The Fluidity of the Ni-Modified Sn-Cu Eutectic Lead Free Solder

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Abstract
One of the factors that has contributed to the establishment of the Ni-modified Sn-Cu eutectic as one of the major alternatives to the widely promoted Sn-Ag-Cu alloys as an RoHS compliant lead-free solder has been its apparent fluidity at temperatures close to its 227°C melting point. This fluidity results in the alloy behaving similarly to lower melting point alloys in which tin dendrites start to freeze out at temperatures higher than the nominal melting point. This in turn has meant that the Ni-modified Sn-Cu eutectic can be used as a wave solder and a HASL alloy at process temperatures not much higher than those that have been used with Sn-37Pb solder. More recently it has been found that this fluidity also permits the use of the alloy in reflow soldering with peak temperatures around 245°C, which is in the middle of the range used with the Sn-Ag-Cu alloys that have a nominal melting point 10°C lower. In a study reported at APEX 2005 it was found that the Ni addition has the effect of suppressing the formation of pro-eutectic β-tin dendrites in the cooling Sn-0.7Cu alloy and promoting solidification as a true eutectic and it was inferred that it was because of this effect that the alloy exhibited good fluidity close to its melting point. In the study reported in this paper the fluidity of the modified and unmodified Sn-0.7Cu alloys is compared using two techniques recognised in solidification science. The Ragone method measures the distance that the molten alloy flows along a tube, a situation which to some extent simulates through-hole penetration in wave soldering and metallography of the resulting sample provides a further correlation between the observed behaviour and the resultant microstructure. The Dendrite Coherency method provides a means of confirming the change in solidification mechanism to heterogenous nucleation when the Ni is present. The results of these tests are consistent with observed positive effect of the Ni in enhancing the performance of the Sn-0.7Cu alloy as a practical lead-free solder.

Introduction

For the thick multilayer boards that now make up a high proportion of the electronic production remaining in the US and Europe the greatest challenge in wave soldering is achieving satisfactory hole fill. Although 75% hole fill is considered acceptable by some industry standards[1] most manufacturers and their customers would prefer to see complete hole fill, with a well formed topside fillet. While it might not be essential for the reliability of the board the complete fill provides a reassuring indication of the good wetting and flow that characterises an ideal solder joint.

Janakiraman et al.[2] identified preheat and contact time as the dominant factors in achieving complete hole fill when soldering thick multilayer boards with "63/37" tin-lead solder with the first "chip" or turbulent wave also having a statistically significant effect. A factor that Janakiraman et al. did not look at, however, is the property of solder known in the foundry industry as "fluidity". In this context fluidity is not the property defined in fluid mechanics as the reciprocal of viscosity but the ability of a molten metal to fill narrow sections of a mould during metal casting[3]. The challenge faced by an electronics production engineer in achieving through hole filling is in many respects similar to that faced by a foundry engineer in getting molten metal to flow into all parts of an intricate casting such as an engine block or cylinder head. Both want a molten alloy to flow as far as possible into a narrow space before it freezes.

A significant difference between these two processes, filling a through hole and filling a mould, is that while the solder should be wetting the walls of the through hole a mould must not be wet by the alloy being cast into it. The capillary forces associated with the wetting of the hole wall are an important factor in achieving a good joint in wave soldering but wetting by itself cannot ensure hole fill if the solder can no longer flow. A mathematical model of through hole filling[3] indicates that the quality of wetting of the hole wall, as indicated by wetting angle, is not a major factor in determining the degree of hole fill.

Fluidity, the ability of a metal to flow into narrow spaces, is affected by many factors including viscosity, surface tension and the presence of surface oxide films[4]. Viscosity and surface tension appear to have only a small effect on this property[2, 6]. In wave soldering one of the functions of the soldering flux, in addition to facilitating the wetting of the substrate and acting as a medium of heat transfer, is dealing with surface oxide films so that the effectiveness of the flux in that regard is another significant factor in achieving hole fill. However, the factors that make the most important contribution to fluidity are the behaviour of the alloy during solidification and the superheat[4].

