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THE EFFECTS OF PHOSPHORUS IN LEAD-FREE SOLDERS

Keith Sweatman, Takatoshi Nishimura and Takuro Fukami
Nihon Superior Co., Ltd
Osaka, Japan
k.sweatman@nihonsuperior.co.jp

ABSTRACT

Phosphorus has long been a "secret ingredient" in tin-lead solder, particularly solder made with recycled metal, as it is a powerful deoxidant that removes dross and brings a sparkle to the surface of the molten solder. With the change to high-silver lead-free solders, which have a strong tendency to oxidize and generate large volumes of dross, phosphorus became a widely used but seldom mentioned ingredient. The solder pot erosion that forced manufacturers to upgrade the materials used in the construction of wave soldering machines is primarily the result of the 100ppm phosphorus commonly included in the formulation of SAC alloys. Now, as solder manufacturers try to distinguish their low- and no-Ag solders from those of those offered by other suppliers, the presence or absence of phosphorus, with or without other antioxidants that have less detrimental side effects, has become a controversial issue. In this paper the authors will report a series of experiments that have been undertaken to determine the effects of phosphorus additions on the behaviour and properties of a widely used lead-free solder.

Key words: Lead-free solder, nickel, dross, phosphorus

INTRODUCTION

One of the many challenges that the electronics industry had to face during the transition to lead-free technologies was learning how to manage the pot of molten solder that is part of wave soldering, selective soldering, dip soldering and hot air solder levelling machines. Issues that emerged early in that transition were excessive drossing and erosion of solder pots, pumps and nozzles.

Dross Control

The constituent of the solders commonly used in electronics assembly that is most vulnerable to oxidation is tin and all the lead-free solders contain at least 95% Sn compared with the 63% Sn of the standard tin-lead solder. Oxidation of solder, particularly when combined with the turbulence associated with the operation of a solder wave, results in the formation of dross, which is a sludgy mixture of unoxidized solder trapped in a web of oxides. This dross interferes with the efficient operation of the wave soldering machine and has to be skimmed off periodically. These skimmings can be processed and the metal content recovered and recycled but the production of dross results in a loss of expensive solder and increases the cost of operating the line so its generation needs to be kept to a minimum.

Phosphorus is a powerful antioxidant that has been widely used for dross control in tin-lead solders and soon became a common ingredient in lead-free solders such as the widely-used Sn-3.0Ag-0.5Cu alloy that became known as "SAC305".

Soldering Machine Erosion

As well as being a powerful antioxidant for solder phosphorus can also break down the oxide film that gives stainless steel its resistance to wetting by molten solder. Once the protective oxide film had been penetrated the molten solder wets the underlying Fe-Cr-Ni alloy, which then begins to dissolve in the solder [1]. The consequence is erosion of parts exposed to the molten solder and even perforation of the walls of the solder pot resulting in leakage of molten solder, which creates serious health and safety issues as well as damaging the machine.

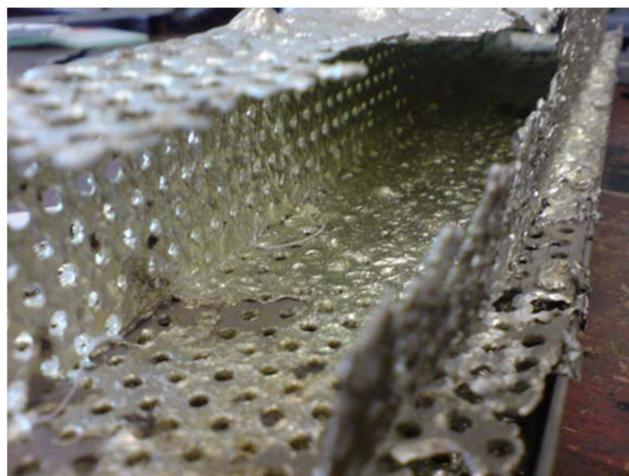


Figure 1. Erosion of stainless steel wave solder machine parts by lead-free solder.

