Evaluation of the Comparative Solderability of Lead-free Solders in Nitrogen

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Abstract
Lead-free soldering technology is still in its infancy with technical and cost issues posing major challenges for the industry. It is expected that soldering in a nitrogen atmosphere might overcome some of the technical barriers and provide soldered products comparable to those using conventional lead-containing materials processed in air. But quantitative data regarding the soldering behaviour of lead-free solders under various atmospheres are sparse. Hence this work was undertaken to build on the previous studies of the solderability of SnAgCu alloys under a range of residual oxygen levels between 10 ppm and 21%. The current work extends the study to other lead-free solders, SnCu, SnZn and SnAgBi, in atmospheres containing as little as 10 ppm oxygen at superheats from 20 to 60 degrees. The results clearly demonstrate the benefit of inerting for these solders. Apart from widening the process window, it can reduce oxidation and improve solderability of lead-free systems to a level close to that of SnPb. In many cases the addition of an inert atmosphere during lead-free soldering can allow a ~30ºC reduction in soldering temperature AND give the same solderability as using SnPb in air. Inerting is especially beneficial at low soldering temperatures or for challenging assemblies such as multi-layer boards. Whilst in the case of soldering with SnZn alloy inerting to < 100 ppm was essential, for SnCn and SnAgBi solders inerting only to <5,000 ppm oxygen offered significant benefits in wetting. For many of the challenging conditions and poor solderability associated with lead-free solders, nitrogen offers an attractive alternative to stronger fluxes and higher processing temperatures.

Introduction

The move to lead-free soldering is gaining momentum every day, driven by a combination of expected European legislation, and global marketing and commercial pressures, particularly from Japan and the Pacific rim counties. However, changing the solder raises a number of issues, of which the most important is arguably its wetting behaviour. Effective implementation of any new lead-free soldering technologies therefore requires credible data on the wetting and solderability behaviour of the lead-free solders used to replace eutectic SnPb - but such data are sparse.

When compared with the universally used SnPb solder, most replacement alloys melt at higher temperatures. Indeed, the melting point of the most widely accepted replacement for conventional SnPb soled, SnAgCu, is about 30-35ºC higher. In addition these lead-free materials have poorer solderability, and are more expensive. But it is the necessity of working at higher temperatures that poses the most serious challenges, including an acknowledged narrowing of the process window and the effect it might have on yield. Combined with the higher soldering temperatures, this places significant demands on the assemblers in terms of tighter process control. Moreover, rising soldering temperatures by 30ºC, say, could result in problems relating to temperature-sensitive components and to increased oxidation effects. Consequently, it is likely that soldering will be carried out using a lower superheat (i.e. the difference between the liquidus and soldering temperatures of the alloy) than has traditionally been the case. Such lower superheats, coupled with the higher surface tensions of all the lead-free solders, result directly in poorer wetting performance and a narrower process window.

There are two main options for widening the process window i.e. to increase the activity of the flux, or to use nitrogen inerting during soldering. The latter, which has the big benefits of not requiring any alterations to the flux chemistry, of giving less risk of flux residues, and of protecting some thermally-sensitive parts, has been the subject of this work.

Some previous studies are relevant. Investigations carried out at NPL[1,2] involved a range of superheats both in air and in an inert atmosphere containing 500 ppm oxygen, whilst other work[3,4] has demonstrated that inerting does improve wetting. But in order to implement new lead-free soldering technologies efficiently it is vital to know the extent of such improvement for each new lead-free solder, and to understand the degree of inerting required. In the absence of production data recourse has to be made to carrying out extensive wetting balance studies in order to compare the solderability of lead-free alloys with that of eutectic SnPb solder as a function of superheat.

For this work three solder alloys have been chosen that, along with SnAgCu, are among the leading contenders as alternative or transitional lead-free solders, viz SnCu, SnAgBi and SnZn, and their target compositions are shown in Table 1 (note the melting point of SnAgBi is not a single value, as this is not a eutectic composition).

Table 1 - Alloy Compositions

Solder alloy	wt% content	Melting point (^{0} C)
SnCu	99.3/0.7	227
SnAgBi	93.5/3.5/3.0	206-213
SnZn	91/9.0	198.5

SnCu has received much attention for wave soldering, where the cost of re-filling a solder bath is a major consideration. Its simple binary nature and the fact that there is unlikely to be any unexpected effects of mixing metals in the soldering process, provide further advantages. But the melting point is high (227OC) which many regard as a big drawback since it results in a very narrow process window. Nearly four years ago Nortel manufactured telephone handsets using this alloy, had a good yield, and have experienced excellent reliability.

