# Atmosphere Effect on Soldering of Flip Chip Assemblies

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## Abstract

An experimental study was conducted to evaluate the feasibility of reducing metal oxides on both the solder and substrate in hydrogen and to investigate the effect of solder size on the solder's oxidation and reduction kinetics. The results of this study can be summarized as follows. 1) The oxides present on a copper substrate can be reduced in hydrogen at or near the normal soldering temperature range. 2) Although in most cases the solder oxides on the surface of a tin-lead solder are very difficult to reduce in hydrogen, the reduction rate of the solder oxides can be significantly increased by decreasing the size of the solder. Therefore, the fluxless soldering of flip chip assemblies by using hydrogen as a reducing agent is very promising, especially when the size of solder bumps on the flip chip is relatively small, such as 40 μm or below. 3) When the solder size falls into the range used for flip chip technology, the oxidation potential of the solder increases significantly. Therefore, minimizing oxygen and moisture concentrations in the reflow environment becomes more critical when flip chip technology is employed.

## Introduction

The trend toward miniaturization is driving the use of technologies such as chip on board (COB) and direct chip attach (DCA). Flip chip bonding is a direct chip attach technology that typically uses solder bumps to provide electrical interconnection between a chip and a substrate. The technology allows for availability of the whole chip surface for I/O interconnections and does not require intermediate chip packaging, so that the flip chip bonding leads to a great increase in circuit density. Besides, the flip chip bonding also provides some advantages over other joining methods. During reflow, the chip can self-align to the substrate due to surface tension of liquid solder leading to a very high-yield manufacturing process. The short distance between the chip and the substrate provides enhanced electrical performance. Therefore, the flip chip bonding is becoming more and more widely used.

However, there are also some challenges involved in the implementation of the flip chip technology. The diameter of a solder bump used for the flip chip bonding normally ranges from 100 to 200 μm and, in some cases, is even as small as 40 μm. Such tiny solder bumps make the soldering of flip chip assemblies relatively difficult. The major difficulty is post-cleaning. Flux residues are likely to be entrapped into the tiny space between the chip and the substrate and are very difficult to clean. These residues can degrade the reliability of flip chip assemblies. The use of no-clean flux has been found to leave residues and cause chip underfill adhesion problems. Therefore, fluxless soldering of flip chip assemblies is highly desirable.

Using a reducing gas, such as hydrogen, to reduce oxides on both solder and substrate is one of the approaches to fluxless soldering and has been occasionally used for some solders with a relatively high melting point. The major limitation is the inefficient and slow reduction rate of solder oxides in hydrogen at the normal soldering temperature range, although the solder oxides are thermodynamically unstable in the presence of hydrogen. However, it was suspected that the reduction of solder oxides in hydrogen could be assisted by decreasing the size of the solder bump (Ref. 1). This conjecture is based on the following reason. When the size of a solder bump is reduced, the surface-to-volume ratio of the solder increases and thus system energy or chemical potential

increases. Therefore, compared with a larger solder bump, the surface of the smaller solder bump should be more chemically sensitive to the soldering environment and thus beneficial to the approach of hydrogen fluxless soldering.

On the other hand, based on the same reason, the surface oxidation of tiny solder bumps on a flip chip in an oxygen-containing atmosphere was also expected to be more severe than that of a solder joint on a normal surface mount package (Ref. 1). During the manufacturing of solder bumps on a flip chip, the solder bumps are either electroplated or printed on the active surface of a flip chip, and then a first reflow is normally required to carry out the alloying effect and to convert the solder bump into a desired shape. An oxide on the bump surface during the first reflow not only may degrade the quality of the solder bumps, but also will reduce the solderability of the flip chip on a substrate. Therefore, minimizing oxygen and moisture concentrations in the reflow environment may be more critical when flip chip technology is employed.

The objective of this study was to evaluate the feasibility of reducing metal oxides on both the solder and the substrate in hydrogen and to verify the effect of solder bump size on the solder's oxidation and reduction kinetics. The following experiments were conducted:

1) investigating the capability of reducing oxides on the substrate material in hydrogen,

2) measuring the reduction rate of solder oxides in hydrogen versus solder bump size, and

3) determining the effect of solder bump size on solder oxidation tendency in an oxygen-containing atmosphere.