One solution to the problem of the machine erosion caused by the phosphorus added to control drossing was to make the solder pot of cast iron, which is more resistant to dissolution or to line the pot with titanium. Pumps and nozzles were made more resistant to wetting and erosion by applying ceramic coatings or a treatment that created a surface layer of metal nitrides that are much more resistant to wetting and dissolution. However this adds substantially to the cost of soldering equipment.

Another approach was to use as the antioxidant germanium, which does not attack the protective oxide on stainless steel but is at least as effective as phosphorus in controlling the

drossing of solder baths. Included in the studies on the effect of phosphorus additions reported in this paper is a widely used commercial solder alloy in which germanium is the antioxidant (Sn-0.7Cu-0.05Ni+<0.01Ge).

Effect on Solder Fluidity

A factor other than the aggressiveness of phosphorus towards the protective oxide coating on stainless steel that influenced the choice of antioxidant has arisen from the use of a microalloying addition of nickel to lead-free solders. It was found that nickel at a level of about 0.05% has a dramatic effect on the behaviour of the Sn-O.7Cu alloy, the nominal eutectic composition [2]. The unmodified Sn-0.7Cu alloy solidifies in two stages, with primary tin dendrites growing first with Sn-Cu_6Sn_5 eutectic finally freezing in the interdendritic spaces. This two stage solidification results in the dull cracked surface of the cast alloy (Figure 2(a)). The smooth bright surface of Sn-0.7Cu-0.05Ni cast under the same conditions indicates that the two stage solidification has been replaced by single stage pseudoeutectic solidification (Figure 2 (b)) which means that in soldering processes the alloy behaves more like the Sn-37Pb eutectic that it is replacing.

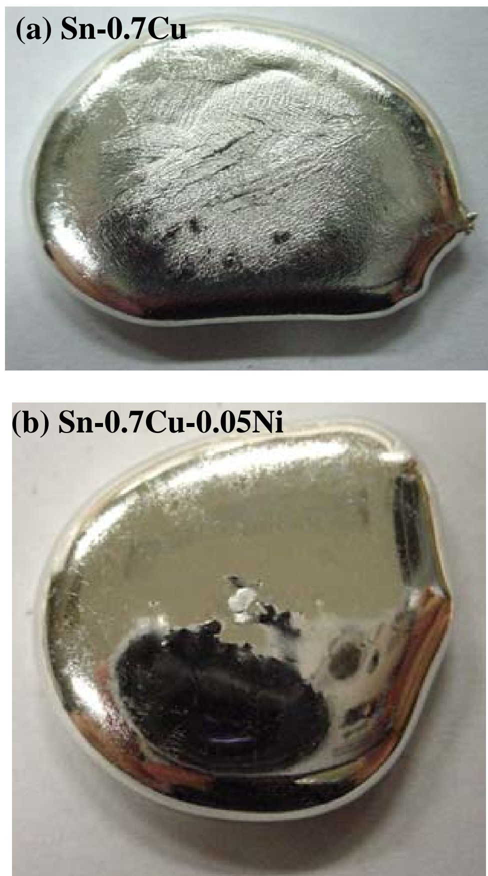


Figure 2. Effect of an addition of 0.05Ni on the as-cast surface of Sn-0.7Cu.

That the nickel had a significant effect on the solidification behaviour of Sn-0.7Cu is also apparent in the Ragone fluidity [3] as a function of nickel content [2] (Figure 3).

It has been found that when phosphorus is added to the Sn-0.7Cu-0.05Ni it reacts with the nickel to form a nickel phosphide [4] (Figure 4).

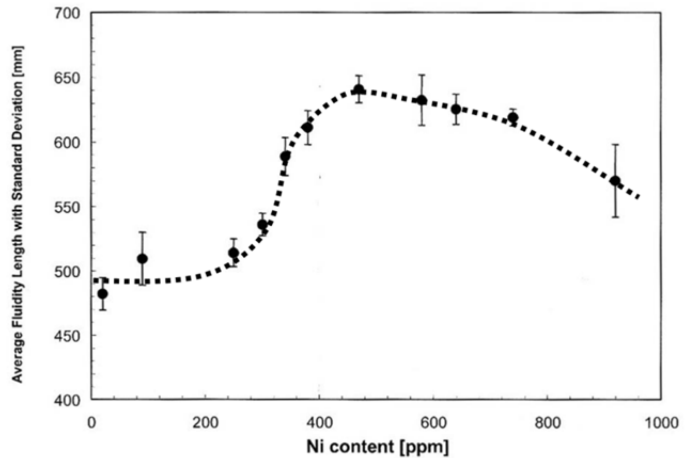


Figure 3. Ragone fluidity of Sn-0.7Cu as a function of Ni content. [2]

