Effects of Controlled Atmospheres on Solder Wetting

Research focusing on inert environments for reflow soldering processes rates the influence of residual oxygen on RMA and low-solids pastes.


In electronics assembly, solder paste is melted in a “low” temperature reflow process over a four- to seven-minute period. The peak temperature is typically ~215°C, and the time the tin-lead solder is liquidus ranges from 30 to 90 seconds. The research reviewed indicates that when solder is reflowed in air, its oxygen content reacts with both the molten solder and solid solder to form predominantly tin and tin (IV)-metal oxides. These oxides hinder the reflow process by decreasing the wetting force of the molten solder and increasing its viscosity, thereby decreasing solder affinity between component leads and solder-coated lands.

Oxygen vs. Wetting Angle

Several oxygen-containing nitrogen reflow atmospheres were evaluated to study the effect of residual oxygen on solder fillet/component wetting angle. In a separate study, the effects of oxygen concentration on solder-component wetting force have been evaluated, and oxygen profiles, with respect to temperature established in an infrared reflow furnace, were taken. Measurements of the wetting angle between the solidified solder and ceramic chip capacitors were taken from cross-sections of components. The measurements showed a favorable correlation between oxygen concentration in the reflow atmosphere and the solder fillet/land wetting angle (table 1).

Preliminary results from wetting balance measurements performed under the controlled-atmosphere conditions of a glove-box apparatus indicate that atmospheres containing low oxygen levels improved wetting force, wetting time, and the standard deviation between measurements. For an RMA assembly flux, wetting time increased by 50 percent, and wetting force increased by 11 percent in a 7 ppm O₂ nitrogen atmosphere vs. air. For a low-solids assembly flux, wetting performance drops with oxygen impurities greater than 40 ppm. Figure 1 illustrates the wettability performance vs. oxygen concentration of a copper test coupon. The test was performed using a GEC Meniscograph, which measures the interfacial force between molten solder and the test specimen to be soldered.

Effects on Paste Residues

Apart from the improved wettability achieved with nitrogen and inert reflow atmospheres, there are additional benefits to be realized. The use of an inert atmosphere can effect a more efficient volatilization of solder paste vehicles. The paste residues from the reflow process are not degraded by oxidation at soldering temperatures and prove to be easier to clean. Oxidation of the rosin during heating involves in its chemistry the conjugated double bonds of the abietic acid system. The reaction produces a combination of peroxides, hydroxy, and keto compounds. The oxidized rosin acid is considerably less sol-
urable in cleaning solvents than the original rosin, and appears as one cause of white residues on the surface of the PCB.

The behavior of commercially available formulations of both rosin-based, mildly activated (RMA) and low-residue, no-clean solder pastes was studied under air, nitrogen, hydrogen, carbon dioxide, and helium reflow atmospheres. (The pastes were not formulated for any specific reflow atmosphere.) The analytical techniques included thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA records the changes in weight percent of a sample as a function of temperature and time, a technique useful for determining the temperature at which solder paste vehicles are volatilized and the amount of paste residue after reflow. (In this evaluation, the term vehicle is used in a generic sense to describe nonmetallic components of solder paste.) In the TGA experiments, the paste samples are heated from ambient to 600°C at a rate of 10°C/min.

The measurement of atmosphere effects on solder paste vehicles is diminished when using solder paste in a TGA experiment since nearly 90 percent of the sample is nonvolatile metal alloy and not vehicle. Accordingly, the percent metal content is factored from the original weight percent values to evaluate the effects of the various atmospheres on the paste vehicles only. The resulting thermograms quantify the percentage of solder paste vehicle that can be expected to remain as residue on the PCB when processed under the various reflow atmospheres studied.

**RMA vs. Low-Solids**

Figures 2 and 3 represent the data collected in the TGA analysis of RMA and low-residue solder pastes at 185°C (near the liquidus temperature—200°C), and 215°C (near the peak solder reflow temperature). The data show that 77.8 percent of the vehicle remained as a residue to be cleaned when using an RMA solder paste reflowed at 215°C in air. The use of nitrogen as an inert atmosphere afforded a 5.3 percent reduction in residue, and when the RMA paste was evaluated under a hydrogen atmosphere, 12.6 percent less residue was observed. The atmosphere effects were more pronounced when evaluating a low-residue solder paste formulation. In this study, 19.2 percent of the paste vehicle remained when reflowed under an air atmosphere at 215°C. This represented a fourfold decrease in residue vs. the RMA solder paste/air trials.

By eliminating oxygen from the reflow atmosphere, a 35 percent decrease in residue remaining was afforded with either the nitrogen or carbon dioxide atmospheres. TGA trials using hydrogen and helium atmospheres resulted in about 50 percent less residue. The comparison of the H2 and He trials indicated that hydrogenation of the paste vehicle leading to an increase in volatility does not occur.