Superheat is the excess of the metal temperature over its melting point at the commencement of the process and in the case of wave soldering the relevant parameter is the solder bath temperature. Superheat is important because, for a given rate of cooling it is the primary determinant of the time available for the metal to flow and fill the mould or the through holes before it solidifies. In both metal casting and wave soldering extra time can be gained by preheating, respectively, the mould or the printed circuit board and that is consistent with the observation of Janakiraman et al.[2]

The feature of the behaviour of the alloy during solidification that is most important in determining fluidity is whether the solidification occurs in a single isothermal process or whether there is a multistage process occurring over a temperature range above the final solidus temperature. This effect is demonstrated dramatically in plots such as that in Figure 1 where fluidity, measured as the distance that the alloy in question flows, is superimposed on the phase diagram. Peaks in fluidity occur at three compositions in this antimony-lead (Sb-Pb) system, the pure metals and the eutectic. This binary eutectic system is very similar to the tin-lead system in which similar results would be expected so that it can be seen why the electronics industry has been using the "63/37" eutectic alloy. In the case of the antimony-lead system of Figure 1, the fluidity of the eutectic is double that of alloys with a composition ±5% of the eutectic composition.

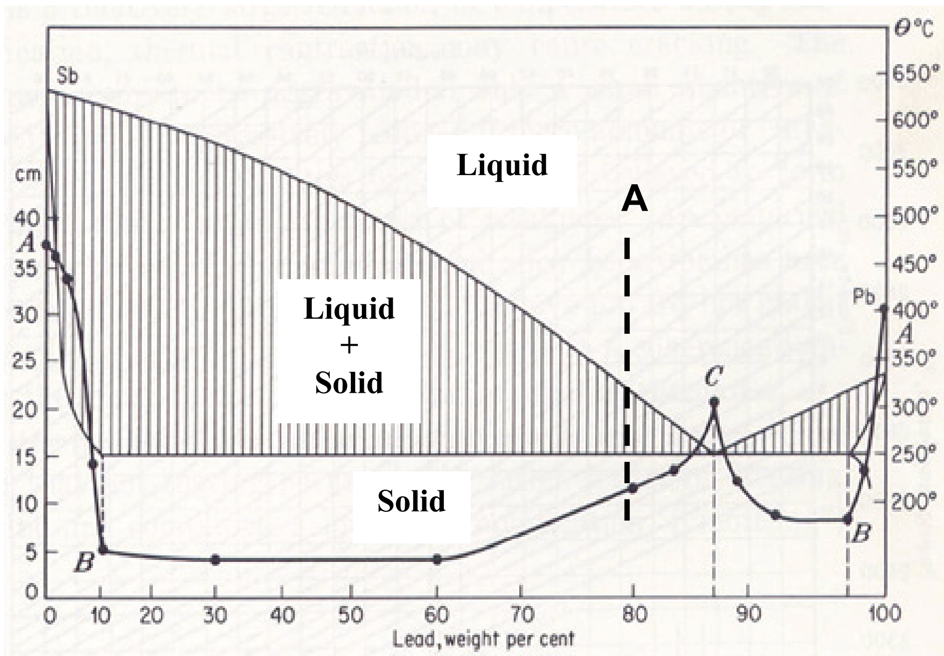


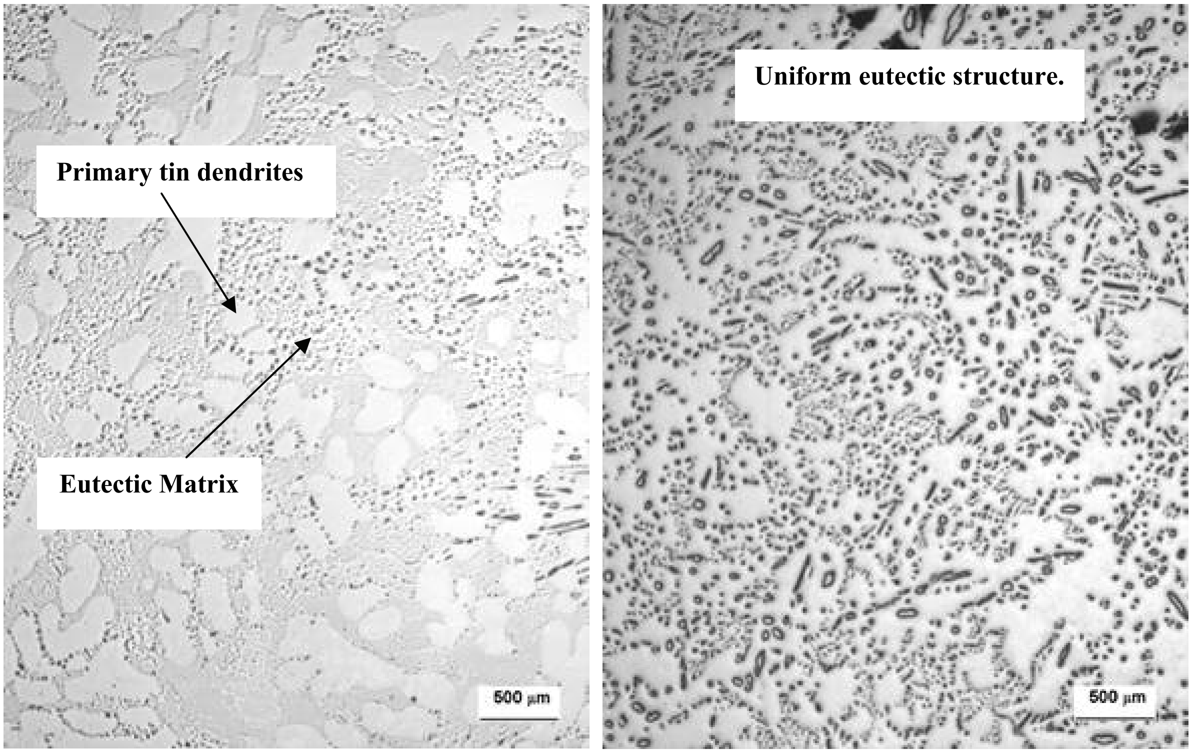
Figure 1 - Fluidity as a Function of Composition in a Binary Eutectic System

This dramatic variation in fluidity can be understood in terms of the behaviour of the metal during solidification. Pure metals have a sharply defined freezing point and transform from liquid to solid in a single step. The unique feature of an alloy of eutectic composition is that it behaves in much the same way as a pure metal although there are two separate phases freezing out simultaneously in the phenomenon known as coupled growth. On either