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Erosion of Copper and Stainless Steels by Lead-Free-Solders

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Abstract

An issue that has emerged from the increasing use by the electronics industry of lead-free solders in mass production wave soldering is the erosion of the copper of printed circuit board patterns and component terminations and the stainless steel of the wave solder bath. In the study reported here the wetting and erosion of copper and Type 304 stainless steel by two widely-used lead-free solders, Sn-3.0Ag-0.5Cu and Ni-stabilized Sn-0.7Cu, was compared with that of Sn-37Pb and Sn-0.7Cu with and without the addition of phosphorus antioxidant. The rate of dissolution of copper by the Ni-stabilized Sn-Cu alloy was found to be lower than that of pure Sn-37Pb alloy while that of the Sn-3.0Ag-0.5Cu and Sn-0.7Cu alloys was higher. The addition of phosphorus increased the copper erosion rate of both lead-free alloys well beyond that of Sn-Pb. The rate of erosion of stainless steel by lead-free solder was confirmed as faster than that of Sn-Pb eutectic solder and phosphorus was found to promote the wetting that precedes erosion. The rate of erosion of stainless steel by the Sn-0.7Cu solder was significantly slowed by the addition of nickel.

Introduction

It is widely argued that a switch by the electronics industry to lead-free solder for the assembly of its circuitry would make a worthwhile contribution to the protection of human health and the global environment and this view is reflected in European Community directives on the recycling of Waste Electrical & Electronic Equipment and the Restriction of Hazardous Substances in electronic equipment that come into force on July 1, 2006.

In the change to lead-free solders the electronics industry has faced the challenges of slower wetting, less spread and in some cases more bridges (shorts) than occur with the lead-containing solders they replace. These challenges have been met, however, and lead-free wave soldering in mass production has been running successfully in Japan since 1999 without compromising the quality or reliability of the assembled circuitry. Two issues that have, however, emerged from this experience of long term mass production with lead-free wave soldering are the faster erosion by some lead-free solders of copper from the tracks and pads of the printed circuit board and the erosion of the stainless steel from which the wave solder bath and fittings are constructed.

In the work reported here the interactions between two widely used lead-free solders, with and without phosphorus antioxidant and copper were studied by immersing copper wire in the molten solders and studying the cross-section of the wire as a function of immersion time. Similar experiments were also undertaken with Type 304 stainless steel wire. An indication of the extent of wetting of Type 304 stainless steel by the molten solders was obtained by exposing the surface to each molten solder and measuring the amount of tin left on that surface after mechanically removing the solidified solder. The intention of the study was to identify aspects of the interaction between the substrates and the solders that could provide ways of dealing with these problems that might otherwise increase the cost to the electronics industry of converting to lead-free soldering.

Experimental Procedure

The solder alloys used in the study are listed in Table 1. Variants of the basic alloys containing phosphorus were included to provide for the widespread practice of adding this element as an antioxidant to control drossing.

Copper wires 0.44mm diameter were prepared by pre-cleaning in a 5% HCl solution and rinsing and were then immersed vertically in each molten solder at 250°C, 280°C and 300°C. Type 304 stainless steel wires 1.0mm in diameter were prepared by pretinning in pure tin with an inorganic flux and were then immersed vertically in each molten solder at 350°C. Wires were removed at various times, allowed to cool to room temperature with any adhering solder being left intact and transverse cross-section prepared for microscopic examination by mounting in epoxy resin and polishing. The extent of erosion was taken to be indicated by the difference between the known initial cross-sectional area of the wire and the area of the remaining core of unreacted metal after exposure to the molten solder. Intermetallic compound on the surface was not included in the measurement of the remaining cross-sectional area of the wire.

To obtain an indication of the extent to which each alloy wets Type 304 stainless steel coupons of 50x50x0.3mm were prepared by lightly polishing with 1500# emery paper and washing in acetone. Sample of each solder, confined in a cylindrical mould were held in contact with the unfluxed surface of the stainless steel coupons for ten hours at 400°C (Figure 1a). After cooling the cylinder of solder was pulled off the stainless steel and the exposed surface analyzed for tin using Sequential X-Ray Fluorescence Spectroscopy (Figure 1b). Since solder does not usually wet stainless steel under these conditions the amount of tin adhering to the surface can be taken as an indication of the extent to which wetting occurred.

