Feasibility of Fluxless Reflow of Lead-free Solders in Hydrogen and Forming Gas

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Abstract

An experimental study was conducted to investigate the feasibility of fluxless reflow of five tin-based, lead-free solders in hydrogen and forming gas (3% hydrogen balanced with nitrogen). Major results of this study are as follows. 1) Solder oxides on the surface of lead-free solders cannot be effectively reduced by hydrogen or forming gas at the normal soldering temperature range (40°C above the solder's melting point). 2) In hydrogen or forming gas, a thin layer of initial solder oxides can be dissolved into bulk liquid solder, and the temperature superheats for dissolving initial oxides of some lead-free solders are significantly lower than that of the eutectic tin-lead solder. 3) At the normal soldering temperature range, copper oxides on the surface of a copper substrate can be successfully reduced in pure hydrogen but not in forming gas. Therefore, fluxless reflow in pure hydrogen seems feasible for some lead-free solders.

Introduction

Fluxes are normally used in soldering processes to remove initial surface oxides on both liquid solder and base metal and to keep the surfaces in a clean state. After soldering, the fluxes are mostly evaporated into vapor phase, but there are always some residues left on the circuit board that may cause corrosion problems. To remove the flux residues, a postcleaning process has to be used. Chlorofluorocarbons (CFCs) were normally used as the cleaning agents, but they are believed to be damaging the earth's protective ozone layer and their use was banned by the Montreal protocol of November 25, 1992. Therefore, fluxless soldering using a reducing gas such as hydrogen or forming gas is desired, because it can eliminate postcleaning and the possibility of flux residues. Although it has been shown that removing tin-oxides on the surface of tin-lead solders in hydrogen is not effective at the normal soldering temperature range (40°C above the solder's melting point, Ref. 1), hydrogen fluxless soldering of other solders may be feasible. Recently, many lead-free solders have been developed due to the proposed legislation introduced in the U.S. Congress in 1990 to regulate the use of lead. Therefore, our present study was aimed at evaluating the feasibility of fluxless reflow of lead-free solders in hydrogen and forming gas (3% hydrogen balanced with nitrogen). Experiments were conducted to evaluate the effect of hydrogen on 1) reducing solder oxides, 2) dissolving solder oxides, and 3) reducing copper oxides.

Since most of the newly developed lead-free solders are based on a ternary or quaternary addition to a tin-based binary system, for an initial study five tin-based binary lead-free solders (48Sn-52In, 91Sn-9Zn, 96.5Sn-3.5Ag, 99.3Sn-0.7Cu, and 95Sn-5Sb) were selected and the feasibility for hydrogen fluxless reflow was compared with that of the eutectic tin-lead solder. The composition and melting point of each solder alloy evaluated in this study are listed in **Table 1**. All the solder alloys used in this study were in the form of fluxless solder preforms (2 mm diameter and 1 mm thick).

The experimental setup used in this study is shown schematically in **Figure 1**. A quartz tube (2" diameter and 12" long) is mounted in a split furnace with a six-inch heating zone in which a temperature rise similar to that in an IR (infrared) reflow soldering furnace can be obtained. To observe and photograph the liquid solder drop, each end of the quartz tube is sealed with an optical-flat glass, and a light source and a video system are mounted at opposite ends of the tube. During each heating cycle, the desired soldering atmosphere is maintained by passing gas through the tube with a constant gas flow rate of 1.8 liter/minute.

Table 1: Composition and Melting Point of Solder Alloys

Solder	Composition (%)	Melting Point (°C)*
eutectic tin-lead	63Sn/37Pb	183
eutectic tin-silver	96.5Sn/3.5Ag	221
eutectic tin-copper	99.3Sn/0.7Cu	227
peritectic tin-antimony	95Sn/5Sb	240
eutectic tin-indium	48Sn/52In	117
eutectic tin-zinc	91Sn/9Zn	199

*Data are based on International Tin Research Institute (ITRI) internal reports.