# Experiments, Results, and Discussions

## Reduction of copper oxides in hydrogen

Copper is a commonly used substrate material for electronics assemblies. To evaluate the reducing capability of copper oxides in hydrogen, differential scanning calorimetry (DSC) was used. 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. Two types of copper samples were used to find the initiation temperature for hydrogen to reduce copper oxides.

As a first step of the study, 100 μm diameter copper powder was used to intensify the heat flow associated with the reduction process. The copper powders were preoxidized to build a thick oxide layer which was measured to be about 5000 angstroms. The preoxidized copper powders were then heated up at 10°C/min in DSC under hydrogen flow. A heat release was detected with increasing temperature due to the exothermic reaction of copper oxides with hydrogen. The temperature at reaching the maximum heat release rate (or the maximum slope on DSC curve) was found to be around 134°C **(Figure 1)**, which was used to represent the initiation temperature of the reaction. This result is quite consistent with the data revealed in the literature (Ref. 2). However, for a flat copper surface, such as used for a substrate, the initiation temperature may not be the same as that of a curved powder surface.

To further evaluate the capability of reducing copper oxides in hydrogen on a flat copper surface, the above experiment was repeated by using a preoxidized copper plate with an oxide thickness around 16000 angstroms. The plate was gently flattened in a press prior to analysis to achieve the maximum thermal contact. As shown in **Figure 2**, an exothermic peak was detected. The peak height was, as expected, relatively small due to the smaller surface area of the copper plate compared with that of the copper powders. The onset tem-

**Figure 1: DSC curve for the reduction of copper oxides on 100 μm copper powders by hydrogen**



General V2.2A DuPont 9900
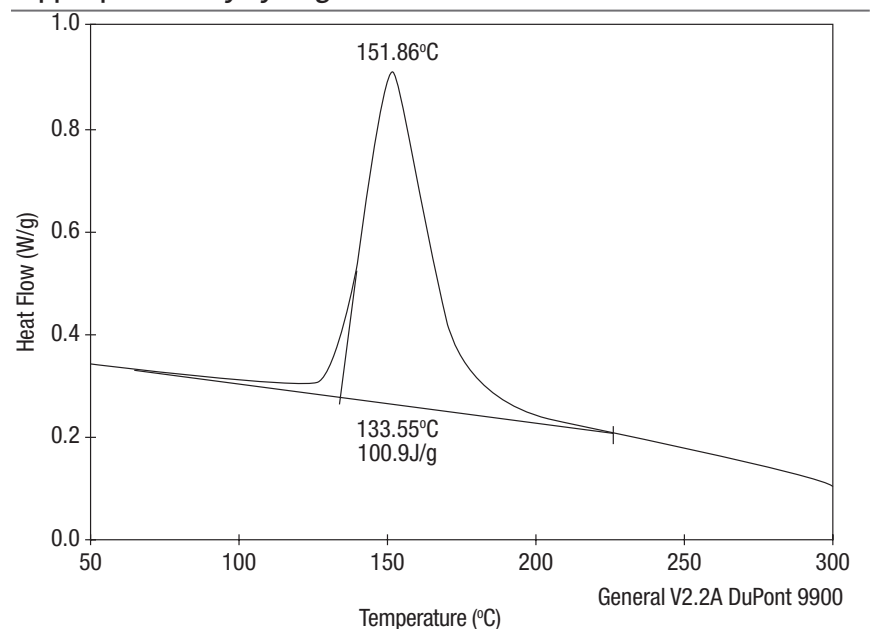
perature of the peak was found to be around 216°C, which is significantly higher than that obtained by using the copper powder. Based on this result, the initiation temperature for hydrogen to reduce copper oxides on a copper substrate should be around 216°C. This temperature is quite close to the peak temperature used for soldering of the eutectic tin-lead solder (220 to 230°C). Therefore, by slightly adjusting the peak temperature or dwell time around the normal soldering condition, the initial copper oxides (~40 angstrom thick) should be able to be removed in hydrogen.

The above experiment verifies the feasibility of reducing copper oxides in hydrogen and also exposes that there is a curvature effect on the reduction kinetics of copper oxides in hydrogen. It seems that when increasing the surface curvature from a copper plate to a fine copper powder, the activation energy of the surface reaction is reduced, thus causing the initiation temperature of the reaction to decrease. To further confirm this phenom- enon, isothermal reduction rates of copper oxides in hydrogen on both copper powder and copper plate were also investigated.

