Effects of Phosphorus on Microstructure and Fluidity of Sn-0.7Cu-0.05Ni Lead-Free Solder

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Phosphorus is often added to wave-solder baths as an anti-oxidation agent. Despite this practice, there is little information on how phosphorus influences the solidification and flow properties of new lead-free solders such as Sn-0.7Cu-0.05Ni. This paper investigates the effects of phosphorus content on microstructure and maximum fluidity length in Sn-0.7Cu-0.05Ni-xP alloys containing 0–0.08 mass% phosphorous. Ppm levels of phosphorous are found to cause Sn-xP, Ni-xP-(Sn) and Cu-xP-(Sn) intermetallic compounds to form in the liquid solder. The IMCs are less dense than liquid Sn and float towards the surface of the melt driven by buoyancy. It is shown that P-free Sn-0.7Cu-0.05Ni solidifies with a near-eutectic microstructure whereas, when P is added to this alloy, a significant volume fraction of primary Sn dendrites form once the P content exceeds ~0.01 mass% P. It is further shown that P additions decrease the ability of Sn-0.7Cu-0.05Ni to flow as it solidifies.

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1. Introductions

Since the discovery that the addition of 0.04–0.1 mass% Ni to Sn-0.7 mass%Cu alloys improves soldering properties, the Sn-Cu-Ni alloy system has become one of the most promising lead-free soldering alloys available.^{1,2)} The addition of between 0.04–0.1 mass% Ni has been shown to improve the soldering characteristics of Sn-Cu alloys by reducing the tendency for “bridging” and to improve the interface between the solder and the base metal.³⁾ The Ni acts to increase the ability of the solder to flow as it solidifies as shown in previous research using the vacuum fluidity test.^{4,5)} The improved capacity of Sn-0.7Cu-(0.04–0.1)Ni to flow as it solidifies is thought to be beneficial during wave soldering, when it is important that the solder is able to completely fill joints and cover connections, and for excess solder to drain away to leave tidy fillets.

Phosphorus is commonly added to solders as an anti-oxidation agent during wave soldering with Sn-37Pb and some new lead-free solder alloys. However, there is little information on how phosphorus influences the solidification and flow properties of Sn-Cu-Ni solders. The purpose of the current research is to investigate the effect of phosphorus on microstructure and maximum fluidity length of Sn-0.7Cu-0.05Ni-(P) alloys.

2. Experimental

Six alloys were used in this study: Sn-0.7Cu, Sn-0.7Cu-0.05Ni and four Sn-0.7Cu-Ni-P alloys containing 0–0.08 mass%P. P was mixed with Sn-0.7Cu-0.05Ni by adding a Sn-5 mass%P master alloy to pre-alloyed Sn-0.7Cu-0.05Ni ingot. The Sn-0.7Cu-0.05Ni was placed in a clay-graphite crucible and heated to 290°C in an electric resistance furnace. The melt was held at this temperature for a minimum of two hours. The Sn-5 mass%P master alloy was then added and the

melt was stirred vigorously by hand for approximately one minute to aid mixing. The system was then held at 290°C for a further hour. Next, the dross was removed from the surface of the melt and two samples of the alloy were collected concurrently in boron nitride coated tapered stainless steel moulds using the method outlined in reference.⁵⁾ One of the samples was used to record the cooling curve using an N-type thermocouple. The other sample was left to solidify and was later used for metallographic examination. This technique resulted in a cooling rate of 0.5°C·s⁻¹ prior to nucleation of the first solid. Samples for chemical analysis were taken from the top of the clay-graphite crucible, after dross had been removed from the melt surface.

Samples were sectioned, mounted in resin and then ground using SiC paper (120–2400 grit). The samples were given a final grinding on 4000 grit SiC paper with soap as a lubricant to prevent the embedding of SiC particles, before a final polish with 0.05 µm colloidal silica. Optical micrographs were taken of these samples before and after etching in a 5% HNO₃ solution. A JEOL 6460LA scanning electron microscope was used to take high magnification backscattered electron images (BEI) and energy dispersive spectra (EDS) of the samples with a particular focus on determining the location of P, Ni and Cu in the microstructures.