side of the eutectic composition the freezing out of the eutectic is preceded by the precipitation of one of the eutectic phases in a primary form, typically dendrites if the phase is a metallic alloy or large crystals if the phase is an intermetallic. These primary phases start to form at a temperature above that of the eutectic to create a mixture of solid and liquid that is sometimes known as the "mushy" stage of solidification and it is not difficult to imagine that the metal would not flow very easily in this condition. For example, in alloy "A" in Figure 1 dendrites of a primary phase start to precipitate at about 310°C, some 60°C higher than the eutectic temperature. Although at the eutectic temperature these primary dendrites make up less than 10wt% of the alloy they reduce its fluidity by nearly 50%.

The Sn-Cu Eutectic as Lead-free Solder

Although recommended by several industry consortia as a lead-free alternative for wave soldering the performance of the tin-copper eutectic in wave soldering was disappointing. The process temperatures and contact times required to achieve satisfactory joints were much higher then were considered acceptable for most printed board assemblies [7]. The fact that temperatures higher than expected were required to achieve satisfactory soldering is an indication that the fluidity of the alloy is an issue; the higher process temperature was providing the superheat that, as reported earlier, has been identified as one of the two main factors affecting fluidity. A breakthrough in the use of the tin-copper eutectic as a practical wave solder occurred when a way was found of dealing with the other factor that has a strong effect on fluidity, the behaviour of the alloy during solidification. It was discovered that the addition of nickel at a specific level has a dramatic effect on the behaviour of the Sn-0.7Cu eutectic[8] and the resulting alloy is now being widely used around the world as a lead-free alloy in wave soldering, Hot Air Solder Levelling (HASL) and, increasingly, in reflow[9]. As of the 3rd Quarter of 2005 there were more than 1,300 soldering lines in commercial production with this alloy.