The lower melting point afforded by the addition of Bi (206-213OC as compared with 217OC for SnAgCu) has made the SnAgBi solder alloy another leading contender as a lead-free replacement. But the presence of Bi does carry penalties. Apart from possible toxicity and environmental worries, there are reliability issues with Alloy42 leadframes, and fillet-lifting can occur following both wave soldering and rework. However, the alloy has been used successfully, for example by Panasonic, with a composition of Sn3Ag2.5Bi2.5In.

SnZn is a very reactive solder and makes special demands on the flux to prevent excessive oxidation. However, NEC has successfully used this alloy for a number of years, for example in the manufacture of Notebooks, although some additions of Bi were sometimes included. The great advantages of SnZn are that it has the lowest melting point (198.5OC) of the majority of the alloys being considered as SnPb replacements, and is relatively cheap.

Experimental

In order to investigate the effect of nitrogen inerting on wettability, the solderability of copper wire (1 mm diameter) using various lead-free solder alloys, was measured using a Mulitcore Must II wetting balance instrument. The wire was cleaned prior to testing using the following sequence:

- 3 minutes with agitation in an ammonium persulphide solution (100g/300ml DI water)
- 15 seconds in acidified water (1 drop conc. HCl/litre of DI water)
- final rinse in IPA, plus air dry

The wetting balance was operated in the globule mode, using the lead-free solders listed in Table 1. Each alloy, in the form of a pellet, was placed on the heated pin of the instrument where it formed a sessile drop. The wetting balance controller was modified so that it could drive two measurement heads, with simple switching between the two heads. One head was on the bench for normal ambient tests, whilst the second was located inside a glove box capable of operation at >5ppm partial pressure of oxygen (see Figure 1). The glove box had two entry ports, both of which could be evacuated and back-filled with nitrogen to allow the introduction of samples with minimal disruption to the atmosphere. The oxygen levels, which were measured at the exit from the glove box, were selected to cover a wide range of partial pressures (see Table 2) and were controlled using "Witt" gas mixing equipment. The Witt mixer was supplied with high purity nitrogen and bottled compressed air.

Figure 1 - Glove Box with Solderability Tester

Table 2 - Oxygen Levels (and log values)

O_2 ppm	Log value
10	1
50	1.699
1000	3
10000	4
210000	5.322

The immersion speed of the samples was 1 mmsec-1, and the immersion depth was 0.5 mm. No pre-heat was used, and the pure rosin flux (complying with IES 68-2-20) was purchased from Multicore Solders as SMMA. Force data were acquired over a 10 second period. Each test condition was repeated five times and the mean value used in the graphical plots. The results presented graphically are both the force at 2 seconds, and the time to 2/3 maximum wetting force. The test temperature was varied from 20 to 60 degrees of superheat. But it should be remembered that the globule test temperature does not equate directly to the temperature in reflow or wave soldering. Whilst during these, on the wetting balance the sample is close to room temperature prior to the test.

Some additional experiments were also carried out using 1mm diameter molybdenum wire to assess the effect of inerting on non-wetting surfaces, and the results obtained using SnPb and SnAgBi solder alloys are presented here.

Results

The data for the alloys are plotted on 3D plots with a mesh overlay across the data points. The wetting force results are plotted on a fixed scale of –1 to 1 milli-Newtons, and a fixed colour scale. Similarly the wetting time data are plotted on a scale between 0 and 10 seconds. Figures 2, 4 and 6 are the 3D plots of wetting force, temperature and oxygen levels, and Figures 3, 5 and 7 are 3D plots of wetting time, temperature and oxygen levels.

Wetting data for SnCu

The wetting force results for SnCu are shown in, where the force is plotted as a function of both superheat and oxygen partial pressure. The bottom corner represents the lowest temperature and normal atmospheric oxygen levels, and under these conditions no wetting is occurring. As the temperature is increased the wetting only improves marginally, and significantly worse than SnAgCu.[1] Between 45 and 60°C a clear benefit can be seen of inerting as the oxygen partial pressure drops to 10,000ppm and wetting effectively turns on. There is no noticeable change in wetting until below 100ppm oxygen, where the wetting here improves slightly at 45 and 60°C, and wetting now starts to occur between 30 and 45°C.

