Effects of Thermal Aging on Copper Dissolution For SAC 405 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 lead free alloy, SAC 405. 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. Additional SAC alloy solders exist. For comparison purposes, SAC 405 was studied under research project 34, which has a 1% increase in silver content. The affect of 4.0% silver within the tin alloy was assessed. The specific SAC 405 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 34 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 405 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:

Solder behavior did not vary greatly between SAC 305 and SAC 405. A second layer intermetallic was not measurable in work order 27, using SAC 305; and similar results were obtained through research project 34. Figure 1 shows the consistency of the intermetallic thickness with SAC 405. Samples were taken out at 50 hour intervals and analyzed. Some samples near the middle of the project were not analyzed, because work order 27 had displayed no quantifiable change. Because of a 1% increase in silver content, SAC 405 used in research project 34 was expected to have less copper dissolution than work order 27. In order to reduce the amount of time necessary to analyze, intermediate samples were analyzed along with samples near the end of the project. A prominent Cu_3Sn_1 layer was not observed in both research project 27 and 34.

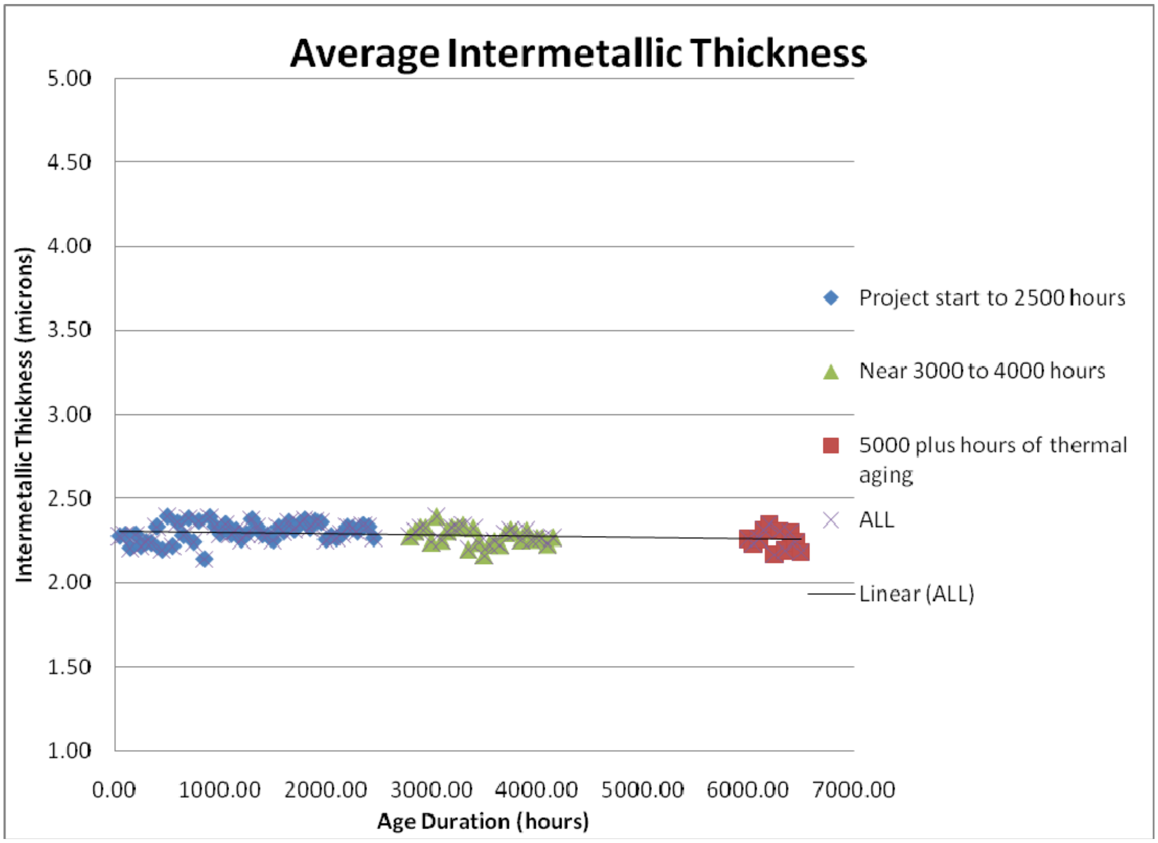


Figure 1: The graph above shows the overall consistency of the intermetallic layer thickness. The measurements were recorded as solely Cu_6Sn_5. A Cu_3Sn_1 layer was never distinct enough to be identified.

The following images were taken of work order 34 samples during SEM analysis. Samples were thermally aged for the duration of the project, so imaging from different periods of the test are included. Over the course of 6500 hours, the intermetallic thickness change was not significant. Results have led to further research projects pertaining to the dependency of second layer formation on application parameters, such as reflow temperature and TAL.

