High-temperature solder alloys are extensively used in die-attach, power semiconductor, and optical device packaging, flip-chip packaging, etc. Current industry standard solders for these applications are mainly high-lead solders (90–97 wt-% Pb) and gold-based eutectic solder alloys such as the 80Au20Sn solder.

The die-attach process involves connecting the silicon die or chips to a lead frame or other substrate with the use of adhesive bonding or solder joining. Soldering is a preferred method for die attach to a lead frame for power devices because of the higher current-carrying capability and better thermal conductivity of a solder alloy than an adhesive. The latter feature proves to be beneficial in dissipating the heat generated by the device.

The solders used for die attach usually have a liquidus temperature of 280°C or higher to allow subsequent mounting of the packaged devices on printed circuit boards, which is done with eutectic SnPb or lead-free SnAgCu (SAC) solders by reflow soldering at a temperature of 200° to 250°C. The most widely used solders for die attach are the high-Pb alloys, e.g., 95Pb5Sn, 88Pb10Sn2Ag, and 92.5Pb5Sn 2.5Ag. However, Pb is poisonous, and is banned in many applications. Although the high-Pb solder alloys for the first level packaging applications are exempted from the current Restriction of Hazardous Substances (RoHS) regulations because of the lack of a reliable replacement for them, the conversion to Pb-free materials in these areas will eventually be implemented.

The Pb-free eutectic Au-Sn (280°C), Au-Si (363°C), and Au-Ge (356°C) alloys can be used as die-attach solders, but the cost is too high. Although other high-temperature lead-free solders in the Sn-Sb, Bi-Ag, Zn-Sn, and Zn-Al systems are also known to be candidates, each has its own drawbacks (Refs. 1, 2). For example, the solidus temperatures of Sn-Sb and Zn-Sn alloys are too low. The Zn-Al alloys are highly corrosive and easily oxidize, while the Bi-Ag alloys have brittleness and low thermal and electrical conductivity issues.

In view of the foregoing, it would be desirable to develop an alternative Pb-free soldering material and process for high-temperature soldering applications, especially for die attach in power semiconductor packaging.

In this work, based on the principles of transient liquid phase (TLP) bonding (Refs. 3–6), a special laminate composite preform has been developed for high-temperature, Pb-free soldering applications, where a melting temperature of 280°C or higher is required. The composite preform is composed of a high-melting, ductile metal core layer and a low-melting solder coating layer at both sides of the core layer. During soldering, the liquid solder layer reacts with the core metal and the substrate materials to form high-melting intermetallic com-
pound phases (IMCs) and consume the low-melting solder phase rapidly. The resultant solder joint is composed of a ductile core layer sandwiched by the IMCs layers at both sides. As shown in Fig. 1A, a composite preform consists of an Ag or Ag-based metal core layer with Sn-Ag based solder layers at both sides. After the composite preform is placed between two substrates (such as between the metallized die and the lead frame), as shown in Fig. 1B, with a suitable amount of flux applied when necessary, the assembly is reflowed in an oven with an appropriate reflow profile (critical parameters being peak temperature and time above the liquidus of solder) with respect to the composition and thickness of the Sn-Ag-based solder layer used.

The reflow peak temperature and time above the liquidus (TAL) of the solder are selected so that after reflow soldering the Sn-Ag-based solder layer is completely converted into a Ag-Sn intermetallics (IMCs) layer in addition to a Cu-Sn IMCs layer, in the case of Cu being the substrate, at the interface between the Cu substrate and the composite preform, as shown in Fig. 2. The solder joint formed this way has a composite IMCs/Ag/IMCs laminate structure consisting of alternating hard-layer (IMCs) and soft-layer (Ag metal), which increases the strength of the solder joint while maintaining the resistance to brittle fracture.

The Ag-Sn IMCs have melting temperatures of 480° up to 724°C, depending on the composition of intermetallic phases formed, as shown in the Sn-Ag binary phase diagram — Fig. 3. The Cu-Sn IMCs have melting temperatures of 415°C (Cu6Sn5) to about 700°C (Cu3Sn). Therefore, the solder joint formed has a remelt temperature much higher than the melting temperature of the starting solder layer (221°C).