The extent to which the alloys could flow as they solidify was studied using the vacuum fluidity test (Ragone method),^{6,7)} where the liquid alloy is forced to flow through a relatively cold tube so that the alloy solidifies as it flows. Experimental parameters were held at:

- (1) Mass of alloy in crucible: 1500 g ± 0.2 g
 - (2) Melt temperature: $T_{liq} + 40^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ (average 267.7°C)
 - (3) Ambient temperature: 22.7°C ± 2.5°C
 - (4) Partial vacuum: -80 kPa ± 2 kPa
 - (5) Outer diameter of borosilicate glass tube: 6 mm ± 0.15 mm
 - (6) Thickness of borosilicate glass tube: 1.5 mm ± 0.1 mm
- Further details of the maximum fluidity length experimental

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Fig. 1 SEM/EDS elemental mapping from the top of a cooling-cup sample with nominal composition of $\text{Sn-0.7Cu-0.05Ni-0.07P}$. (a) secondary electron SEM image, (b) P, (c) Cu and (d) Ni.

Fig. 2 SEM/EDS elemental mapping from the centre of a cooling-cup sample with nominal composition of $\text{Sn-0.7Cu-0.05Ni-0.07P}$. (a) secondary electron SEM image, (b) P, (c) Cu and (d) Ni.

Fig. 3 Lattice image and corresponding selected area electron diffraction pattern (SAD) taken from an intermetallic at the flow tip of sample with nominal composition Sn-0.7Cu-0.05Ni-0.07P. The crystal structure is monoclinic, and EDS point analysis yielded Sn:49 at%, Cu:49 at%, Ni:2 at% and P:0 at%, indicating that the phase is η' -(Cu,Ni)₆Sn₅'.

Table 1 Chemical compositions of the samples (mass%) measured by ICP-AES.

Sample name	Nominal compositions			Measured compositions		
	Cu	Ni	P	Cu	Ni	P
Sn0.7Cu	0.6975	0.0032	0.000	0.6975	0.0032	0.0002
Sn0.7Cu0.05Ni	0.6954	0.0503	0.000	0.6954	0.0503	0.0002
Sn0.7Cu0.05Ni0.007P	0.6944	0.0502	0.007	0.7015	0.0501	0.0023
Sn0.7Cu0.05Ni0.02P	0.6926	0.0501	0.020	0.6983	0.0457	0.0087
Sn0.7Cu0.05Ni0.07P	0.6857	0.0496	0.070	0.6817	0.0330	0.0212
Sn0.7Cu0.05Ni0.08P	0.6843	0.0495	0.080	0.6644	0.0371	0.0253

procedure are outlined in reference.⁴⁾ Experiments were repeated six times for each composition. Fully solidified fluidity samples were later prepared for optical microscopy and field emission transmission electron microscopy (FE-TEM: Tecnia20). High resolution lattice images and electron diffraction patterns were used to study the intermetallic phases and EDS was used for elemental analysis.

3. Results and Discussion

3.1 Intermetallic compounds

Adding ppm levels of phosphorous to Sn-0.7Cu-0.05Ni was found to influence the intermetallic compounds that form during solidification. SEM-EDS analysis of cooling-cup samples revealed the presence of various P-bearing intermetallic particles. Figures 1(a)–(d) and 2(a)–(d) show SEM/EDS element maps from a sample with nominal composition Sn-0.7Cu-0.05Ni-0.07P. Figure 1 is from the top of the sample and appears to contain a number of distinct intermetallic phases: (i) the Cu-rich regions containing only background-levels of Ni or P are probably Cu₆Sn₅; (ii) the P-rich region containing only background-levels of Ni and Cu is probably a Sn-*x*P phase; and (iii) the region rich in P and Ni is likely to be one of the wide range of binary Ni-*x*P or ternary

Fig. 4 The measured chemical composition of the melt as a function of the amount of master alloy added. Dashed lines indicate the nominal composition.

