Presented in the ECWC 10 Conference at IPC Printed
Circuits Expo®, SMEMA Council APEX® and
Designers Summit 05

The Effect of Ni on the Microstructure and Behaviour of the Sn-Cu Eutectic Lead-free Solder

Keith Sweatman and Tetsuro Nishimura
Nihon Superior Co., Ltd.
Osaka, Japan

Abstract
While the Ni-stabilized Sn-0.7Cu alloy is now well established as a viable lead-free solder in large scale commercial printed circuit board assembly the effect of Ni is not yet fully understood. It is likely that the effect is related to the preferential incorporation of the Ni into the crystal structure of the Cu_6Sn_5 intermetallic but this effect needs to be further quantified and related to the observed behaviour in production soldering. In this paper the results of DSC and microstructural analysis are reported and the possible connection with the performance of the solder proposed. These results suggest that the Ni influences the nucleation and growth of the intermetallic with consequential impacts on solder flow and joint appearance.

The Search for a Lead-Free Solder
When, in the 1990's the electronics industry first faced the prospect of having to switch to lead-free solders the tin-copper system was one of the first considered. The advantages of this alloy system seemed manifold (Table 1). In fact if there were no other considerations the tin-copper eutectic would probably be the first choice for a lead-free solder. Tin-copper alloys had been quite widely used as a solder in the plumbing industry when lead-containing solder was banned from use in contact with potable water so there was some experience of their successful use in metal joining. Certainly from the point of view of designing a solder alloy the tin-copper system has the basic requirement: a high tin content to provide the intermetallic bond that characterises a good soldered joint and an alloying addition to improve the rather limited mechanical properties of pure tin as well as a lowering the melting point by some 5°C.

However, the primary recommendations of the industry consortia in Japan, Europe and the USA were alloys based around the tin-silver-copper eutectic. There were several factors which influenced that choice. One factor was the melting point of the tin-silver-copper eutectic (217°C), which is some 10°C lower than that of the tin-copper eutectic. At that stage in the development of lead-free soldering technology it was considered important to choose an alloy with a melting point as close as possible to that of the tin-lead eutectic it would be replacing (183°C). Another factor was that wetting balance studies indicated that a silver addition enhances the wetting properties of tin-copper alloys. Silver also increases the mechanical strength of the alloy which was considered to be a useful advantage in what was otherwise regarded as the inconvenient change to lead-free. The tin-copper eutectic was listed as a possibility for wave soldering but general relegated to low end applications.

Undoubtedly another factor contributing to the preference for tin-silver-copper alloys was that early experience with the tin-copper eutectic in production soldering processes was not encouraging. In wave soldering it was found to be difficult to get good wetting and through-hole penetration and the incidence of shorts (bridging) was unacceptably high. And to get anything like reasonable results solder bath temperatures high enough to damage laminates and components had to be used (280°C and higher).

Although on the basis of those observations and experiences the tin-copper eutectic did not seem to be very promising as a lead-free solder that could be used in the assembly of advanced printed circuit boards the advantages of the system are such that there was a strong incentive to try to improve its performance. And since one of the key advantages of the tin-copper eutectic is its simplicity any worthwhile improvement would have to be achieved without substantially changing the basic composition.

Table 1 – Advantages of the Tin-Copper Eutectic as a Lead-Free Solder

Minimal environmental impact – both raw materials readily available
Recyclability of circuitry not compromised - both constituents already present in electronic circuitry
No toxicity issues- both constituent widely used in food contact applications
Simple to manage solder bath composition – only two constituents
Good mechanical properties – stronger than tin-lead and more compliant than tin-silver-copper
A eutectic with a melting point (227°C) low enough for most applications
Relatively tolerant of lead contamination
Lowest cost raw materials

A Strategy for Turning the Tin-Copper Eutectic into a Usable Lead-Free Solder

Evidence such as that in Figure 1 suggests that the problem with the basic tin-copper eutectic is that although thermodynamically of eutectic composition it does not behave as a eutectic in practical soldering. If it were freezing as a true eutectic there would be no evidence of primary β-tin dendrites but in the microstructure of the unmodified alloy there is clear evidence of such dendrites (Figure 2). Fortunately experience in other fields of commercial alloy development provided a clue to a means of improve the properties of the tin-copper eutectic. For example, in the aluminium-silicon