Preoxidized copper samples, in powder and plate form, were heated up in DSC under a nitrogen flow to a selected temperature (above the corresponding initiation temperature). After the temperature was stabilized, the nitrogen flow was switched to a hydrogen flow. As long as the hydrogen flow started, a heat release could be detected. The duration of the exothermic peak was then recorded, which represented the time required to complete the reduction process. The isothermal reduction rate could thus be calculated from the ratio of the oxide thickness on the preoxidized sample over the reduction time. Such determined reduction rate is independent from the total surface

**Figure 2: DSC curve for the reduction of copper oxides on a copper plate by hydrogen**
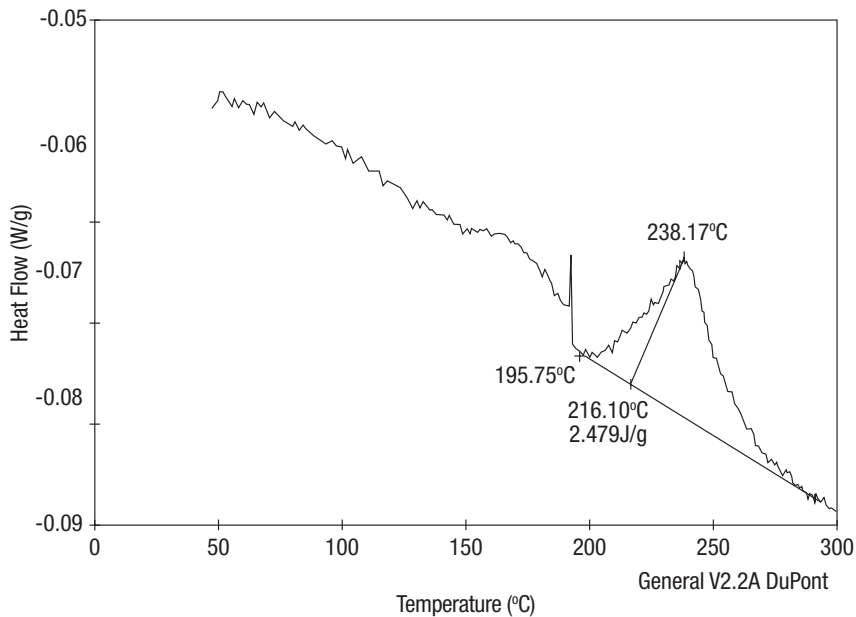


**Figure 3: Reduction rate of copper oxides on each copper sample as a function of temperature**
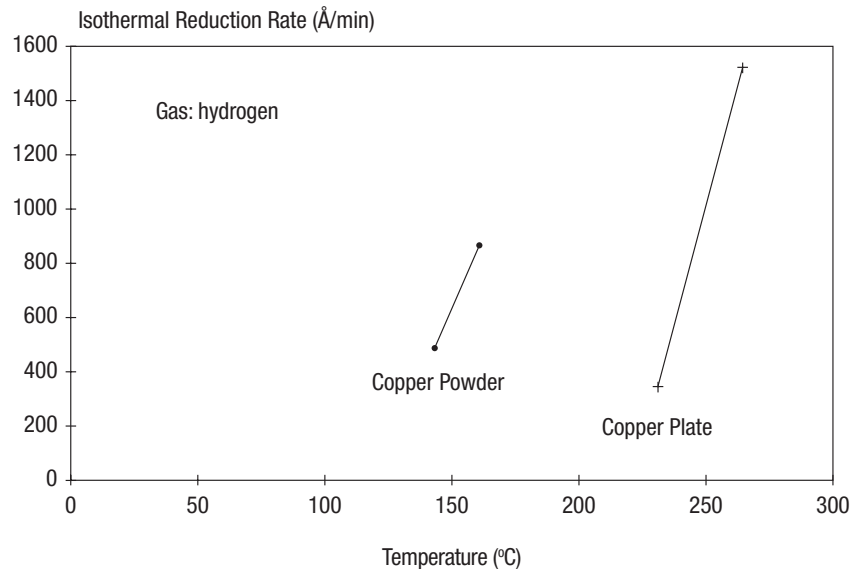


area involved in the reaction. Therefore, a comparison of the reduction rates between the two copper samples represents a difference in chemical potential rather than a difference in oxide concentration (amount of surface oxides per volume of the solder).

