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Reduced Oxide Soldering Activation (ROSA) PWB Solderability Testing

Cynthia L. Hernandez, F. Michael Hosking, Jim Reed, D. Morgan Tench, John White

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Reduced Oxide Soldering Activation (ROSA) PWB Solderability Testing

Cynthia L. Hernandez and F. Michael Hosking Physical and Joining Metallurgy Department Sandia National Laboratories Albuquerque, NM 87185-1411

> Jim Reed Texas Instruments Austin, Texas 78714-9149

D. Morgan Tench and John White Rockwell Science Center Thousand Oaks, CA 91358

ABSTRACT

The effect of ROSA pretreatment on the solderability of environmentally stressed PWB test coupons was investigated. The PWB surface finish was an electroplated, reflowed solder. Test results demonstrated the ability to recover plated-through-hole fill of steam aged samples with solder after ROSA processing. ROSA offers an alternative method for restoring the solderability of aged PWB surfaces.

ACKNOWLEDGMENTS

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INTRODUCTION

In typical soldering processes for the electronics industry, many different components must be soldered simultaneously and quickly to minimize costs and avoid thermal damage to circuit boards. Many factors influence good solderability such as layout, process parameters and materials. The electronics industry has traditionally relied on activated rosin fluxes to remove oxides from PWB and component surfaces during soldering. The molten solder can then react and form a strong metallurgical bond with the "clean" metal surfaces (Ref. 1).

Chemical fluxes used during the electronic soldering process generally contain very reactive, hazardous constituents that require special handling and storage. Corrosive flux residues that remain on soldered parts can degrade product reliability and must, therefore, be removed with chlorofluorocarbon (CFC) or other hazardous solvents that contribute to ozone depletion or release volatile organic compounds into the atmosphere (Ref. 2). With the push toward more environmentally compatible processes, several alternatives to rosin-based fluxes have been developed. They consist mainly of no-clean and water-soluble fluxes but are not completely free of environmental concern and are effective only under limited conditions (Ref. 2-3). This paper describes a reduced-oxide soldering activation (ROSATM) process that removes oxides from tin, tin-lead, and copper surfaces without the use of a chemical flux. The process offers an environmentally benign alternative, since oxygen gas is the only resulting effluent. This work supported the National Center for Manufacturing Sciences' (NCMS) Printed Wiring Board (PWB) Interconnect Systems CRADA project.

THE ROSA PROCESS

In the ROSA process, surface oxides are electrolessly reduced to the metallic state by a highly reducing vanadous ion solution that is non-corrosive to most metals and is regenerated electrochemically, much like the charging and discharging of a battery. Metallic oxides that interfere with solder wetting are reduced back to a pure metal by the highly reducing aqueous acidic solution. The preferred electrolyte is a vanadous sulfate solution with a pH of 0.5 (Ref. 4).

Figure 1 represents the overall ROSA process. The electrochemical regeneration cell is divided into two compartments separated by a microporous glass sheet that acts as a semipermeable ionic barrier, inhibiting migration of vanadium ions from the catholyte to the anolyte.

In contrast to conventional fluxes that require aggressive chemicals to dissolve oxides in the time prior to soldering, oxides are completely removed prior to the soldering operation while no waste chemicals are generated. The ROSA process, therefore, offers the potential for fluxless or "no clean" soldering when subsequently performed in an inerted or controlled atmosphere, such as nitrogen. The need for CFC solvents to remove corrosive flux residues is, therefore, eliminated.

MATERIALS AND TEST PROCEDURE

A forty hole plated-through-hole (PTH) solder float test coupon supplied by Texas Instruments (TI) was used to evaluate the ROSA process at Rockwell's Science Center at Thousand Oaks, CA. The coupon is illustrated in Figure 2. The test vehicle was fabricated using conventional PWB materials and fabrication technologies. The substrate was an epoxy resin laminate, 1.3" long x 0.55" wide x 0.060" thick, reinforced with glass fiber cloth (FR-4). It had a single reflow solder plated (RSP) surface finish. Latex gloves were used when handling all specimens to minimize contamination from oils, greases, salts or other foreign debris. Teflon coated tweezers were used to transport all samples.