Experiments, Results, and Discussions

Reducing Solder Oxides

Whether or not an oxide can be reduced by hydrogen depends on the stability of the oxide at the given temperature and hydrogen/water partial pressure. However, the reduction rate can be extremely slow even when the oxide is thermodynamically unstable, which makes the reduction process practically ineffective (Refs. 2 and 3). From a kinetics point of view, an initiation temperature should exist for each solder above which the reduction rate of solder oxides is acceptable for a normal soldering process.

To find the initiation temperature, isothermal reduction rates of solder oxides at various temperatures in hydrogen were investigated in this study. The isothermal reduction rate was determined by observing the rate of the shape change of a preoxidized fluxless solder preform on glass at a given temperature when exposed to hydrogen. As shown in **Figure 2**, a molten solder with an oxide layer on its surface tends to maintain its initial solid shape because the oxide layer prevents liquid flow underneath it. However, a molten solder with an oxide-free surface normally forms a nearly spherical shape driven by liquid surface tension. This shape characteristic was used in this study to monitor the progress of reducing surface oxides on each solder.

A thick initial oxide layer on the surface of each solder preform is desirable for this study, because it minimizes the dissolution effect of solder oxides and makes the shape change more distinguishable. To develop a thick oxide layer, each solder preform was preoxidized by heating up in air from room temperature to a temperature that is about 140°C higher than its melting point and

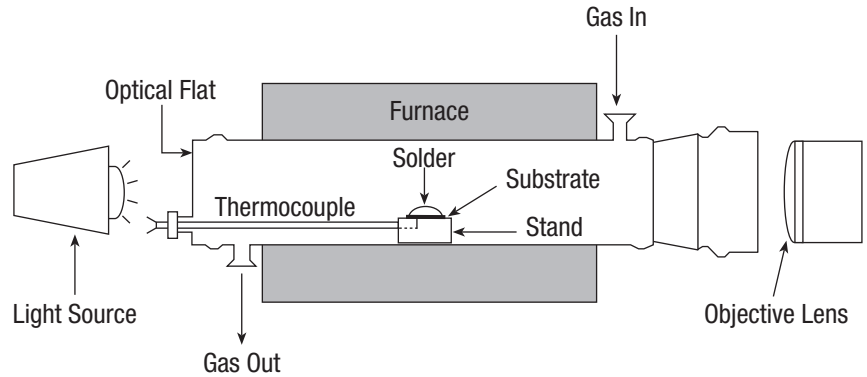Figure 1: Schematic illustration of the experimental setup.

Figure 2: Photographs showing the shape change of a fluxless molten solder when the initial oxide layer is reduced in hydrogen, (a) before and (b) after the reduction of the initial oxide layer.
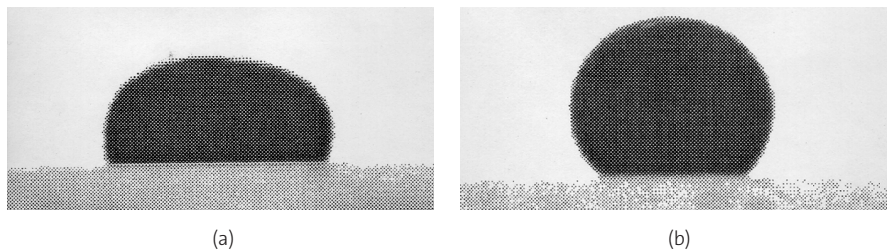

(a)   (b)

Table 2: Dominant Type of Solder Oxides on Preoxidized Solder Preforms

Solder	Dominant Type of Oxide
63Sn/37Pb	tin oxides
96.5Sn/3.5Ag	tin oxides
99.3Sn/0.7Cu	tin oxides
95Sn/5Sb	tin oxides
48Sn/52In	indium oxides
91Sn/9Zn	zinc oxides

cooling to room temperature in nitrogen. After this preoxidation, the thickness and the dominant type of oxide formed on each solder were determined by Auger Electron Spectroscopy (AES). The dominant type of oxide on each solder (determined by AES, as shown in **Table 2**) is quite consistent with that predicted based on thermodynamics (Ref. 4). According to thermodynamics, an element of a liquid alloy having a lower (or more negative) free energy of oxide formation should migrate to the liquid surface to form oxides.