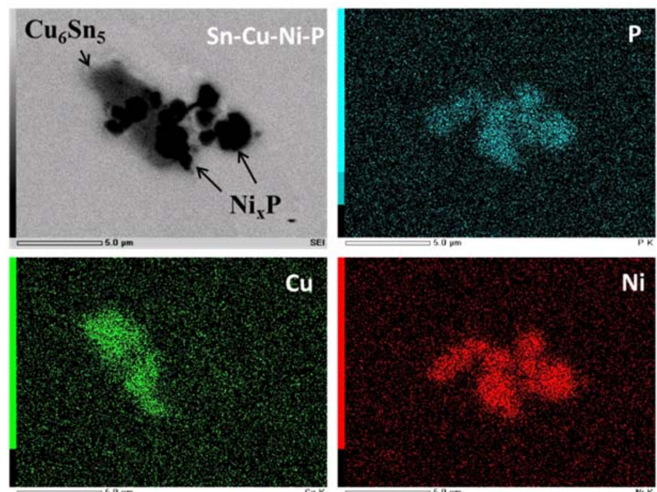


Figure 4. SEM and element mapping of nickel phosphide precipitate in Sn-0.7Cu-0.05Ni-0.07P [4].

Combined in this way the nickel is no longer available to play a role in promoting pseudoeutectic solidification with a consequent negative effect on Ragone fluidity (Figure 5).

The effect of the deactivation of the nickel by the phosphorus is apparent in the microsections in Figure 6. After the addition of the phosphorus the microstructure of the Sn-0.7Cu-0.05Ni shows evidence of a return to the two stage solidification characteristic of the basic Sn-0.7Cu alloy.

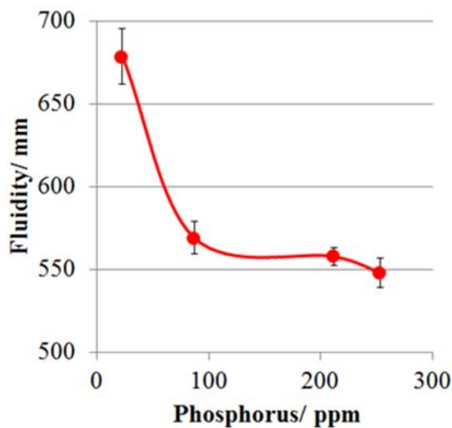


Figure 5. Ragone fluidity of Sn-0.7Cu-0.05Ni as a function of phosphorus additions [4]