Table 1- Composition of Solder Alloys Tested

Alloy Code	Sn	Pb	Ag	Cu	Ni	Fe	P
Sn-37Pb	Bal.	37	<0.001	0.002	<0.001	0.003	<0.001
Sn-3.0Ag-0.5Cu	Bal.	0.03	3.00	0.52	<0.001	0.004	<0.001
Sn-3.0Ag-0.5Cu+100ppmP	Bal.	0.03	3.05	0.56	<0.001	0.005	0.009
Sn-0.7Cu	Bal.	0.03	<0.001	0.65	<0.001	0.004	<0.001
Sn-0.7Cu-0.05Ni	Bal.	0.03	<0.001	0.65	0.05	0.004	<0.001
Sn-0.7Cu-0.05Ni+100ppmP	Bal.	0.03	<0.001	0.65	0.05	0.003	0.009

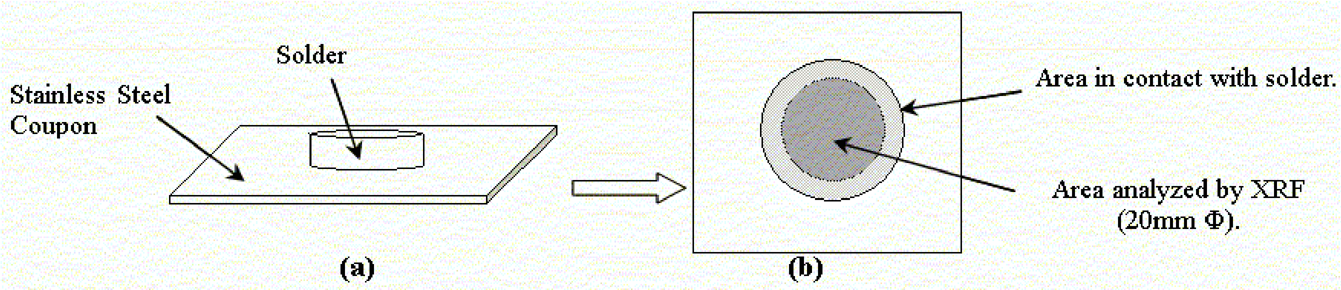

Figure 1-Schematic Representation of Procedure for Studying the Wetting of Stainless Steel by Solder

Experimental Results and Discussion

Erosion of Copper Wire

Significant differences between the rate at which the various alloys erode copper are apparent in the plots of cross sectional area as a function of immersion time in Figure 2.

Sn-3.0Ag-0.5Cu was the most aggressive towards copper of the alloys tested in this study. and the addition of phosphorus did not further increase the rate of erosion.

The Sn-0.7Cu alloy is also aggressive towards copper but the addition of 0.05% nickel slowed the rate of copper dissolution to the point where the resulting alloy was the least aggressive of the alloys tested. At a solder temperature of 250°C the phosphorus addition increased the erosion rate of the Sn-07Cu-0.05Ni to a level about the same as that of the Sn-0.7Cu alloy but had no effect on the already high rate at 300°C, well above the temperatures at which this solder would normlly be used in wave soldering.

Contrary to expectations the Sn-37Pb did not have the lowest rate of copper erosion with that honour falling to the Sn-0.7Cu-0.05Ni alloy. The erosion rate of the Sn-37Pb was, however, lower than that of the Sn-3.0Ag-0.5Cu.

