Effects of Thermal Aging on Copper Dissolution For SAC 305 Alloy

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Abstract:
Aging characteristics of new lead free solder alloys are in question by many experts because of higher amount of tin's effect on the diffusion of other metals, primarily copper, to create undesirable boundary intermetallics over long periods of time and even moderately elevated temperatures. A primary layer of intermetallics, Cu6Sn5 forms as the liquid solder makes contact with the solid copper substrate. This reaction however ceases as the solder temperature falls below that of liquidus. A secondary intermetallic Cu3Sn1, an undesirable weak and brittle layer, is thought to form over time and may be accelerated by even mildly elevated temperatures in electronic modules such as laptops under power. This project was designed to quantify the growth rate of Cu3Sn1 over an extended period of time in a thermal environment similar to a laptop in the power on mode.

Objective:
Create a model of a copper printed circuit board that has been reflow soldered under conditions that duplicate automated printed circuit board assembly operations employing the new lead free alloy, SAC 305. Thermally age the samples to simulate the environment likely to be found in an operating electronic device under normal ambient conditions and measure the growth of intermetallic layers at specific time intervals.

Background:
Older solder alloys contained about a third less tin than the new lead free alloys, about 63% versus 96.5%. Although no lead free alloy is as universally accepted for all applications as older lead-solder alloys, SAC 305 has become the defacto standard paste for most general purpose lead free manufacturing. Specifically, this alloy consists of 96.5% tin (Sn), 3.0 % silver (Ag) and 0.5% copper (Cu). The nomenclature is based on the first letters of each element from the periodic table SAC and the relative percentages of each which tell the user immediately which alloy is involved. The specific SAC 305 paste used in this experiment was AIM brand 257-2, #3 screen with a no clean flux. For additional background please refer to the explanation of research project 27 in Figure 6 of the Appendix.

Method:
Test specimens O.062" thick FR-4 fiberglass printed circuit board copper clad with 1.0 oz copper thickness (0.0014") over the entire surface. Blanks were prepped by milling out 1/2" squares of the copper clad on the blanks to minimize thermal losses due to dissipation and insure more even heat distribution. After

milling, the surface of each copper square was coated with liquid solder flux (Kester 951) to aid in removing any oxidation caused by the handling or milling process. A 4 gram dollop of the SAC 305 alloy solder paste was deposited in the center of each square. Samples were then reflow soldered simultaneously on a pair of identical board blanks (65 squares each) using a Heller 1800EXL automated solder paste reflow oven with a standard lead free profile set for a maximum board surface reflow temperature of 235^0 C with a TAL (time above liquidus) of around 50 seconds (see attached KIC Slimkic Thermal Profile). After soldering was completed the individual ½" samples on the main coupons were individually numbered and sectioned into the 130 individual samples that were then exposed to thermal aging in a Blue M Convection Oven at a constant 50^0 C (122^0 F) to mimic the temperature found inside a functioning laptop computer or other electronic device for an extended period of time. At precise 50 hour intervals one sample would be removed from the Blue M Oven and again be sectioned through the center of the solder mound with a Buehler Isomet 1000 wafer saw. One half of the sample was cold mounted using Buehler Epo-Kwick sample mounting epoxy, polished, and examined using a Zeiss VP40 Scanning Electron Microscope and Princeton Gamma Tech energy dispersive x-ray (EDX) analysis to determine the presence and chart the growth of the secondary intermetallic layer Cu3Sn1. The process of removing and prepping samples at the 50 hour intervals continued for a total of 6,500 hours.

Due to the irregular shape of the primary intermetallic layer, measurements were taken electronically using the SEM for both the primary (Cu6Sn5) and secondary (Cu3Sn1) intermetallic layers at 18 different locations on each sample. From these data points, an average thickness is determined for each sample. In order to limit error, operators maintain a standard procedure, in which the 18 measurements are taken from three different locations on the sample. At each location, six measurements are recorded, two points are of intermediate thickness, another two represent the thinnest intermetallics, and the remaining two values will estimate the thickest section of intermetallics.

Results:

For reference purposes, average thickness measurements for Cu_6Sn_5 and Cu_3Sn_1 have been included in the appendix, in addition to reflow profile temperature and time above liquidus during the application of solder. The thickness measurements from table 1 have been graphically depicted in Figure 4. Over the 6500 hour aging duration, there were negligible variations in thickness between the intermetallic thickness measurements. The secondary layer Cu3Sn1 did not become prominent throughout the entire thermal aging process. It would be expected that over time the second layer intermetallics will form and continue to grow over time. With a reflow temperature of 235^oC and a TAL of 60 seconds or less, the samples did not have a Cu_3Sn_1 layer appear noticeably. It is assumed that under these parameters, adequate reflow temperature and TAL thresholds were not breached to form the second layer of intermetallics.