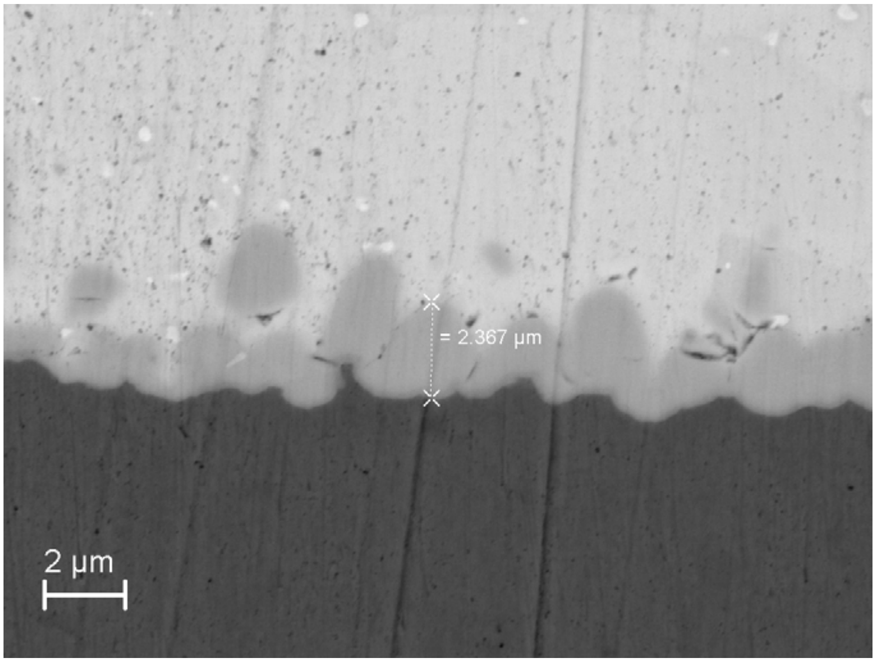


Figure 2: The image was taken of sample 3, which was thermally aged for 150 hours. With the SEM, a magnification of 12.35KX was reached. The average thickness of the Cu_6Sn_5 layer is near 2.367 micron and the Cu_3Sn_1 layer is not prominent enough to be measured.

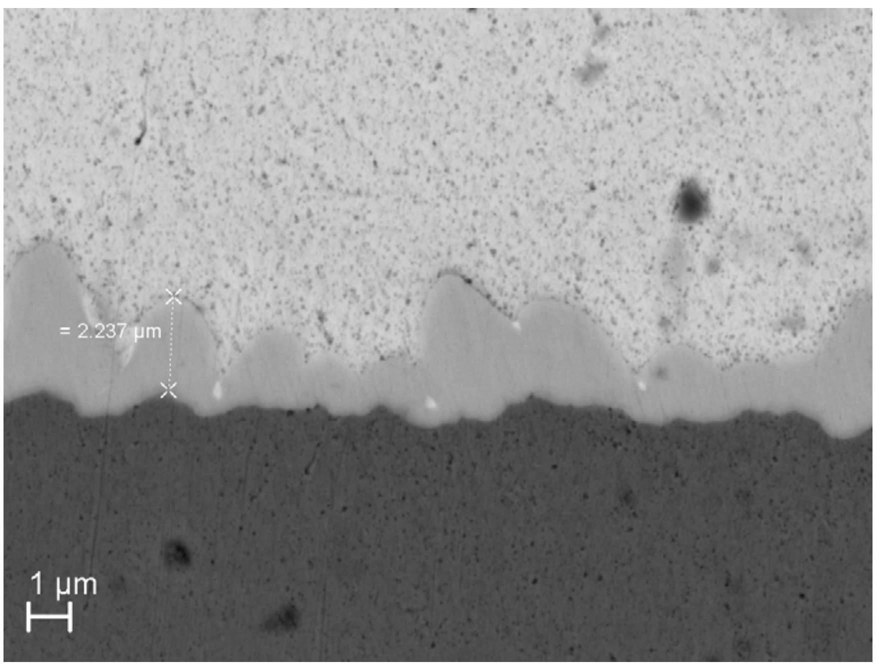


Figure 3: Sample 60 was thermally aged for 3000 hours. The image was captured at 12.74KX magnification. The average thickness of the Cu_6Sn_5 layer is near 2.237 micron, which is near the thickness of other samples.

