ENVIRONMENTALLY COMPATIBLE SOLDER MATERIALS FOR THICK FILM HYBRID ASSEMBLIES

F. Michael Hosking, Paul T. Vianco, Jerome A. Rejent, and Cynthia L. Hernandez
Materials and Process Sciences Center
Sandia National Laboratories
Albuquerque, NM

ABSTRACT
New soldering materials and processes have been developed over the last several years to address a variety of environmental issues. One of the primary efforts by the electronics industry has involved the development of alternative solders to replace the traditional lead-containing alloys. Sandia National Laboratories is developing such alternative solder materials for printed circuit board and hybrid microcircuit (HMC) applications. This paper describes the work associated with low residue, lead-free soldering of thick film HMC's. The response of the different materials to wetting, aging, and mechanical test conditions was investigated. Hybrid test vehicles were designed and fabricated with a variety of chip capacitors and leadless ceramic chip carriers to conduct thermal, electrical continuity, and mechanical evaluations of prototype joints. Microstructural development along the solder and thick film interface, after isothermal solid state aging over a range of elevated temperatures and times, was quantified using microanalytical techniques. Flux residues on soldered samples were stressed (temperature-humidity aged) to identify potential corrosion problems. Mechanical tests also supported the development of a solder joint lifetime prediction model. Progress of this effort is summarized.

INTRODUCTION
The electronics industry has devoted significant resources in an attempt to develop lead-free solders and low-residue, "no clean" soldering technologies (Leonard, 1994; Sohn, et al., 1994; Vianco, et al., 1994; Artaki, et al., 1994; Lee, et al., 1994; Rupp and McClain, 1994; Gutierrez and Tulkoff, 1994; Steen, 1994; and Iman, et al., 1995). The driving force behind this international effort has been a myriad of proposed and enacted environmental laws and regulations. Activities related to printed wiring board (PWB) applications have been the focus of the effort. Technological solutions developed for PWB's will not necessarily satisfy requirements for hybrid thin and thick film systems. For example, technology-specific HMC substrate materials and surface finishes will necessitate different solders and processing conditions compared with PWB requirements. Although similar environmental issues face the two substrate materials, the overall development of hybrid environmentally-compatible technologies generally lags behind the larger PWB effort.

Sandia National Laboratories is a multiprogram engineering and science laboratory for the U. S. Department of Energy. It supports a wide range of military, energy, and environmental programs. Two of Sandia's primary responsibilities are to design microelectronic components and assure that the manufactured hardware meets high reliability requirements. The components incorporate both PWB and HMC technologies. Sandia has been very interested, consequently, in the environmental issues that affect the electronics fabrication and assembly industries. As part of its "Environmentally Conscious Manufacturing" program, Sandia has developed alternative soldering and cleaning materials and processes for PWB and HMC applications. The PWB effort, coordinated with other industry and government agency partners, has yielded several promising solutions. The HMC task, although not as mature as the PWB work, is yielding similar technical promise. This paper presents the status of Sandia's HMC low-residue, lead-free soldering effort. The technology is intended for thick film networks in high reliability applications.

TEST MATERIALS
The hybrid test vehicle was a 96% alumina substrate with an Au-Pt-Pd thick film metallization. The Au-Pt-Pd film was double printed and fired at 850°C. Two test vehicles were designed to evaluate the different test conditions. The first alumina substrate was an area-of-spread wetting sample with four 10 x 10 mm Au-Pt-Pd fired pads. The second substrate was an aging sample.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
having ninety eight smaller 2 x 2 mm metallized pads that were individually sectioned and aged at the prescribed times and temperatures.

Seven solder alloys were selected initially for the investigation. The baseline solders, by weight percent, were 63Sn-37Pb, 50In-50Pb, and 96.5Sn-3.5Ag. The remaining lead-free solders were based on the Sn-Bi-Ag, Sn-Au-Ag, Sn-Au-Bi, and Sn-Bi-Au-Ag alloy systems. The precious metal additions were intended to retard the dissolution reaction between the Au-Pt-Pd thick film and the Sn constituent of the high Sn-based solders. Soldering temperatures were dependent on the melting range of the particular solder alloy. The peak hot zone settings ranged from 216-220°C for the Sn-Bi-Au-Ag, Sn-Pb, and Sn-Au-Bi alloys, 230-233°C for the In-Pb and Sn-Bi-Ag alloys, and 240-245°C for the Sn-Ag and Sn-Au-Ag alloys.