The thickness of the primary intermetallic Cu6Sn5 remained remarkably consistent over the span of 6500 hours, as visible in Figure 4. The images below in figures 1-3 are included to show the columnar distribution of the intermetallics. The appearance of intermetallics does change from sample to sample, but it is not attributed to the thermal aging cycle.

Growth of the second layer intermetallic was not identifiable. Therefore, its presence under these parameters would probably not be a threat to the functional integrity of the electronic device at least for at least a number of years. This is provided that the TAL and Reflow Temperature guidelines followed in this study are observed by the manufacturer.

Discussion:
Prior to the completion of research project 27, assumptions had been made concerning the initiation of intermetallic formation and the source of material for intermetallic layers. Researchers theorized that the Cu_6Sn_5 intermetallic layer formed during the solder application process; and as the component aged, the Cu_3Sn_1 layer would form. During research project 27, the question of where the tin is acquired to form the detrimental Cu_3Sn_1 layer was considered. Based on the data obtained, an adequate answer cannot be determined solely due to discrepancies with Cu_3Sn_1 identification. An insufficient amount of second layer intermetallics were recorded throughout the 6500 hour aging period. These results were unexpected. Theoretical diffusion is dependent on temperature and time, which would cause intermetallic growth to continue throughout the thermal aging process. Although Cu_6Sn_5 growth was not anticipated, the growth of Cu_3Sn_1 was expected. To explain the lack of Cu_3Sn_1 formation, the mechanisms of interface diffusion must be examined. Along the interface between the solder ball and the copper pad, the first layer of intermetallics forms. The formation of the initial intermetallic occurs in order to reduce the residual stresses along the interface. As the Cu_6Sn_5 layer becomes stable upon cooling, our researchers theorize that it must store a sufficient amount of energy to form the Cu_3Sn_1 layer. At the mild reflow temperatures and time above liquidus parameters designated for this project, the energy required to form the Cu_3Sn_1 layer was not produced. This mechanism explains the lack of second layer intermetallics present within the results of work order 27. In addition to this assumption, the growth of Cu_3Sn_1 was to come as a result of the depletion of the first layer of intermetallics. If activation energy is necessary for the formation of Cu_3Sn_1, then the required energy may be stored within the first layer of intermetallics. The energy stored in first layer intermetallics gives evidence that material from Cu_6Sn_5 may still be the source for the Cu_3Sn_1 layer.

Based on the assumption that activation energy must be achieved during the reflow process to have Cu_3Sn_1 intermetallic compounds form, we are planning other research projects that will obtain information to assist in solving for activation energy of the Cu_3Sn_1 intermetallic. Preliminary samples subjected to higher reflow temperatures and longer times above liquidus have shown strong evidence of the existence of a Cu_3Sn_1 initiation threshold.

In addition to research pertaining to solder bond strength, projects have begun that will identify the conditions needed for the origination of the second layer. As more understanding about the second layer of intermetallics is acquired, work may then address its effect on the bond strength of solder.