The faster copper erosion rate of the Sn-37Pb compared the Sn-0.7Cu-0.5Ni and even with the Sn-0.7Cu is probably related to the fact that as the copper content of an alloy increases towards saturation at a particular temperature the rate of copper dissolution decreases. With minimal initial copper content the copper dissolution rate of the Sn-37Pb used in this experiment is likely to be higher than that of the Sn-0.7Cu-0.05Ni or even the Sn-0.7Cu which already have copper levels close to saturation. That copper erosion has not been an issue in wave soldering with Sn-37Pb is probably due to the fact that the level of copper in a working wave solder bath fairly quickly rises to around 0.2-0.3% at which level the rate of further copper dissolution is reduced. Although copper is considered an impurity in tin-lead solder, at levels up to around 0.3% it does not have any detrimental effect on soldering or the soldered joint and has the beneficial effect of increasing the strength of the solder while reducing further copper dissolution.

The micrographs in Figure 3 are those of copper wires the cross-sectional area of which had been reduced to 40% or less of the original area at a temperature of only 250°C. Of the alloys tested the Sn-0.7Cu-0.05Ni left the thickest intermetallic layer with the addition of phosphorus increasing the thickness further.

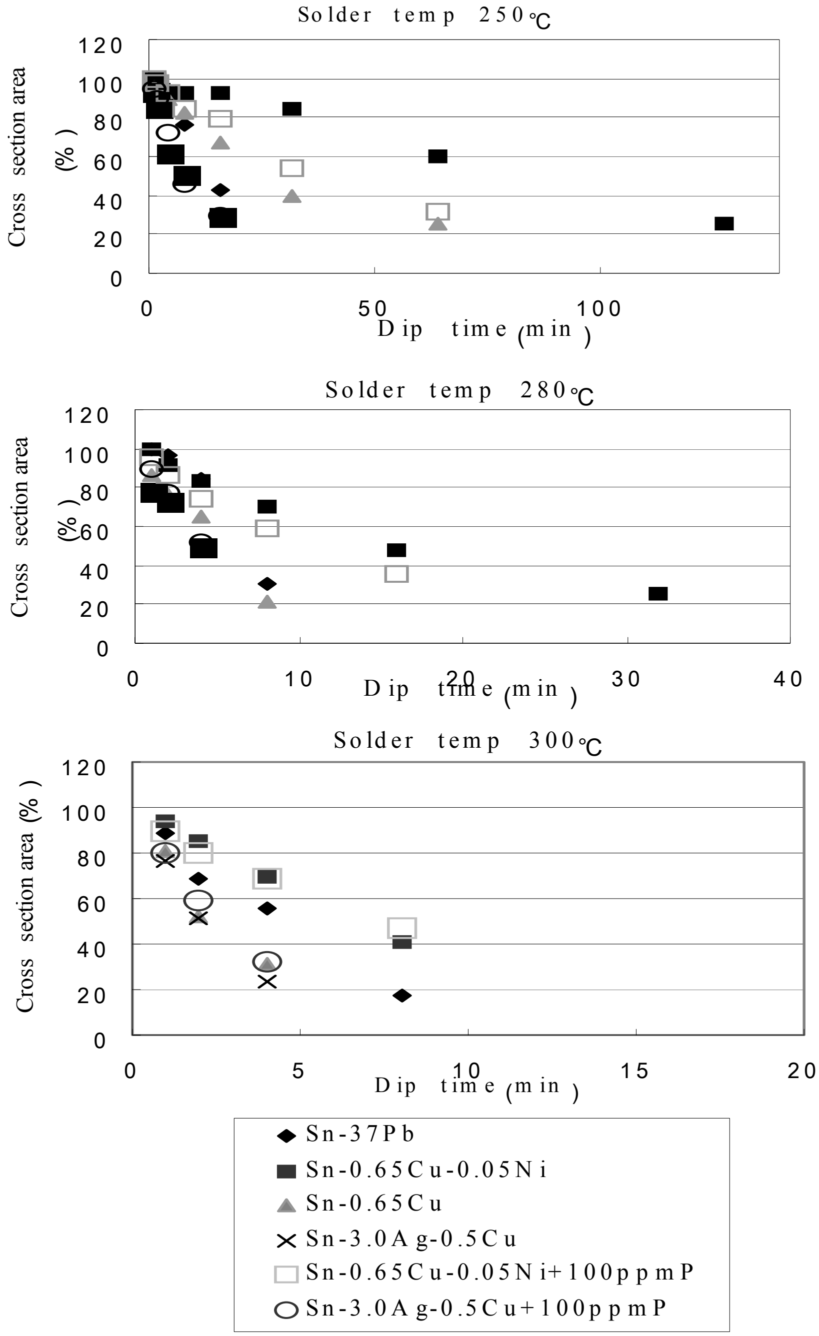

Figure 2- Cross-sectional Area of Copper Wire as a Function of Immersion Time at 250°C, 280°C and 300°C