As shown in **Figure 3**, at each temperature, the reduction rate of copper oxides on the copper powders is indeed much higher than that on the copper plate. Therefore, this result supports the above inference that the activation energy of the reduction for a curved surface must be smaller than that for a flat surface, so that at a certain temperature a higher percentage of the oxide molecules at the curved surface is in the activated state and thus the reaction rate can be promoted.

## Reduction of solder oxides in hydrogen

From a kinetics point of view, the reduction of solder oxides, or in most cases tin oxides, on the surface of a tin-lead solder in hydrogen should be more difficult than that of copper oxides on a copper substrate. The reason is attributed to the relatively high bond strengths of the tin oxides compared to that of the copper oxides (Ref. 3). Therefore, higher activation energies or temperatures are expected to be required for hydrogen to break the bonds of tin oxides. In the previous section, the curvature effect on the reduction kinetics of copper oxides has been demonstrated. For reducing solder oxides, this curvature effect should be more important, since it implies that the reduction of the surface oxides may be assisted when the solder bump size is reduced, such as in the case of using flip chip technology where very small (40µm) solder bumps can be encountered.

To investigate the effect of solder bump size on the reduction rate of surface oxides, the previous DSC method cannot be applied, because at the temperature of interest, the solder is in the liquid phase. Therefore, another experimental method was exploited based on the shape characteristic of a molten solder bump, which can be described by **Figure 4**. An electroplated solder bump on a flip chip has a typical mushroom shape (**Fig. 4a**). When the solder bump is reflowed in a nitrogen-based oxygen-containing atmosphere, the shape of the solder bump becomes ellipsoidal (**Fig. 4b**), because an oxide layer formed on the surface of the solder bump prevents liquid flow underneath it and makes the solder maintain its initial shape. However, as the reflow is conducted in hydrogen, the solder bump with an oxide-free surface forms a nearly spherical shape driven by liquid surface tension (**Fig. 4c**). This shape characteristic was used in this study to monitor the progress of reducing surface oxides on a molten solder bump in hydrogen. A high lead solder with a composition of 90Pb/10Sn and a melting point of 305°C was selected. The solder was made into three samples:

1) 1200 µm disk shaped solder preform placed on a glass slide,

2) 160 µm electro- plated solder bumps bonded on a flip chip, and

3) 40 µm electroplated solder bumps bonded on a flip chip.

Each sample was preoxidized to build a thick oxide layer to minimize the dissolution effect of solder oxides into bulk liquid solder (Ref. 4) and make the shape change of the oxidized sample more distinguishable during a hydrogen reduction process. The thickness of the oxide layer ranged from a few hundred to a thousand angstroms. The dominant type of the oxides formed on the three samples was all found to be tin oxides. After preoxidation, each oxidized sample was placed in a quartz tube furnace and isothermally reduced in hydrogen at selected temperatures for various time periods and then quenched to room temperature. Both heating to and cooling from the reduction temperature were conducted in nitrogen. For the solder preform, the shape change of the molten solder during reduction in hydrogen was monitored in situ by a video system mounted at the outside of the furnace. However, due to the limited magnification of the video system, an in situ observation of the shape change on the tiny solder bumps of a flip chip during reduction in hydrogen cannot be achieved. As a substitution, the shape of the as-quenched bumps on a flip chip after each test was examined by an optical microscope. Therefore, the time required for each sample to change from its initial oxidized shape to an oxide-free shape could be found and an isothermal reduction rate could be cal culated from the ratio of the oxide thickness on the preoxidized sample over the reduction period.
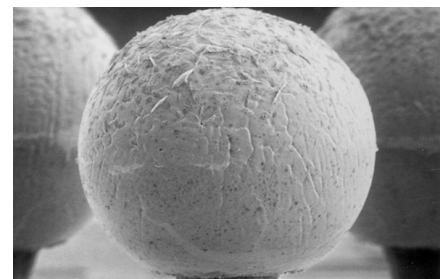
**Figure 4: SEM micrographs of a) an electroplated solder bump, b) a solder bump after being reflowed in a nitrogen-based oxygen-containing atmosphere, and c) a solder bump after being reflowed in hydrogen**
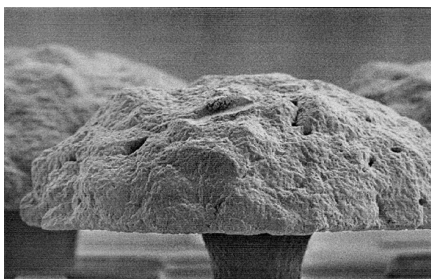