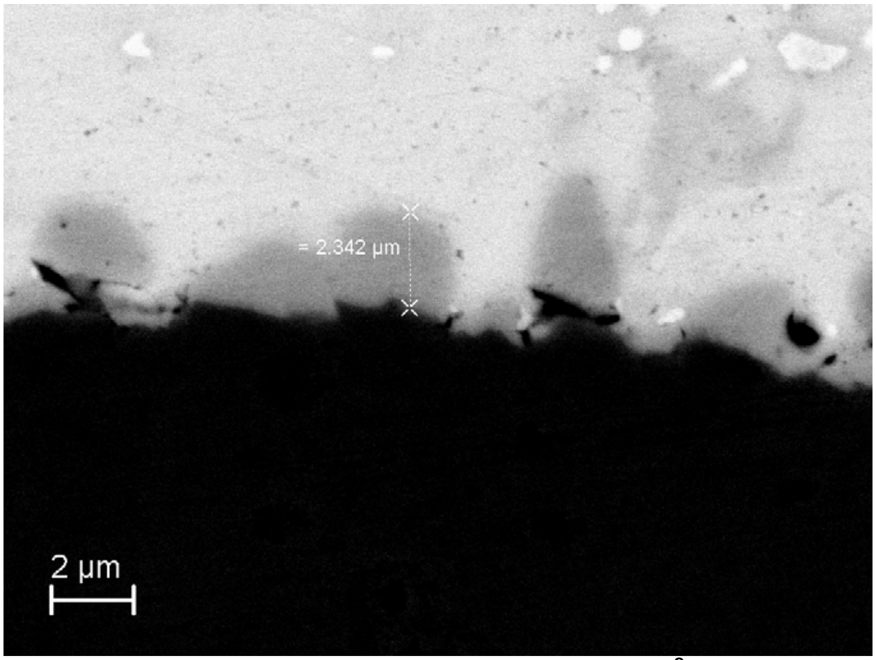


Figure 1. Sample 2 was aged at 100 hours at a temperature of 50^{o}C. An intermetallic measurement of 2.34 micron is labeled.

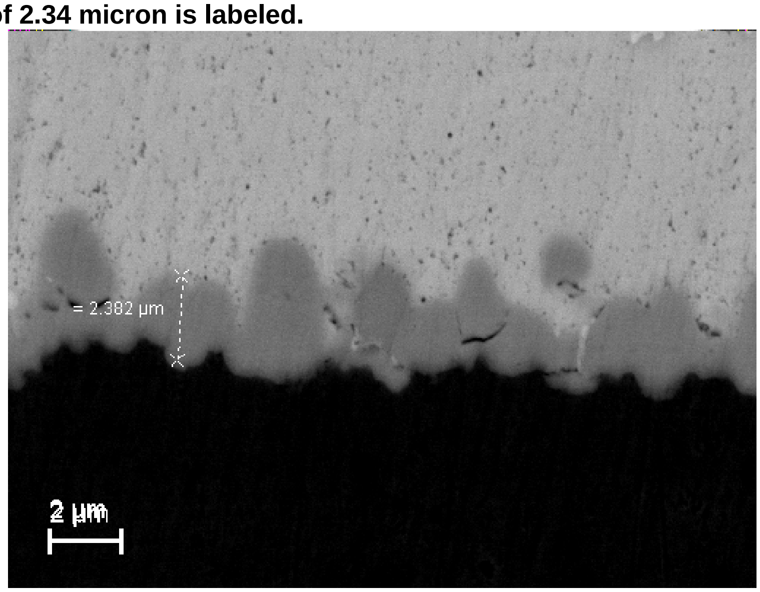


Figure 2. Sample 64 was aged for 3200 hours under the same conditions as sample 2. Although columnar distribution varies from sample to sample the average intermetallic thickness does not vary far from the 2.38 micron measurement of sample 64.

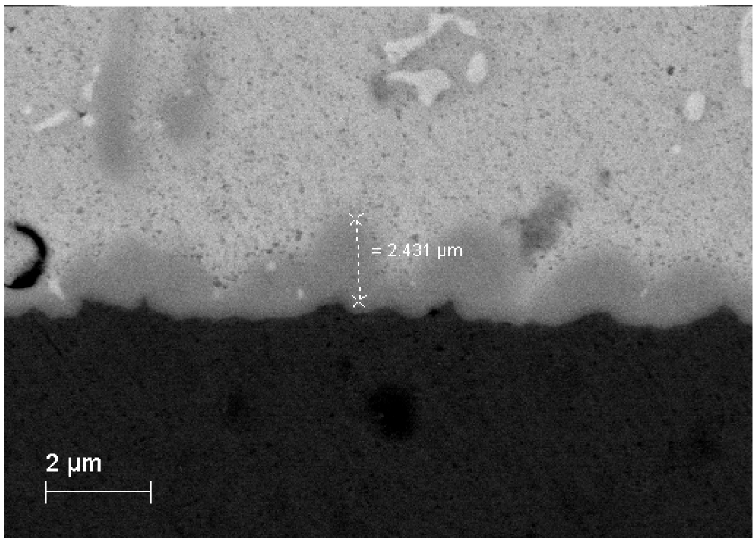


Figure 3. Sample 123 was thermally aged at 6150 hours. The Cu_6Sn_5 measurement did not vary appreciably from the previous samples.