Laboratory studies of the Sn-Cu-Ni alloy have confirmed that the effect of the nickel addition is to suppress the growth of pro-eutectic tin dendrites and promote solidification as a true eutectic[10, 11]. This effect is apparent in the change in the microstructure that occurs with the nickel addition (Figure 2). The primary tin dendrites that dominate the microstructure of the unmodified alloy virtually disappear when nickel is present at the appropriate level. The resulting microstructure is almost perfect eutectic with clear evidence of coupled growth of the two eutectic phases, tin and the intermetallic Cu_6Sn_5.



Sn-0.7Cu **Sn-0.7Cu+Ni**

Figure 2 - Effect of Nickel Addition on the Tin-Copper Eutectic

The objective of the study reported here was to confirm whether there is indeed a measurable increase in fluidity associated with the change in solidification effected by the nickel addition.

Experimental Procedure

In the foundry industry fluidity is typically measured as the distance that the molten metal will flow along a channel[5]. However, Ragone[6] devised a method of measuring fluidity that by coincidence better simulates that geometry of a through hole in a printed circuit boards. In this method the molten alloy is drawn by a vacuum into a tube and the distance that it travels before freezing measured. The apparatus based on this method is illustrated schematically in Figure 3.

Since the Ragone method was developed for aluminium alloys preliminary experiments were undertaken to determine the solder temperature, the internal diameter and length of the glass tube and the vacuum pressure most appropriate for tin-based alloys. On the basis of those experiments the solder temperature was set at 300°C and the vacuum pressure at 50kPa. The fact that the solder temperature is higher than normally used in wave soldering does not affect the relevance of the experiment to practical soldering since for all alloys the temperature has to cool to the melting point within the available length of tube. Superheat at this level was found to be necessary to get a significant flow length given the thermal mass of the glass tube.
The internal diameter of the tube was 3mm diameter and the dimensions of the tube as indicated in Figure 4. In this experiment the measure of fluidity recorded is the length "L_f" indicated in Figure 4.

The alloys studied are listed in Table 1. The Sn-Ag-Cu alloy, commonly known as "SAC305" was included for comparison purposes since it is an alloy that has been widely promoted for wave soldering.

Table 1 - Alloys Subjected to Fluidity Testing

Sn-0.7Cu
Sn-0.7Cu-0.010Ni
Sn-0.7Cu-0.025Ni
Sn-0.7Cu-0.060Ni
Sn-0.7Cu-0.100Ni
Sn-3Ag-0.5Cu

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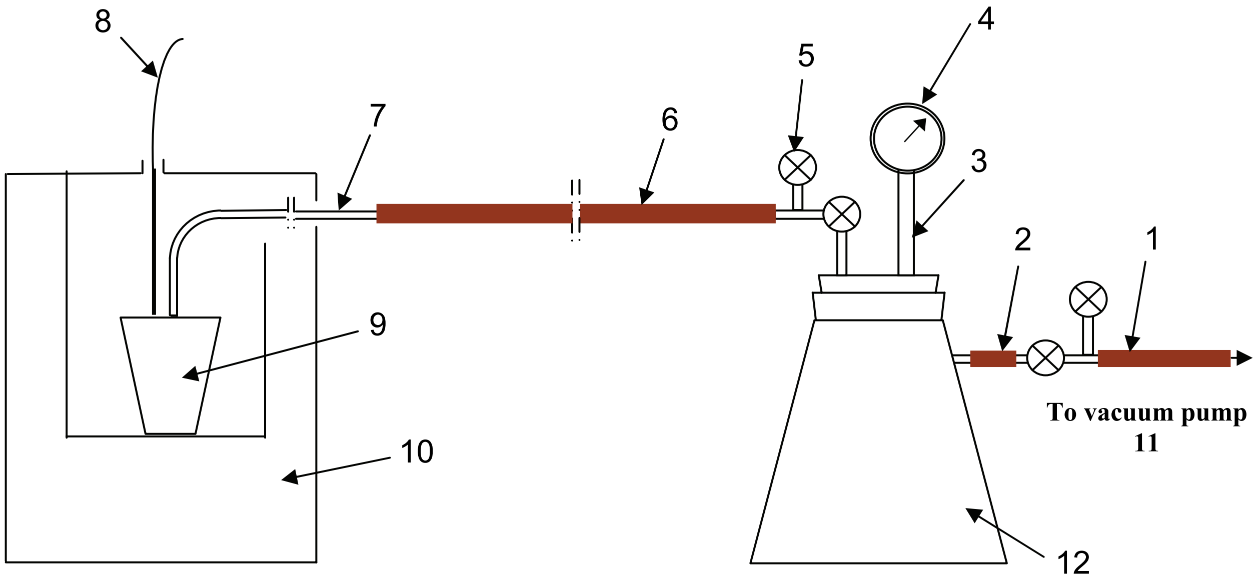