Two surface conditions were evaluated: (a) as fabricated with the RSP finish or (b) steam aged (SA) at 93°C for eight hours. The second condition was intended to simulate severe environmental stressing and is typically used by industry to screen the solderability of PWB surface finishes. Samples solder tested at Sandia were dipped and gently agitated for 5-10 seconds in 25% solids rosin flux. After slow withdrawal from the flux, they were held vertically for approximately 15 seconds and blotted along their bottom edges to remove excess flux. Solderability tests were conducted by floating the samples on a standard thermostatically controlled solder pot at 245°C in air for 5 seconds. The samples were then removed and allowed to cool. Flux residues were removed by ultrasonically cleaning in trichloroethylene followed by a subsequent rinse in isopropyl alcohol.

The remaining samples were tested at Rockwell. ROSA immersion times were determined by sequential electrochemical reduction analysis (SERA). As fabricated float samples were immersed in the ROSA solution for 30 seconds while the steam-aged samples were immersed for 60 seconds prior to testing. Samples were then floated per the previously described procedure. In addition to the solder floated coupons, a second set of samples were processed through an inerted mini-wave soldering machine. The wave soldered samples were tested without flux in a nitrogen atmosphere containing 200 ppm oxygen. The samples were preheated to 100°C and passed over a 260°C eutectic Sn-Pb solder wave. The approximate time over the wave was 5-7 seconds. Due to fixturing limitations, only half of each sample was soldered (twenty out of forty holes per test vehicle). Similar ROSA immersion times were used to prepare the wave soldered samples.

RESULTS AND DISCUSSION

Test coupons were visually inspected under a microscope at a magnification of 7-10x. They were inspected per a modification of the ANSI/J-STD-003 PWB Solderability Test procedure (Ref. 5) to accommodate the specific testing conditions of the NCMS PWB Surface Finishes team. Class 1 & 2 accept/reject criteria specifies a minimum of 95% of each termination exhibiting good wetting. The balance of the surface may contain only small pin holes, dewetted areas, and rough spots, provided such defects are not concentrated in one area. There shall be no non-wetting within the evaluation area. Solder shall fully wet the wall area of the plated-throughholes, and plug holes less than 1.5 mm (0.06") in diameter. Solder can be recessed from the top or bottom of the plated-through-holes, provided there is evidence of positive wetting. Class 3 inspection criteria requires that Class 1 and 2 shall be met. Additionally, the solder must wet over the knee of the hole and onto the land around the top of the hole. Figure 3 illustrates the difference between a Class 1/2 and a Class 3 inspection on actual float samples. The cross-sections are from samples tested for this investigation.

Table 1 shows RSP and SA float and wave soldered inspection results. The data includes baseline testing of untreated ROSA samples. The baseline solder float coupons were tested at Sandia. The results are reported as the percentage of unfilled holes, plus or minus one standard deviation. Two inspectors independently examined the tested coupons. They were in generally good agreement on the Class 1/2 test results.

The baseline float coupons were then reinspected using the Class 3 criteria. One inspector failed approximately 15% of the RSP PTH's and 40% of the steam aged coupons, while the other inspector failed only 1% of the RSP PTH's and 60% of the steam aged PTH's. These significant differences in the Class 3 inspection data demonstrate the difficulty in interpreting Class 3 wetting and were attributed primarily to individual technique. Subsequent inspection was limited to only Class 1/2 interpretation. Even under this less stringent inspection criteria, steam-aged RSP PTH surfaces clearly demonstrated poorer solder wettability, especially when wave soldered without flux. ROSA treatment did, however, reduce the number of unfilled holes on the SA samples.

