Originally published in the Proceedings of the SMTA International Conference, Orlando, FL, October 24-28, 2010

New Developments in High-Temperature, High-Performance Lead-Free Solder Alloys

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ABSTRACT

A new Lead-free electronic solder alloy that addresses the challenges of applications requiring superior lead-free solder joint reliability on both epoxy- and ceramic-based substrates is now available in a variety of forms.

The high reliability & high operating temperature Lead-free alloy known commercially as InnoRel-Innolot® is a Tin-Silver-Copper (SAC) metallurgical system with small amounts of Antimony, Bismuth and Nickel added to it. The additional elements harden the alloy and improve its creep strength. Developed by a working group of researchers that include industry suppliers, users and academic partners, this results in significantly improved reliability of solder joints at standard temperatures of 125°C (vs. SAC and SnPb) especially with ceramic chip components. Additionally, this alloy enables operating temperatures of up to 165°C, a substantial improvement over the traditional SAC alloys' peak operating limits of 125°C.

The alloy represents an excellent solution for circuit assemblies that are located under the hood of automobiles or in other similarly harsh environments, but until recently its application has been limited to Surface Mount Technology only. When applied to ceramic substrates, there is no major benefit in reliability vs. SAC alloy; therefore its usage had been limited to epoxy-based circuit assemblies.

Recent advancements in alloy composition now make it possible to improve its reliability on ceramic substrates that are metalized with thick films or direct bonded copper. Broadening its applications even further, a novel wire drawing process that enables the production of flux-cored wire for manual and automated soldering has been developed and commercialized.

This paper reviews the composition, hardening mechanisms, and performance on the alloy. It then introduces the two innovations that now make it available also for hand soldering and hybrid assembly.

INTRODUCTION

As the electronic content of automobiles continues to increase, the reliability requirements of those electronics also increase. Many sensors and controllers are mounted in areas that experience high operating temperatures, and regularly fluctuate between hot and cold extremes. The demands of harsh service environments challenge the capabilities of Tin-Lead solder alloys, and are considered too harsh for traditional Lead-Free SAC alloys, which have poorer creep resistance than Tin-Lead. In response to the lack of a viable Lead-free alternative and the regulatory and supply chain pressures to remove Lead from electronic solder systems, a working group was formed to develop a solution.

The group of suppliers, users and academic researchers worked to identify a Lead-free alloy that was capable of operating at temperatures up to 165°C, melted at or below 220°C, had better creep resistance and was comparable in cost to the current Lead-free alloys, and presented no greater health or toxicity concerns than the current products. They started with a baseline Tin-Silver-Copper (SAC) 405 alloy, and considered numerous alloying elements. The resulting alloy contains additions of Nickel (Ni), Antimony (Sb), and Bismuth (Bi).

ALLOY

Composition

Each added element was selected for its ability to modify certain properties of the alloy:

- **Nickel** - is only marginally soluble in Tin and increases the alloys's strength by forming intermetallic phases with the Tin, but it also increases the melting temperature.
- **Antimony** – is soluble in Tin to increase the alloy's strength, and it slightly raises the melting temperature.
- **Bismuth** – is also soluble in Tin to increase its strength, but decreases the melting temperature enough to compensate for the effects of the Ni and Sb additions.

Table 1. Alloy composition

Alloy Composition		
Element	**Min %**	**Max %**
Sn	Balance (90.1 – 91.6)	
Ag	3.6	4.0
Cu	0.6	0.8
Ni	0.1	0.2
Sb	1.3	1.7
Bi	2.8	3.2

The alloy's composition is shown in table 1. Its melting range is 206 to 218°C. Its operating temperature can be as high as 165°C.

As with most SAC solder alloys, too much Copper or Nickel can affect the fluidity and wetting characteristics of the liquid alloy. This consideration is particularly important in wave and selective soldering processes, which typically gain Copper and Nickel as the metals dissolve from the PWB and component surfaces during processing. Additionally, mixing with Lead (Pb) solder or plating material is not advisable, as the alloy contains Bismuth. When Pb is present, a SnPbBi phase can form that has a melting temperature of 96°C. Although it is highly unlikely that this phase could form from a solder with only a 3% Bi content,[1] the formation of such a phase could weaken solder joints that experience service temperatures over 96°C. Therefore it is recommended to insure that no Lead is present on any components of the assembly.