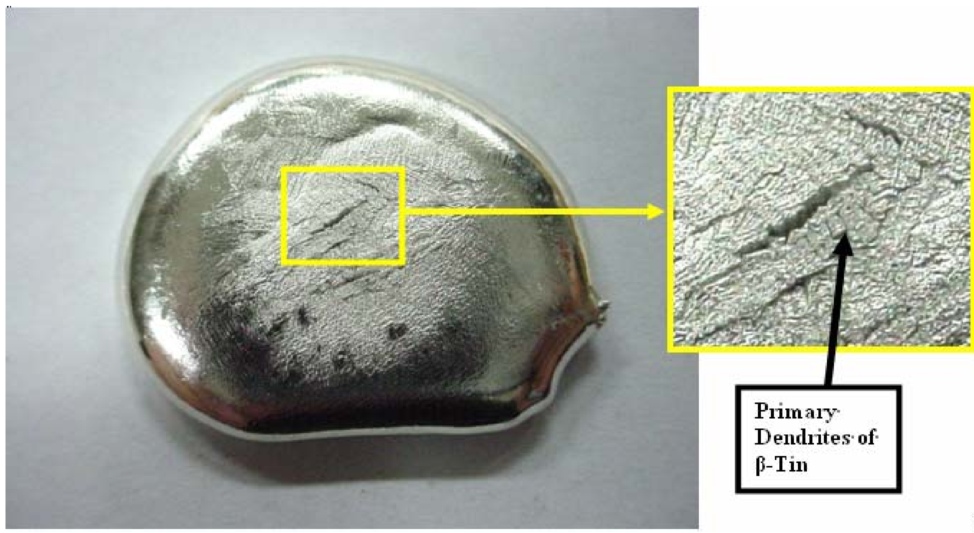


Figure 1- As Cast Structure of Unmodified Tin-Copper Eutectic

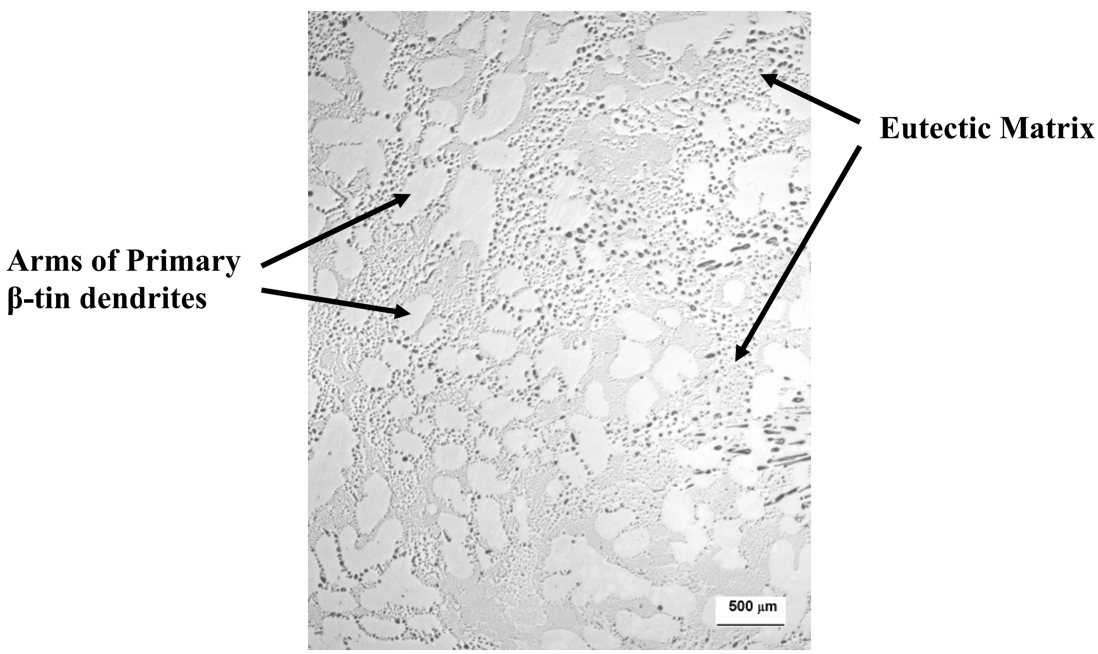


Figure 2- Microstructure of Unmodified Tin-Copper Eutectic

system there is eutectic around 12% silicon but in practical production the alloy freezes with large crystals of primary silicon and consequently inferior properties. It has been found that a small addition of sodium suppresses the precipitation of these primary silicon crystals so that the alloy freezes with a true eutectic structure, which results in properties that make aluminium-silicon a commercially successful alloy. Although the exact mechanism of the modification of the aluminium-silicon eutectic is not fully understood the fact that a trace element addition can effect such a dramatic change in the behaviour of an alloy provides some encouragement that something similar might be achievable in the tin-copper system. There is some degree of parallel between the two systems in that in both cases one of the phases in both eutectics is in some ways non-metallic in character. Whereas the phases in the tin-lead eutectic are essentially metallic tin (with some dissolved lead) and metallic lead (with some dissolved tin) one of the phases in the tin-copper eutectic is the intermetallic compound Cu_6Sn_5. Since it is likely that β-tin is freezing out as primary dendrites because the Cu_6Sn_5 phase is slow to nucleate an addition that facilitated nucleation would help the alloy freeze as a true eutectic. To be effective that addition would have incorporate itself into the structure of the intermetallic. The existence of a nickel-tin intermetallic compound, Ni_3Sn_2, with the same close-packed hexagonal structure as Cu_6Sn_5 (Figure 3) and very similar lattice constants (Table 2) suggested that nickel atoms could replace some copper atoms in the copper-tin intermetallic. This may well disturb the structure sufficiently to facilitate nucleation of the intermetallic before the primary β-tin dendrites start to form and so trigger isothermal freezing with a true eutectic microstructure.

