Fluxless Soldering of Flip Chip Assemblies

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Abstract
A study was conducted to investigate the feasibility of using a forming gas (H$_2$/N$_2$ mixture) to assist fluxless soldering of flip chip assemblies. Results from laboratory investigations show that, for hydrogen (in forming gas) to reduce solder oxides, there is an initiation temperature below which the reduction is insignificant and above which the reduction process is accelerated. The initiation temperature decreases with decreasing size of the solder bump. For a flip chip bonded with 40 µm solder bumps (90Pb/10Sn), the initiation temperature is about 370°C. At this temperature the isothermal reduction rate in pure hydrogen is about 3.3 nm/minute, in terms of reduction in oxide thickness. The isothermal reduction rate is directly proportional to the percentage of hydrogen in the forming gas. It is also demonstrated that soldering in hydrogen is superior in soldering quality to nitrogen when the reflow temperature is at or above 370°C. Specifically, hydrogen soldering intensifies the interfacial reactions at the bonding surface and provides a higher self-alignment ability, as compared to nitrogen soldering. These laboratory findings were transferred to production trials. Preliminary results of the production trials show acceptable solder wetting.

Introduction
Flip chip bonding of IC chips to chip carriers has gained tremendous popularity in recent years. The flip chip process, conceived and developed by IBM as a C4 (Controlled Collapse Chip Connection) joining process, is traditionally done using a rosin flux. The purpose of the flux is to assist bonding by reducing the oxides on the solder and substrate metallization and to hold the chip in place during the reflow process. After joining, the flux residues are removed by using cleaning solvents such as xylene or perchloroethylene (PCE).

Due to environmental concerns and restrictions, efforts are being made in the electronic industry to eliminate usage of these cleaning solvents and to develop no-clean fluxes or fluxless bonding processes. IBM recently qualified a C4 assembly process that eliminated the use of xylene or PCE (refs. 1 and 2). This process uses a mildly activated no-clean flux in combination with a hydrogen reflow atmosphere. At bonding temperatures, hydrogen reduces oxides on the solder and the copper metallization of bonding pads, and thus acts very similar to the rosin flux in promoting bonding. The role of the no-clean flux in this process is not very clear other than that it holds the chip in place during the reflow process. This no-clean flux, if used in excessive amounts, was found to leave residues and cause chip underfill adhesion problems.

To eliminate these problems associated with no-clean flux and to understand the solder interactions with the hydrogen gas, solder reflow experiments were done in forming gas (H$_2$/N$_2$) without any flux (dry process). The main objective of this experimental study was to find an acceptable forming gas composition and a temperature range to accomplish the fluxless reflow of a solder-bonded (90Pb/10Sn) chip on a substrate with gold-plated solder pads. Two approaches were used in this study. In the first approach, laboratory investigations were conducted to obtain fundamental understandings on the mechanisms of the fluxless soldering. The second approach involved using a production reflow furnace to verify the laboratory findings and to further develop the process.
Laboratory Investigations

During the fluxless soldering of the flip chip assembly in a forming gas environment, four reactions take place at the surface of a liquid solder, which determine the fate of the solder oxides and the quality of a solder joint. These four reactions are: 1) oxidation of solder as a result of the existence of a trace amount of oxygen and moisture in the forming gas, 2) dissolution of solder oxides due to an increase in oxygen solubility when the reflow temperature is above the melting point of the bulk solder, 3) reduction of solder oxides by the reducing effect of hydrogen in the forming gas, and 4) reflow soldering caused by interfacial reactions between the liquid solder and the solder pad. In our laboratory investigations, all four reactions were studied, and each one is described in a following section.

The experimental setup used in this laboratory study is schematically shown in Figure 1. A quartz tube (2” diameter and 12” long) is mounted in a split furnace with a 6” heating zone in which a temperature rise similar to that in an IR (infrared) reflow soldering furnace can be obtained. 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. When house-line nitrogen or pure hydrogen from a gas cylinder is introduced into the furnace, gas impurity levels at the outlet of the furnace are measured, as summarized in Table 1. 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 an optical system (a telescope and a video camera) are mounted at opposite ends of the tube, respectively.

Solder Oxidation

Thickness and composition of solder oxides

On the flip chip assembly, the 90Pb/10Sn solder bumps were electroplated and then first reflowed in hydrogen to carry out the alloying effect and to convert them into equilibrium hemispherical shapes. Both the electroplating and the first reflow processes can cause solder oxidation due to oxygen and moisture contamination in the gas phase. The oxide layer on the bump surface needs to be reduced by a forming gas before reflow soldering (called “second reflow”) starts.