Preliminary soldering evaluations were performed at approximately 245°C for 15 seconds on a hot plate to screen the wetting behavior of the candidate solders. Subsequent tests were conducted in a controlled conductive-convection reflow system, under a protective 30 SCFH flowing nitrogen gas cover. Time above the melting temperature of each alloy was restricted to 30-45 seconds. Sample speed through the oven was 3.8 mm/s.

A typical circuit board soldering profile was used to heat the test pieces in the reflow machine. The profile consisted of an initial ramp rate of approximately 90°C/min, from ambient conditions to approximately 30°C below the melting temperature of the solder. The temperature was held for 15-30 s to facilitate activation of the applied flux before continuing the ramp at a rate of 120°C/min to the final peak soldering temperature. The time spent between the melting and soldering temperatures was generally 30-45 seconds.

Solderability tests were conducted with three types of solder flux. They included a baseline rosin mildly activated flux (RMA; 25% solids in an alcohol base), a low solids flux (LS; 2.3% adipic acid solids in an alcohol base), and a citric acid-based flux (CA; 40% carboxylic acid in a water base). The RMA flux was best suited for the reflow profile described above, although the other two fluxes were adequately processed using the same profile. Adjustments to the front end of the profile to address water evolution from the CA flux and the effective activation of the non-rosin flux activators in the LS and CA fluxes improved their soldering results.

TEST CONDITIONS

The investigation consists of four interrelated activities; wetting, corrosion, aging, and mechanical testing. Wetting behavior was determined by area-of-spread experiments. Flux residue corrosion behavior was characterized by temperature-humidity aging. Microstructural development along the solder and thick film interface was examined after solid state aging over a range of elevated temperatures and times. Mechanical testing is still in progress and involves the characterization of prototype joints on populated and soldered test vehicles. The development of a neural network model was also initiated for predicting solder joint fatigue lifetime.

The area-of-spread tests involved placing a known quantity of solder, 6.4 x 6.4 x 0.25 mm, at the center of a burnished and flux-coated Au-Pt-Pd pad. The solder preforms were also coated with flux. The samples were then processed through the appropriate reflow profile and cleaned prior to assessing solder wettability. Wettability was determined by measuring the contact angle at the outer intersection between the solidified solder droplet and the metallized pad. The angle provides an excellent indicator of wettability and was measured either directly with a goniometer or from optical images of sectioned samples.

Corrosion tests were conducted in an environmental test chamber. Samples were prepared similarly to the wetting samples described above, using the different solders and fluxes. The only change to the process was the elimination of the post-soldering cleaning step. The soldered samples, with flux residues, were then placed in the test cell and exposed to an 85°C/85% relative humidity environment for seven days. The aged samples were removed from the cell and visually examined for corrosive products.

Solid state aging was conducted with individual samples sectioned from the smaller pad-geometry test vehicle. Since the formation and growth of brittle intermetallics along the joint interface and in the solder could seriously affect joint reliability, determining the time-temperature effects on microstructure is critical to understanding the fundamental response of the different joints to aging. Several times and temperatures were selected to simulate or accelerate the aging process. Samples were soldered, cleaned, and then individually aged in air at 55, 70, 85, 100, 135, and 170°C for 5, 10, 25, 50, 100, 200, 500, 1000 and 2000 hours. The aged samples were then cross-sectioned and examined for microstructural changes.

The mechanics of the different solder joints is still under investigation. Solders that demonstrated acceptable wetting and aging properties during the first phase of the investigation were chosen for subsequent mechanical evaluations. Test joints were fabricated by soldering surface mount components to corresponding Au-Pt-Pd features on hybrid test vehicles, using the reflow profiles developed for making the wetting and aging samples. Once again, the potential for forming brittle intermetallics that could lead to premature joint failures was the principal concern with these high Sn-containing alloys. As part of the effort, a neural network flow model for predicting solder joint lifetime was developed. Test variables included strain rate, hold time, and test temperature, with two thermal cycling ranges of 55°C/125°C and 0°C/100°C.