In a series of experiments with additions of nickel ranging from 0.01 to 1% it was found that within a certain range of nickel levels there is a dramatic change in the way the alloy behaves in freezing and in the microstructure of the alloy (Figure 4). This discovery is protected in most countries by patents held by Nihon Superior Co., Ltd.[1]

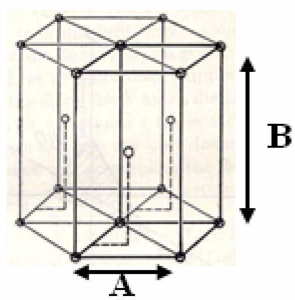


Figure 3 - Hexagonal Close Packed Crystal Structure of Cu_6Sn_5 and Ni_3Sn_2

Table 2 - Similarity of Copper-Tin and Nickel-Tin Intermetallics

		Cu_6Sn_5	Ni_3Sn_2	
Lattice Constants (nm)	a	0.4125	0.4190	1.6% difference
	b	0.5198	0.5086	2.2% difference

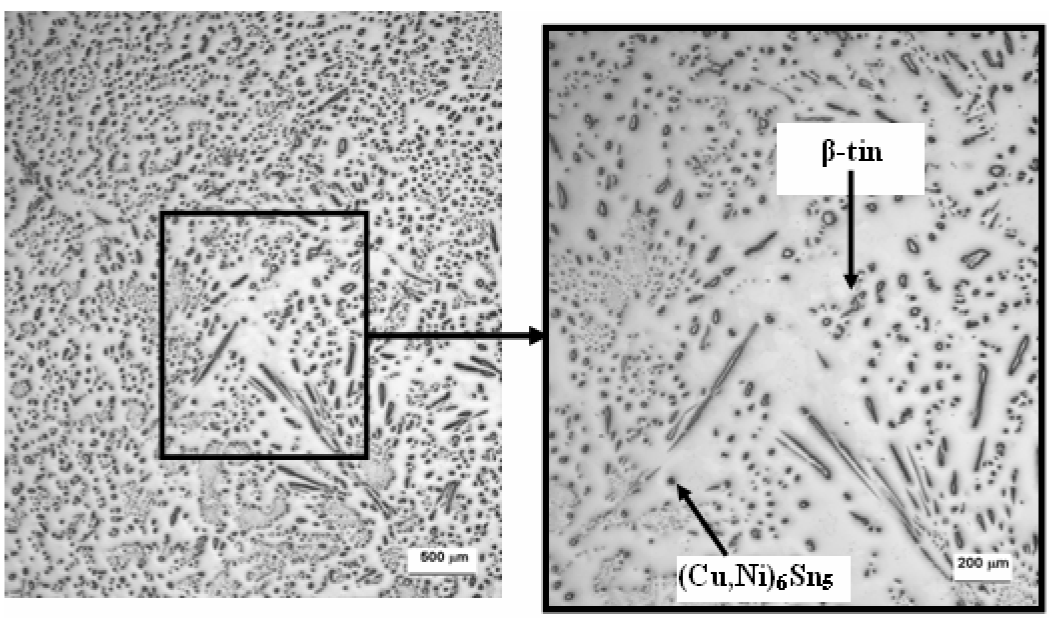
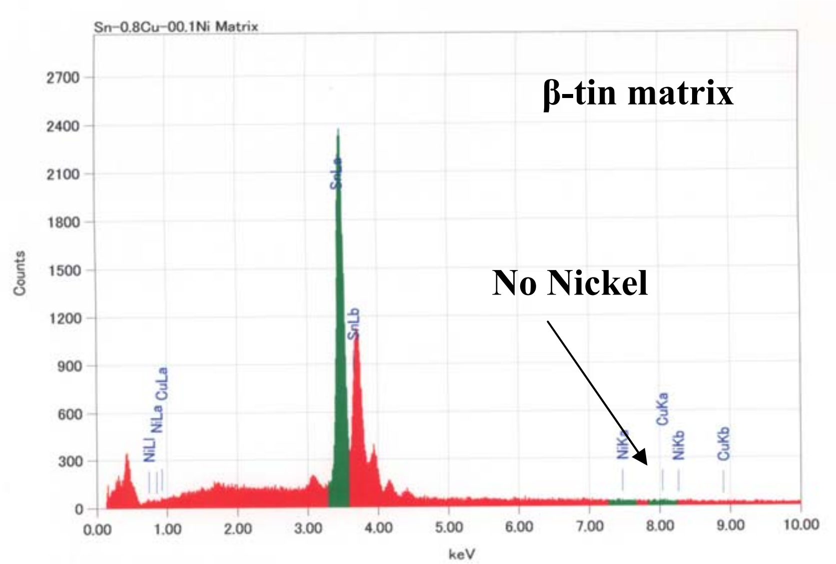
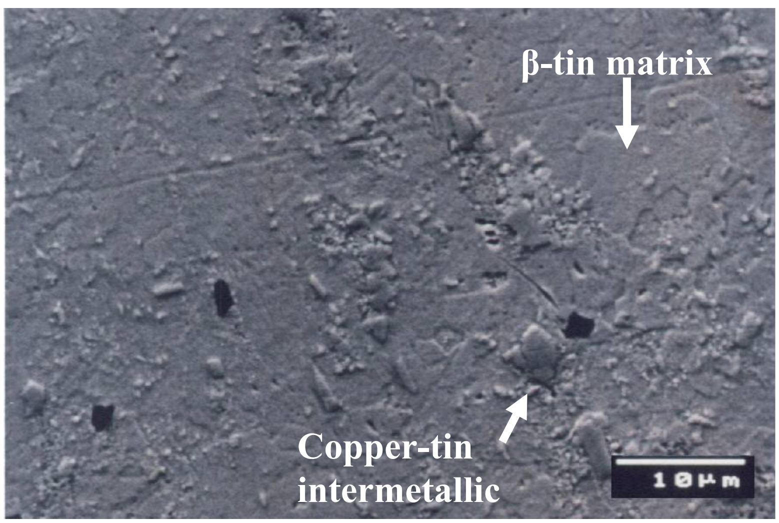