The wetting time data for SnCu are shown in Figure 3. For the wetting forces the temperature and oxygen concentrations have been reversed. This has been done, necessarily in order to effect sensible visualisation of the results. If the axes had been maintained from the force data, the trend would be of diminishing values from the bottom corner of the graph, hence obscuring reducing data values from a high initial value. The wetting time data follow very similar trends to the force data. There are, however, some minor interesting differences. The decrease in wetting time as the oxygen concentration is reduced below 10,000ppm is not as marked as with the force data. The wetting time data shows the impact of inerting, as compared to the force data, at 20°C superheat, where the wetting time is reduced from 8 to 5 seconds as the oxygen concentration is reduced to below 10,000ppm.

Overall with SnCu there is demonstrable benefit of inerting to below 10,000ppm oxygen, and a target of 5,000ppm is recommended.

Wetting data for SnAgBi

The SnAgBi alloy results are presented in Figure 4 and figure 5. Regarding the force data in Figure 4, the SnAgBi alloy wets better in atmosphere than SnCu compared with Figures 2 and 3. There is a much smaller area on this plot where non-wetting occurs from 20 to 40°C and 21% to 10,000ppm oxygen concentration, compared to SnCu. Unlike SnCu, wetting does occur reasonably well above 45°C without the benefit of nitrogen. The introduction of nitrogen, again to the 10,000ppm level, does marginally improve the wetting above 45°C, and there is evidence that oxygen levels around 1000ppm are beneficial at lower superheats of 30°C. There is also an increase in wetting force as the oxygen concentration drops below 50ppm where even higher wetting forces are achieved.

The wetting time data for SnAgBi are presented in Figure 5. These results are similar to those of the force data, but do not reflect the benefits achieved with oxygen levels below 50ppm in the wetting force data. The wetting time data for SnAgBi is also very similar to the SnCu results.

The wetting of SnAgBi is intrinsically superior to that of SnCu, as can be seen for the results in air. Consequently in this case the benefits of inerting are not so strong. However, where the effect of nitrogen is evident, it does occur at similar oxygen levels. Again there is a general improvement in wetting as the oxygen level is dropped below 10,000ppm, and again a level of 5,000 ppm is recommended. The data again support the conclusion that there is some benefit of inerting using an oxygen concentration of 50ppm.

Wetting Data for SnZn

The wetting force data for SnZn are presented in Figure 6. It is immediately apparent that SnZn alloy does not wet very well and that only soldering with 45°C superheat and less than 1000ppm oxygen does wetting occur at all. Indeed, even at 60°C superheat and 20ppm oxygen the wetting is still poor compared to the other two alloys. This poor wetting is due to the oxidation potential of zinc. This alloy was also found to be detrimental to the equipment. The solder globule sits on an iron pin, and this pin is shrink fitted into an aluminium block. There are naturally high stresses with such an arrangement around the pin, but normally this does not cause problems.

However, with this alloy significant corrosion of the aluminium block did occur, and at the end of this testing the aluminium block and its iron pin had to be replaced due to the damage done by the alloy.

The wetting time data for SnZn in Figure 7 depict identical behaviour to the force data, with adequate wetting occurring only at the highest temperatures and lowest oxygen levels.

The reactiveness of zinc clearly impacts on the wetting, its propensity to oxidise significantly impeding the wetting process. Hence, it is not surprising that inerting has such an important effect on wetting. There is a clear conclusion that any solder alloy that includes zinc will require full inerting, with better than 100ppm levels oxygen.