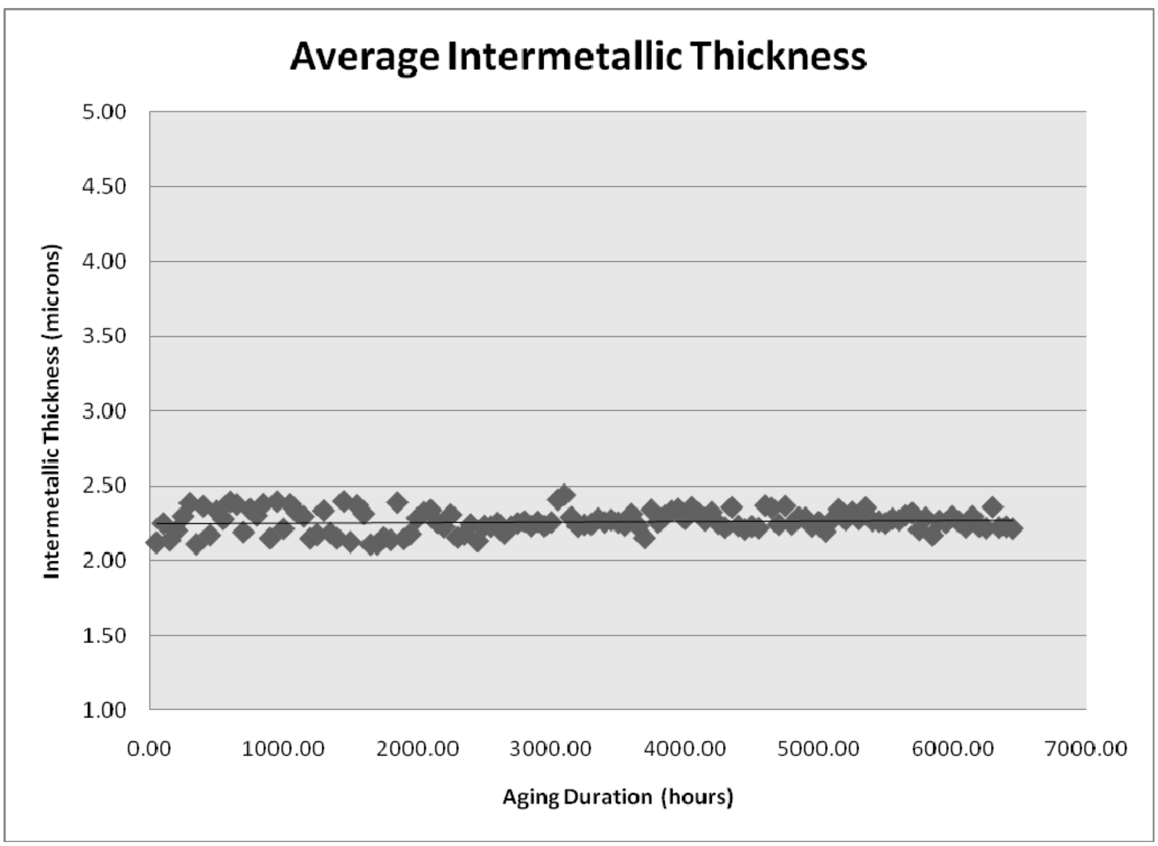


Figure 4. The graph above depicts the average thickness of first layer intermetallic for each sample. Only slight variations were visible between samples over the aging duration.

Appendix

Table 1: The data below records the thickness of the first intermetallic layer throughout the 6500 hour duration of the project. No appreciable variations in the intermetallic layer thicknesses were discovered.

Research Project #27 Copper Dissolution #3

ALL SAMPLES THERMAL AGED

Time Above Liquidus: 50-60 sec

*Excessively small values

Reflow Temperature 235C With SAC 305

Sample	Aging duration (hours)	Intermetallic Layer Thickness (microns)
		1st
1	50.00	2.18
2	100.00	2.12
3	150.00	2.25
4	200.00	2.13
5	250.00	2.20
6	300.00	2.30
7	350.00	2.38
8	400.00	2.11
9	450.00	2.36
10	500.00	2.17
11	550.00	2.33
12	600.00	2.28
13	650.00	2.39
14	700.00	2.37
15	750.00	2.19
16	800.00	2.34
17	850.00	2.30
18	900.00	2.38
19	950.00	2.15
20	1000.00	2.39
21	1050.00	2.21
22	1100.00	2.37
23	1150.00	2.32
24	1200.00	2.29
25	1250.00	2.15
26	1300.00	2.17
27	1350.00	2.33
28	1400.00	2.18
29	1450.00	2.15
30	1500.00	2.39
31	1550.00	2.12
32	1600.00	2.37
33	1650.00	2.31
34	1700.00	2.11
35	1750.00	2.11
36	1800.00	2.15
37	1850.00	2.14
38	1900.00	2.39
39	1950.00	2.14
40	2000.00	2.18
41	2050.00	2.28
42	2100.00	2.32
43	2150.00	2.34
44	2200.00	2.25
45	2250.00	2.22
46	2300.00	2.31
47	2350.00	2.15
48	2400.00	2.17
49	2450.00	2.24
50	2500.00	2.13
51	2550.00	2.23
52	2600.00	2.23