Figure 3 - Fluidity Measurement Apparatus

1- Vacuum hose – length 520mm, 6.3mm inside diameter, directly connected to the pump
2- Vacuum hose – length 55mm, 6.3mm inside diameter
3- Vacuum hose – length 100mm
4- Vacuum Gauge (TecSis, Germany, Ø63mm, precision 1.6%, 0 to -100kPa)
5- Tap
6- Vacuum hose – length 1069mm, 6.3mm inside diameter
7- Pyrex tube elbow (800mm x 150mm, 3mm ID)
8- Thermocouple (thermocouple controller Anritherm HL600, Anritsu)
9- Clay-bonded graphite crucible
10- Nabertherm resistance furnace
11- Java double stage Pump, DD300
12- Buchner flask, 2 litres

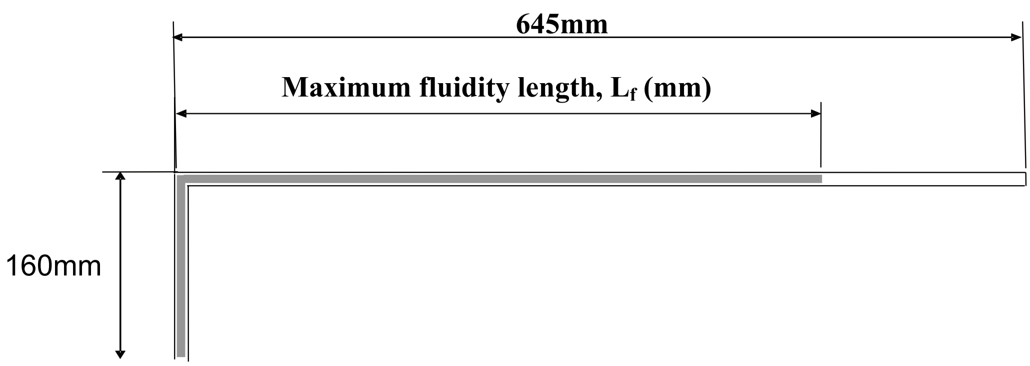

Figure 4 - Fluidity Measurement Tube Dimensions and Method of Measuring Fluidity

Results
The results are presented graphically in Figure 5 with a best bit curve indicating the trend. In summary the observations are that:

- The fluidity or the tin-copper eutectic alloy, as measured by the modified Ragone method increases with the level of nickel addition to a peak at a nickel level at 0.06% and then declines at higher nickel levels.
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- At the optimum nickel level the fluidity of the Ni-modified Sn-0.7Cu eutectic is about one third greater than that of the basic Sn-0.7Cu.
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- The fluidity of the SAC305 alloy is similar to that of the basic unmodified Sn-0.7Cu alloy.