The preoxidized preforms were placed on glass slides and heated in nitrogen

to various temperatures, and then the nitrogen flow was switched to a hydrogen flow after the temperature was stabilized. As soon as the hydrogen flow was introduced, the shape of the molten solder was monitored in situ, and the time needed for the molten solder to change from its initial oxidized shape to a stable final shape was recorded. An average reduction rate can be obtained from the ratio of the initial oxide thickness over the reduction period. The obtained reduction rate of solder oxides on each solder is plotted in **Figure 3** as a function of temperature.

In a normal soldering process, the

thickness of the initial oxide layers on a solder joint ranges from 20 to 30 angstrom and the reflow time is about 1 to 1.5 minutes. In this case, the reduction rate of solder oxides should exceed 20 angstrom per minute to ensure solderability. If we assume that a reduction rate of 20 angstrom per minute is acceptable, the initiation temperature for hydrogen to effectively reduce solder oxides on each solder can be obtained. As shown in **Table 3**, zinc oxides on the surface of 91Sn/9Zn are the most difficult ones to reduce; the initiation temperature is as high as 510°C. To reduce indium oxides on 48Sn/52In, the initiation temperature is around 470°C. The initiation temperature to reduce tin oxides on 63Sn/37Pb, 96.5Sn/3.5Ag, 99.3Sn/0.7Cu, and 95Sn/5Sb, however, is only 430°C.

The difference in the initiation temperatures among the solder oxides studied is believed to be related to the metal-oxygen bond strength (or heat of oxide formation) of each oxide. The higher the strength of a metal-oxygen bond (or the lower the heat of oxide formation), the higher the initiation temperature should be (Ref. 5). Comparing **Table 3** with **Table 4** (Ref. 6), this relationship between initiation temperature and bond strength is demonstrated.

It should be pointed out that the reduction rate and the initiation temperature are functions of not only solder alloy but also the size of solder. A tiny solder drop, such as a solder bump of 40µm in size used in flip chip technology, has a relatively high surface-to-volume ratio and thus possesses a large thermodynamic driving force for surface reduction. Therefore, the reduction rate of solder oxides on such small solder drops can be much higher and the initiation temperature can be significantly lower than that determined here (Ref. 7).

Figure 3: Reduction rate of solder oxides on each solder as a function of temperature.
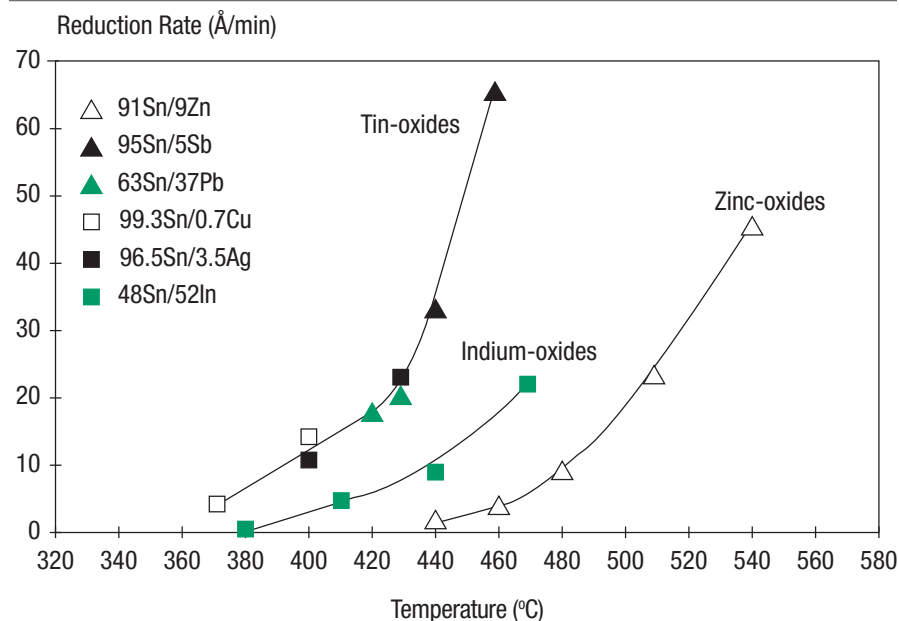
Table 3: Initiation Temperature for Hydrogen to Reduce Solder Oxides