Figure 4 illustrates how ROSA pretreatments lowered the solder defect rate. The unfilled hole data is plotted as a function of the surface finish and test conditions (RSP/SA processed, ROSA pretreated, and float/wave tested). The RSP and SA defect rates on the floated samples were virtually zero after ROSA pretreatment, although relatively low unfilled hole values (1.3-1.9%) were also observed on the soldered samples without ROSA treatment. The low defect rate was attributed to the initial robust RSP surface finish and the rosin-based flux used during solder float testing.

The hole fill behavior of the wave soldered RSP and SA samples was generally poorer than for the solder float substrates. Substantially higher soldering defects were observed, particularly on the SA wave soldered samples, even after ROSA pretreatment. Since steam aging produces oxides that are generally an order of magnitude thicker than typical naturally-aged surfaces, and consequently harder to reduce, soldering defects on naturally-aged PWB's should be significantly lower after ROSA processing than observed on the steam aged samples.

The percentage of unfilled holes on the SA wave soldered samples varied from 68.8% (untreated) to 42.5% (ROSA pretreated). Even with these higher defect rates, the general soldering trend improved hole fill after ROSA processing. RSP and SA wave solder defects were reduced after ROSA pretreatment from 6.3% unfilled holes to 1.7% and from 68.8% to 42.5%, respectively. Cross-sections of steam-aged samples, before and after ROSA pretreatment, are shown in Figure 5. Although the hole fill of the ROSA treated sample barely satisfies the minimum Class 1/2 criteria, there is significantly more solder in the ROSA treated hole than in the untreated sample.

The above results clearly demonstrate the potential of the ROSA process as a solderability restoration tool. Either through uncontrolled storage conditions (i.e., temperature, humidity, time) or preassembly processing (e.g., handling, air baking), the solderability of PWB surface finishes can quickly degrade. Surface oxidation and sulfidation are very common problems that lead to serious soldering defects. With ROSA, these unsolderable surface coatings can be electrochemically removed. ROSA also offers the potential for soldering without flux. An inline system could ROSA-treat PWB's, pass the cleaned boards directly through to the assembly stage, and then solder them under a controlled atmosphere. This "clean" system would eliminate the need for applying flux to the PWB or widen the processing window for using the more environmentally compatible water soluble and low solids fluxes. The results from this study suggest that the latter option is probably the more practical approach, since full solderability restoration of the steam aged samples was not achieved without using a flux. Although the study was only intended as a process feasibility demonstration, optimization of the ROSA, handling, and soldering parameters could further reduce the number of unfilled holes. Aging samples at temperature/humidity conditions that yield a more natural surface oxide should also reduce the defect rate. The effect of ROSA pretreatment on other PWB surface finishes, particularly copper, needs to be further investigated.

CONCLUSIONS

Float and wave solder testing results indicate that ROSA pretreatments generally lower defect rates in PWB PTH's. ROSA processing improved the solderability of solder-plated surfaces that were steam aged at 93°C for 8 hours. The investigation clearly demonstrated the merits of ROSA on the solderability restoration of PWB surface finishes.

REFERENCES

- 1. Wassink, R.J.K., <u>Soldering in Electronics</u>, Electrochemical Publications Limited, Scotland, 2nd Edition, pp. 204-205 and 227-232 (1989).
- 2. Yost F.G., Hosking F.M., and Frear D.R., (Eds), <u>The Mechanics of Solder Alloy Wetting and Spreading</u>, Van Nostrand Reinhold, pp. 78-83 (1993).
- 3. Hosking F.M., Frear D.R., Iman R.L., Keicher D.M., Lopez E.P., Peebles H.C., Sorensen N.R., and Vianco P.T., "Integrated Environmentally Compatible Soldering Technologies Final Report", <u>Sandia Report SAND93-4039</u> (May 1994).
- 4. Tench D.M., Anderson D.P., Jambazian P., Kim P., White J., Hillman D., Lucey G.K., Gher T., and Pierkarski B., "A New Reduced-Oxide Soldering Activation Method", <u>Journal of Metals</u>, pp. 36-41 (June 1995).
- 5. <u>Solderability Tests for Printed Wiring Boards</u>, ANSI/J-STD-003, The Institute for Interconnecting and Packaging Electronic Circuits (IPC).