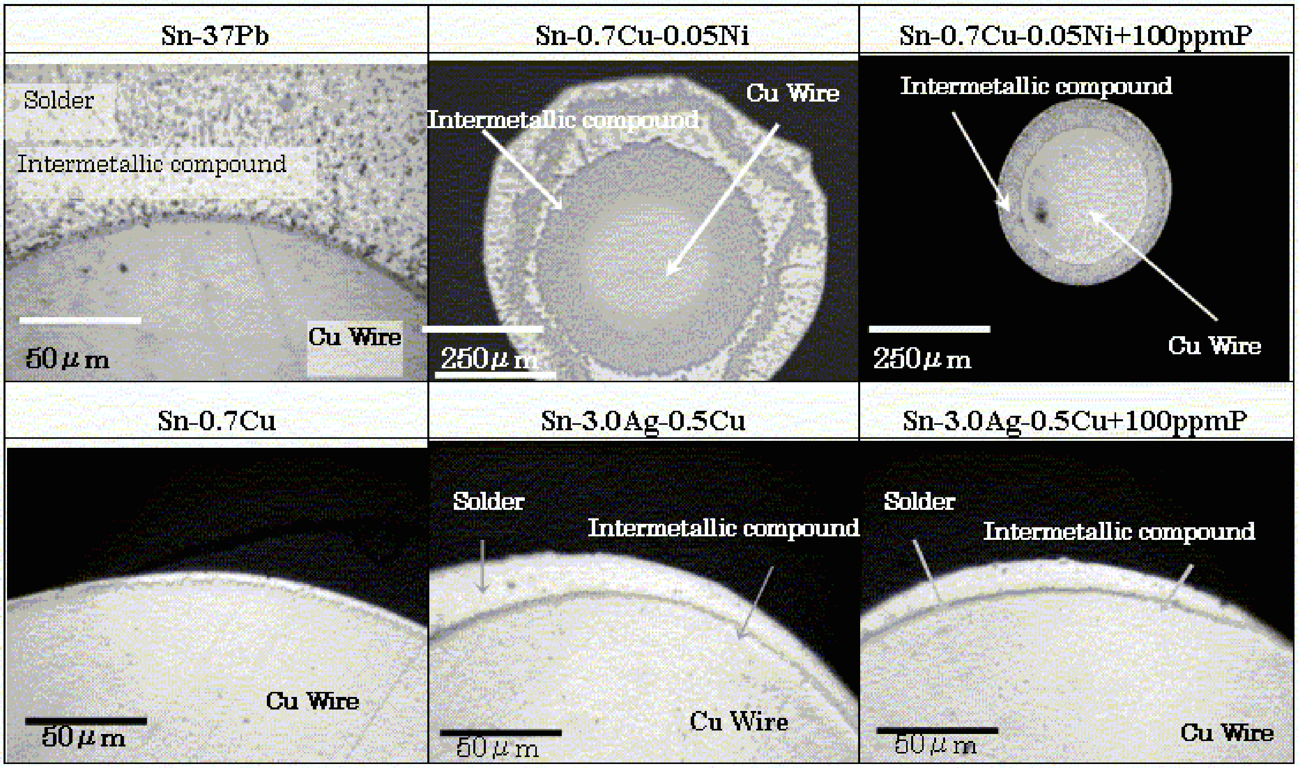

Figure 3- Microstructure of Eroded Copper Wire

Erosion of Stainless Steel Wire

The general trend of cross-sectional area of the stainless steel wire was similar to that for copper (see Figure.4) but the scatter of the data increased as the immersion time increased. This scatter is probably the result of the non-uniformity of stainless steel erosion. Again the most aggressive solder is Sn-0.7Cu but the rate of erosion was slowed by the addition of nickel. Both the Sn-0.7Cu-0.05Ni and the Sn-3.0Ag-0.5Cu eroded type 304 stainless steel more rapidly than Sn-37Pb. In both cases, however, the addition of phosphorus slowed the rate of erosion to that of Sn-37Pb.