Solder	Dominant Type of Oxide	Initiation Temperature(°C)*
63Sn/37Pb	tin oxides	~430
96.5Sn/3.5Ag	tin oxides	~430
99.3Sn/0.7Cu	tin oxides	~430
95Sn/5Sb	tin oxides	~430
48Sn/52In	indium oxides	~470
91Sn/9Zn	zinc oxides	~510

*The experimental error is ± 5°C.

Table 4: Heats of Formation for Several Oxides

Oxide	Heat of Formation (Kcal/g mole)
SnO	−68.4
In_2O_3	−74.2
ZnO	−83.2

Dissolving Solder Oxides

Because the initiation temperatures for hydrogen to effectively reduce solder oxides on lead-free solders are significantly higher than the normal soldering temperatures, the hydrogen reduction mechanism on reducing initial solder oxides cannot be applied in fluxless soldering processes unless a high temperature is used. However, there is another mechanism of removing initial solder oxides in inert or reducing atmosphere, that is, dissolution of initial solder oxides into bulk liquid solder. It is understood that during heating of a metal element, such as tin, its oxide solubility increases significantly at the melting temperature and continues to increase with increasing temperature (**Figure 4** from Ref. 8). This phenomenon implies that under inert or reducing atmosphere, a thin layer of initial solder oxides may be totally dissolved by increasing the temperature to a certain level.

To investigate the temperature required to totally dissolve the initial oxides on each solder, a fluxless solder preform was placed on a glass slide, heated in nitrogen (O_2 concentration below 10 ppm) from room temperature to a temperature above the solder's melting point, and then held at this temperature to observe if there was any shape change

on the molten solder. If there was no shape change, the temperature was further increased until a critical temperature was reached, above which the molten solder changed from its initial oxidized shape to a nearly spherical shape. The difference between the critical temperature and the melting point of a solder is defined as temperature superheat to dissolve the initial oxides. The temperature superheats of all solders investigated are summarized in **Table 5**. Although the experiment was conducted in nitrogen, the result should be the same when using hydrogen or forming gas instead of nitrogen.

As shown in **Table 5**, the oxides present on the surface of 91Sn/9Zn could not be completely dissolved by heating. Oxides on surfaces of 96.5Sn/3.5Ag, 99.3Sn/0.7Cu, and 95Sn/5Sb could be easily dissolved, and the temperature superheats were below 20°C. However, the temperature superheats to dissolve oxides of 48Sn/52In and 63Sn/37Pb were relatively high (>77°C). A low temperature superheat is always preferred to reduce formation of "cold" solder joints and temperature-induced damage. The temperature required to totally dissolve initial solder oxides on each solder depends on both the thickness of the initial solder oxide layer and the oxide solubility for each solder alloy at a given temperature.

The thickness of initial oxide film formed on each solder was determined by AES. As shown in **Table 6**, the initial oxide layer on 91Sn/9Zn is very thick, about 70 angstrom, while the initial oxide layers on other solders are only about 20 to 30 angstrom. This is one of the reasons why the surface oxides of 91Sn/9Zn could not be completely dissolved by heating in a nitrogen- or hydrogen-containing atmosphere.