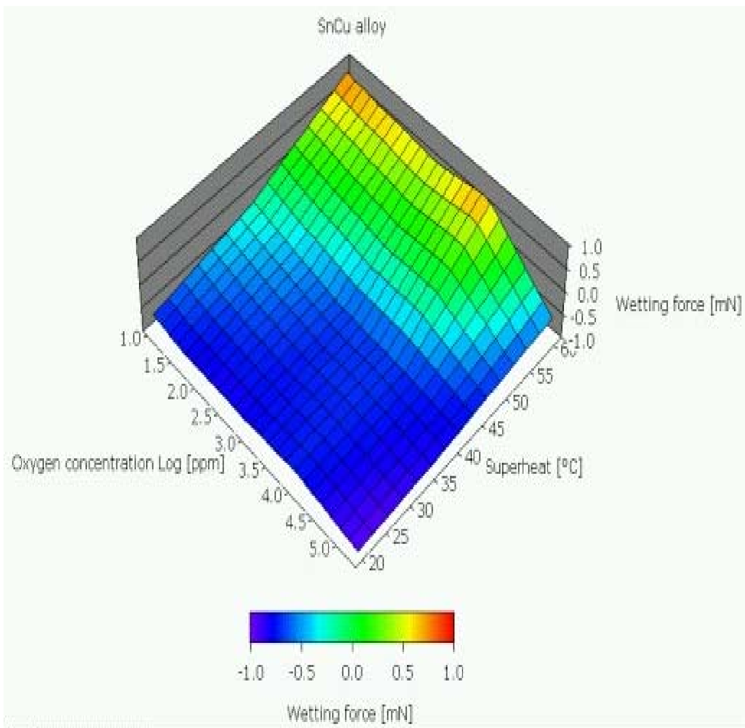

Figure 2 - 3D Plot of Wetting Force, Temperature and Oxygen Levels for SnCu

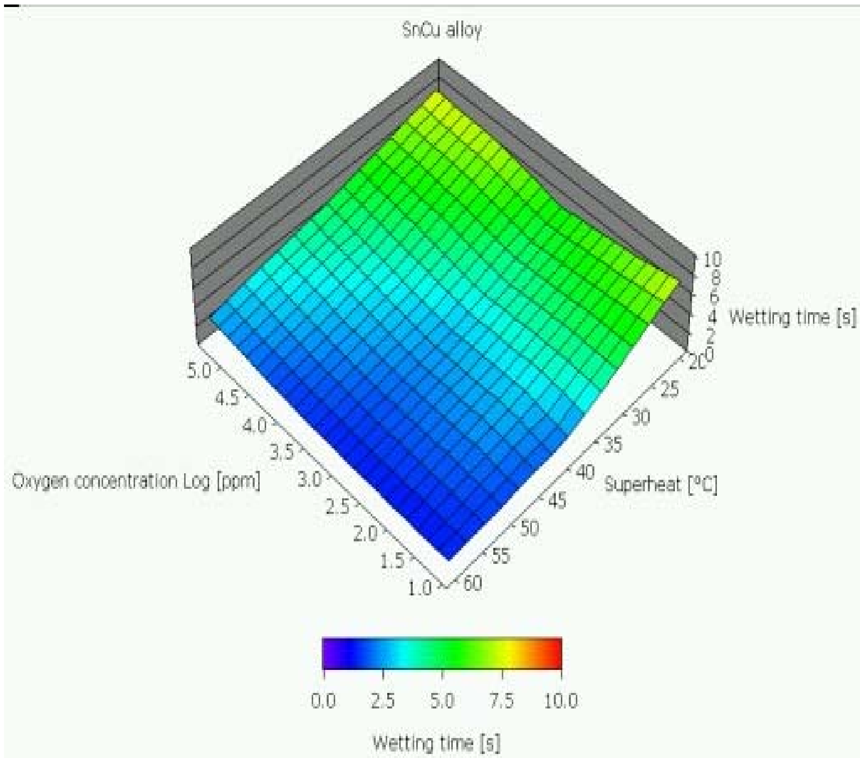

Figure 3 - 3D Plot of Wetting Time, Temperature and Oxygen Levels for SnCu