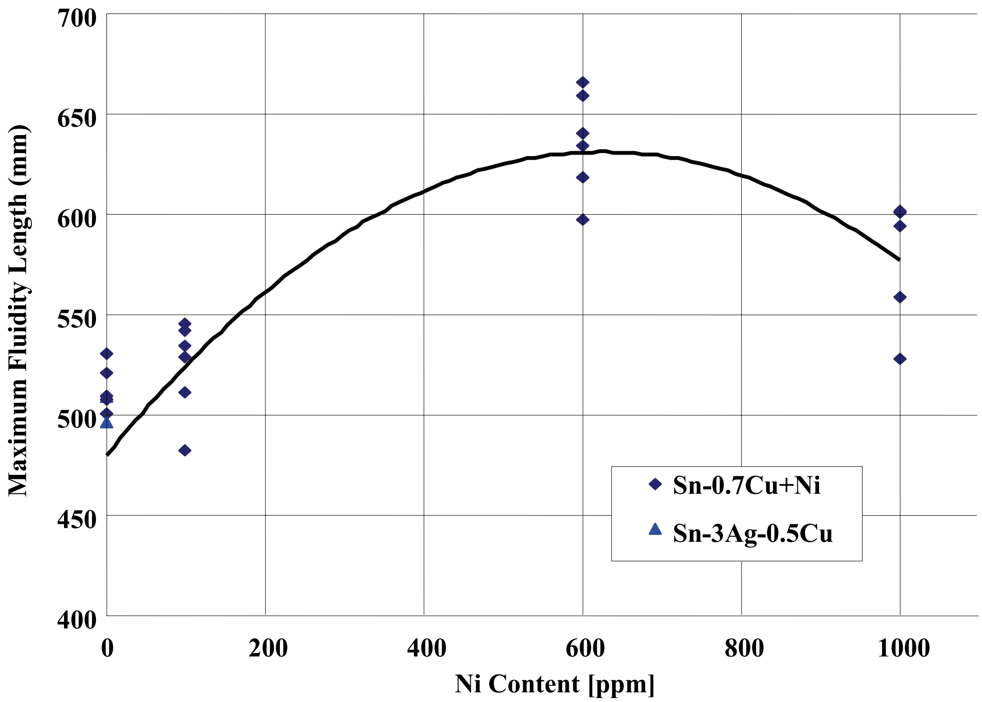

Figure 5 - Fluidity of the Tin-Copper Eutectic Alloy as a Function of the Nickel Addition

Discussion
The increase in fluidity at the level of nickel specified by the inventor of this alloy as the optimum[12] confirms that there is a measurable improvement in a specific property that is relevant to the alloy's performance as a solder. This greater fluidity is undoubtedly a factor in that makes it possible to use the Ni-modified Sn-0.7Cu eutectic at process temperatures much lower than those required by the unmodified alloy.

The decline in fluidity at higher nickel levels is consistent with the observation that the beneficial effect of the nickel on solidification behaviour of the alloy also declines at higher nickel levels[10, 11].

The fact that the fluidity of the SAC305 alloy, Sn-3.0Ag-0.5Cu, as measured in this study is similar to that of the unmodified Sn-0.7Cu eutectic alloy suggests that the reported satisfactory performance of this alloy in wave soldering is mainly the result of its lower melting point (~218-219°C). At the same process temperatures, the lower melting point means that the effective superheat (the excess of the process temperature over the melting point of the solder) is ~8°C greater than the Sn-0.7Cu alloy at the same process temperature. As noted earlier, the effect of superheat can be diminished by preheating and that provides an explanation for the practical experience that with the appropriate process parameters the performance of the Ni-modified Sn-0.7Cu alloy can match that of the SAC305 alloy in the filling of through holes.

Although this report has focussed on the importance of fluidity in filling through holes this property of a molten solder is also important in determining the extent of the wave soldering defects known as "bridges" ("shorts") and "icicles". The relationship between these phenomena and the composition of the alloy are the subject of a separate study.

Another application in which the fluidity of a solder alloy is important is the application of a solderable finish to a printed circuit board by the process of Hot Air Solder Levelling (HASL). The success of the Ni-modified Sn-0.7Cu alloy in that process (more than a 100 lines in commercial production as of the 3rd Quarter of 2005) provides practical confirmation of the improved fluidity measured in this study. A coating that is superior to that typically obtained with "63/37" in terms of the uniformity of coating thickness can be obtained at process temperatures of only 260-265°C.

Conclusions

The addition of a specific level of nickel to the tin-copper eutectic results in a measurable increase in the fluidity of the alloy, as measured by the Ragone, method which correlates well with reports of the good performance of this alloy in wave soldering and Hot Air Solder Levelling.

The superiority of the fluidity of the Ni-modified Sn-0.7Cu alloy over that of the lower melting point Sn-3.0Ag-0.5Cu alloy provides an explanation of the observation that a similar degree of success in through hole filling can be achieved with these alloys at similar process temperatures.

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