For a liquid alloy with metal oxides

Figure 4: Sn-O phase diagram.
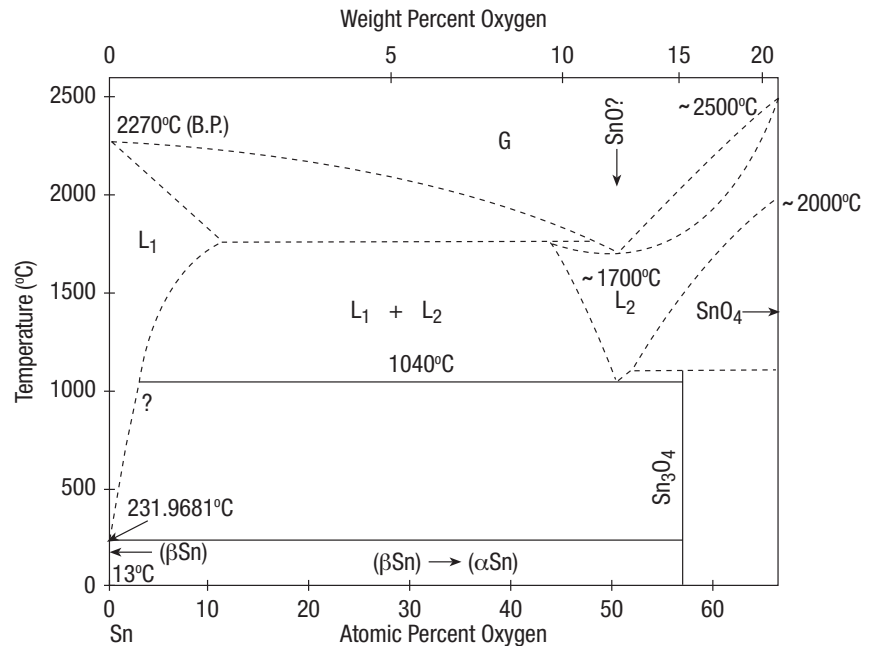
Table 5: Temperature and Temperature Superheat in N_2 for Dissolving Initial Solder Oxides

Solder	Melting Point (°C)	Temperature for Dissolving Oxides (°C)*	Superheat (°C)*
63Sn/37Pb	183	~260	~77
96.5Sn/3.5Ag	221	~240	~19
99.3Sn/0.7Cu	227	~245	~18
95Sn/5Sb	240	~250	~10
48Sn/52In	117	~210	~93
91Sn/9Zn	199	>500**	>301**

*The experimental error is ± 5°C.

** The highest temperature used in the experiment was 500°C.

Table 6: Thickness of Initial Oxide Film

Solder	Oxide Thickness (angstrom)
63Sn/37Pb	30
96.5Sn/3.5Ag	30
99.3Sn/0.7Cu	20
95Sn/5Sb	20
48Sn/52In	20
91Sn/9Zn	70

formed on its surface, the solubility of the metal oxides in the liquid alloy at a given temperature is determined by 1) melting point and enthalpy of fusion of the metal oxides and 2) intermolecular forces between the metal oxides and the liquid alloy (Ref. 9). The higher the concentration of the oxide-forming element in the alloy, the larger the attraction force between the oxides and the liquid alloy, and thus the larger the oxide solubility.

96.5Sn/3.5Ag, 99.3Sn/0.7Cu, and 95Sn/5Sb solders all form tin-oxides and their bulk concentrations of the oxide-forming element, tin, are all overwhelming (≥95%). Therefore

the solubility of surface tin-oxides in these solders is relatively high and their temperature superheats to totally dissolve the initial oxides are relatively low.

In contrast, 91Sn/9Zn solder forms zinc-oxides, 48Sn/52In solder forms indium-oxides, and 63Sn/37Pb solder forms tin-oxides, and the bulk concentration of the oxide-forming element for 91Sn/9Zn is very low (9%), for 48Sn/52In, and for 63Sn/37Pb is not overwhelming (52% and 63%). Therefore, dissolving surface oxides of 91Sn/9Zn is extremely difficult and relatively high temperature superheats are required for dissolving surface oxides of 48Sn/52In and 63Sn/37Pb.

Reducing Copper Oxides

To further understand the feasibility of fluxless reflow in a hydrogen-containing atmosphere, reduction kinetics of copper oxides on copper substrate by hydrogen and forming gas was also investigated. Differential scanning calorimetry (DSC) was used to find the initiation temperature for hydrogen to reduce copper oxides. DSC measures heat adsorbed or released during a heating cycle. The temperature at which heat flow changes represents the initiation temperature of a chemical reaction. To intensify the heat flow associated with a chemical reaction, 100μm diameter copper powder was used instead of a copper plate. The copper powders were preoxidized to build a thick oxide layer.