Fig. 5 Typical microstructures from near the flow tip of maximum fluidity length samples. (a) Sn-0.7Cu, (b) Sn-0.7Cu-0.05Ni, and (c) nominal composition Sn-0.7Cu-0.05Ni-0.07P (measured Sn-0.68Cu-0.033Ni-0.021P).

Ni- x P-(Sn) phases that are known to exist.^{8,9)} Figure 2 is from the centre of the sample and appears to contain two distinct intermetallic compounds: (i) Cu-rich regions are probably Cu_6Sn_5 , and (ii) the Ni-rich region containing P is probably a binary Ni- x P or ternary Ni- x P-(Sn) phase,^{8,9)} similar to Fig. 1. Further work is required to isolate and identify the phases present. A significantly higher volume fraction of P-bearing compounds was observed in the top regions than elsewhere in cooling-cup samples.

Figure 3 shows the lattice image, selected area diffraction pattern (SAD) and EDS results from an intermetallic at the flow tip of a fluidity sample with nominal composition Sn-0.7Cu-0.05Ni-0.07P. The TEM/SAD result shows that the phase has a monoclinic crystal structure and the EDS analysis yielded a composition of $\text{Sn}_{49}\text{Cu}_{49}\text{Ni}_2$. The Sn rich Sn-Cu binary phase diagram,^{10,11)} shows that Cu_6Sn_5 has two crystal structures, with an allotropic transformation at 186°C. For the compositions studied here, the high temperature hexagonal η - Cu_6Sn_5 phase is expected to form during solidification and to transform to the low temperature monoclinic η' -(Cu,Ni) $_6\text{Sn}_5'$ phase on cooling.^{11–13)} The monoclinic $\text{Sn}_{49}\text{Cu}_{49}\text{Ni}_2$ intermetallic in Fig. 3 is consistent with the room temperature monoclinic η' -(Cu,Ni) $_6\text{Sn}_5'$ phase.^{11–13)} No phosphorus containing intermetallics were found in fluidity samples.

3.2 Composition

Table 1 shows the melt composition as measured by ICP-AES. The measured compositions do not correlate closely with the nominal compositions, despite the fact that the alloys were made simply by mixing a Sn-5P master alloy with pre-

alloyed Sn-0.7Cu-0.05Ni ingot. Note that the quoted nominal values already account for the decrease in Ni due to the Sn-5P master alloy addition. Table 1 and Fig. 4 show that the measured Ni contents are lower than the nominal values, and adding increasing Sn-P master alloy tends to amplify this difference. The highest P additions also led to a reduction in Cu content in the melt. Additionally, the composition of P in the melt was significantly lower than the nominal composition.

During experiments, it was noticed that the surface dross of phosphorous containing alloys had a much greater lustre than that in the Sn-0.7Cu or Sn-0.7Cu-0.05Ni alloys. Combining this observation with the presence of a high volume fraction of P-bearing particles at the top of samples in §3.1, it is likely that low-density P-bearing particles floated towards the surface of the melt and were removed when dross was removed from the melt. As dross was removed before chemical analysis and cup samples were taken and before fluidity experiments were run, adding P changes the P, Ni and Cu contents during these experiments. The removal of dross is also common practice in industrial wave-soldering operations.

3.3 Microstructure

Figures 5 and 6 show optical micrographs from fluidity samples and three locations within cooling-cup samples, respectively. Although the scale of the microstructure and the cooling rate during solidification differs between the two experiments, each alloy exhibited similar microstructural characteristics. The microstructure of binary Sn-0.7Cu con-

Fig. 6 Optical micrographs from the top, middle and bottom of cooling-cup samples made using five Sn-0.7Cu-xNi-yP alloys. Compositions are in mass% with measured compositions in bold and nominal compositions in bracketed italics.

sists of primary Sn dendrites and interdendritic eutectic. In Sn-0.7Cu-0.05Ni samples no dendrites are discernable and the intermetallics are distributed more evenly throughout the microstructure. In nominal Sn-0.7Cu-0.05Ni-xP alloys, the microstructure was found to depend on the P content. At a measured level of 0.002 mass% P, the microstructure appears near-eutectic and Sn-dendrites were not observed. At the higher measured levels of 0.021 and 0.025 mass% P, however, the microstructure is clearly hypoeutectic, containing a significant volume fraction of Sn dendrites.