The thickness and composition of the solder oxides present on the surface of both as-plated and first-reflowed solder bumps were determined using Auger microscopy. Two sizes of solder bumps were investigated: 1) 200 µm for as-plated and 160 µm for first-reflowed bumps, and 2) 60 µm for as-plated and 40 µm for first-reflowed bumps. The results are summarized in Table 2. As the size of the as-plated solder bump is decreased from 200 µm to 60 µm, the initial oxide thickness increases from 5 nm to 10 nm. After first reflow, the oxide layer in each case is further built up, and the smaller solder bump shows a larger increment in the oxide thickness, indicating a higher oxidation rate. This is reasonable because the smaller solder bumps have a larger surface-to-volume ratio and thus thermodynamically a higher tendency to reduce surface energy by surface oxidation. However, the bump size may not be the only factor influencing oxidation rate since the electroplating processes for the two bump sizes are not exactly the same, which may result in a slightly different bump composition. It is also shown in Table 2 that if the oxidation rate is relatively slow (thin oxide layer), only tin oxides are present on the surface. When the oxidation rate is faster (thick oxide layer), however, both tin and lead oxides are present. The amount of lead oxides increases with increasing oxidation rate. This can be explained as follows. With a rapid surface oxidation, the diffusion of tin from bulk to the surface is relatively slow as compared to the surface oxidation, thus resulting in mixed oxides at the surface. This observation of the dependence of the solder oxide composition on the oxidation rate is consistent with that reported in the literature (ref. 3).

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**Table 1:** The gas impurity levels at the outlet of the tube furnace.

<table>
<thead>
<tr>
<th>Inlet Gas</th>
<th>Outlet H₂O ppm</th>
<th>Outlet O₂ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>House nitrogen line</td>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>Pure hydrogen tank</td>
<td>5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

**Table 2:** The oxide thickness and the outmost surface composition of 90Pb/10Sn solder bumps.

<table>
<thead>
<tr>
<th>Solder bumps size</th>
<th>As-plated oxidation</th>
<th>First-reflowed oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (µm)</td>
<td>Oxide composition</td>
<td>Thickness (µm)</td>
</tr>
<tr>
<td>Large bump (200/160)</td>
<td>5 nm 100% tin oxides</td>
<td>10 nm 78% tin oxides</td>
</tr>
<tr>
<td>Small bump (60/40)</td>
<td>10 nm 93% tin oxides</td>
<td>30–50 nm 21% tin oxides</td>
</tr>
</tbody>
</table>
Shape of molten solder

When a fluxless solder is melted, it forms a droplet. The presence of oxygen in the solder drop (below approximately one monolayer, refs. 4 and 5) reduces the liquid surface tension, thus affecting the shape of the drop. This is demonstrated in the following experiment.

A flip chip containing 60 µm as-plated solder bumps was placed in the tube furnace with bumps facing up and heated to 400°C either in nitrogen and held for 8 minutes or in hydrogen and held for 3 minutes. After heating and holding, the chip was then quenched to room temperature. The shape of the as-quenched bump was examined using SEM. As shown in Figure 2, the shape of the bump after being reflowed in hydrogen is much more spherical than that in nitrogen. The spherical bump shape obtained in hydrogen is believed to be due to the reducing effect of hydrogen, which removes the initial oxides and prevents further oxidation of solder bump during the reflow. In the flip chip bonding technology, the shape of each solder bump after the first reflow is very critical. An oxide-free bump surface with a large bump height is preferred for better bonding and higher fatigue resistance (refs. 6 and 7).