a) electroplated



b) reflowed in N$_2$



c) reflowed in H$_2$

**Figure 5** shows the reduction rate of solder oxides on each sample as a function of temperature. The result proves that the smaller the solder size is, the larger the isothermal reduction rate will be. For example, at 370°C the rate of reducing solder oxides on a 40 µm solder bump can be as high as 40 angstroms per minute. However, on the surface of a 1200 µm solder (a size similar to that of a normal solder joint), the reduction rate at the same temperature is only 3 angstroms per minute. Therefore, the solder size does play an important role in the reduction kinetics of solder oxides. It is believed that when the size of a solder is reduced, the surface-to-volume ratio of the solder increases and thus system energy increases, so that lower activation energies or temperatures are required for hydrogen to break the bonds of surface oxides and make the oxides in the activated state. In other words, at a certain temperature, there should be a higher percentage of surface oxides on a smaller solder being activated compared to a larger solder. Therefore, the reduction rate of surface oxides increases with decreasing the size of a solder.

**Figure 5: Reduction rate of solder oxides on each sample as a function of temperature**
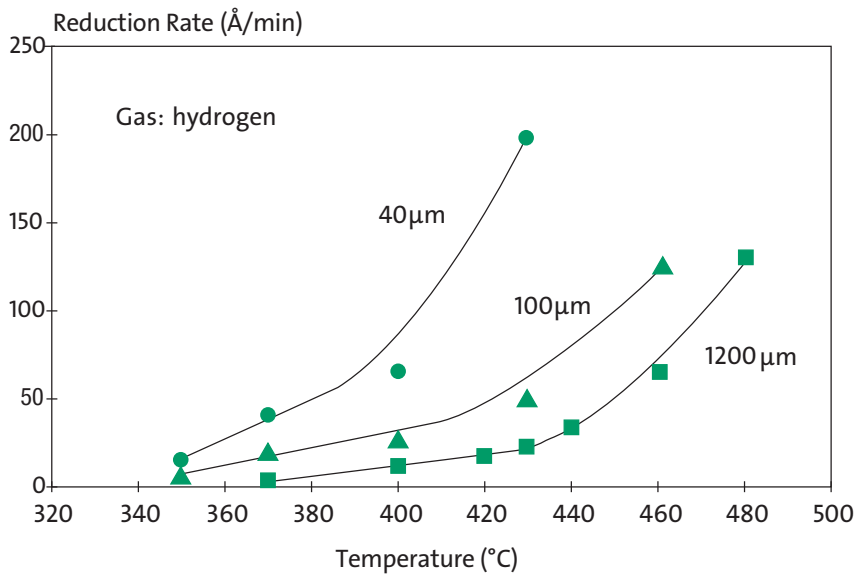


### Solder oxidation in an oxygen-containing atmosphere

Solder oxidation is a common problem encountered in soldering of flip chip assemblies, especially in the case where flux is eliminated in the solder. During the manufacturing of solder bumps on a flip chip, the solder bumps are either electroplated or printed on the flip chip, and then a first reflow is performed to carry out the alloying effect and to convert the solder bumps into a desired shape. The first reflow is normally conducted in an inert or a reducing atmosphere for a fluxless solder. When a nitrogen- based inert atmosphere is used for the first reflow, solder oxidation will occur due to a trace amount of oxygen present in the furnace atmosphere. This oxidation on the bump surface may cause problems such as: nonuniform bump shape, insufficient bump height, and non-smooth bump surface. Even when the first reflow is conducted in a hydrogen- based reducing atmosphere, solder oxidation still cannot be totally prevented at the cooling zone of a reflow furnace. The reason is that when temperature is lower than a certain value, solder oxides become thermodynamically stable for the normal hydrogen/water partial pressure range which is achievable in a production used reflow furnace. The solder oxidation under the hydrogen-based reducing atmosphere may not affect having a desired bump shape because the oxidation occurs when the peak temperature of the reflow has been passed and desired bump shape has been obtained. However, an oxidation on the bump surface will always interfere with the physical contact at the interface of the solder bump and substrate and thus reduce the solderability during the subsequent solder joining process.