In the cross-sectional photomicrographs of stainless steel wire that had been immersed in some of these solders at 350°C for 32 hours (Figure 5) the intermetallic layer resulting from the reaction between the solder and the stainless steel can be observed between the stainless steel core and the solder adhering to the surface. This intermetallic is probably $FeSn_2$. In the alloys containing phosphorus there is an additional crystalline layer at the interface between the intermetallic compound and the solder. SEM-EDX analysis confirmed that this phase contains phosphorus. The reduction in cross sectional area is less in these alloys containing phosphorus and it is inferred that this is because the phosphorus-rich phase acts as a protective barrier against erosion. Although the erosion of the stainless steel is reduced a thick layer of a britttle phosphorus-rich compound is produced which experience suggests tends to exfoliate and open up the surface to further erosion.

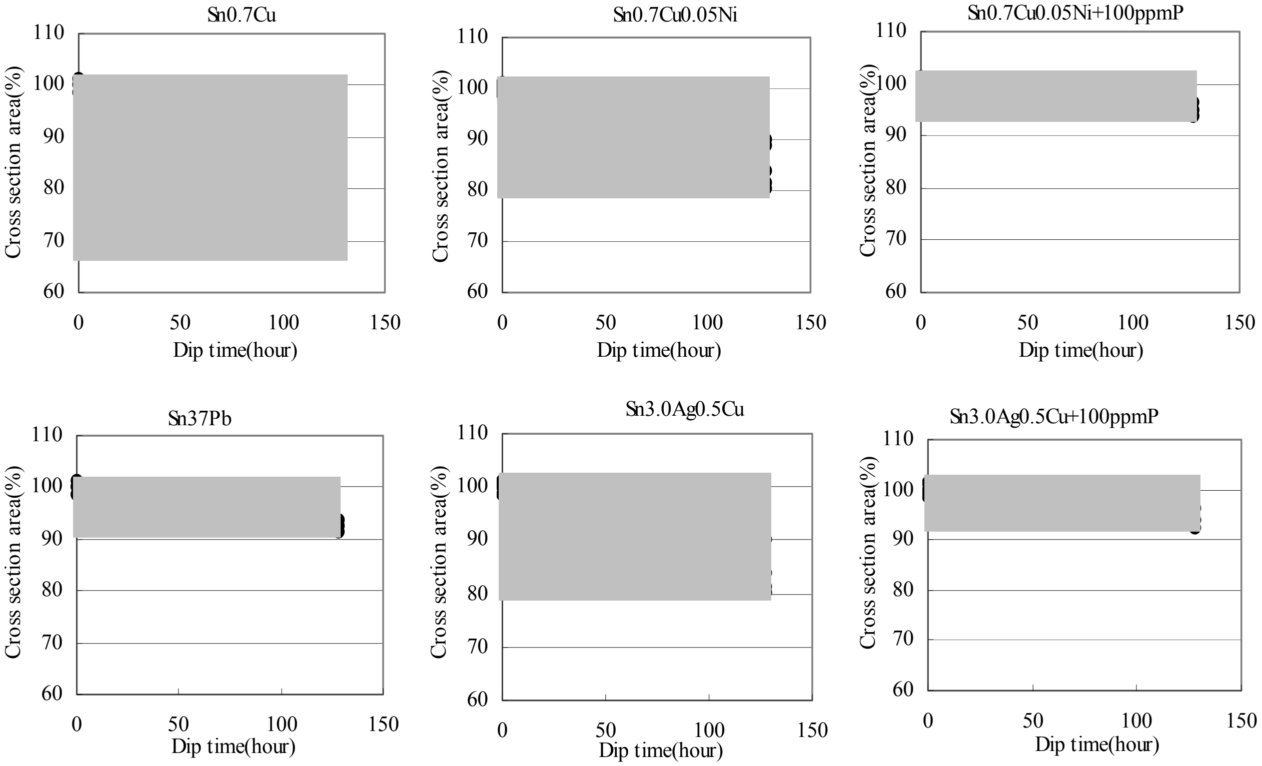

Figure 4- Cross-sectional Area of Stainless Steel Wire as a Function of Immersion Time at 350°C