Dissolution of Solder Oxides

A 90Pb/10Sn fluxless solder preform (2 mm diameter and 1 mm thick) was placed on a glass slide, heated in nitrogen from room temperature to a temperature above the solder melting point (305°C), and held at this temperature until the solder drop reached a stable shape; then the drop was photographed in situ in the tube furnace. The recorded solder drop is presented in Figures 3a to 3f for various temperatures. As the temperature is increased from 310 to 460°C, the solder drop becomes more hemispherical, indicating that the liquid surface tension is increased. This observation is in contrast to the normal temperature dependence of a liquid surface tension (ref. 8). Normally, as the temperature is increased, the surface tension of a liquid decreases due to a decrease in the molecular binding force at the surface. Since no reduction occurs in nitrogen atmosphere, this surface tension increase is presumably attributed to an increased dissolution of initial surface oxides with increasing temperature. To verify this hypothesis on the dissolution of surface oxides, the following experiment was performed.
A fluxless solder preform on a glass slide was heated in pure hydrogen from room temperature to 460°C and then held at this temperature for 30 minutes to ensure a complete removal of the initial surface oxides. Subsequently, the temperature was gradually decreased. During the cooling step from 460 to 310°C, the shape of the molten drop was recorded at each intermediate temperature (Figures 4a to 4f) corresponding to the heating experiment conducted in nitrogen (Figures 3a to 3f). Comparing Figure 3 with Figure 4, it can be seen that the shape of the molten drop in nitrogen approaches that in hydrogen as the temperature is increased. This observation suggests that at a high temperature, the surface of the molten drop in nitrogen is nearly as clean as that in hydrogen, indicating a dissolution of the initial surface oxides into bulk liquid solder and an increased solubility with increasing temperature. This observation is consistent with a previous study reported in the literature (ref. 9).

**Reduction of Solder Oxides**

**Initiation temperature**

Although in the normal soldering temperature range the reduction of solder oxides by hydrogen is thermodynamically feasible (solder oxides are unstable), the reduction rate, in many cases, can be extremely slow, which makes the reduction practically ineffective (refs. 10 and 11). From a kinetics point of view, an initiation temperature should exist above which the reduction process is rapid. A previous study reported the initiation temperatures for hydrogen to reduce tin oxides and lead oxides (ref. 12). However, the reported initiation temperatures may not be applicable to the electroplated solder bumps because the geometry and surface composition are different. Therefore, in this study, the initiation temperatures for hydrogen to reduce solder oxides on both 90Pb/10Sn solder preforms and solder bumps (40 µm) were investigated. The experiments were conducted by observing the shape change of a preoxidized molten solder during isothermal reduction in hydrogen at a given temperature. The rate of the shape change reflects the rate of the reduction process. This method was found to be simple and cost-effective as compared with the Auger analysis.
An initial experiment was performed using 90Pb/10Sn fluxless solder preforms (2 mm diameter and 1 mm thick). To develop a thick oxide layer, the solder preforms were first preoxidized by heating up from room temperature to 370°C in air and cooling down to room temperature in nitrogen. The thick oxide layer minimizes the effect of solder oxide dissolution and makes the shape change more distinguishable. The preoxidized preforms on glass slides were heated in nitrogen to various testing 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 recorded in situ, and the time needed for the molten solder to change from its initial oxidized shape to a stable final shape was determined. As summarized in Table 3, the initiation temperature to reduce oxides in the preoxidized solder preform is about 400°C. At or above this temperature, the reduction rate of solder oxides is accelerated. This result is consistent with that reported for hydrogen reduction of tin oxides (ref 12).

To obtain a further understanding, the initiation temperature for hydrogen to reduce solder oxides on a 90Pb/10Sn solder bump (40 µm) was also investigated. The as-plated solder-bonded chips were first reflowed at 400°C for 8 minutes in a nitrogen environment containing 100 ppm oxygen and then cooled down to room temperature. As shown in Figure 5a, such a reflowed bump shows a typical oxidized shape. The reflowed chip was then isothermally reduced in pure hydrogen at three reduction temperatures (340°C, 370°C, and 400°C) for 6 minutes and quenched to room temperature. Both heating to and cooling from the reduction temperature were conducted in nitrogen. The shape of the as-quenched bump after the reduction was examined by SEM. As shown in Figure 5, after reduction at 340°C for 6 minutes, the initially oxidized bump shape remains unchanged. However, after reduction at 370°C for 6 minutes, a significant change in bump shape is observed. When the reduction is done at an even higher temperature of 400°C for 6 minutes, the shape of the bump is similar to that obtained at 370°C, which indicates that the reduction of surface oxides by hydrogen at 370°C is nearly completed after 6 minutes. Therefore, the initiation temperature for hydrogen to reduce solder oxides in a solder bump is determined to be 370°C. The temperature range from 340 to 370°C is considered to be a transition region.

Table 3: Time to reach a near-equilibrium drop shape of the preoxidized preform in H₂ versus reduction temperature.