53	2650.00	2.25
54	2700.00	2.18
55	2750.00	2.23
56	2800.00	2.25
57	2850.00	2.26
58	2900.00	2.23
59	2950.00	2.26
60	3000.00	2.23
61	3050.00	2.26
62	3100.00	2.41
63	3150.00	2.44
64	3200.00	2.29
65	3250.00	2.23
66	3300.00	2.24
67	3350.00	2.24
68	3400.00	2.28
69	3450.00	2.26
70	3500.00	2.27
71	3550.00	2.25
72	3600.00	2.23
73	3650.00	2.31
74	3700.00	2.23
75	3750.00	2.15
76	3800.00	2.34
77	3850.00	2.25
78	3900.00	2.30
79	3950.00	2.33
80	4000.00	2.35
81	4050.00	2.28
82	4100.00	2.36
83	4150.00	2.32
84	4200.00	2.27
85	4250.00	2.32
86	4300.00	2.25
87	4350.00	2.22
88	4400.00	2.36
89	4450.00	2.23
90	4500.00	2.21
91	4550.00	2.23
92	4600.00	2.22

93	4650.00	2.37
94	4700.00	2.35
95	4750.00	2.24
96	4800.00	2.36
97	4850.00	2.24
98	4900.00	2.29
99	4950.00	2.28
100	5000.00	2.23
101	5050.00	2.26
102	5100.00	2.19
103	5150.00	2.27
104	5200.00	2.34
105	5250.00	2.27
106	5300.00	2.32
107	5350.00	2.28
108	5400.00	2.35
109	5450.00	2.27
110	5500.00	2.26
111	5550.00	2.25
112	5600.00	2.28
113	5650.00	2.27
114	5700.00	2.30
115	5750.00	2.32
116	5800.00	2.20
117	5850.00	2.29
118	5900.00	2.17
119	5950.00	2.27
120	6000.00	2.25
121	6050.00	2.29
122	6100.00	2.26
123	6150.00	2.22
124	6200.00	2.29
125	6250.00	2.23
126	6300.00	2.22
127	6350.00	2.36
128	6400.00	2.22
129	6450.00	2.23
130	6500.00	2.21

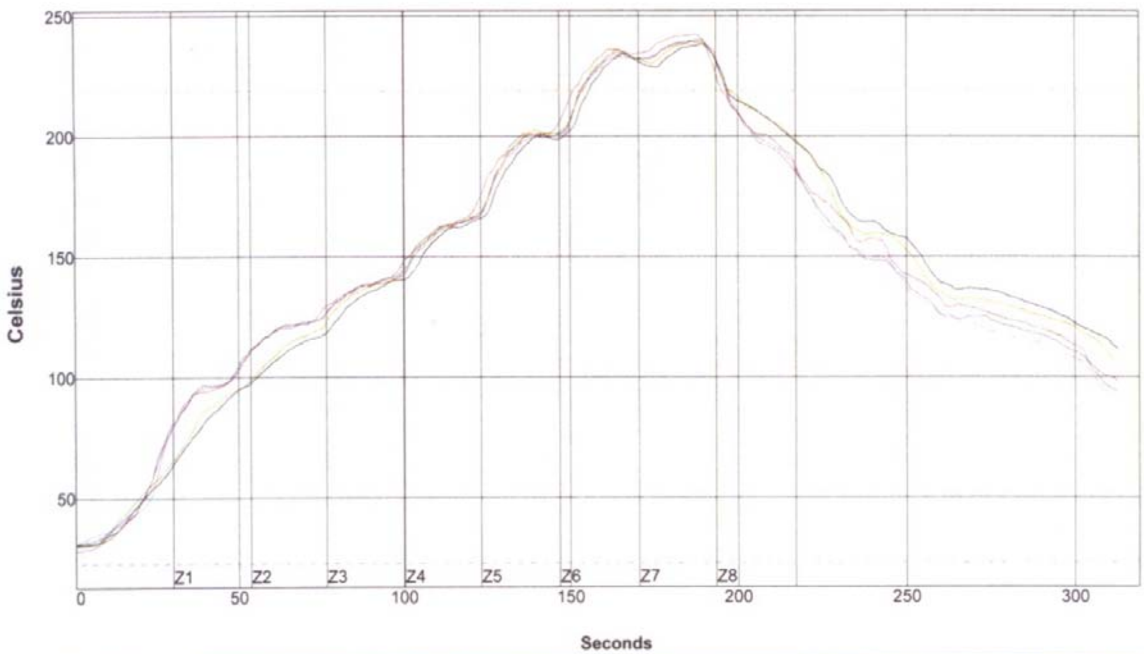
Copper reflow WO 27 Wed Oct 29 2008 10:34:43