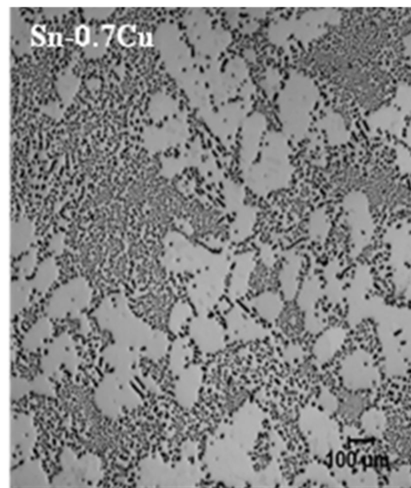
Effect on Cu_6Sn_5 Stabilization

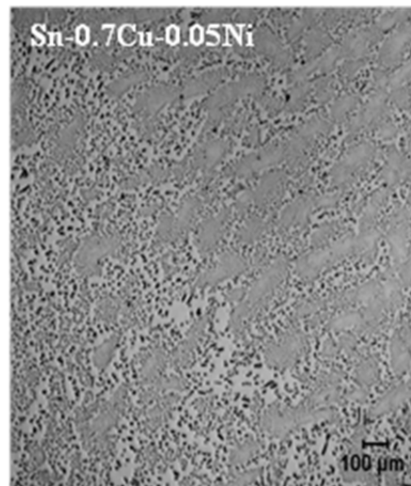
In addition to its effect in the fluidity of the Sn-0.7Cu solder alloy, nickel stabilizes the hexagonal η form of the Cu_6Sn_5 that forms the intermetallic layer in solder joints on copper substrates [3]. In the absence of nickel the stable form of the Cu_6Sn_5 at temperatures below 186°C is the monoclinic η' phase. The volume change associated with that transformation creates stress which can fracture the intermetallic reducing the resistance of the solder joint to impact loading. The nickel therefore plays an important role in maintaining the integrity of the intermetallic layer (Figure 7). With the deactivation of the nickel by a phosphorus addition the stabilization effect is lost with the consequent risk of a phase change and consequent cracking of the intermetallic layer.

EXPERIMENTAL PROGRAM

While considerable practical and experimental evidence for the negative effects of phosphorus additions on lead-free solder and the equipment in which they are used has been accumulated further experimentation has identified new issues:

- The effect of phosphorus additions on copper dissolution
- The effect of phosphorus additions on wetting of copper substrates
- The effect of phosphorus additions to solder on the erosion of soldering tool tips
- The effect of phosphorus additions to solders in which drossing is already being controlled by a germanium addition





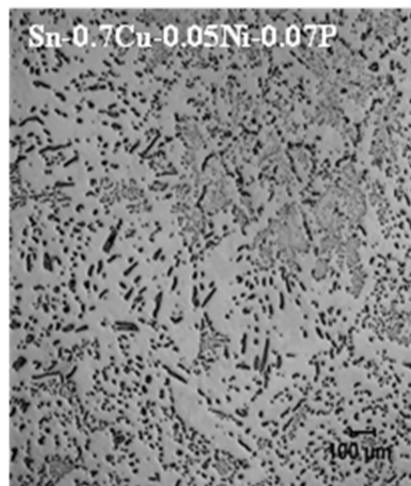


Figure 6. Effect of phosphorus in the microstructure of Sn-0.7Cu-0.05Ni [4]

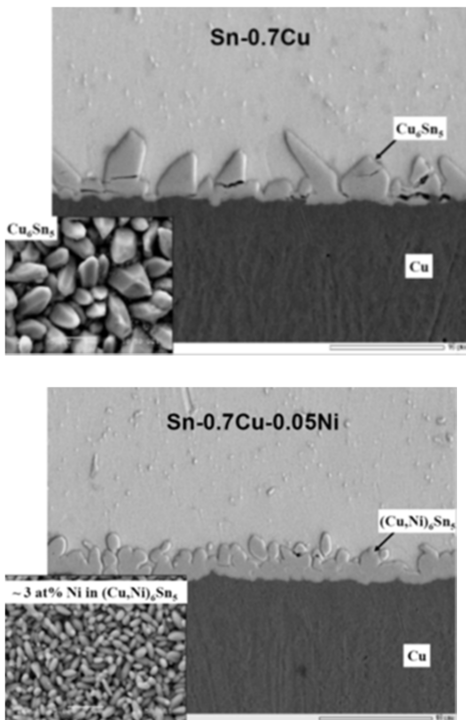


Figure 7. Effect of nickel on the stabilization of the intermetallic layer

Effect of Phosphorus on Copper Dissolution

Copper wire 0.44mm diameter was precleaned with 5% HCl solution and dipped in Sn-065Cu, Sn-0.65Cu-0.05Ni and Sn-0.65Cu-0.05Ni+100ppm P at 250°C. Samples were immersed for increasing times and them removed and cross-sectioned to measure the area of copper remaining. The results plotted in Figure 8 indicate that while the nickel addition substantially slowed the rate of dissolution the addition of phosphorus returned the rate to close to that for the alloy without the nickel addition.