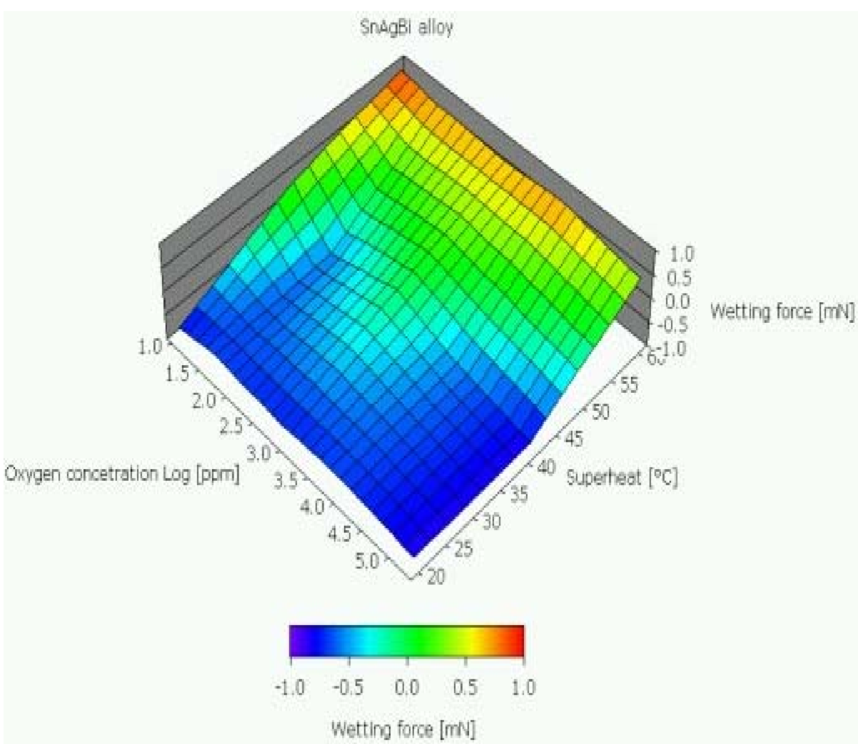

Figure 4 - 3D Plot of Wetting Force, Temperature and Oxygen Levels for SnAgBi

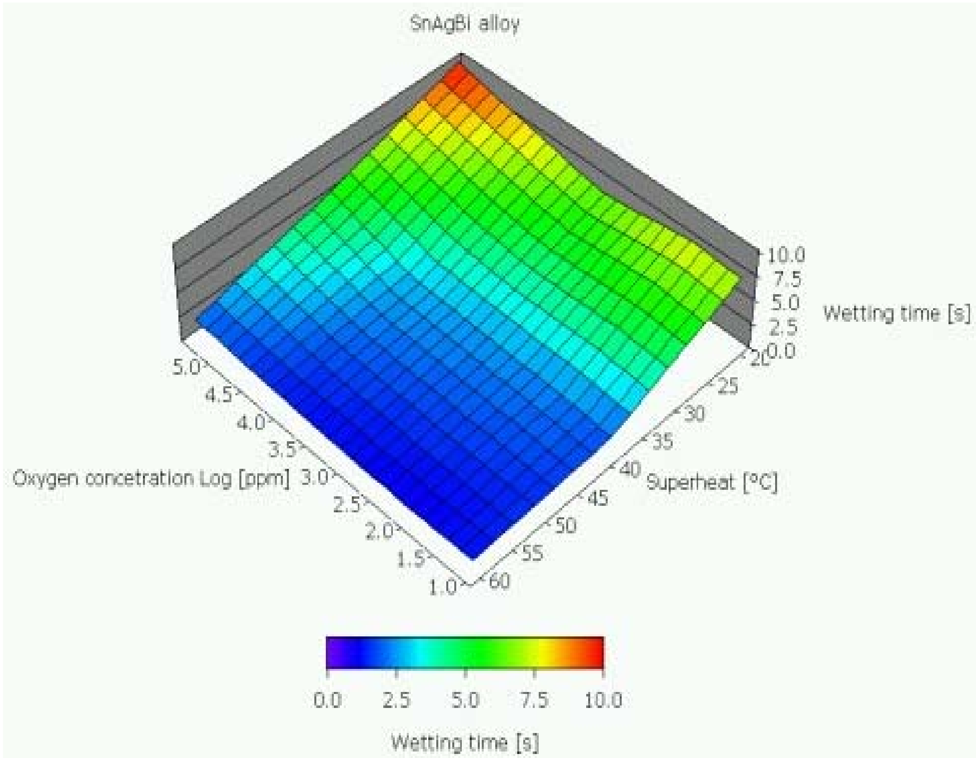

Figure 5 - 3D Plot of Wetting Time, Temperature and Oxygen Levels for SnAgBi