Unlike the conventional TLP bonding process, the solidification reaction in the present soldering process with the composite preform takes place as a result of intermetallics formation via wetting, substrate metal dissolution, and liquid diffusion stages of interactions among the liquid solder, core metal, and substrates. The functions of the core layer in the composite preform include accelerating the consumption of liquid Sn phase during isothermal solidification in the reflow soldering process, improving the ductility and fracture toughness in the final composite joint, and providing support for the outer thin solder layers. These can be provided by a high-melting, ductile metal that has a high rate of reaction with Sn to form intermetallic phases with a melting temperature of 280°C or higher. The solder layers in the composite preform provide a transient liquid phase that is converted into high-melting intermetallic phases upon interactions between the liquid phase and the core metal, and substrate metals in the solder joint during the reflow soldering.

**Preparation for the Experiment**

An Ag ribbon 25 to 80 μm thick was used as the core layer in a laminate composite foil in this work. The ribbon was coated with a Sn3.5Ag eutectic solder layer at both sides by different methods, e.g., dip soldering, electroplating, or roll cladding. Various thicknesses of Sn-Ag solder layers ranging from 5 to about 30 μm were obtained by controlling the processing conditions of the coating process. Preforms of different sizes, primarily of ¼-in. square, were then made from the laminate composite foil by punching. An example cross-section micrograph is shown in Fig. 4 for each of the composite preforms made by dip soldering and electroplating, respectively.

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**Fig. 1** — Schematic representations of a laminate composite preform and the assembly to form a solder joint between two substrates.
A very thin intermetallic layer, about 1–1.5 μm thick, can be seen at the interface between the Ag layer and the solder layer coated by dipping. Commercial purity (CP) Cu coupons 15 mm (long) by 12 mm (wide) by 0.6 mm (thick) were used as substrates to be joined. Silicon dies ¼-in. square by 0.4 mm thick have also been used as components to be joined to Cu or direct bonded copper (DBC) substrates. The Si die has a metallization layer structure of Ti/Ni/Ag, with approximate thickness of Ti 0.1 μm/Ni 0.2 μm/Ag 0.8 μm.

The Cu substrates were first cleaned for 2 min in 10% HBF₄ acid, then rinsed with deionized water, and finally cleaned with isopropyl alcohol (IPA). The preforms were simply cleaned with IPA. The substrates were printed with a rosin mildly activated (RMA) flux of the preform size at the center of the surface to be joined. A piece of composite preform was sandwiched between the two fluxed substrates or between a component and the substrate. A pressure of zero (no pressure) to about 0.3 MPa was applied on the sample. The sample was then placed in an infrared (IR) reflow oven, heated to a peak temperature of approximately 300°–380°C for about 5 to 9 min above the liquidus temperature of 221°C, then cooled. The reflow soldering was conducted in N₂ atmosphere. Fluxless soldering was also tried in the same reflow oven in a N₂ atmosphere.

Following the standard cross-sectional metallographic sample preparations, the microstructures of solder joints with composite preform were investigated by light optical microscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDS) analysis. Microhardness measurements of some phases in solder joints were conducted using a Vickers indenter under a 10-g load. The Vickers hardness number (VHN) was reported as an average value of 8 indentations. The remelt temperatures of selected soldered joints were investigated by using differential scanning calorimetry (DSC). Samples for DSC analysis were prepared by grinding off most of substrate metals in the Cu-Cu soldered joints and then punching out small pieces of the joint. Differential scanning calorimetry tests were performed at a heating rate of 10°C/min, scanning from room temperature to
450°C in a TA Q2000 differential scanning calorimeter. The voiding in the solder joints was examined by X-ray inspection.

To evaluate the tensile strength of solder joints, two Cu bars with a ¼- × ¼- in. cross-sectional area and a length of 1 in. were joined with a composite solder preform under the processing conditions described above. A graphite mold was used to facilitate the assembly of samples and pressure application. For comparison, similar Cu-Cu butt joints were soldered using Au-Sn eutectic solder preforms of ¼ in. × ¼ in. × 50 μm thick under a reflow peak temperature of 320°C and TAL of 1.5 min. The tensile tests were performed at a strain rate of 1×10⁻³ s⁻¹. For reliability evaluation, temperature cycling (TC) tests were conducted in air with a cycling temperature range from –55° to 125°C and a dwelling time of 5 min at each extreme temperature (45 min per cycle).