Figure 4 - Fully Eutectic Microstructure in Nickel-Modified Tin-Copper Eutectic

EDX analysis confirms that all of the nickel added to the alloy concentrates in the intermetallic phase (Figure 5) so that the intermetallic can be considered to be $(Cu,Ni)_6Sn_5$.





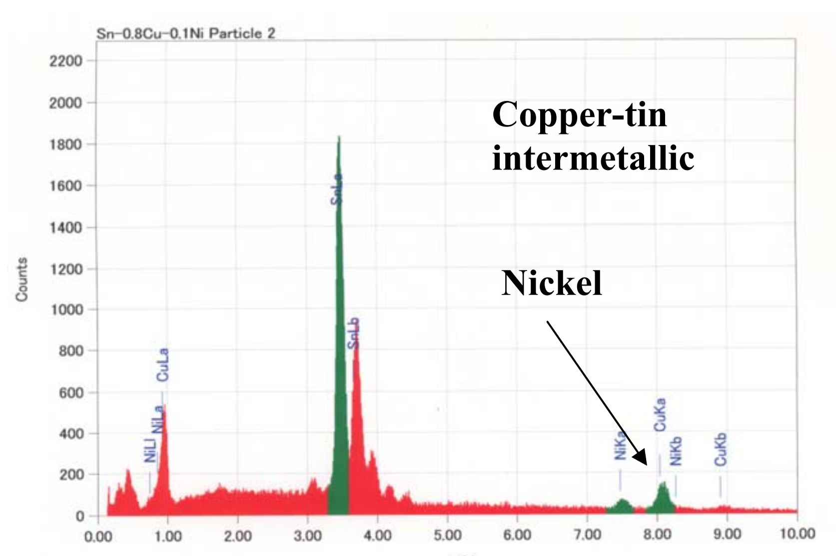


Figure 5 - Concentration of Nickel in the Copper-tin; Nickel Concentrates in the Intermetallic Phase

The eutectic character of the alloy is confirmed by DSC which shows no evidence of primary β-tin freezing out prior to the eutectic (Figure 6)

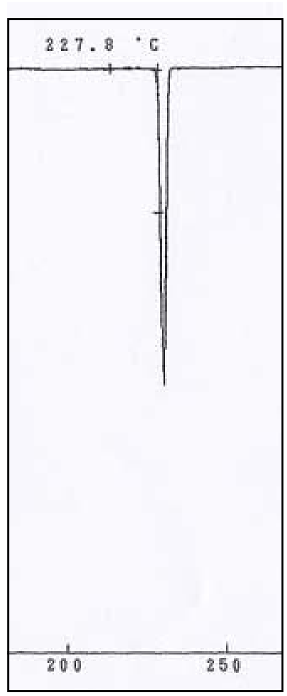


Figure 6 - Differential Scanning Calorimetry Plot of Nickel-Modified Tin-Copper Eutectic

Effect of Nickel Modification on the Behaviour of the Tin-Copper Eutectic
The change in the microstructure of the modified tin-copper eutectic results in fillets with a smooth bright finish comparable with that of the tin-lead eutectic (Figure7). The similarity of joint appearance to that of tin-lead makes inspection of soldered joints, manual or automatic optical, easier than with the alternative tin-silver-copper alloys that have notoriously dull, grainy fillets, often, in the case of the Sn-3.0Ag-0.5Cu alloy, crazed with shrinkage cracks.

From the practical point of view, however, the most important effect of the nickel modification is the reduction in the incidence of defects such a shorts and insufficient hole fill. Figure 8 is a plot of the ratio of the soldering defect rate experienced during the implementation of lead-free soldering on a commercial mass production wave soldering line to the defect rate experienced with a particular board when soldered with conventional tin-37%lead solder. The first step in the optimisation process, which resulted in a 41% reduction in the incidence of defects, was the replacement of the basic tin-copper eutectic with the nickel-modified variant. The potential of the nickel-modified tin-copper eutectic for high yield wave soldering is demonstrated by the ultimate achievement of a defect rate lower than that typically experienced with tin-lead solder. The subsequent steps taken to reduce the defect rate are a reflection of the acknowledged need to modify machine design, process parameters and circuit layout to accommodate the fact that the properties of lead-free solders are different from those of the tin-lead solder they are replacing.