Table 1.

Reflow Solder Plated (RSP) and Steam Aged (SA) Float and Wave Soldered Fill Results (% Unfilled Holes)

	No ROSA Pre-Treatment		After ROSA Pre-Treatment	Std. Dev.
RSP - Float	1.3	1	0	0
RSP - Wave	6.3	6	1.7	2
SA - Float	1.9	3	0.6	0
SA - Wave	68.8	16	42.5	6

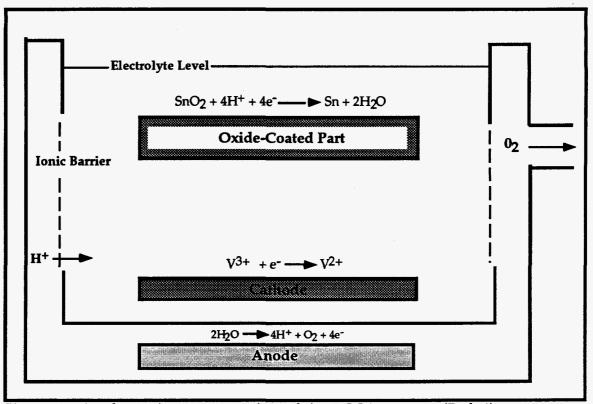


Figure 1. A schematic representation of the ROSA process (Ref. 4).

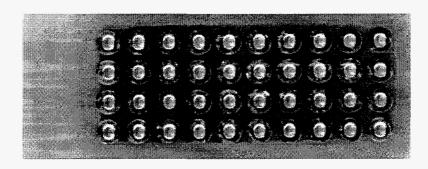


Figure 2. Forty hole plated-through-hole solder float test coupon used to evaluate ROSA process.

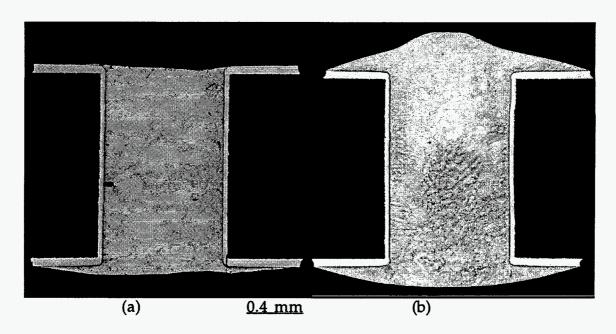


Figure 3. Cross-sections of PTH float samples showing (a) Class 1/2 and (b) Class 3 hole fill.

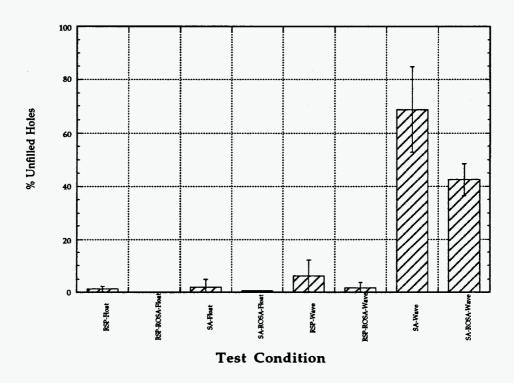


Figure 4. Float and wave test results before and after ROSA pretreatments. Test results illustrate how ROSA pretreatments generally lowered defects.

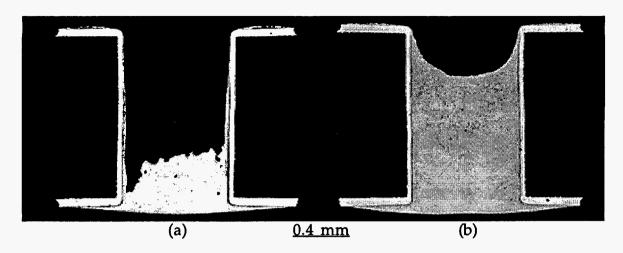


Figure 5. Cross-sections of steam aged coupons (a) before and (b) after ROSA.

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