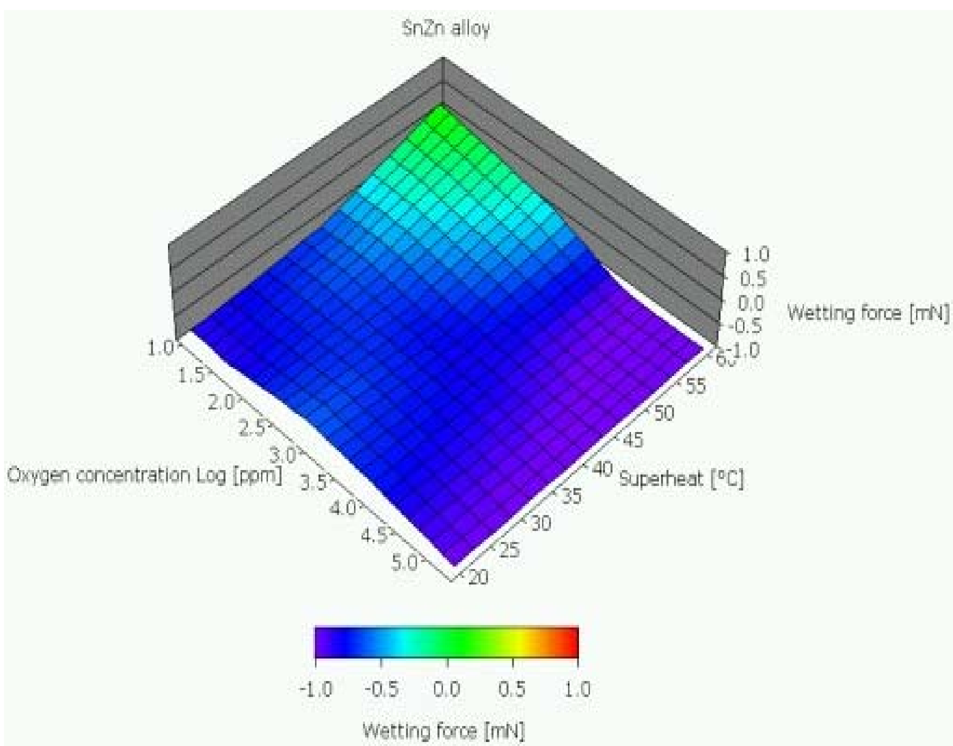

Figure 6 - 3D Plot of Wetting Force, Temperature and Oxygen Levels for SnZn

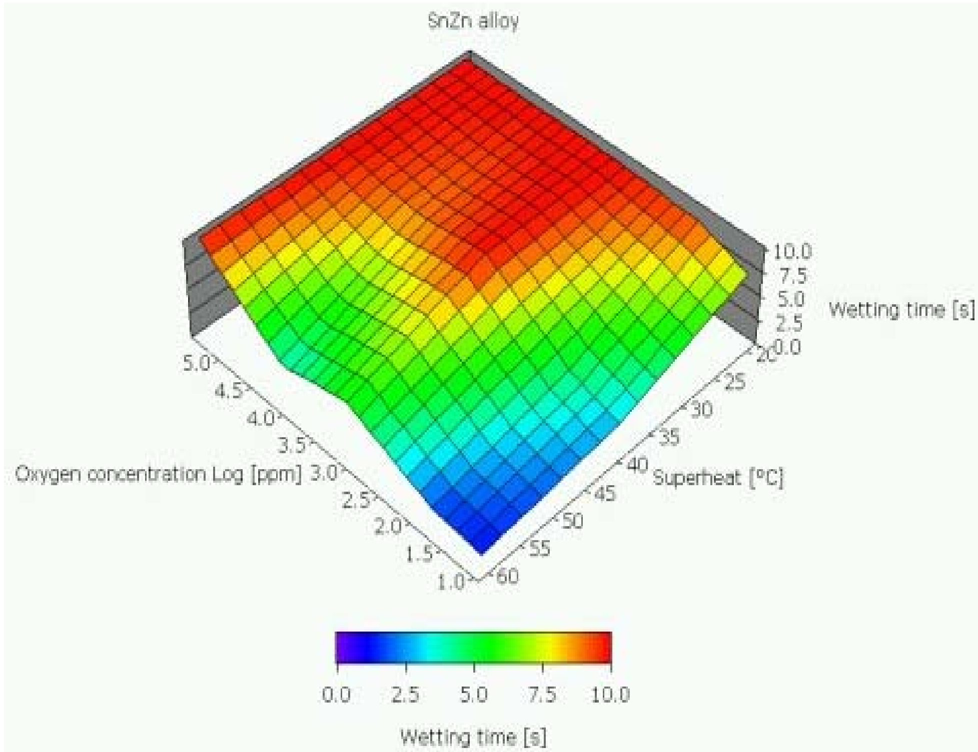

Figure 7 - 3D Plot of Wetting Time, Temperature and Oxygen Levels for SnZnWetting Data for