The most immediately noticeable effect of the nickel addition on the behaviour of the tin-copper eutectic in wave soldering is the reduction in the incidence of solder bridges even at solder bath temperatures similar to those used with tin-lead solder (Figure 9)

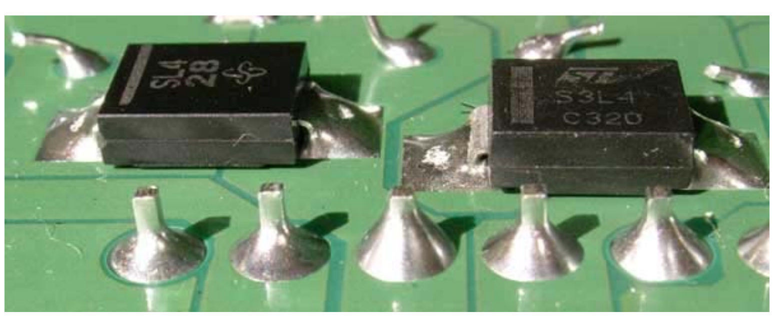


Figure 7- Smooth Bright Fillets Produced By Nickel-Modified Tin-Copper Eutectic

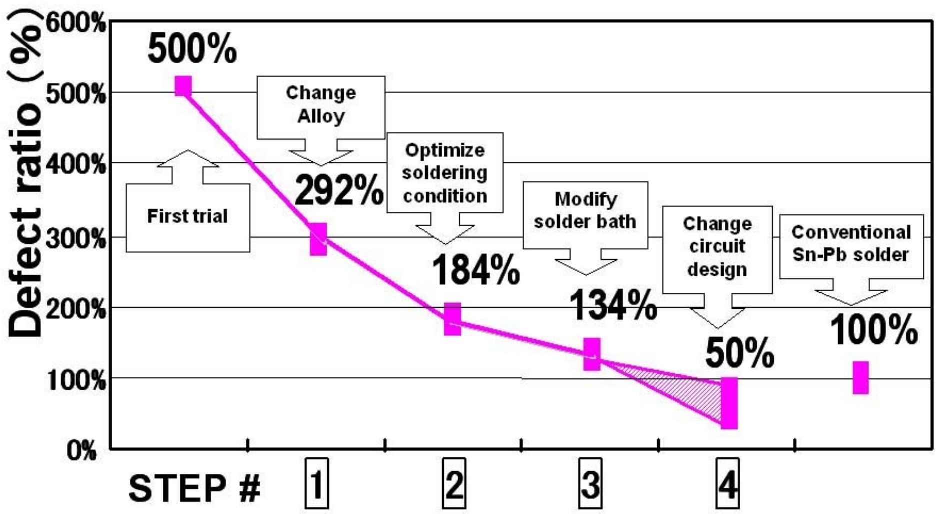


Figure 8 - Defect Rates during Implementation of Lead-Free Wave Soldering
Step #1 was the change from Sn-0.7Cu to the Ni-modified Sn-0.7Cu

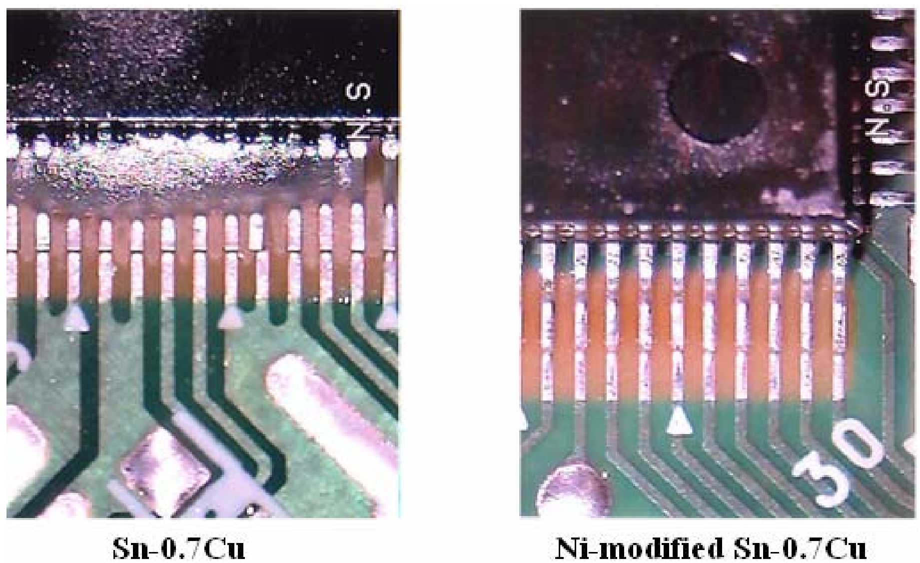


Figure 9 - Effect of Ni Addition on Bridging Behaviour of Sn-Cu Eutectic Solder
Solder Bath Temperature 250°C, 2-3 Seconds Contact Time

Given that better through-hole filling is cited as one of the reasons for adding silver to the tin-copper system it is interesting to note that with the nickel addition the behaviour of the solder appears to at least match that of the most popular tin-silver-copper solder in that regard (Figure 10).