<table>
<thead>
<tr>
<th>Isothermal reduction temperature</th>
<th>Time to reach the equilibrium shape</th>
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<tbody>
<tr>
<td>370 degrees centigrade</td>
<td>No shape change was observed after 60 minutes</td>
</tr>
<tr>
<td>400 degrees centigrade</td>
<td>40 minutes</td>
</tr>
<tr>
<td>430 degrees centigrade</td>
<td>30 minutes</td>
</tr>
<tr>
<td>460 degrees centigrade</td>
<td>15 minutes</td>
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</table>

Figure 5: SEM micrographs of an as-quenched solder bump (a) after being first-reflowed and (b to d) after being reduced in H₂ for 6 minutes at various temperatures.
It is interesting that the above two experiments result in two different initiation temperatures. One is 400°C for a solder preform and the other is 370°C for a 40 µm solder bump, although their bulk solder compositions are similar. It can be concluded that the initiation temperature depends on the size of the solder involved. The smaller the solder drop, the lower the initiation temperature (i.e., the higher the reduction tendency). This conclusion is quite similar to that obtained for solder oxidation, in which we found that a smaller solder drop has a higher oxidation tendency. The two phenomena may be attributed to the same cause. That is, a smaller solder drop has a higher surface energy, thus thermodynamically having a larger tendency to reduce surface energy by obtaining a more stable phase at the surface. However, the bump size may not be the only factor influencing oxidation/reduction rates because the bulk compositions for the two bump sizes are not exactly the same.

Reduction rate

Since the initiation temperature for hydrogen to reduce solder oxides on a 40 µm solder bump was found to be around 370°C, this temperature was therefore selected to study the isothermal reduction rate as a function of the forming gas concentration. A flip chip containing as-plated solder bumps was preoxidized at 400°C for 8 minutes in a nitrogen environment containing 100 ppm oxygen and then cooled to room temperature. In this case, the thickness of the oxide layer on the surface of each solder bump (40 µm) is determined to be about 20 nm by Auger microscopy. The oxidized chip was subsequently heated in nitrogen to 370°C, held at 370°C in a selected hydrogen concentration of forming gas for a period of time, and then cooled to room temperature in nitrogen. The shape of each quenched bump was examined by SEM and the time required for a solder bump to change from its initial oxidized shape to an approximately final shape for a given hydrogen concentration was thus determined. The result is shown in Figure 6, where the term “90% reduction” is an approximate value to represent the near completion of the reduction since a 100% reduction would take a relatively long time to finish. The result shows that the higher the hydrogen concentration, the shorter the reduction time will be. The time to reach a 90% reduction of oxides at 370°C is inversely proportional to the percentage of hydrogen in the forming gas, i.e., $t \propto \frac{K}{P_{H_2}}$. For a 40 µm solder bump with a 20 nm thick oxide layer, it takes about 6 minutes to reduce 90% of oxides at 370°C in pure hydrogen. Therefore, the average reduction rate is about 3.3 nm per minute.
Reflow Soldering

Soldering of a solder-bonded chip on a Au/Ni-coated Cu foil

As a preliminary study, the solderability of a solder-bonded chip on a metal foil was investigated. The metal foil has exactly the same composition and coating layer as those of the solder pad on currently used production printed circuit boards. The chips bonded with 40 µm bumps were tacked on the Au/Ni-coated Cu foils and soldered at 370°C in house-line nitrogen. As shown in Figure 7a, after the chip is soldered and pulled apart from the substrate, the solder material is left in an irregular pattern on each pad. This poor solderability can be attributed to the thicker oxide layer present on the surface of the bumps, which impedes the interaction between the solder and the substrate. In contrast, when hydrogen is used as a soldering environment at 370°C, the solderability is significantly improved. After the chip is soldered in hydrogen and pulled apart from the substrate, only mushroom-shaped pads are left in the chip side (Figure 8a), and all the solder material is found to be firmly bonded on the substrate (Figure 8b).