Hardening Mechanisms

The additions of the alloying elements improve the creep resistance of the solder by one of two means: dispersion hardening and solid solution hardening.

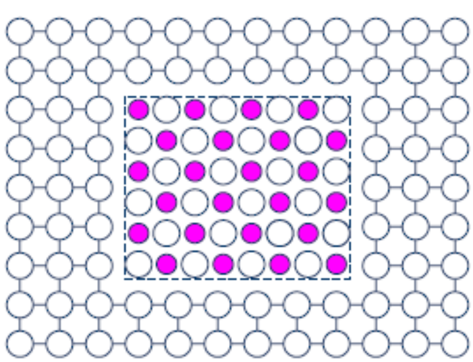

Figure 1. Diagram of dispersion hardening

Dispersion hardening, also known as precipitation hardening, occurs when elements that do not dissolve in Sn – in this case, Ni – form intermetallic phases that precipitate out upon cooling, as illustrated in figure 1.

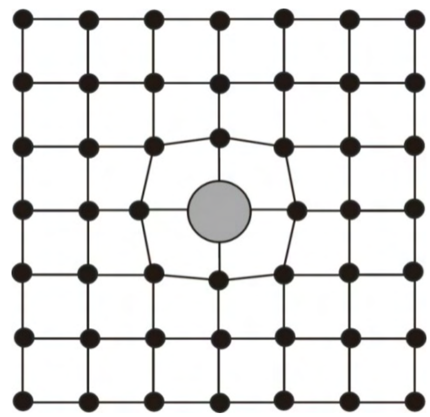

Figure 2. Diagram of solid solution hardening

Solid solution hardening occurs when the added elements – in this case, Sb and Bi – dissolve in the Sn solid solution and increase its strength, as illustrated in figure 2.

Microstructures

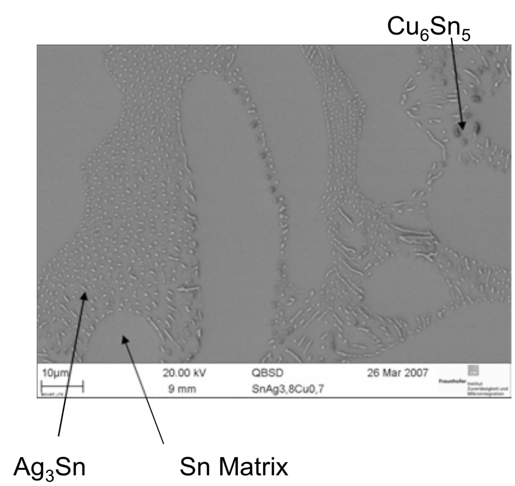

Figure 3. Typical SAC alloy microstructure

The typical SAC alloy microstructure in figure 3 shows the Sn matrix with Ag_3Sn and Cu_6Sn_5 intermetallics dispersed throughout it.

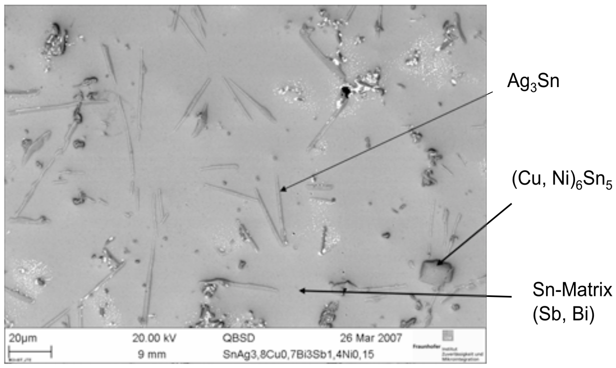

Figure 4. Modified SAC alloy microstructure

The modified microstructure seen in figure 4 shows the Sn matrix with Sb and Bi dissolved in it, along with Ag_3Sn and $(Cu,Ni)_6Sn_5$ phases.

Performance

The addition of the alloying elements improves the strength of the solder joints over SAC and SnPb alloys.