The preoxidized copper powders in DSC were heated up at 10°C/min under a flow of either pure hydrogen or forming gas. When pure hydrogen was used, a heat release was detected as the temperature was increased to about 134°C (Figure 5). The heat release is believed to be due to the exothermic reaction of copper oxides with hydrogen. Therefore, the initiation temperature of the reduction process

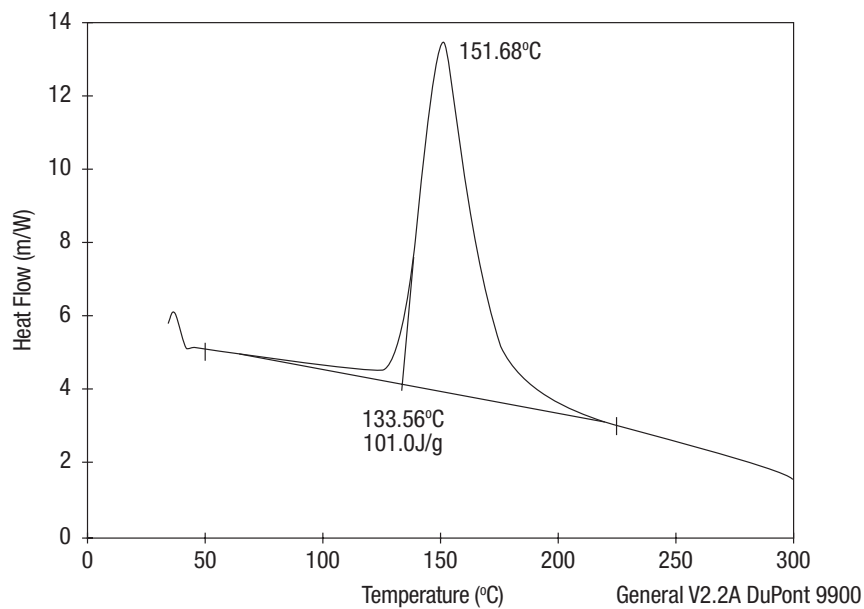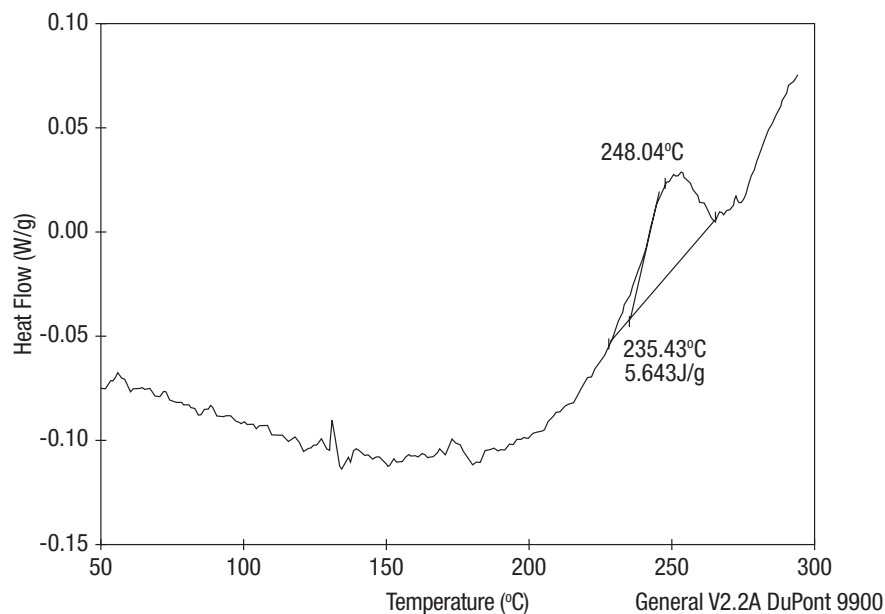Figure 5: DSC curve for the reduction of copper oxides by hydrogen.