Wetting Data for molybdenum wire

The wetting results are shown for the Mo wire in Figure 8 and 9 for the SnPb and SnAgBi alloys. With both alloys the wetting is very poor, never achieving positive wetting. In the case of the SnPb alloy there is a clear beneficial effect of inerting, but no further increase with reducing the oxygen concentration below 10,000ppm.

The results with the SnAgBi alloy show a more complex response, but there is again a general trend of improving wetting with reducing oxygen concentration, although the overall effect is weaker than that observed with SnPb solder.

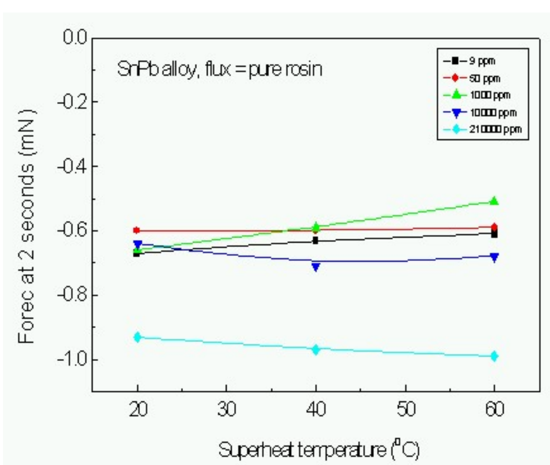

Figure 8 - Effect of Nitrogen Inerting on the Wettability of Mo wire with SnPb Solder Alloy

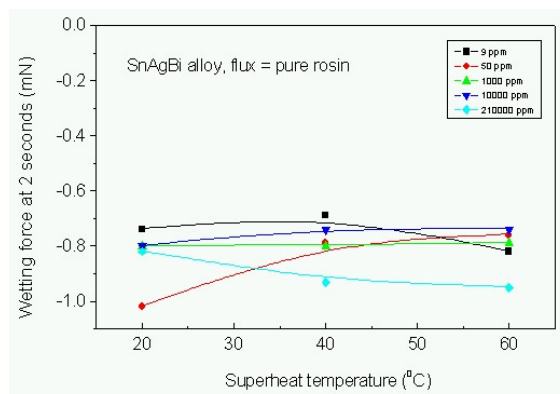

Figure 9 - Effect of Nitrogen Inerting on the Wettability of Mo wire with SnAgBi Solder Alloy

Discussion

This work has investigated the soldering behaviour of three leading lead-free alternatives for replacing SnPb, particularly under conditions of nitrogen inerting. The results have not only provided an insight into how these solders will perform when used in PCB assembly, but also enabled them to be ranked. Moreover, the experimental arrangement employing a wetting balance developed at NPL, enables the effects of nitrogen inerting to be quantified.

The results have highlighted some interesting differences between the performances of the three solders. Not surprisingly, SnCu and SnAgBi displayed superior wetting behaviours compared with that of SnZn solder. Whilst the low melting point of the SnZn alloy is very attractive, the oxidation issues result in poorer wetting. This might not be a worry with consumer goods or equipment used in benign office-type environments, but it does mean that widespread use of this solder, particularly in applications demanding high reliability, is unlikely. It is also apparent that for this solder nitrogen inerting will be highly desirable, if not mandatory, and at levels better than 100 ppm oxygen.

The SnAgBi and SnCu solders behaved similarly in terms of superheat with the former always giving the better performance. If the melting point is taken into account then the SnAgBi solder always out-performs the SnCu in terms of wetting. Interestingly the two alloys behaved similarly as nitrogen was introduced into the soldering process, with improvements in wetting force and time as the oxygen concentration was reduced to < 10,000 ppm. The improvement was significant and would undoubtedly impact on the process yield. Using SnCu solder, wetting was only just acceptable when soldering under normal atmosphere; however inerting had an immediate effect.