RESULTS AND DISCUSSION

The wetting and residue/corrosion investigations have been completed. The paper focuses on these results. The
data include contact angle measurements, microstructural observations, and visual inspection of environmentally stressed coupons. The solid state aging and mechanical analyses are still in progress. The aging study characterizes microstructural features of the different soldered interfaces through phase identification and measurement of the physically changing reaction layers. The mechanical tests are addressing issues associated with demonstrating the ability to fabricate prototype joints, measuring nominal joint strengths, and predicting “service” lifetime. The impact of these latter activities on delivering a “useable” technology will be discussed.

Initial wetting experiments with the Sn-Au-Ag solder revealed extensive intermetallic compound (IMC) formation, consisting of relatively large IMC needles and smaller IMC particles dispersed throughout the bulk solder. Consequently, subsequent testing was not performed with this alloy. Data from the remaining solder wettability experiments are summarized in Table 1 and Figure 1. The error bars represent one standard deviation.

The measured angles revealed several interesting trends. Wetting behavior was generally “good” for all the solders, except the 50In-50Pb alloy, when soldered with the RMA flux. The average contact angle for the group was 39°, while the 50In-50Pb solder yielded an angle of 62°. “Good” wettability is typically associated with a contact angle between 30° and 40°. An angle greater than 60° is generally considered poor wetting.

A second observation on the wettability results was that the citric acid-based flux consistently produced better wetting results than the RMA and LS fluxes, yielding generally lower contact angles. Once again, the 50In-50Pb solder had higher wetting angles. Finally, the poorest wetting behavior was observed on samples coated with the low solids flux. The contact angles of this last set were generally greater than 90°, although the LS flux did yield “adequate” wetting for the control 63Sn-37Pb and developmental Sn-Bi-Au-Ag alloys.

Representative cross-sections of several wetting and aging samples are shown in Figure 2. The optically imaged contact angles correlated very well with the measured goniometer data. From the imaged and measured wetting results, the RMA and CA fluxes demonstrated the best spreading behavior, regardless of solder composition. The cross-sections revealed a common problem with the CA flux, however. Although wetting was visually good, the CA flux left significant porosity in the solidified solder droplets. If the same porosity was present in an actual solder joint, it could affect the mechanical strength of the joint. The porosity is probably caused by the evolution of entrapped water vapor from the flux during heating and soldering (Wassink, 1989). Since the original RMA reflow profile was not optimized for the CA flux, the void problem was anticipated.

The RMA profile has a lower preheat temperature, approximately 80°C, than normally recommended for a flux with a water-based carrier, such as the CA flux, which typically should have a preheat closer to 100°C. One of the functions of the preheat stage is to evolve the nonreactive base of a flux before the reactive constituents are activated and the solder melts. Otherwise, “bubbles” that evolve during the latter soldering stage are entrapped as the solder solidifies. Since alcohol was the base of the RMA flux, the lower preheat was sufficient for the baseline condition. Subsequent tests with the CA flux used a modified thermal profile with a preheat stage closer to 100°C. Joint porosity was reduced significantly. The results clearly demonstrated the importance of optimizing the thermal profile to enhance solder wettability of each solder and flux system. For example, the LS flux can also be sensitive to heating, requiring a relatively linear profile, with a narrow activation window that was better matched by the CA reflow profile. By using this modified profile, the contact angle from a 96.5Sn-3.5Ag alloy and LS flux test was reduced from 120°, observed with the RMA profile, to 65°.

Isothermal solid state aging experiments (55-170°C for up to 2000 hours) have been completed. Characterization of the as-soldered and aged microstructures are being conducted through metallographic analyses. An example of the joint microstructures for an as-soldered and aged Sn-Au-Bi/Au-Pt-Pd sample is shown in Figure 3. The Au-Pt-Pd thick film metallization was nominally 15-20 μm (600-800 μm) thick. Up to a fifth of the metallization was consumed during the reflow soldering operation. The dissolution rate of the thick film was slowed by the initial Au addition to the Sn-based solder composition. A thin intermetallic reaction layer was formed along the solder-thick film interface. Precious metal constituents in the solder and dissolution of the thick film by the solder also generated additional intermetallic precipitates (needles and particles) in the bulk joint. Growth of the intermetallic was considerable as the aging temperature and time were increased. Understanding the evolution of these structural changes is very important to the mechanical response of the joint and developing a methodology for predicting service reliability.