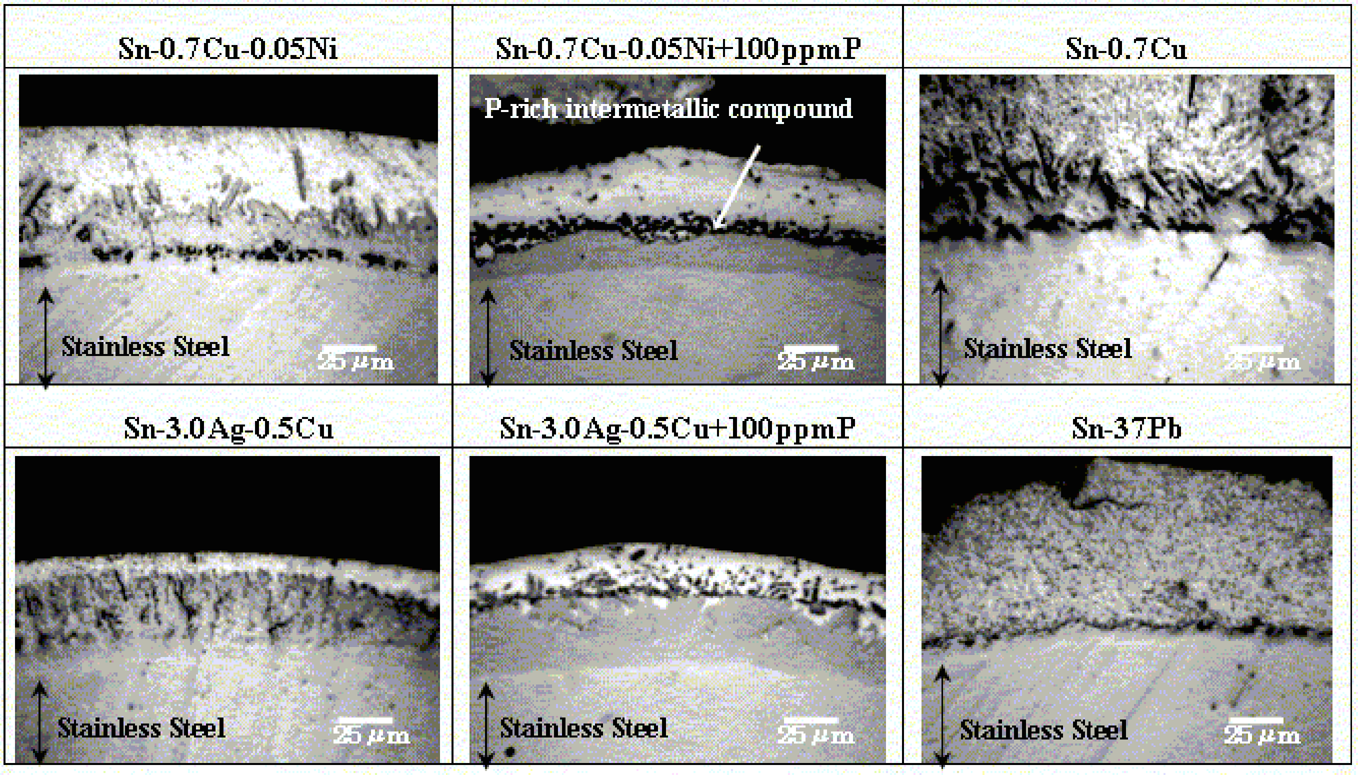

Figure 5 - Microstructure of Type 304 Stainless Steel Wire after Exposure to Solder at 350C for 32 Hours

Wetting of Stainless Steel

The relative amount of tin detected on the surface of the stainless steel after exposure to the molten solder at 400°C for 10 hours is presented in Figures 6 and 7. Amongst alloys without the phosphorus addition the Sn-3.0Ag-0.5Cu alloys showed the greatest degree of wetting as indicated by the extent of adhesion to the stainless steel surface (Figure 6).