Figure 6:DSC curve for the reduction of copper oxides by forming gas.

in pure hydrogen should be around 134°C. This initiation temperature was found to increase with decreasing concentration of hydrogen. When reduction of copper oxides was conducted under forming gas, an exothermic peak was found with an onset temperature of 235°C (**Figure 6**). In addition, the amount of heat released under forming gas was found to be significantly reduced compared with that under pure hydrogen (**Figures 5 and 6**), which indicates, as expected, that the rate of reduction of copper oxides in forming gas is much slower than that in pure hydrogen.

Similar to the reduction of solder oxides, the initiation temperature of reducing copper oxides should be a function of not only hydrogen concentration but also surface curvature. For a flat copper surface, the initiation temperature may be significantly higher than that of a curved powder surface (as used in this study). To further demonstrate the reducing effect of hydrogen on a flat copper surface, another experiment was conducted. As shown in **Figure 7**, two parallel copper foils were set vertically by a holder on a fluxless solder preform of 96.5Sn/3.5Ag that

was supported by a glass slide. The vertical space between the two copper foils was maintained by a spacer.

As the setup was heated under various atmospheres, such as hydrogen, forming gas, nitrogen, and air, results were quite different (**Figures 8a to 8d**). In pure hydrogen at about 265°C, the molten solder crept up along the narrow space between the two foils due to capillary force (**Figure 8a**). However, under a flow of forming gas, the movement of the molten solder within the capillary space was very slow and nonuniform (Figure 8b). The equilibrium height of the liquid solder rise in forming gas was also reduced compared with that in pure hydrogen (**Figures 8a and 8b**). Furthermore, when the same experiment was conducted under a flow of nitrogen or air, the capillary phenomenon could not be observed at all, even when the temperature was as high as 350°C (**Figures 8c and 8d**). Under the flow of normal air, the molten solder maintained its initial solid shape (Figure 8d). However, the molten solder bulged up when it was

melted in nitrogen (**Figure 8c**).

The above result can be explained as follows. When capillary wetting is conducted in normal air, both surfaces of copper and solder are oxidized and the surface oxides prevent solder flow and interface contact between molten solder and copper so that capillary wetting is impossible. Under a flow of nitrogen, initial solder oxides on the surface of molten solder can be dissolved into bulk liquid solder which causes the molten solder to bulge up, but capillary wetting on a substrate still cannot be achieved due to the presence of copper oxides on the copper surface. Under a forming gas environment, the initiation temperature of reducing copper oxides (≥235°C) is higher than the melting point of 96.5Sn/3.5Ag solder (221°C). The molten solder starts melting and creeping before copper oxides are totally removed so that the surface oxides are blocked from the atmosphere by molten solder and capillary wettability is reduced. When capillary wetting is conducted in hydrogen, however, the initial oxides on both surfaces of copper and

solder are removed before the solder is melted so that the molten solder can creep up nicely along the capillary space.

Figure 7: Schematic illustration of the experimental setup used for capillary test.


Copper Plate

R

h

Solder Preform
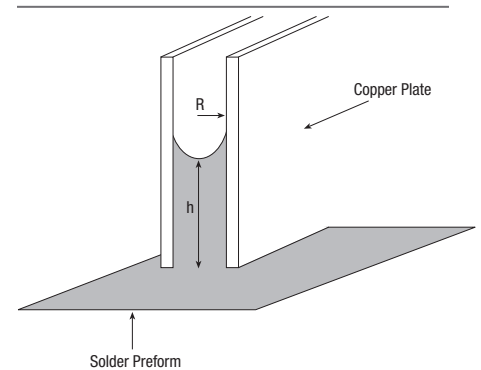
Conclusions

The feasibility of fluxless soldering of five tin-based, lead-free solders in hydrogen and forming gas was investigated and compared with that of eutectic tin-lead solder. The major results of this study are summarized as follows.