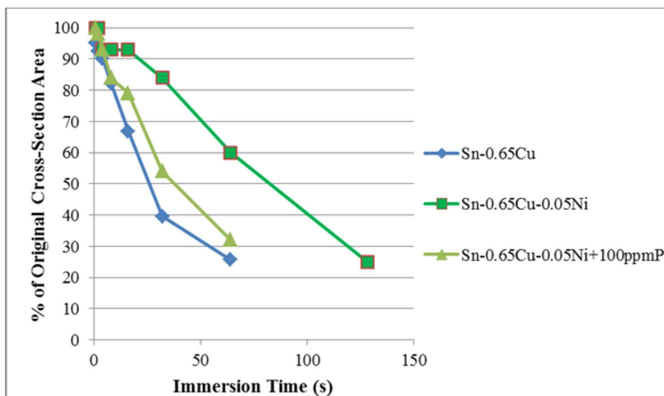


Figure 8. Cross-sectional area as a percentage of the original area of 0.44mm copper wire as a function of immersion time in the indicated solder alloy at 250°C.

Effect of Phosphorus on Wetting

Copper wires 0.6mm diameter were fluxed with a JIS Z 3197 Standard Type B flux and wetting behaviour at a solder temperature of 255°C was measured with a Rhesca Sat-5100 wetting balance with an immersion speed of 2mm/s to a depth of 2mm.

The force-time plots for Sn-0.7Cu-0.05Ni and Sn-0.7Cu-0.05Ni+Ge with and without the addition phosphorus are presented in Figure 9. In Figure 10 the wetting behaviour is interpreted in terms of the time to zero crossing. The phosphorus addition slows wetting but since the nickel addition does not appear to have an effect on wetting speed the slower wetting cannot be attributed to the deactivation of the nickel by reaction with the phosphorus. An explanation consistent with the accelerating effect of a phosphorus addition on copper dissolution is that wetting is slowed by a reaction between the copper and the phosphorus.

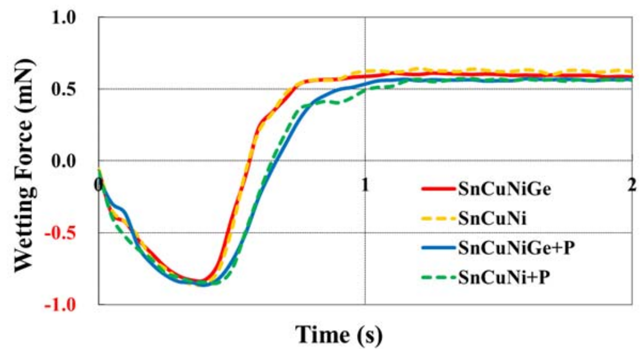


Figure 9. Wetting balance force/time plots

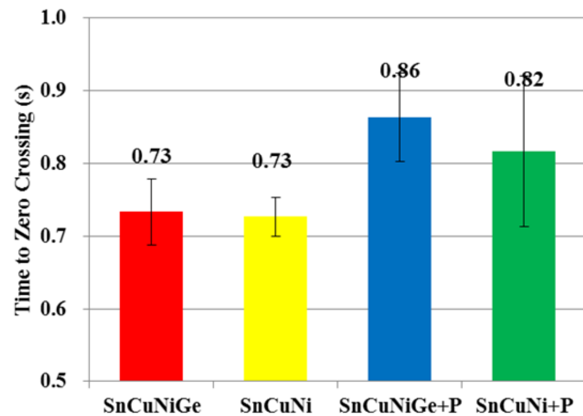


Figure 10. Effect of phosphorus addition on the zero crossing time in wetting balance testing of Sn-0.7Cu-0.05Ni with and without an addition of <0.01Ge on a copper substrate.

Effect of Phosphorus on Tip Erosion

A robotic soldering station (Figure 11) was set up to apply repeatedly to an iron plated soldering tip 15mm of 0.8mm diameter flux-cored lead-free solder. The reference solder alloy was Sn-0.7Cu-0.05Ni+<0.01Ge and the test alloy was Sn-0.7Cu-0.05Ni+<0.01Ge+<0.01 P. The core flux was J-STD-004 ROL1. The flux percentage was 3wt% and the tip temperature was 380°C. Tips were removed for cross-sectioning after 10,000, 15,000 and 30,000 operations. The effect of the P addition to the solder is apparent in Figure 12. The phosphorus promotes wetting of the protective iron

plating, which then dissolves quickly in the solder effectively destroying the tip (Figure 12(c).