Previous research by the authors^{5,14} has shown that, as the Ni content in Sn-0.7Cu-xNi decreases from 0.05 mass%, the volume fraction of primary Sn dendrites in the microstructure increases. This result was shown to be consistent with the phase equilibria of the Sn-Cu-Ni system,¹⁵ where Sn-0.7Cu-0.05Ni is closer to a eutectic valley than Sn-0.7Cu.^{4,5} However, the increased volume fraction of Sn-dendrites with increasing P content in Figs. 5 and 6 cannot be solely explained by the decreased Ni content, as the P containing samples in Figs. 5(c) and 6 contain a higher volume fraction of Sn dendrites than that previously reported for P-free Sn-0.7Cu-(0.03–0.04)Ni alloys.⁵

3.4 Maximum fluidity Length

Figure 7(a) shows that adding P to a Sn-0.7Cu-0.05Ni melt significantly decreases the ability of the alloy to flow as it solidifies. P additions decrease the maximum fluidity length with the most dramatic decrease in the range 20 to 90 ppm P (measured composition). Extensive studies on the influence of alloy composition on maximum fluidity length (L_f) have shown that pure metals and eutectic alloys have the highest

values of L_f , and that L_f decreases as the composition deviates from these points.^{6,7,16} The microstructural observations in §3.3 revealed that adding increasing levels of P to Sn-0.7Cu-0.05Ni melts leads to a transition from a near-eutectic microstructure to one containing a significant volume fraction of Sn dendrites. Therefore, the decreasing L_f with increasing P additions appears to occur because the composition moves away from a eutectic valley.

Figure 7(a) does not show the change in L_f at constant Ni content, however, because P additions reduced the Ni content of the melt (see Table 1 and Fig. 4). The L_f of Sn-0.7Cu-xNi alloys has previously been shown to be highly sensitive to the Ni content,^{4,5,17} and it is therefore important to assess the role of the changing Ni content on the change in L_f with P additions. Figure 7(b) shows the influence of Ni content on L_f in P-free Sn-0.7Cu-xNi using data from reference.⁴ Figure 7(b) also shows the P-containing data from Fig. 6(a), where L_f values are plotted against the measured Ni content. In both cases a marked transition in L_f occurs with increasing Ni content, and this transition occurs at higher Ni content in the P-containing alloys. However, similar to Fig. 7(a), Fig. 7(b) does not show L_f vs. Ni at constant P, and therefore Figs. 7(a) and (b) do not allow us to decouple the influences of P and Ni on L_f .

4. Conclusions

0–800 ppm P has been added to liquid Sn-0.7Cu-0.05Ni alloys in the form of a Sn-5 mass%P master alloy. P additions were found to influence following:

(1) Ni-xP-(Sn), Cu-xP-(Sn) and Sn-xP intermetallic com-

Fig. 7 Maximum fluidity length (L_f) in Sn-0.7Cu-xNi-yP alloys using the experimental conditions given in reference 4. (a) L_f versus P content, (b) L_f versus Ni content.

pounds were observed in P-containing alloys. A higher volume fraction of these phases was distributed near the top surface of samples, indicating that these particles float in liquid Sn. These phases can be removed from the melt when dross is removed.

- (2) TEM/SAD analysis of intermetallics in fluidity samples demonstrated the presence of monoclinic η' - $(\text{Cu,Ni})_6\text{Sn}_5'$ in Sn-0.7 mass%Cu-0.05 mass%Ni-0.07 mass%P. TEM/EDS analysis showed that this phase contained negligible P and only 2 at% Ni.
- (3) The maximum fluidity length decreases when P is added to Sn-0.7Cu-0.05Ni melts. The most dramatic decrease in fluidity length occurs in the range 20 to 90 ppm P (nominal addition of 70 to 200 ppm P).
- (4) Sn-0.7Cu-0.05Ni solidifies with a near-eutectic microstructure whereas, when P is added to this alloy, a significant volume fraction of primary Sn dendrites forms once the P content exceeds ~ 0.01 mass% P.

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