The benefits of improved fluidity at temperatures in the 250-260°C range that the nickel addition imparts to the tin-copper eutectic has also been found to be of benefit in the hot air solder levelling (HASL) process for applying a protective solderable finish to printed circuit boards. Not only is the finish as smooth and bright as that obtained with tin-lead solder but it has been found that the coating thickness variation, a problem that has limited the application of the HASL finish, is much less with the nickel-modified tin-copper alloy (Figure 11).

In a HASL finish as well as in soldered joints where intermetallic growth can be a cause of loss of solderability and joint embrittlement the effect of the nickel addition in inhibiting the rate of growth of intermetallic (Figure 12) is an advantage.[2]

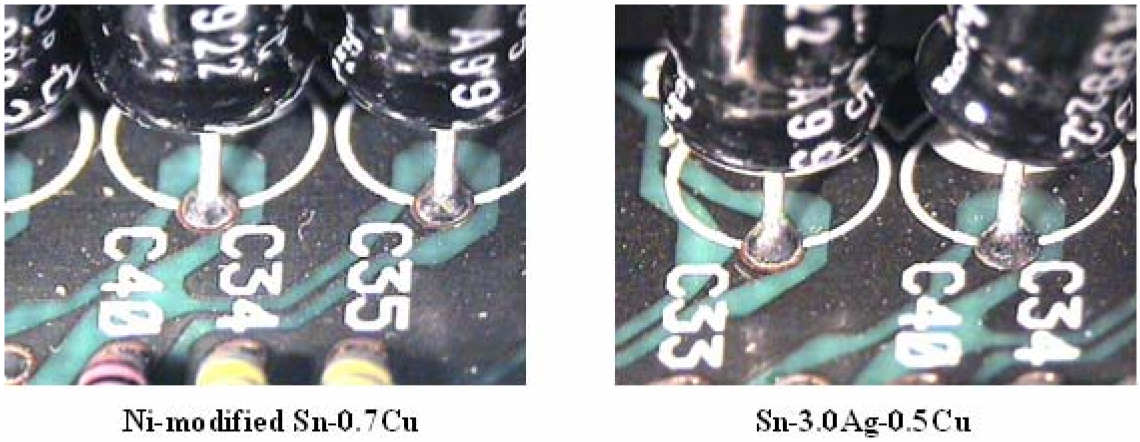


Figure 10 - Comparative Through-Hole Filling and Topside Fillet Formation in Wave Soldering

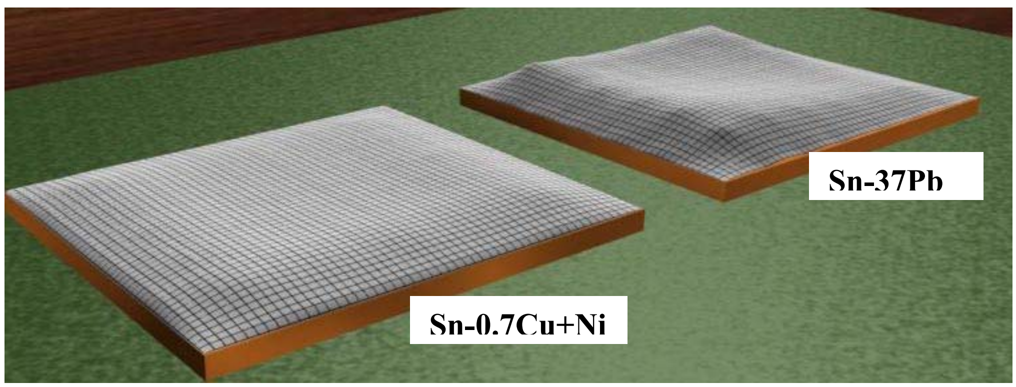


Figure 11- Improved Uniformity of HASL Coating Thickness of Nickel-Modified Tin-Copper Eutectic[3]

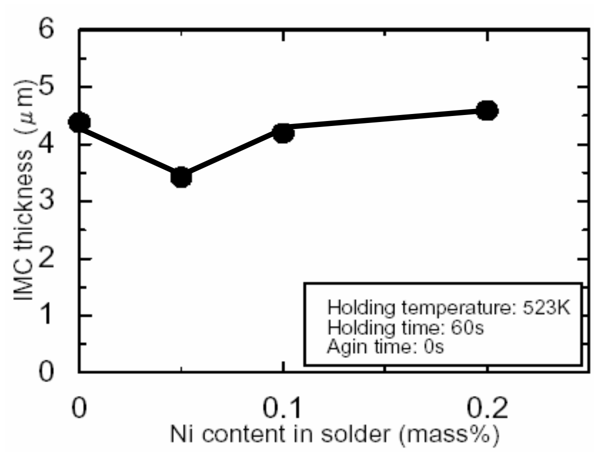


Figure 12 - Effect of Nickel in Tin-Copper Eutectic Solder on the Growth of Intermetallic on a Copper Substrate (Nishikawa et al[2])

The nickel addition has also been found to reduce the rate of erosion of copper substrates by the molten alloy (Figure 13). This effect is presumably related to the effect of nickel on intermetallic growth as intermetallic formation is the first step in copper dissolution of copper. As well as reducing damaging erosion of copper tracks during soldering and hot air solder levelling the lower rate of copper dissolution makes it easier to keep the copper content of a wave solder bath within specification by the use of a copper-free replenishment alloy. This provides a substantial economic advantage over the widely promoted Sn-3.0Ag-0.5Cu which, because of the high copper erosion rate, typically requires periodical draining and replacement of solder from a solder bath to keep the composition within specification.