Figure 11. Robotic soldering station

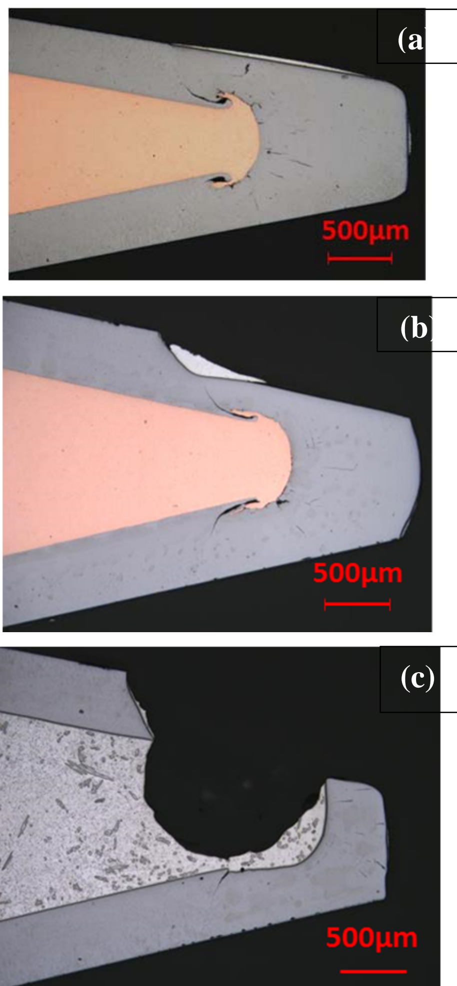


Figure 12. Effect of phosphorus addition to alloy on soldering tool tip erosion. (a) tip before testing, (b) and (c) tip after 15,000 soldering operations with Sn-0.7Cu-0.05Ni+<0.01Ge and Sn-0.7Cu-0.05Ni+<0.01Ge+ <0.01 P respectively.

Effect of Phosphorus on Drossing

A 400kg content solder pot (Figure 13) was filled with Sn-0.7Cu-0.05Ni+<0.01Ge and run for 8 hours under stable conditions at a temperature of 255°C. Dross accumulated on the surface of the solder, particularly near the area where the solder wave flows back in solder bath (Figure 14). All the dross generated during this period was carefully skimmed from the surface of the solder and weighed. To confirm the reproducibility of the method this procedure was repeated two more times with the solder in the pot being returned to its original level after each run. Phosphor-tin was then added to the solder bath to bring the phosphorus level up to a range of 0.001-0.003% and the procedure of three runs of 8 hours was repeated with the same pump settings and wave height (Figure 15).

The drosses collected were transferred to a crucible and heated in an electric furnace to 500°C (Figure 16). The dross was stirred so that over a period of about 30 minutes unoxidised solder was released leaving a dry powder that was presumed to be mainly solder oxides (Figure 17). The powder and recovered solder were weighed separately and the averaged results over the three runs of each alloy are plotted in Figure 18. The total weight of solder lost as dross was increased by nearly 68% by the phosphorus addition,

Figure 13. Nozzle of wave soldering machine

Figure 14. Dross accumulated on SnCuNiGe alloy after 8 hours operation at 255°C.

Figure 15. Dross accumulated on SnCuNiGe+P alloy after 8 hours operation at 255°C.

Figure 16. Crucible and furnace for sweating of dross to separate powder oxides from unoxidized solder.

Figure 17. Oxide powder left after sweating out unoxidized solder from dross collected from SnCuNiGe (left) and SnCuNiGe+P (right).

Samples of the drosses were mounted and polished for SEM examination and EDX analysis (Figures 19 and 20). The presence of phosphorus in the dross is consistent with the results of the referenced study [4] that found that the phosphorus reacts with nickel to form nickel phosphide that is lost to the dross, effectively removing the nickel from the solder with consequent loss of the performance and reliability benefits this alloying addition brings to lead-free solder.