Two types of samples were made for the TC tests. One type was the ½- × ½- in. Si die joined to a DBC substrate with the composite preform. In another type of sample, an alumina substrate with Ag-Pt thick-film pads was used to join to Cu coupons with the composite solder preform to produce solder joints for TC tests. The tested solder joints in the TC chamber were periodically checked at an interval of 100 cycles for any separation or failure.

**Evaluation of the Test Results**

**Microstructures of TLP Bonds with Composite Preform**

Figure 5 shows the light optical micrograph (Fig. 5A) and SEM back-scattered electron (BSE) micrograph (Fig. 5B) of a solder joint made with a composite preform between two Cu substrates after reflow soldering with a peak temperature of 380°C and TAL of about 9 min. The solder joint has a total thickness of about 100 μm, with a remaining Ag core layer at the center and two layers of intermetallic phases at each side of the joint. The two layers of intermetallic phases have an average thickness of 16 μm (adjacent to the Ag layer) and 3 to 4 μm (adjacent to the Cu substrate), respectively. The thick, Ag-Sn intermetallic phase layer and the Ag layer have a very slight difference in contrast in the back-scattered electron micrograph. Quantitative energy dispersive X-ray spectroscopy (EDS) analyses indicated that the Ag-Sn intermetallic phase...
formed has a composition which corresponds to the \( \zeta \) phase in the binary Ag-Sn phase diagram — Fig. 3. The thin Cu-Sn IMC phase formed adjacent to the Cu substrate in Fig. 5 was identified to be Cu$_3$Sn by the EDS analysis. As can be seen, a fully “isothermally-solidified” joint (i.e., without remaining low-melting solder phases) with the microstructure features described in Fig. 2 was achieved. The thickness of the Ag-Sn intermetallic (\( \zeta \) phase) layer is much larger than that of the Cu$_3$Sn layer, which indicates that the reaction rate of Ag and the liquid solder is significantly higher than that of Cu and the liquid solder.

The microhardness measurement results showed the Ag-Sn intermetallic layer (\( \zeta \) phase) has an average Vickers hardness of 215 VHN, while the average value for the Ag layer in the TLP joint is 80 VHN. The Ag layer in a starting composite preform has an average Vickers hardness of 124 VHN. The Cu-Sn intermetallic layer is too thin to be measured by microhardness testing in the present work. However, Cu$_3$Sn and Cu$_6$Sn$_5$, IMC phases were reported to have a Vickers hardness of 343 and 378 VHN (Ref. 8), respectively. Compared to the Cu-Sn intermetallics, the Ag-Sn intermetallic phase has a much lower hardness value, and thus tends to be more ductile. As shown in Fig. 3, the \( \zeta \) phase with a close-packed hexagonal crystal structure is stable over a wide composition range from 12.8 to 19 wt-% Sn at room temperature. Intermetallic compounds that are stable over a range of compositions tend to be moderately ductile and, therefore, have a benign effect on joint properties (Ref. 9). Figure 6 shows the microstructure of a solder joint made under similar reflow soldering conditions but with a composite preform of slightly increased solder layer thickness between two Cu substrates. As the solder layer thickness increased to about 20 \( \mu \)m, heterogeneous intermetallic phases were found in the solder joint. As shown in Fig. 6B, a light-gray phase exists between the dark-gray Cu-Sn IMC phase and the white Ag-Sn intermetallic phase. This intermetallic phase was also seen to penetrate into the grain boundary area of the Ag-Sn intermetallic phase.

Figure 7 shows the representative EDS spectra of the three intermetallic phases observed in Fig. 6B. Quantitative analyses of the spectra, combined with the phase diagram examination, demonstrated these phases to be the \( \zeta \) phase (white), Cu$_8$Sn$_5$ (light-gray), and Cu$_3$Sn (dark-gray) IMC phases, respectively. The total thickness of the two Cu-Sn intermetallic layers is only about \( \frac{1}{4} \) of
the thickness of Ag-Sn intermetallic phase layer.