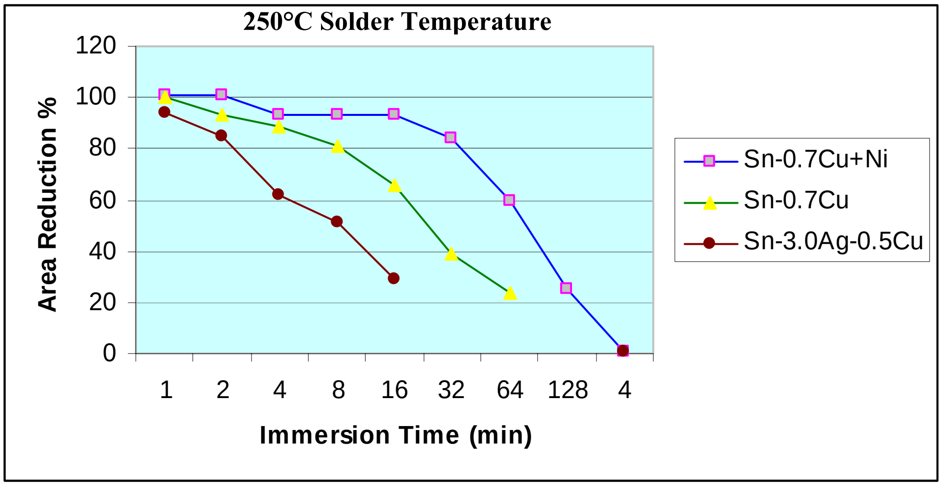


Figure 13 - Effect of Nickel Addition on the Copper Erosion Rate of the Tin-Copper Eutectic

Process Temperatures for the Nickel-Modified Tin-Copper Eutectic

A concern that the higher melting point of the tin-copper eutectic would necessitate correspondingly higher process temperatures has proved not to be justified. Experience of commercial lead-free soldering indicates that the early concern about finding lead-free alloys with melting points as close as possible to that of the tin-lead eutectic they were replacing was largely unwarranted. Optimum process temperatures appear to be determined by more factors than the melting point of the solder since the temperatures recommended for a range of lead-free alloys currently being promoted do not vary as widely as their melting points (Table 2). Despite having the highest melting point of the alloys listed the temperatures recommended for wave soldering with the nickel-modified tin-copper eutectic are similar to those recommended for alloys with lower melting points. The recommended range for reflow soldering with the nickel-modified tin-copper eutectic does extend higher than the other alloys but in practice the alloy is being successfully reflowed with a peak temperature of 245°C in well designed ovens.

Table 2 - Relationship between Melting Point and Process Temperature for Some Commercial Lead-Free Solders

Alloy System	Melting Point °C	Wave Soldering		Reflow Soldering	
		Solder Temperature °C	Superheat °C	Peak Temperature °C	Superheat °C
Sn-Pb	183	255±5[2]	72±5	210-220[2]	27-37
Sn-Cu[1,4]	227	255±5[3]	28±5	240-250[3]	13-23
Sn-Ag-Cu	217	255±5[2]	38±5	235-245[2]	18-28
Sn-Cu-Ag-Bi[4]	217-228	260±5[3]	(32)±5	Not recommended[3]	
Sn-Ag-In-Cu[4]	205-210	250±5[3]	(40)±5	230-250[3]	20-40

1. With patented addition of Ni
2. Typical industry practice
3. Supplier recommendation
4. Proprietary alloy

Reliability of the Nickel-Modified Tin-Copper Eutectic

The properties of the nickel-modified tin-copper eutectic lie somewhere between those of tin-lead and those of the tin-silver-copper alloys. The strength is higher than tin-lead but lower than tin-silver-copper but ductility is greater than tin-silver-copper and comparable with that of tin-lead.