1. Solder oxides on the surface of lead-free solders cannot be effectively reduced by hydrogen at the normal soldering temperature range. Therefore, the hydrogen reduc-tion mechanism on reducing initial solder oxides cannot be applied in a fluxless soldering process unless a high temperature is used.

2. Hydrogen or forming gas can prevent solder from further oxidation during reflow, and therefore a thin layer of initial solder oxides can be dissolved into bulk liquid solder. The temperature superheats for dissolving initial oxides of 96.5Sn/3.5Ag, 99.3Sn/0.7Cu, and 95Sn/5Sb solders are significantly lower than that of the eutectic tin-lead solder.

3. The initiation temperature for reducing copper oxides in hydrogen and forming gas are 134°C and 235°C, respectively. Therefore, copper ox-ides can be successfully reduced in

Figure 8: Photographs showing capillary wetting of 96.5Sn/3.5Ag in (a) hydrogen, (b) forming gas, (c) nitrogen, and (d) air.

(a)

(b)

(c)

(d)
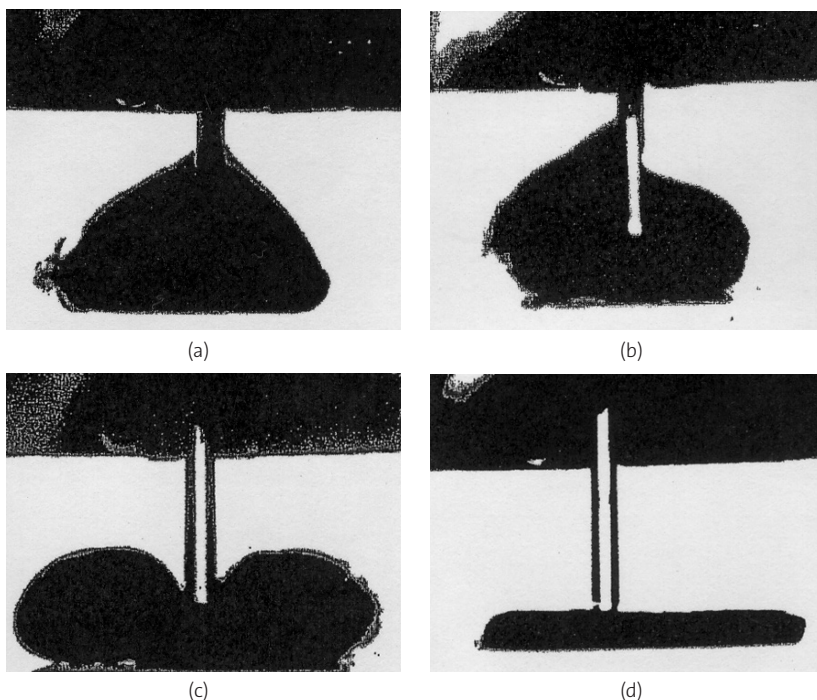
pure hydrogen at the normal soldering temperature range. Under a forming gas environment, however, the initiation temperature of reducing copper oxides is higher than most lead-free solders' melting points, thus making the reduction process difficult.

In conclusion, fluxless soldering in pure hydrogen seems feasible for some lead-free solders, such as 96.5Sn/3.5Ag, 99.3Sn.0.7Cu, and 95Sn/5Sb. These three solders investigated have relatively large oxide solubilities because their bulk concentrations of the oxide-forming element, tin, are overwhelming. Therefore, their temperature superheats for dissolving initial solder oxides are relatively low. In addition, the melting points of the three solders are significantly higher than the initiation temperature of reducing copper oxides in hydrogen so that the reduction of copper oxides can be completed before solder starts melting and spreading.

However, it must be pointed out that a flux used in the normal soldering process has two major functions. The first function is to remove initial surface oxides on both solders and base metals and keep the surfaces in a clean state. The second function is to reduce surface tension of a liquid solder so that solder can easily spread out on base metal surface. Hydrogen cannot decrease the surface tension of a liquid solder. Therefore, adding a surfactant into the lead-free solders may be a way to ensure satisfactory wetting for hydrogen fluxless reflow.

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