With a further thicker solder layer (over 25 μm) in the composite preform, residual low-melting solder phases remained in the solder joint after soldering, as shown in Fig. 8. This joint was made with a composite preform of unequal solder layer thicknesses. The side with a thicker solder layer has a solder interface thickness of about 35 μm between the Ag layer and the top Cu substrate after soldering. In this bond line, in addition to the three intermetallic phases, an amount of low-melting solder phase was observed, which had not been converted into high-melting intermetallic phases. Interestingly, a small amount of Cu₅Sn and Cu₆Sn₅ IMC phases was also seen in the middle of this interface line. The residual low-melting phase can be converted into high-melting phases by using a higher reflow temperature or a longer TAL or a combination of both. Alternatively, the low-melting phases can be eliminated by a post-joining thermal treatment.

Figure 9A shows the light optical micrograph, and Fig. 9B shows the SEM back-scattered electron micrograph of a solder joint made with a composite preform between an Alloy 42 substrate and a Cu substrate. At the Cu side, near-fully converted intermetallic phases can be seen with only isolated residual solder “islands” in the interface line. At the Alloy 42 side, however, a thin layer of residual solder phase about 2 to 3 μm remained between the (Fe, Ni)Sn₂ intermetallic layer (Ref. 10) and the Ag-Sn intermetallic (ζ phase) layer, as marked in Fig. 9B. The thickness of the (Fe, Ni)Sn₂ intermetallic layer is thinner than that of the two Cu-Sn intermetallics, demonstrating that the rate of interactions between the liquid solder and Alloy 42 is lower than that between the liquid solder and Cu.

Figure 10 shows the microstructure of a die-attach joint made by using a composite preform with a solder layer thickness of about 20 μm and a 40-μm-thick Ag core layer. The joint was reflowed under similar processing conditions described above. Good metallic bonding was achieved between the silicon die and the composite preform as well as between the Cu substrate and the composite preform, although a small amount of residual low-melting phases can be seen in some discontinuous locations at the silicon die side. Quantitative EDS analyses indicate that the residual low-melting solder phase has a composition of 86.9Sn13.1Ag (wt-%), the Ag content of which is about 4 times that of the original 96.5Sn3.5Ag solder layer.

### Remelt Temperatures of Solder Joints

Figure 11 shows the DSC heating thermographs of samples from three different solder joints. Two samples were taken from Cu-Cu joints soldered with a composite preform reflowed with a same TAL of 8 min, but different peak temperatures, 300° and 380°C, respectively. For comparison, the third sample was
taken from a Cu-Cu joint soldered with a composite solder paste consisting of a mixture of a flux and two metal powders.

Before mixing with the flux, the two powders were blended uniformly, which had a composition of 80 wt-% Sn3.5Ag solder powder and 20 wt-% Ag powder. The total metal content in the composite solder paste was 85 wt-%. As shown in Fig. 11, the solder joint made with the (Sn3.5Ag+20%Ag) solder paste has a big endothermic peak at about 225°C (with an onset temperature being around 220°C) and a smaller endothermic peak at about 357°C.

The big endothermic peak corresponds to the melting of the eutectic phase (Sn3.5Ag), while the smaller endothermic peak results from the melting of primary solidification phase Ag3Sn — Fig. 3. The formation of the primary phase Ag3Sn is due to the dissolution of the Ag particles in the liquid solder during the reflow process. Therefore, the remelt temperature of the (Sn3.5Ag+20%Ag) composite solder paste joint is the same as the melting temperature of Sn3.5Ag solder. On the other hand, no endothermic peak can be seen in the DSC thermograph for the sample of solder joint made with the composite preform under a peak reflow temperature of 380°C.

This result demonstrates that the solder joint has a remelt temperature higher than 450°C, and no low-melting phase exists in the joint. However, a tiny endothermic peak is observed at about 220°C in the DSC thermograph for the sample of solder joint made with the composite preform under a peak reflow temperature of 300°C, which indicates that there is still a small amount of residual solder phase in the joint. Previous experimental results also showed that increasing the bonding temperature is the most effective way to eliminate the low-melting phases in TLP bonds (Ref. 4).