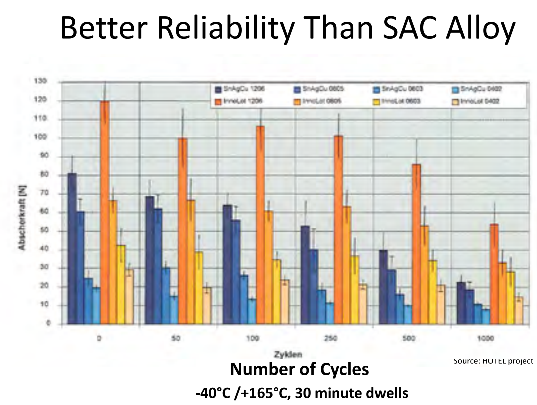

Figure 5. Comparative shear strengths SAC405 and modified alloy on ceramic capacitors after thermal cycling[2,3]

Figure 5 shows the results of shear tests that were performed on capacitors sizes 0402 through 1206 after fixed numbers of thermal cycles from -40°C to 165°C. The 6-part alloy outperforms the SAC initially, and especially after repeated cycles it continues to retain far more shear strength than the SAC alloy.

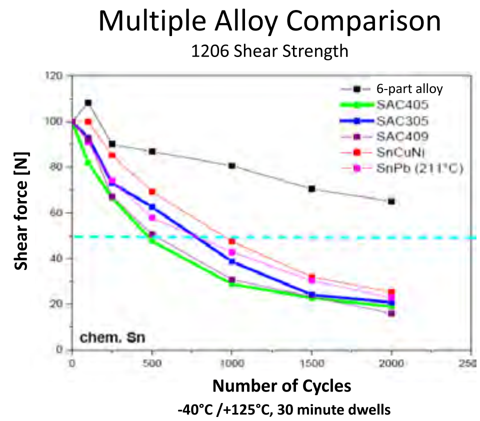

Figure 6. Comparison of shear strengths of multiple alloys on 1206 capacitors after thermal cycling[2,3]

Figure 6 shows the results of shear tests on a multitude of solder alloys. When tested with 1206 capacitors with Sn finishes, the 6-part alloy outperforms all others.

After 1000 cycles thermal cycles of -40 to +125°C, the alloy retains more than 80% of its initial solder joint shear strength, compared to 50% for the conventional SAC solders. After 2000 cycles, the alloy retains about 70% of its initial strength, compared to average 25% of SAC305, SAC405, SAC409.

SAC+Ni+Sb+Bi Summary

This alloy provides reliability improvements for applications using both standard operating temperatures and elevated ones. The reliability of solder joints connecting ceramic components to epoxy-based substrates depends heavily on the thermal expansion of the two different materials. The ceramic components have relatively low Coefficients of Thermal Expansion (CTEs), whereas the epoxy-glass PWB materials have comparatively high CTEs. When a circuit assembly is heated, the board expands a great deal more than the component that is soldered to it. The mismatch in expansion puts shear stresses and strains on the solder joints. After repeated cycles, the joints begin to show signs of fatigue, cracks begin to propagate, and the joints' initial strength degrades - sometimes to the point of complete failure.

The improved creep strength of the 6-part alloy enables it to accommodate the CTE mismatches much better than the traditional SAC alloys to which it is compared. The benefits are two-fold:

- At standard operating temperatures of 125°C, long term reliability is greatly improved.

- At elevated temperatures up to 165°C, long term reliability is now possible.

The alloy ensures proper reliability and addresses the manufacturing challenges of maintaining costs and compatibility with existing processes. It offers higher operating temperatures than Tin-Lead, slightly lower melting temperatures than typical Lead-Free solder alloys, and better reliability than both classes of solders. While it is clearly the best option for applications like under-hood automotive electronics, it still presents some challenges.

As previously discussed, mixing the alloy with Lead is a concern, but given the elimination of Lead in the supply chain and the relatively small amount of Bismuth in the solder, it is a minor concern. Other challenges associated with the 6-part alloy include sensitivity to Cu and Ni rise, impracticality in wave soldering, increased monitoring requirements in selective soldering, limitations in hand and point soldering capability, and no real benefits on the ceramic substrates of hybrid circuits. Some of the challenges can be addressed, while others will continue to remain associated with the alloy.