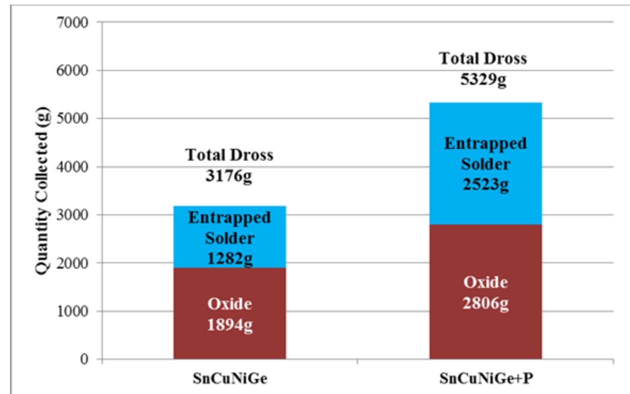


Figure 18. Comparison of dross generation before and after phosphorus addition.

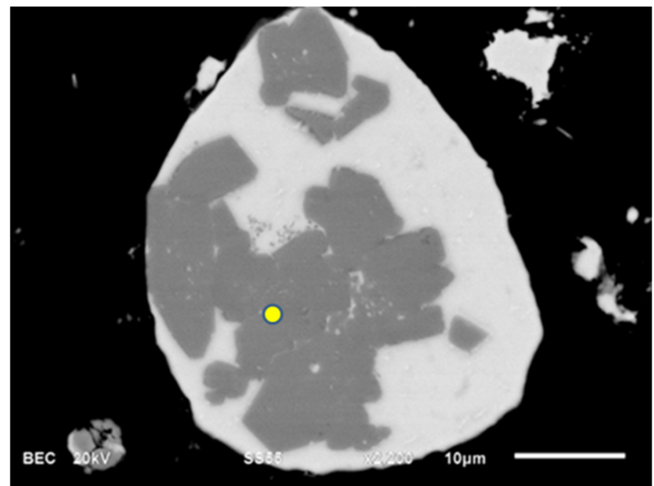


Figure 19. SEM of dross particle with point of EDX analysis indicated.

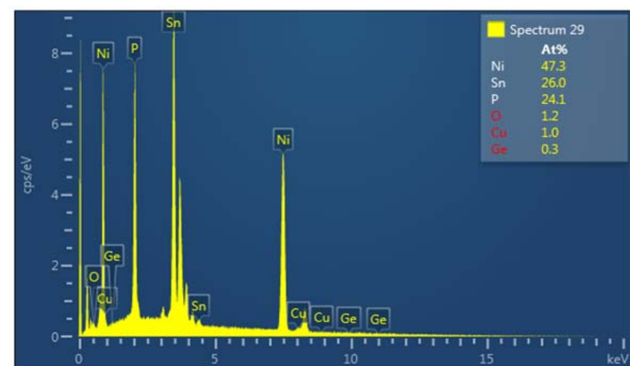


Figure 20. EDX spectrum from dross collected from SnCuNiGe+P alloy showing the strong phosphorus peak.

CONCLUSIONS

The results of laboratory tests and evaluation in soldering processes confirm the conclusions of earlier work that phosphorus does not have a place as an alloying addition in lead-free solders, particularly those that rely on nickel to

promote eutectic solidification or stabilize the hexagonal η form of the Cu_6Sn_5 intermetallic.

- Phosphorus additions to lead-free solders promote the wetting and consequent erosion of stainless steel machine parts.
- When added to tin-copper-nickel solders phosphorus reacts with the nickel reducing the beneficial effects that it has on solder fluidity and Cu_6Sn_5 stability.
- Wetting of copper is slowed.
- Erosion of iron plated soldering tool tips is accelerated.
- The rate of dross production in tin-copper-nickel alloy that already have germanium as their antioxidant is increased. Rather than working with the germanium synergistically to achieve an even lower rate of drossing, the phosphorus appears to act as an accelerant with the rate of dross production increasing by more than 60%.

Germanium is an effective antioxidant that does not cause the detrimental side effects that occur when phosphorus is used as an alloying addition to control oxidation or for any other purpose.

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