### Voiding in the Composite Preform Joints

One problem encountered with the use of the composite solder preform is voids in the solder joints. Figure 12 shows the X-ray images of soldered joints with a composite preform under different processing conditions. The joints made with no flux and without any pressure displayed the highest amount of voids, while those made with flux and with an appropriate pressure (0.3 MPa) had the lowest level of voids. A small pressure ensures close contact between the composite preform and the substrates for joining and reduces voids as well. Voids are generally caused by trapped gas in nonwetted areas or outgassing of flux that is entrapped in the solder joint during reflow. Another type of voids is caused by solidification shrinkage of the molten solder. When flux is used, the outgassing substance is generally generated by the evaporation of the solvent and the rheological additives in the flux that may evaporate in the heating process during soldering. Previous investigations have indicated that the reflow process, the flux, and solder material are the most significant factors affecting void formation (Ref. 11).

Figure 13 shows cross-sectional micrographs of the soldered joints with voids. In the voids caused by nonwetting or poor wetting, little intermetallic formation can be seen on the substrate, as shown in Fig. 13A. Otherwise, the relatively big voids were caused by the out-
gassing of flux entrapped in the solder joint.

In the soldering process with a composite preform, the Ag core layer remains solid during the entire reflow process and the liquid solder layer is thin, which both make the entrapped gas more difficult to escape out of the joint. The voids located in the last “isothermal” solidification regions are generally a result of solidification shrinkage or lack of enough liquid solder in the interface line, as shown in Fig. 13B. Further work is needed to optimize the joining process and composite preform design in order to reduce the voiding occurrence in the solder joints.

### Tensile Strength and Reliability of Solder Joints

Table 1 lists the ultimate tensile strengths of the Cu-Cu butt joints soldered with the composite preform under a peak temperature of 380°C and TAL of 8 min. The tensile strengths of the Cu-Cu joints made with the AuSn solder preform are also shown in Table 1 for comparison.

The soldered joints with the composite preform had an average tensile strength of 9.6 ksi. This value is lower than expected, which should be close to the strength of Ag for an ideal joint shown in Fig. 2, although it is higher than the value for solder joints with Sn3.5Ag, 8.0 ksi (Ref. 12). The defects, especially voids, in the solder joints with composite preform are believed to be the reason for the lower strength value. In comparison, the joints soldered with eutectic Au20Sn alloy preform had an average strength of 13.5 ksi. The joint strength is expected to be improved by reducing the voiding content in the solder joint through optimization of the joining process and composite preform design.

The temperature cycling tests are currently under way. No solder joint failures have been observed so far after 1850 cycles for the Si die/DBC joints soldered with a composite preform, and 1500 cycles for the Cu/Al2O3 joints soldered with a composite preform. Figure 14 shows examples of samples for each type of joints after the current number of cycles.

### Conclusions

A special laminate composite preform has been developed for high-temperature lead-free soldering applications, where a melting temperature above 280°C is required. The laminate composite preform is composed of a high-melting, ductile metal core layer and a low-melting solder coating layer at both sides of the core layer. The resultant solder joint is composed of a ductile
The microstructures in TLP joints soldered with a SnAg/Ag/SnAg composite preform were characterized. The reaction rate of Ag and the liquid solder is significantly higher than that of Cu and the liquid solder, which leads to a much thicker Ag-Sn intermetallic (\(\zeta\) phase) layer and thin Cu-Sn intermetallics layer in the TLP soldered joints. The \(\zeta\) phase with an average microhardness of 215 VHN is more ductile than other intermetallic phases. The Cu-to-Cu TLP joint soldered with the composite preform has a remelt temperature higher than 450°C. An appropriate pressure helps to ensure close contact between the composite preform and the substrates for joining and to reduce voids in the solder joint as well. The soldered joints have a tensile strength of 9.6 ksi, which is expected to be improved by reducing the voiding content in the solder joint through optimization of the joining process and composite preform design. Temperature cycling testing that is under way shows promising solder joint reliability for die-attach applications.

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