On wave & selective soldering, some restrictions apply, especially concerning the Ni content. The alloy contains 0.15% Ni. If this alloy is used in wave or selective soldering at temperatures above 300°C, there are no issues surrounding intermetallic formation, as they are fully dissolved in this temperature range. At lower temperatures there is a certain segregation of these compounds, depending on the concentration of the element in the alloy. At 265°C, for example, nickel contents of less than 0.7% will be stable. At concentrations greater than 0.7% however, excess Ni will precipitate into intermetallic compounds until an equilibrium status is reached.

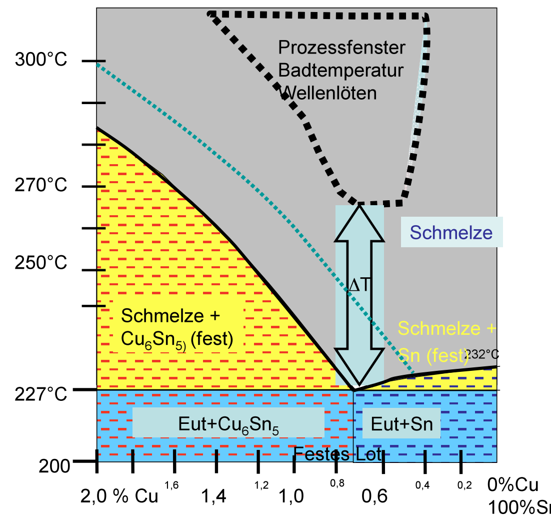

Figure 7. Tin-Copper phase diagram

The liquidus temperature of the alloy is dependent on both Nickel and Copper content. The presence of Nickel will change the alloy's liquidus temperature, shifting it as indicated by the dotted green line in figure 7.

Selective soldering with the alloy is easier than wave soldering: the lower flow of molten solder and process' precise contact areas limit the amount of Copper and Nickel that can be dissolved into the solder pot. Additionally, it is easier to keep the solder bath temperature at 300°C or higher in selective soldering, and is often typical in selective soldering processes.

Alternatively, through-hole components can be soldered by a pin-in-paste method or by hand or automated point soldering.

Hand and point soldering has historically presented a challenge for this alloy, but the development of new solder wire manufacturing methods have addressed the problems. And solutions to the problems associated with the lack of reliability improvement when used with ceramic substrates are currently under development.

FLUX CORED WIRE AND REWORK FLUX

Since its introduction in 2006, the new alloy has not been available in the form of cored wire. It is too hard to draw by traditional methods, so hand or point soldering has been performed with small "sticks" of solder. The sticks present handling and feeding issues which have hindered large-scale implementation of the alloy in production.

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A new, special wire manufacturing process has been developed to produce cored wire from the 6-part alloy. It is now available in spools with wire diameters of 12, 20 and 40mils (0.3, 0.5 and 1.0mm).

Figure 8. Cored solder wire made from 6-part Lead-free alloy

The process-compatible wire shown in figure 8 now enables:

- Standard touch up and rework operations
- Easier site redressing
- Add-on of heat-sensitive components after reflow
- Add-on of water-sensitive components after wash
- Robotic soldering operations

To further ease the integration of the new alloy system in high reliability applications, the consideration of flux compatibilities has been addressed. In addition to being halide and halogen-free, the cored wire flux uses a chemistry identical to that of the printing and dispensing solder pastes and the rework flux. The usage of the same chemistry eliminates the potential for failures like shorts or electrical leakage that occur when incompatible formulations are applied in add-on, touch up or repair operations.

CERAMIC SUBSTRATES

Comprehensive reliability testing of the 6-part alloy showed that it dramatically improves solder joint fatigue performance when used on epoxy-based circuit substrates, but did not demonstrate a significant performance improvement when used on ceramic circuit substrates.

One of the primary issues associated with ceramic circuits is the dissolution of Ag-based terminations into the solder, also known as Silver leaching. As the silver slowly dissolves into the joint, the AgSn intermetallic phase grows thicker and can embrittle the solder joints. A modification has been made to the standard SAC alloy to help control and decrease the growth of intermetallic phases, especially AgSn phases. The new alloy is called InnoRel HT1.