Something that is emerging from the increasing experience with lead-free solders in service is that the high strength of, for example, the tin-silver-copper alloys, is not an advantage in all stress situations. One of the under-appreciated advantages of tin-lead solder was its compliance, i.e. its ability to absorb strain without rapidly work hardening to the point of crack initiation is triggered and to absorb by accommodating strain stress that would otherwise have to be carried by the component. Cracking of chip capacitors overstressed in this way is one of the defects that are being commonly encountered in circuitry assembled with tin-silver-copper solders. Similarly in four point bend tests tin-lead is outperforming tin-silver-copper in terms of the number of cycles the joint can tolerate and in vibration testing the nickel-modified tin-copper eutectic is outperforming both tin-lead and tin-silver-copper. The experience of some 150 million boards assembled with the nickel-modified tin-copper eutectic in service in a wide range of circumstances without report of joint failure provides anecdotal evidence that the alloy has a combination of properties that are capable of providing high reliability. This is being confirmed in reliability testing that is currently underway and which will be reported in late 2005. Early results of thermal cycle testing (Figure 14) indicate that the performance of the nickel-modified tin-copper eutectic exceeds that of tin-lead and is comparable with that of tin-silver-copper.

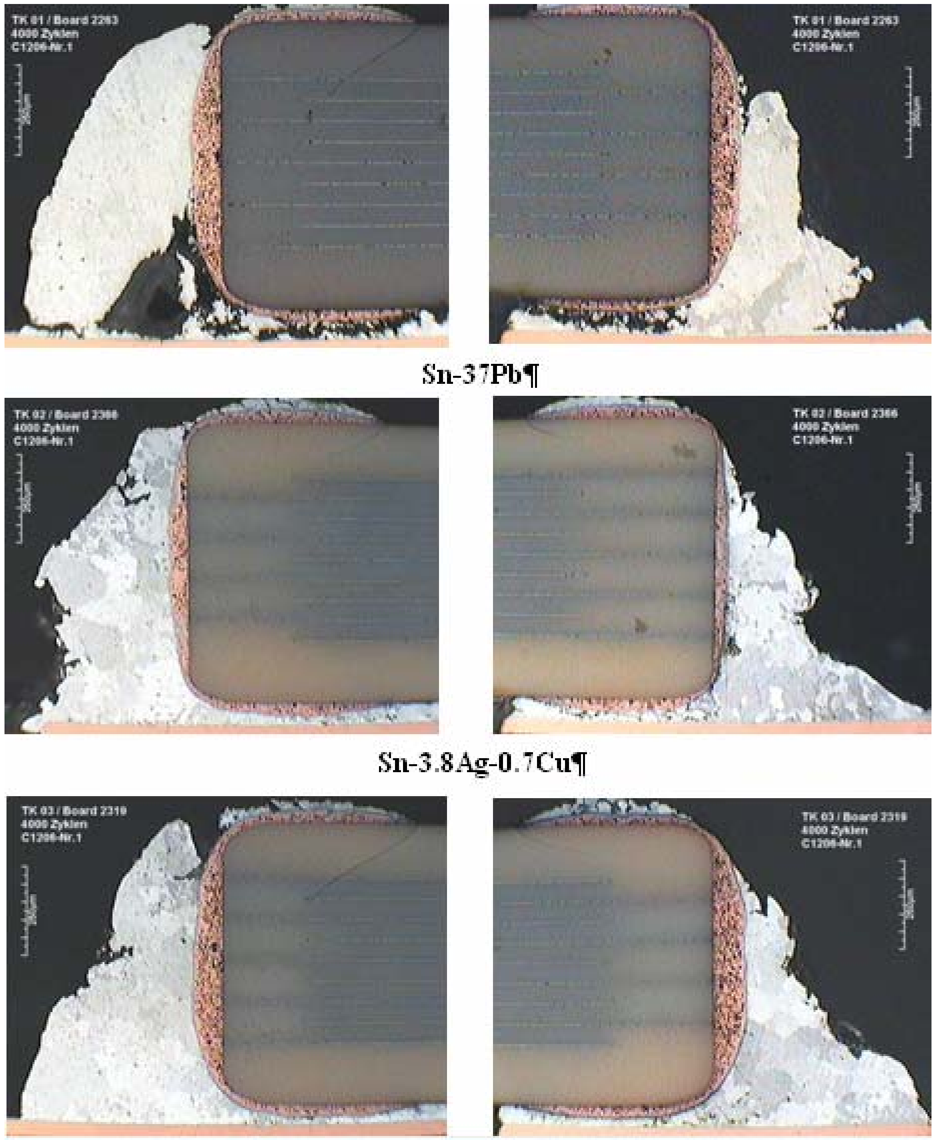


Figure 14 - Performance of Nickel-Modified Tin-Copper Eutectic Solder Compared with Tin-Lead and Tin-Copper-Silver

Acknowledgements
The authors wish to acknowledge the contribution of staff of the Nihon Superior Technology Centre in undertaking the experimental work on which much of this paper is based. The authors also wish to acknowledge the contribution of the BFE Consortium for the micrographs of Figure 14. The work reported here would not have been possible without the continuing support and encouragement of the chairman of Nihon Superior Co., Ltd, Mr. Toshiro Nishimura.

References

1. Japanese Patent No. 3152945, US Patent No. 6180055
2. H. Nishikawa, J.Y. Piao and T. Takemoto, "Effect of Ni Concentration on Reaction Between Sn-Cu-Ni Solders and Cu Base Metal". Proceedings of Soldertec/IPC International Conference on Lead Free Electronics, Amsterdam, June 2004.
3. Figure 11 courtesy Cemco Ltd., Waterlooville, UK