When phosphorus is present the extent of wetting of the Sn-3.0Ag-0.5Cu is increased by a factor of ten and the extent of wetting of the Sn-0.7Cu-0.05Ni is also increased dramatically.

The phosphorus appears to change the nature of the interface between the solder and the stainless steel substrate (Figure 8).

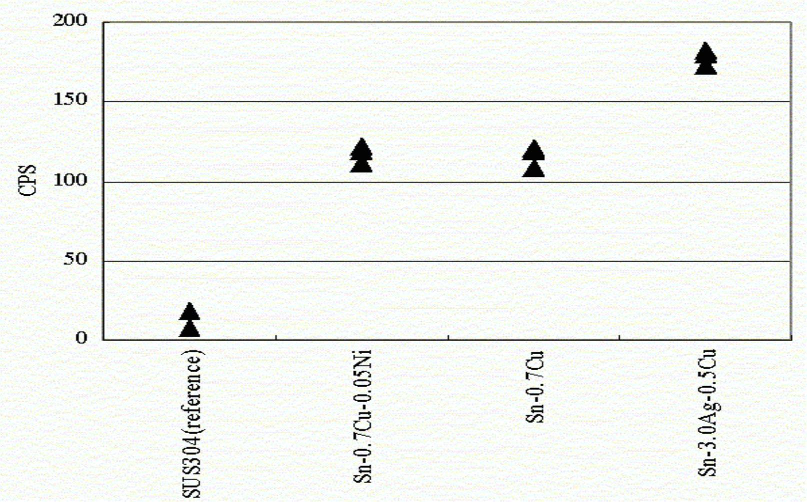

Figure 6 - Level of Tin Detected on Stainless Steel Surface after Exposure to Solders Alloys without Phosphorus

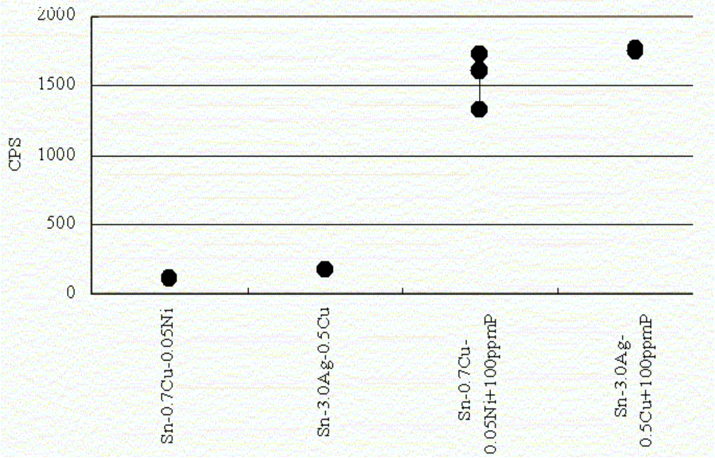

Figure 7 - The Effect of Phosphorus Additions to Sn-0.7Cu and Sn-3.0Ag-0.5Cu on the of Level of Tin Detected on the Stainless Steels