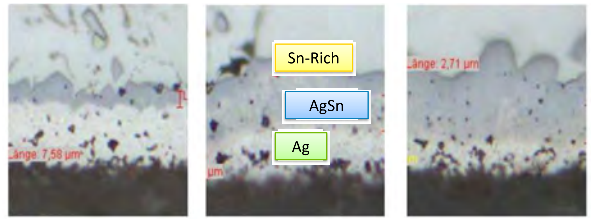

Figure 9. Growth of intermetallic region after temperature cycling -40/+150°C. Images shown from left to right are at time zero, after 1000 cycles and after 2000 cycles.

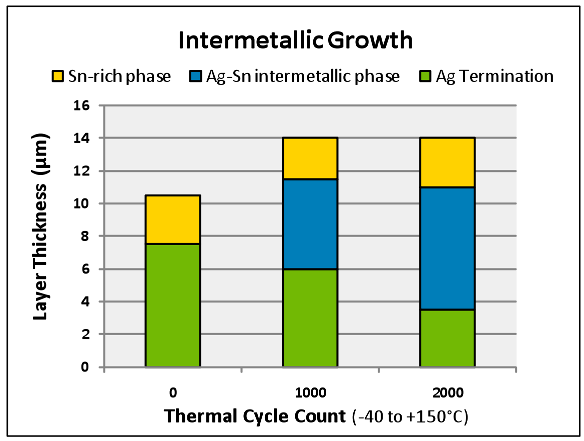

Figure 10. AgSn intermetallic growth from Silver terminations and InnoRel HT1 solders after thermal cycling.

Figure 9 shows micrographs of the alloy's solder joints' intermetallic regions after thermal cycling from -40 to +150°C. The average measured thickness of each layer is shown in figure 10. After 2000 cycles, the Ag layer thickness decreases to approximately 3 µm, whereas with an unmodified SAC alloy the Ag termination would be almost completely dissolved.

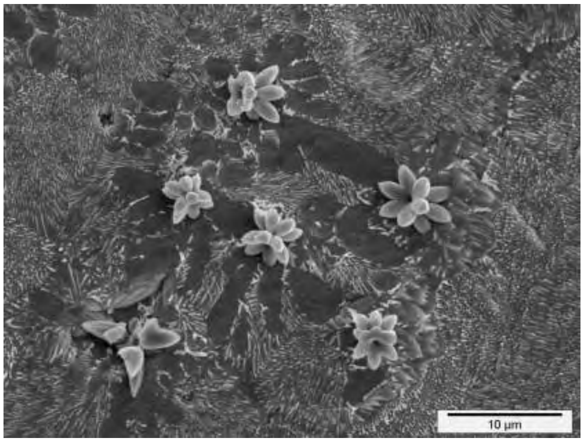

Figure 11. Microstructure of SnAgCu + In + crystal modifier with star looking phases.

The additions to the alloy include Indium (In) and special crystal modifiers. The In helps to suppress the leaching process, and the crystal modifiers help form crystallization nuclei, creating small, star shaped crystals as shown in figure 11.

Figure 12. Microstructure of SnAgCu + In

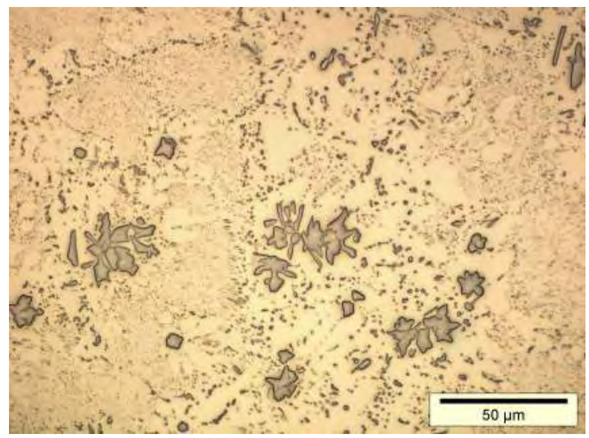

Figure 13. Microstructure of SnAgCu + In + crystal modifier

Figures 12 and 13 show the microstructures of the SnAgCu + In, with and without the crystal modifier. The influence of the crystal modifier is apparent in the differing microstructures.[3]