A note of caution should be made in the use and interpretation of these data. In PCB assembly the processing temperature is often poorly defined, and will often extend over a range. Indeed, the DT across an assembly is sometimes of the order of 10OC. Therefore marginal soldering temperatures can be easily realised, with the processing temperature only 10 to 20 degrees above the melting point. In this case the presence of nitrogen can make a decisive difference in maintaining wetting and widening the process window.

At even lower oxygen levels (< 50 ppm) there was again an improvement in wetting using SnCu and SnAgBi, but the effect was more subtle and less likely to be significant, especially when the cost of nitrogen inerting is taken into account. However, this improvement may be important when processing particularly difficult assemblies, such as large multi-layer boards.

The lower cost associated with SnCu solder will probably maintain the popularity of this alloy for wave soldering. Although its wetting behaviour was broadly similar to that of SnAgBi, the melting point is 17 degrees higher at 227OC demanding the use of a lower superheat. However, the latter may not compromise the wetting too much since the dynamic energy of the wave will compensate for the loss of the thermal energy.

The need to achieve superior wetting with higher soldering temperatures, lower superheats and alloys with higher surface tension, will require new fluxes. These will have to have more solids in order to withstand the higher temperatures, and be more active to achieve adequate wetting with the new alloys and the lower superheat. There may be another issue here. In achieving adequate activity in the flux, there is a possibility that harmful flux residues may be left behind causing low surface insulation resistance (SIR). This makes the case for nitrogen inerting when using lead-free solders, even more compelling. It is expected that in the future in order to achieve good wetting the balance between flux activity and nitrogen inerting will swing more and more towards increased inerting.

With the longer pre-heats, higher soldering temperatures and the more challenging wetting conditions associated with lead-free soldering technologies, the use of nitrogen is likely to become more widespread than is currently the case. To alleviate potential wetting problems, which are more severe with lead-free solders, the user has three options – increase the soldering temperature, increase the activity of the flux, or use nitrogen inerting. Changing the flux is not an easy option, since the flux is often specified, and any new fluxes will require qualification. Increasing the temperature is a possibility, but it is likely that with lead-free soldering the maximum temperature is already being used in current profiles. Hence in many cases the only viable option will be to use nitrogen inerting.

The results with the Mo wire show that nitrogen inerting can influence the wetting of normally non-wetting surfaces. This effect is presumably a reduction in the surface tension of the solder as any interaction with the Mo is unlikely due to the tenacious nature of the Mo oxide.

Conclusions

- With the more restrictive soldering conditions and narrower process windows associated with lead-free soldering technologies the use of nitrogen inerting will play an increasingly important role in attaining satisfactory soldering. Nitrogen inerting can largely compensate for the poor solderability experienced when using lead-free solders.
- Of the three options available to improve wetting (increasing flux activity, increasing soldering temperature, reducing oxygen concentration) the use of nitrogen is the most preferable technically.
- In achieving adequate wetting, it is necessary to have a balance between flux activity and nitrogen inerting. With the more challenging wetting conditions of higher surface tension, together with the lower superheats, of lead-free alloys compared to those of SnPb, the use of nitrogen may become inevitable.

- Developments in flux chemistry may partially offset the need for inerting.
- In order to achieve good yield and acceptable reliability when using SnZn solder alloys it will be necessary to use nitrogen inerting with oxygen levels better than 100 ppm.
- When using SnCu and SnAgBi solder alloys an improvement in wetting can be achieved with nitrogen inerting at oxygen levels of only 10,000 ppm. However, a level of 5,000 ppm oxygen is recommended as an ideal compromise between product quality and cost.
- Inerting to 50 ppm oxygen when using SnAgBi and SnCu solders will provide a benefit when soldering particularly difficult assemblies e.g. multi-layer boards.
- The relative cheapness of using SnCu solders will ensure this alloy continues to be considered as a leading lead-free alternative to SnPb by many users of wave soldering. The dynamic energy in wave soldering may help offset the poorer solderability compared with other alloys, even at room temperature. The marginal wetting of SnCu in air and its higher melting point could make the use of inerting inevitable, depending on the flux employed.

Acknowledgements
We would like to acknowledge the assistance of Milos Dusek in producing the 3D plots and Brian Richards for useful discussions.

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