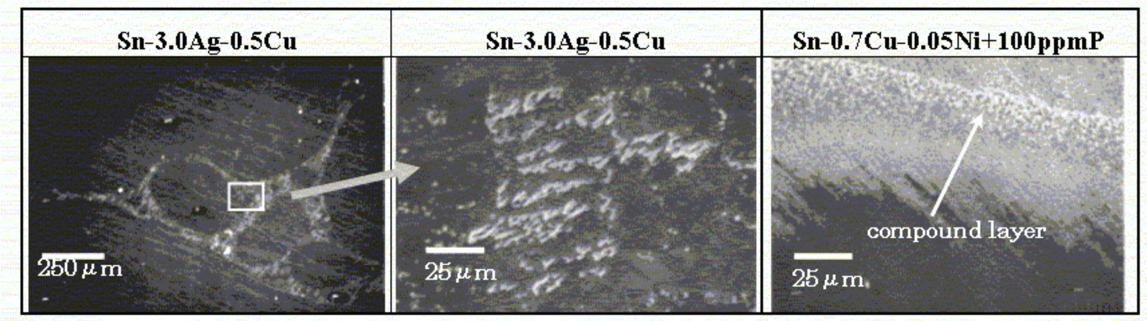

Figure 8- Scanning Electron Micrographs Images of Interface between Stainles Steel and Lead-free Solders

Although, as indicated by the amount of tin detected on the surface, the Sn-3.0Ag-0.5Cu alloy has wetted the stainless steel, the appearance of the surface in SEM continues to reflect the underlying microstructure of primary tin dendrites surrounded by ternary eutectic. When phosphorus is present the surface left after pulling off the solder is dominated by the phosphorus-containing compound.

While phosphorus promotes the wetting of the stainless steel it acts as a barrier to dissolution.

Conclusions

1. An addition of nickel to Sn-0.7Cu reduces the tendency of the alloy to wet and erode copper and stainless steel.
2. At 250°C the addition of 100ppm phosphorus greatly increases the rate at which the Sn-0.7Cu-0.05Ni alloy erodes copper. This accelerating effect decreases with increasing temperature and disappears completely at 300C.
3. Sn-37Pb erodes copper at a greater rate than Sn-0.7Cu-0.05Ni, but more slowly than Sn3.0-Ag-0.5Cu.
4. Sn-3.0Ag-0.5Cu wets unfluxed Type 304 stainless steel to a greater extent than Sn-0.7Cu or Sn-0.7Cu-0.05Ni.
5. An addition of phosphorus to lead-free alloys increases the extent to which they wet Type 304 stainless steel but under the conditions of the experiment reduces the subsequent rate of erosion.

It should be noted that erosion of copper creates two separate problems. The obvious problem is a reduction in the thickness of copper in tracks, pads and through holes which has been found to reduce the reliability of the board in some cases, e.g. by the weakening of the shoulder or plated-through hole. Erosion of copper can also push the copper content of the solder bath beyond the specified maximum with a consequent increase in the incidence of defects such as bridges (shorts) incompletely filled through holes. If the rate of dissolution of copper in the solder bath is not too great the copper level can be maintained within specification by the use of a top-up solder that is low in copper. However, with the high rates of dissolution experienced with some lead-free solders the use of a low-copper top-up solder is not enough to keep the alloy within specification and to bring the alloy back into specification a portion of the solder bath has to be removed and replaced by fresh solder. This adds significantly to the cost of operating a wave solder line.

In regard to erosion of copper, the Ni-stabilized Sn-0.7Cu is at least as safe as Sn-37Pb solder.

Once they have wetted the surface lead-free solders erode stainless steel faster than does Sn-37Pb. However there are major differences between alloys in the rate at which various lead-free solders wet stainless steel and erosion does not commence until the stainless steel has been wetted. This difference has major implications for the selection of a lead-free alloy for wave soldering.

Further studies of the intermetallic layer produced on stainless steel by lead-free solders containing phosphorus suggest that the protective effect that occurs in the simple static immersion experiment reported here may not apply in practical wave soldering. The protective phosphorus-containing intermetallic is brittle and in a working wave soldering bath would tend to flake off exposing the underlying steel to further erosion.

In any case, because of its accelerating effect on wetting the use of phosphorus as an antioxidant in solder in the manufacture of solder and to reduce drossing in service should be avoided. A commercial solder based on the Ni-stabilized Sn-0.7Cu, Nihon Superior “SN100C”, has a very low dross rate while not containing phosphorus.

Whichever lead-free alloy is chosen for wave soldering a stainless steel the solder bath should be checked regularly for signs that it has been wetted by the solder as erosion will certainly occur at that point.

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