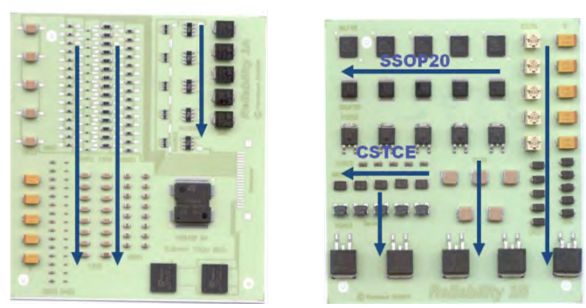

Figure 14. Test coupon for temperature cycling on hybrid substrate

The modified alloy is significantly outperforming SAC alloys in initial reliability testing on hybrid substrates (fig. 14), which includes 2000 thermal cycles of -40/+125°C and -40/+170°C. Two independent studies are producing corroborating results. Detailed evaluations are ongoing, and conclusions of the tests are not yet available at the time of publication.

The most recent advancement in the development of the new alloy is the extension of the tests to Direct Bond Copper (DBC) substrates, which are used in power electronics and hybrid and electric automobiles. Initial results in DBC applications are very promising, indicating increased reliability in power modules, motor controls, and semiconductor applications. Again, testing is ongoing and detailed results are not yet available at the time of publication.

CONCLUSIONS

The high reliability, high operating temperature Lead-free solder alloy is comprised of Sn with 3.8% Ag, 0.7% Cu, 0.15% Ni, 1.5% Sb, and 3.0% Bismuth. This alloy has great potential to outperform not only existing SAC and SnCu solder alloys in long-term reliability, but also surpasses SnPb as well. Moreover, it enables higher operating temperatures than traditional alloys, up to 165°C.

While originally deemed unacceptable for use in flow soldering systems due to its 6-part composition and the SAC family's overall sensitivity to Cu/Ni rise, the material has proven itself successful in selective soldering operations. Its overall acceptability was limited by its inability to be drawn into wire for hand or point soldering, but new wire manufacturing technology has enabled production of flux-cored wire for both manual and automated soldering. The availability of cored wire vastly improves the acceptability of the alloy, as it is now considered "production worthy" for most soldering operations.

The cored wire contains a high reliability, halide- and halogen-free flux that uses the same active chemistry as the alloy's solder paste, eliminating the electrochemical reliability concerns of mixing different flux formulations on the same assembly. A similar flux formulation is also used in the solder paste designed for hybrid circuits.

The solder paste designed for hybrids combines a member of the compatible flux family with a new generation alloy that adds Indium and a crystal modifier. The modified alloy limits silver leaching and embrittling AgSn intermetallic growth to improve the long-term reliability of solder joints on ceramic circuit substrates. Initial testing shows improved reliability over traditional SAC alloys.

Similar reliability testing has begun on DBC substrates that are commonly used in the power electronic circuits in many alternative energy vehicles. Preliminary results also indicate improved performance over traditional SAC alloys.

Introduced in 2008, the 6-part alloy provided a solution to high reliability, Lead-free SMT applications in harsh environments. Since that time, continued development efforts have produced flux-cored solder wire and selective soldering processes to support a variety of electronic assembly types. Developments in the pipeline at the time of publication include a newly modified SAC alloy to improve reliability on ceramic and DBC substrates.

REFERENCES

[1] M. Cantrell, "Japan's Best-Kept Pb-Free Secret," California Eastern Labs

[2] Consortia HOTEL publication ISBN3-934142-52-4 200

[3] Consortia LIVE publication ISBN-13: 978-3-934142-57-2

[4] J. Trodler, A. Goedecke, C. Hofmann, P. Rombach, R. Hirsch, L.C. Cheung, R. Meisenzahn, S. Widuch; W.C. Heraeus GmbH; Dr. P. Lange, E. Schall; Hella KGaA Hueck&Co.; Dr. H. Wohlrabe; TU Dresden, Zuverlässigkeitsuntersuchung auf Basis von Baugruppen für die Automobilindustrie, PLUS, Aug 2010