Based on the same reason as the effect of solder size on the reduction of solder oxides, the surface oxidation of a tiny solder bump in an oxygen-containing atmosphere was also expected to be more severe than that of a solder joint on a normal surface mount package. Therefore, the effect of solder size on the oxidation tendency was also studied by using the same samples as used previously for studying reduction of solder oxides in hydrogen. Because solder oxidation is normally a diffusion-controlled process rather than a reaction-controlled process (such as it is for the reduction of solder oxides), the rate of solder oxidation, in most cases, is not a constant value which decreases with increasing oxidation time or oxide thickness. Therefore, it is not quite reasonable to compare isothermal oxidation rates among the solder samples with different sizes. Therefore, the thickness of the oxide layer formed on each sample after an isothermal oxidation treatment was investigated.

Each sample was placed in the quartz tube furnace and heated at 450°C in hydrogen for 5 minutes to remove initial oxides. The sample inside the furnace was then cooled under a nitrogen flow to 400°C. When the furnace temperature reached equilibrium, the nitrogen flow was switched to an oxygen- containing atmosphere, which was 100 ppm oxygen in nitrogen, for 8 minutes to oxidize the solder. Finally, the furnace was cooled in nitrogen to room temperature. After this oxidation treatment, the thickness of the oxide films formed on each solder bump was determined using Auger Electron Spectroscopy (AES).

**Figure 6: Oxide thickness formed on each sample after an oxidation treatment versus the size of the solder bump**
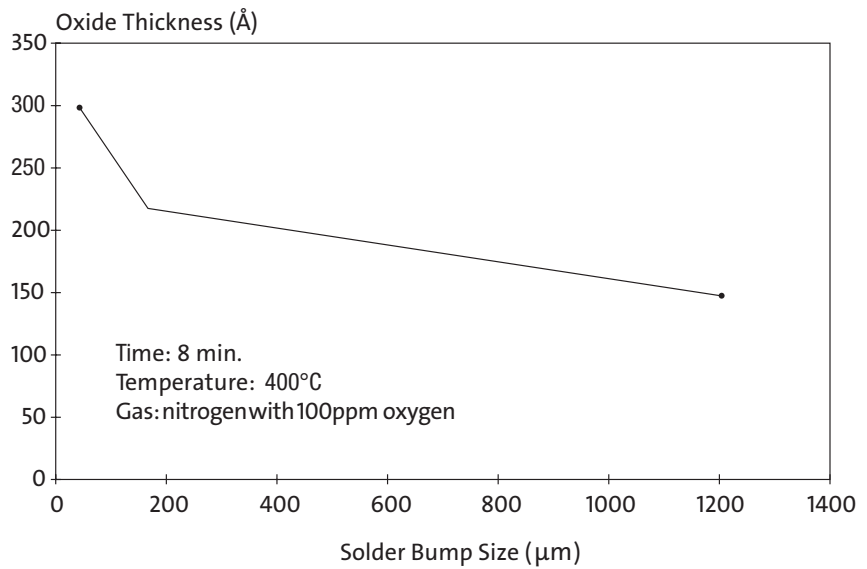


**Figure 6** shows the oxide thickness after the oxidation treatment versus the size of the solder bump. The result indicates that when the solder size falls into the range used for flip chip technology, furnace oxidation of the solder bump will be enhanced significantly. Therefore, minimizing oxygen and moisture concentrations in the reflow environment is indeed more critical when flip chip technology is employed.

## Conclusion

The results obtained in this study can be summarized as follows.

1. The oxides present on a copper substrate can be reduced in hydrogen at or near the normal soldering temperature range.

2. The reduction rate of solder oxides in hydrogen can be significantly increased by decreasing the size of a solder. The reason is attributed to an increase in system energy or chemical potential as the size of the solder is shrunk. Therefore, the fluxless soldering of flip chip assemblies by using hydrogen as a reducing agent is very promising, especially when the size of solder bumps on the flip chip is relatively small, such as 40 μm or below.

3. When the solder size falls into the range used for flip chip technology, the oxidation potential of the solder increases significantly. The reason is believed to be the same as that of reducing solder oxides. Therefore, minimizing oxygen and moisture concentrations in the reflow environment becomes more critical when flip chip technology is employed.

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