified BiAg paste, the LPDB paste consists of two types of powder, high melting point and low

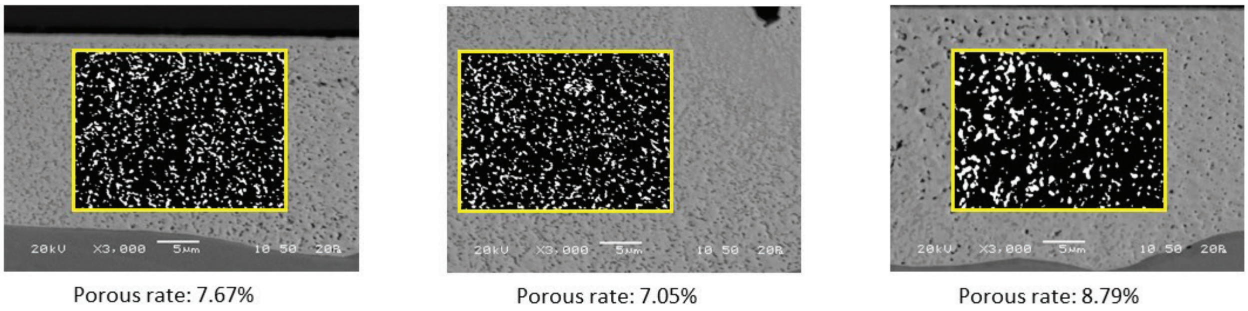

Figure 11. Porosity check after pressurized sintering on Ag sintering joint.

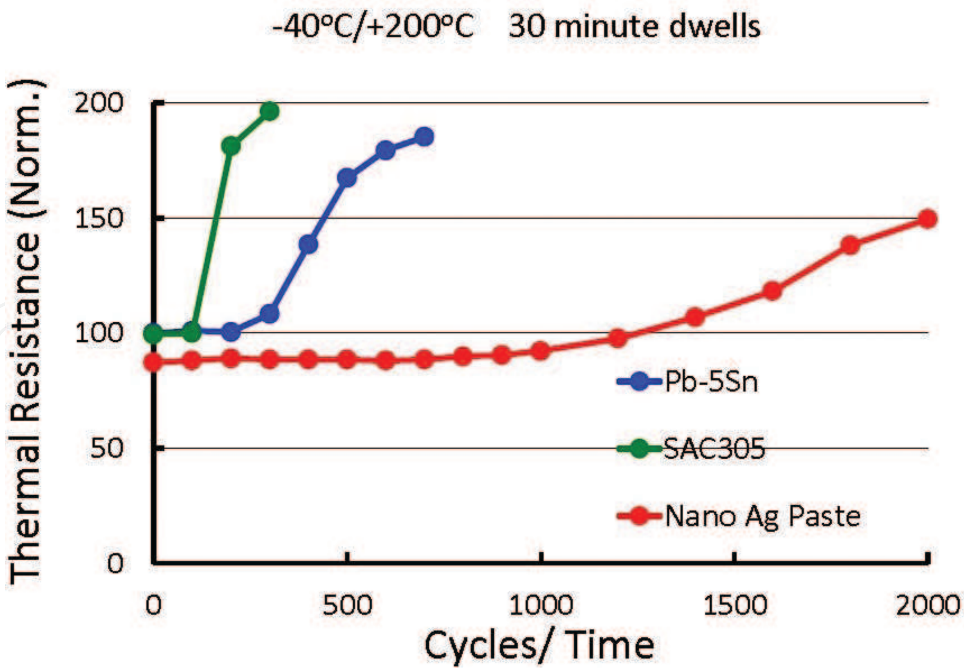

Figure 12. Change in thermal resistance of high temperature die attach material in a function of thermal cycling. 10×10 mm silicon die on Al_2O_3 substrate with Cu plate heat sink was used as test vehicle. The sintering condition was 300°C, 40MPa pressure assisted and 3 min sintering duration.

melting point. Unlike the modified BiAg paste where both types of powder will melt during the bonding process, the high melting point powder of LPDB will never melt during the bonding process but only the low melting point powder will melt and react with soldering pads and simultaneously react with the high melting powder to form a new IMC. During the bonding process, homogenization of the molten occurs. IMC will be formed because of the reaction between the molten low melting point powder and high melting point powder. And, this newly formed IMC has much higher melting point than the low melting point powder. Therefore, the molten will start to solidify even before the cooling starts due to the change of melting point. After the bonding process, the joint will only remelt at a temperature higher than the bonding temperature. This is why this material is also called transient liquid-phase diffusion bonding material. Nihon Superior Co., Ltd. has participated a project run by Ames lab from Iowa State University in developing this LPDB material. Ames lab is mixing the high melting point Cu-10Ni powder into the commercial SN100C® fine powder to make this LPDB material. The bonding process will transform all SN100C® powder into high melting point $(Cu, Ni)_6Sn_5$ IMC which will only remelt at 525°C [8]. This is a very important characteristic to make it a potential high temperature Pb-free die attach material. Moreover, the Ni addition into Cu_6Sn_5 has significantly improved the properties of this IMC. It has made it a more robust joint because the Ni has inhibited the polymorphic transformation of the allotropic Cu_6Sn_5 as discussed earlier in this chapter. According to Choquette and Iver [8], the Ni addition into Cu_6Sn_5 should improve the ductility and strength of the joint as well. This LPDB material can be a potential drop-in solution in replacing the high Pb solder because it can complete the bonding at conventional reflow temperature (240–260°C), but it will only re-melt at 525°C.

4. Conclusion

Due to RoHS compliance, electronic industries have stopped adopting the stable and familiar SnPb-6337 solder, which was used as electrical interconnect for decades and migrated to Pb-free solder. There are many developments of Pb-free solder with the objective to fulfill the manufacturability and reliability expectation from the users. This kind of development has flooded the market with many alloy compositions and increased the difficulty for user to select a right Pb-free alloy, which can meet their expectations. Since 2006, generally, there are three generations of Pb-free solder being introduced into market. The first generation of Pb-free solder is the conventional SAC alloy with high Ag bearing ranging from 3.0 to 4.0%. Then, the market is moving into low SAC alloy due to the surge of Ag price in early 2010s and the poor drop impact resistance of these conventional SAC alloys. Recently, due to the aggressive growth of auto electronics and avionics, a new set of requirement in term of solder joint reliability is defined against the Pb-free solder. This is the third generation of Pb-free alloy, which is an alloy system catering for long thermal fatigue life and robust in drop impact resistance. On the other hand, there are still many IC and electronic components still adopting high Pb solder (soft solder) as die attach material. The industries are actively looking for Pb-free alternatives to replace it. Alloy systems such as AuSn, BiAg, ZnAl, Ag sintering material, and LPDB material are the potential candidates on the list.

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