Corrosion tests were conducted on soldered flux residues. The tests were conducted in an environmental chamber at 85°C and 85% relative humidity in ambient air for a duration of seven days. The solder-flux-thick film test samples were fabricated using the baseline reflow soldering conditions. Flux residues on the soldered samples were visually inspected in natural or fluorescent lighting, before and after aging. As expected, the LS flux left the smallest quantity of residues after soldering. The RMA processed samples were least affected by the temperature-humidity exposure and did not show any appreciable changes in appearance. There was, however, a slight darkening of the LS flux residues. This change in appearance was not chemically quantified.

The greatest visual change occurred with the CA flux residues. These residues not only darkened, but also mixed with the water vapor in the test cell and spread over the test surface. There did not appear to be a chemical reaction.
between any of the flux residues and the solders or Au-Pt-Pd thick film. Further surface analysis is recommended to determine if the above observations could affect the electrical performance of an active soldered circuit. The RMA and CA fluxes normally require cleaning after soldering, while the LS flux does not. The exception is for high reliability product, which normally requires post-cleaning of all visible residues to assure that flux activators are not encapsulated near critical circuitry.

Populated test vehicles are being assembled to evaluate actual solder joints. The joints will be thermally and mechanically tested. The circuit design has a daisy-chained configuration to permit the measurement of electrical continuity during testing. The Au-Pt-Pd thick film circuit was double printed to a minimum thickness of 23 μm on 1 mm thick alumina substrates. A dielectric was deposited around the metallized features. The test components consist of a variety of dummy chip capacitors and ceramic leadless chip carriers (LCC’s). The chip capacitors have 100% Sn terminations. The LCC’s have gold castellations with 16, 20, 32, or 68 input/outputs (I/O’s). Baseline solder powders/pastes were fabricated with the Sn-Pb, Sn-Ag, Sn-Bi-Ag, and Sn-Bi-Au-Ag compositions. The pastes will be screen printed on the test substrates and reflowed with the components in place. Reflow profiles are being developed for the populated circuit to satisfy the different peak topside temperature soldering requirements.

Finally, a reliability model, based on neural networks (Fausett, 1994 and Robinson, 1995), was proposed for assessing the response of surface mount devices under a variety of random service conditions. While a number of failure mechanisms is possible, the dominant failure mode for surface mount technology is typically fatigue caused by the cyclical thermal expansion differences between the component, solder, and substrate materials. These differences induce cyclic shear strains that lead to an accumulation of fatigue damage. Several empirical models have been developed to describe the expected fatigue life of typical solder joints. Most of the resulting functions relate the different parameters to only a median life expectancy. This is of particular concern, since two solder alloys could exhibit different life characteristics, but the same median fatigue life. Neural networks, however, should increase the accuracy in modeling these complex failure relationships. The inputs to the neural network model are probability density functions describing typical system characteristics. The model output is a statistical description of system performance, such as predicting the failure of a solder joint. The technique can "train" the baseline network by processing experimental data back through the interconnected structure and adjusting the model until a minimum criterion is achieved. Experimental data consequently drives the life prediction, rather than arbitrarily defined parametric functions. An example of the proposed model is illustrated in Figure 4, with joint strength, coefficient of thermal expansion, and temperature distributions as the input parameters and fatigue life as the predicted model output.

A combination of experimental design, neural network modeling, and probabilistic design theory, therefore, can offer an improved approach for predicting solder joint life and providing a more direct link between the experimental results and solder joint reliability. Initial modeling has involved working with three input parameters: (a) solder coefficient of thermal expansion, (b) component/substrate coefficient of thermal expansion, and (c) cyclic temperature extremes. The output variable is fatigue life or cycles to failure. Mechanical test data will be collected for input to the model for "tuning" of the neural network.

**CONCLUSION**

Area-of-spread wetting experiments were conducted with several fluxes and lead-free solders on a Au-Pt-Pd thick film. Wetting was generally good with rosin and citric acid-based fluxes. The low solids flux yielded the poorest wetting results, although a slight improvement in wetting was obtained by adjusting the reflow profile. Isothermal aging of prototypic joints revealed substantial intermetallic growth along the joint interface and in the bulk joint, particularly with increasing aging temperature and time. Corrosion testing (temperature/humidity aging) of soldered low solids flux residues caused darkening of these flux deposits. The citric acid residues not only darkened, but also mixed with the water vapor in the test cell and spread over the test surface. There did not appear to be a chemical reaction between any of the flux residues and the solders or Au-Pt-Pd thick film. Populated test substrates are being assembled to gather data for developing a neural network reliability model for predicting solder joint lifetime.