Two factors—heat-transfer ability of the reflow atmosphere and solder paste residue oxidation—contribute to the mechanism that gives rise to these observations. The thermal conductivities of these atmospheres are listed in table 2 relative to air, and suggest that hydrogen and helium are more efficient heat-transfer media. This efficient heat transfer results in an enhancement of the volatilization of solder paste nonmetals.

Hydrogen, or nitrogen/hydrogen forming gas blends, has been employed as a reducing atmosphere in high-temperature soldering and brazing applications. However, thermodynamic calculations show that hydrogen is not reducing to the solder oxides in the temperature regime of the solder reflow process. Experimental data supporting these calculations indicate that the onset of metal oxides reduction by molecular hydrogen begins at 138°C for Cu (I) oxides, 144°C for Cu (II) oxides, 319°C for Pb (II) oxides, and 400°C for Sn (IV) oxides. Therefore, hydrogen functions as an inert, high-heat-transfer fluid at typical circuit board reflow temperatures.

**DSC Evaluation**

Solder paste and rosin samples were evaluated using differential scanning calorimetry to study paste residues and the adverse effect of oxidation on vehicle volatilization. DSC records heat energy lost or gained as a consequence of endothermic or exothermic reactions oc-
curing in the sample. Physical processes that are endothermic include solid-to-liquid and liquid-to-gas phase changes. (Oxidation is an exothermic process for nearly all organic reactions.)

DSC thermograms of both RMA and low-residue solder pastes show exotherms within the temperature regime of reflow soldering, indicating residue oxidation. At elevated temperatures, a significant exotherm is observed. Exotherms are not observed in thermograms acquired using nitrogen and hydrogen atmospheres. DSC data also clearly indicate the oxidation of rosin in air vs. nitrogen. These studies show that oxidation of organic components of solder paste formulations can contribute to larger amounts of residue on the substrate after reflow.

There are some obvious advantages to minimizing residue after solder reflow for manufacturers that require cleaning. When using a no-clean solder paste formulation, the reduction of residue in a more cosmetically appealing product. Also, test probes must deal with less tacky residue, resulting in more effective in-circuit testing. In general, paste residue can be minimized by maintaining a minimum heat exposure and by conducting reflow in an inert atmosphere. Solder pastes formulated with vehicle chemistries that complement the effects of the inert atmospheres can result in no-clean, essentially no-residue, soldering processes.

Effects on Solder Defect Rates

Several test programs have been conducted at customer sites to demonstrate the advantages of using nitrogen or IR solder reflow. Customers found that the most significant benefit of nitrogen atmospheres is the reduction of soldering defects. Long-term evaluations of nitrogen reflow atmospheres at Xetel Corp. (Austin, Texas), for example, show a reduction of 75 percent in overall soldering defects resulting in a savings of over $20,000 per month in rework labor costs.

Xetel was most concerned with decreasing defects due to solder nonwetting. This defect was important to its process engineers because each inspector had to determine what qualified as a nonwetting defect. Test-detectable defects such as solder bridges and opens were also recorded. The identification and correction of these defects were major criteria in the atmosphere evaluation.

Figure 4 shows the defect data acquired over a two-month period. Air and nitrogen reflow atmospheres were altered for two-week intervals in the IR furnace during normal production schedules. The PCBs were Type I and Type II boards of medium complexity, with each board averaging approximately 200 solder joints. Boards from many different production lots were processed in each atmosphere. More than 6700 boards were run in air (nearly 1.5 M solder joints) and more than 12,700 were run in nitrogen (over 2.5 M solder joints).

The overall solder defect level for the IR operation fell from 1250 ppm in air to 275 ppm in nitrogen, with nonwetting defects reduced by greater than 85 percent. This result is directly attributable to reflow soldering in nitrogen and the subsequent minimization of solder oxidation. The data indicate that other solder defects were also decreased significantly when assemblies were processed in nitrogen. Solder bridging was reduced by nearly 78 percent, and solder defects due to insufficient solder decreased 77 percent.

Conclusions

The presence of low oxygen concentrations in soldering atmospheres causes oxidation of tin-lead alloy systems used in electronic soldering. These surface oxides are predominantly SnO and SnO₂. The exclusion of oxygen by use of an inert atmosphere has a positive effect on the solder reflow process. Inert atmospheres have been demonstrated to decrease wetting angle and increase wetting force. Overall solder defect levels were reduced by more than 75 percent in production trials using inert soldering atmospheres. Inert atmospheres have also been demonstrated to be effective in reducing the amount of solder paste residue remaining after solder reflow by reducing flux oxidation. When a nitrogen atmosphere is used in conjunction with a low-residue solder paste, the amount of vehicle remaining as residue is reduced by 35 percent. Hydrogen and helium reflow atmospheres afford similar TGA thermograms, indicating the solder paste volatiles are more efficiently evolved when a high-heat-transfer atmosphere is employed. New flux and vehicle chemistries, ideally low in nonvolatile rosin, should complement the benefits that can be realized when reflow soldering is performed in an inert atmosphere.

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