Company: REIC
Oven Name: Heller 1800EXL

Site: Production Floor
Process Window Name: SAC 305

Setpoints (Celsius)								
Zone	1	2	3	4	5	6	7	8
Top	120.0	135.0	150.0	180.0	230.0	265.0	255.0	175.0
Bottom	120.0	135.0	150.0	180.0	230.0	265.0	255.0	175.0

Conveyor Speed (inch/min): 31.00



PWI= 425%	Preheat 23-150C		Reflow Time /219C		Peak Temp		Tot Time /219C		Preheat 150-200C-(2)	
upper left	102.71	71%	42.83	-14%	239.54	282%	42.83	-414%	41.68	-274%
lower left	101.97	70%	43.49	-10%	240.17	307%	43.49	-410%	39.01	-280%
upper right	103.06	72%	44.41	-4%	239.28	271%	44.41	-404%	33.55	-292%
lower right	104.98	75%	41.31	-25%	238.17	227%	41.31	-425%	39.07	-280%
middle	101.08	68%	44.41	-4%	242.34	393%	44.41	-404%	33.66	-292%
Delta	3.90		3.11		4.16		3.11		8.13	

Figure 5. The figure above shows the temperature profile of the solder reflow for the samples that were produced for research project 27. The reflow profile may be reviewed to verify that research project 27 had a reflow temperature of 235 ^{o}C and a TAL of 90 to 120 seconds.

Standard Subcontractor Research Project

Subcontract No. 07S-0575

Phase No. 3 Research Project No. R027 Date: 10/13/2008

Title: Copper Dissolution #3

Scope of work:

This is the next in a series of copper dissolution experiments designed to build a predictor model for the life expectancy of lead free solder joints in actual devices. In previous experiments we confirmed that the thickness of first intermetallic layer, Cu_6Sn_5, was a function of time above liquidus and maximum reflow temperature. Growth of the second intermetallic layer thickness, Cu_3Sn_1, was a function of time and ambient temperature. For this project we will be trying to duplicate the actual manufacturing process that the OEM might use to build the product. So rather than use the DRS22 rework station, we will need to create a Heller oven profile using a copper clad coupon for SAC305 solder to achieve a basically "normal" reflow profile that will achieve a maximum peak temperature of 235^0C for 90 to 120 seconds (longer is better than shorter). A special separate coupon will be provided for profiling purposes so we don't oxidize the actual test coupons.

We will be using two copper clad coupons milled in to separate test areas similar to the ones from the previous copper dissolution tests. Once again each available test area should be given a dot of liquid Pb free compatible flux and a dollop of SAC 305 roughly the size of a pencil eraser on top of the flux dot. Boards should immediately be reflowed on the above specified profile. After reflow the coupons should be sectioned into individual small squares following the milled lines and numbered sequentially on the back.

We have ascertained through anecdotal reports from IT sources that temperatures inside a card chassis, laptop, or other small electronic device can run between 30^0C (86^0F) and approximately 50^0C (122^0F) maximum. For this study we chose the worst case higher temperature. Place the small sample squares into the Blue M at 50^0C. If necessary, acquire some flat oven pans to accommodate the small size of the samples. We will run all samples simultaneously for the duration of this test. The first sample, number 1, should be removed after 50 hours. The second sample should be removed at 100 hours, the third at 150 hours and so on. Each sample will be sent after removal to SDSM&T for SEM analysis and charting of the progression of growth in the secondary intermetallic layer. There are over 130 samples so with the 50 hour interval we can maintain just under 6500 hours of test time before all samples are depleted. The study will however terminate when we achieve total dissolution of the copper layer if that occurs prior to 6500 hours.

Ship to Liz Nielsen at SDSM&T for analysis

Figure 6. The research project work order is included above. It provides a detailed description of the procedure and objective for the project. Information in the paper references this work order number.