Soldering of a solder-bonded chip on a printed circuit board

As a final approach to these laboratory studies, the soldering performance of a solder-bonded chip on a printed glass substrate was investigated. As shown in Figure 9a, a chip bonded with 40 µm solder bumps is tacked on a printed glass substrate with the solder-bonded surface of the chip up and the conducting surface of the substrate down. In the horizontal direction of Figure 9a, a misalignment between the chip and the substrate can be seen. When this tacked sample was reflowed at 370°C in nitrogen, only a small degree (3 µm) of self-alignment was achieved (Figure 9b). Figure 10a shows another tacked sample having an initial misalignment in the vertical direction. When reflow soldering was conducted at 370°C in hydrogen, about 12 µm self-alignment was obtained (Figure 10b). The higher self-alignment ability in hydrogen is believed to be due to the higher surface tension of liquid solder, as a result of reduction of oxide by hydrogen.
Production Trials

The results from laboratory investigations (section 2) demonstrate that 100% hydrogen in forming gas provides the highest reduction rate of solder oxides on the 40 µm solder bumps (90Pb/10Sn) and the initiation temperature of the reduction is around 370°C. Therefore, pure hydrogen and reflow temperatures above 370°C were used for solder bonding in production trials. The first step of the production trials was to establish acceptable oxygen and moisture (dewpoint) levels (oxygen < 10 ppm and moisture < 150 ppm) within a reflow furnace using pure hydrogen. The oxygen and moisture levels were measured by pulling a sample of the furnace atmosphere via a vacuum pump at one-foot intervals using a 0.25 inch O.D. stainless steel probe. A Teledyne 311B trace oxygen analyzer and a Nyad Series 100 hygrometer (dewpoint) were used for the measurement. The second step of the production trials was to obtain an expected reflow temperature profile, and the third step was to reflow solder-bonded chips on printed circuit boards and to examine the solder wetting by pulling the chips apart from the substrates. Both a laboratory-scale reflow furnace and a production furnace were used in the production trials.

The initial experiments were done in a laboratory-scale reflow furnace (Lindberg) with minimal gas and temperature controls. By adjusting gas flow rates of different zones and adding baffles on the entrance and the exit of the furnace, the lowest oxygen and moisture levels obtained in this furnace were about 6.4 ppm and 129 ppm, respectively. The temperature profile established in this furnace has a reflow temperature of 377°C for 30 seconds. After reflow, acceptable wetting on the pads of the substrate was found. Failure modes for the reflowed samples included intrasolder joint failures and substrate pad pull-outs. These preliminary results indicate that this fluxless soldering process can achieve acceptable solder joints.

As a further development, the process parameters established in the laboratory-scale furnace were transferred to a production furnace (Lindberg Model 816). However, the acceptable oxygen and moisture levels have not yet been obtained in this production furnace. With a pure hydrogen flow, the average oxygen level was about 14 ppm and the average moisture level was about 991 ppm. The moisture level was much above the acceptable limit. Under this soldering environment, a reflow trial consisting of 15 units was run with a reflow temperature of 386°C for 24 seconds. After pulling a reflowed chip apart from a substrate, it was found that solder wetting on the substrate pads was not uniform and repeatable. As shown in Figure 11, some of the gold-plated pads (white) are still exposed without a uniform coverage of solder (black). The major failure was found at the interface between solder and pad instead of the intrasolder breaks. This result indicates an unacceptable wetting due to the high moisture level present in the furnace, which causes solder oxidation. Further experiments are in progress to reduce the oxygen and moisture levels, which is the most critical part of the production trials.
Conclusions

During fluxless soldering in a forming gas environment, four reactions take place at the surface of the liquid solder: solder oxidation, dissolution of solder oxides, reduction of solder oxides, and reflow soldering.

1) Solder oxidation is caused by trace amounts of oxygen and moisture present in the soldering environment. A smaller solder bump has a higher oxidation rate than that of a larger bump. The higher the oxidation rate, the larger the percentage of lead oxides that will be present on the surface of a solder bump (90Pb/10Sn).

2) A dissolution of initial surface oxides into bulk liquid solder occurs when the temperature is above the melting point of the solder. The oxide solubility increases with increasing temperature.

3) For hydrogen (in forming gas) to reduce solder oxides on 40 µm solder bumps (90Pb/10Sn), the initiation temperature is about 370°C. The initiation temperature increases with increasing size of the solder. At 370°C, the isothermal reduction rate in pure hydrogen is about 3.3 nm/minute, in terms of reduction in oxide thickness. The isothermal reduction rate is directly proportional to the percentage of hydrogen in the forming gas.

4) When the reflow temperature is at or above 370°C, hydrogen soldering intensifies the interfacial reactions at the bonding surface and provides a higher self-alignment ability, as compared with nitrogen soldering.

5) Preliminary production trials indicate that if acceptable oxygen and moisture levels (oxygen < 10 ppm and moisture < 150 ppm) are obtained, the fluxless soldering of the flip chip assisted by hydrogen can achieve good solder joints.

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