**ACKNOWLEDGMENTS**

The authors would like to acknowledge the contributions of Darrel Frear, David Robinson, Eddie Lopez, Martin Montoya, and Alice Kilgo. The manuscript was reviewed by Eddie Lopez.

**REFERENCES**


Table 1.
Contact Angle on Au-Pt-Pd as a Function of Solder Alloy and Flux

<table>
<thead>
<tr>
<th>Solder Alloy (wt. %)</th>
<th>Peak Reflow Temp. (°C)</th>
<th>Flux Type **</th>
<th>Contact Angle (deg ± std. dev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63Sn-37Pb</td>
<td>220</td>
<td>RMA</td>
<td>36.5 ± 1.3</td>
</tr>
<tr>
<td>63Sn-37Pb</td>
<td>230</td>
<td>LS</td>
<td>52.5 ± 9.7</td>
</tr>
<tr>
<td>50In-50Pb</td>
<td>230</td>
<td>CA</td>
<td>12.5 ± 3.0</td>
</tr>
<tr>
<td>96.5Sn-3.5Ag</td>
<td>240</td>
<td>RMA</td>
<td>62.3 ± 2.1</td>
</tr>
<tr>
<td>96.5Sn-3.5Ag</td>
<td>240</td>
<td>LS</td>
<td>94.3 ± 28.7</td>
</tr>
<tr>
<td>50In-50Pb</td>
<td>240</td>
<td>CA</td>
<td>69.0 ± 3.6</td>
</tr>
<tr>
<td>96.5Sn-3.5Ag</td>
<td>240</td>
<td>RMA</td>
<td>34.8 ± 1.0</td>
</tr>
<tr>
<td>Sn-Bi-Ag</td>
<td>232</td>
<td>LS</td>
<td>120.0 ± 6.7</td>
</tr>
<tr>
<td>Sn-Bi-Ag</td>
<td>232</td>
<td>CA</td>
<td>20.8 ± 2.6</td>
</tr>
<tr>
<td>Sn-Bi-Ag</td>
<td>232</td>
<td>RMA</td>
<td>38.5 ± 1.3</td>
</tr>
<tr>
<td>Sn-Au-Bi</td>
<td>220</td>
<td>LS</td>
<td>113.8 ± 4.9</td>
</tr>
<tr>
<td>Sn-Au-Bi</td>
<td>220</td>
<td>CA</td>
<td>31.3 ± 1.3</td>
</tr>
<tr>
<td>Sn-Au-Bi</td>
<td>220</td>
<td>RMA</td>
<td>38.5 ± 1.3</td>
</tr>
<tr>
<td>Sn-Au-Bi</td>
<td>220</td>
<td>LS</td>
<td>81.8 ± 19.6</td>
</tr>
<tr>
<td>Sn-Au-Bi</td>
<td>220</td>
<td>CA</td>
<td>33.3 ± 2.6</td>
</tr>
<tr>
<td>Sn-Bi-Au-Ag</td>
<td>216</td>
<td>RMA</td>
<td>48.5 ± 1.7</td>
</tr>
<tr>
<td>Sn-Bi-Au-Ag</td>
<td>216</td>
<td>LS</td>
<td>63.0 ± 10.4</td>
</tr>
<tr>
<td>Sn-Bi-Au-Ag</td>
<td>216</td>
<td>CA</td>
<td>34.5 ± 1.7</td>
</tr>
</tbody>
</table>

**RMA - Rosin Mildly Activated; LS - Low Solids; CA - Citric Acid
Figure 1. Solder wettability as a function of solder alloy and flux.

Figure 2. Cross-sectioned wetting results at 220°C for 63Sn-37Pb solder on Au-Pt-Pd thick film with (a) RMA, (b) LS, or (c) CA flux and Sn-Au-Bi solder on Au-Pt-Pd thick film with (d) RMA, (e) LS, or (f) CA flux.
Figure 3. Cross-sections of Sn-Au-Bi solder on Au-Pt-Pd thick film in the (a) as-soldered and (b) 100°C/500 hr. aged conditions.

Figure 4. Neural network model for predicting fatigue life of a solder joint.