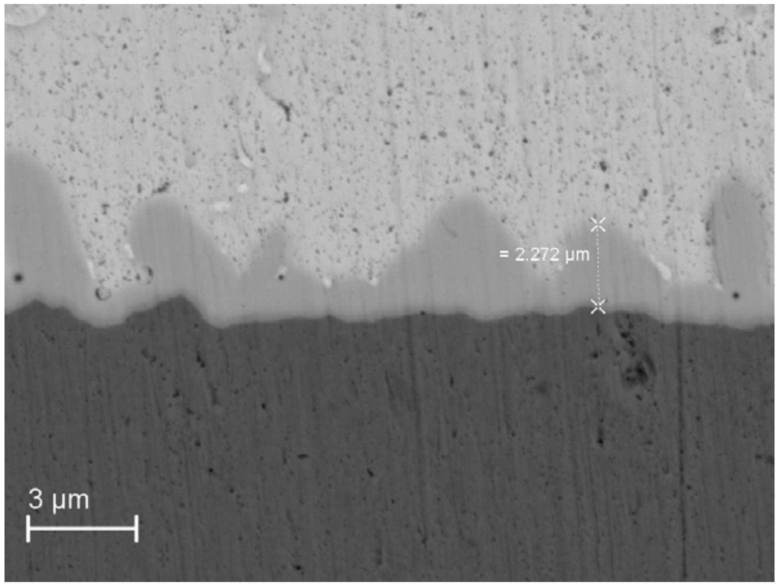


Figure 4: Thermally aged for 6150 hours, sample 123 was expected to depict a great change. With a magnification of 12.42KX, the first layer intermetallic remained consistent with prior samples. The average thickness of the Cu_6Sn_5 layer is near 2.272 micron.

Discussion:

Research project 34, with SAC 405, was expected to behave similar to project 27, with SAC 305. This theory was validated by the analysis of samples that had been thermally aged at 50^oC for 50 hour intervals. Overall, quantifiable growth was not visible. Project specimens coincided with data from other studies. An example of this is that the Cu_6Sn_5 intermetallic layer formed during the solder application process and no further growth is apparent. Other research has suggested that the intermetallic which forms after solidification is the Cu_3Sn_1 intermetallic phase. From research project 34, measurements were not obtainable for the Cu_3Sn_1 layer, parallels research project 27.

As previously stated in research project 27, 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, first layer intermetallics form. 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. Another suggestion is that the Cu_3Sn_1 intermetallic exists at the interface, but it may be minuscule in size or it may be in a metastable state.

Additional research projects are in progress. These studies will further assess the amount of energy required to form a distinct Cu_3Sn_1 layer upon initial application of the solder, as well as consider thermal aging temperatures that reach greater temperatures. Projects that will quantify activation energy will be used to also estimate the amount of diffusion that will take place over a period of time. Additional projects are necessary to correlate the thickness of the Cu_3Sn_1 intermetallic to bond strength estimations.

Conclusions:

The comparison between SAC 305 and SAC 405 concluded that the addition of 1% silver will not significantly alter intermetallic formation. The project simulated the environment that a standard computer would operate under, and it was determined that operating at $50^{o}C$ for 6500 hours would not stimulate a prominent Cu_3Sn_1 layer.

Appendix

Surface Temp 405 4 x 6 Copper Blank — **Wed Mar 04 2009 11:16:33**

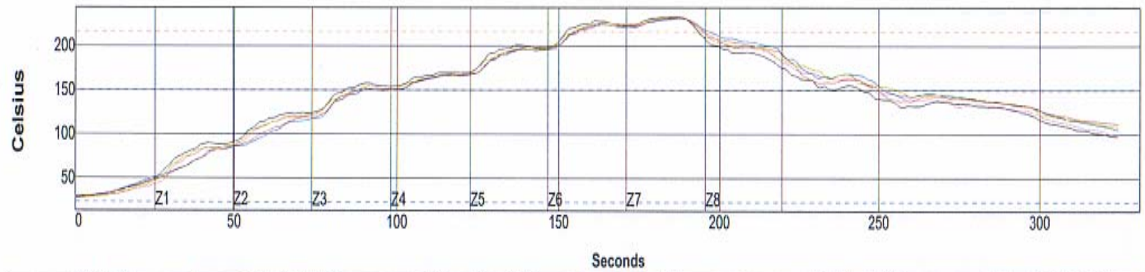
Company: REIC
Oven Name: Heller 1800EXL

Site: Production Floor
Process Window Name: SAC 405 Copper Blank

Setpoints (Celsius)

Zone	1	2	3	4	5	6	7	8
Top	115.0	145.0	185.0	185.0	230.0	260.0	250.0	170.0
Bottom	115.0	145.0	185.0	185.0	230.0	260.0	250.0	170.0

Conveyor Speed (inch/min): 32.01



PWI= 71%	Preheat 23-150C		Reflow Time /217C		Peak Temp		Tot Time /217C		Preheat 150-175C-(2)	
Upper Left	88.88	-38%	38.91	-41%	233.10	-59%	38.91	-41%	36.96	-54%
Upper Right	91.42	-27%	40.95	-27%	232.55	-66%	40.95	-27%	34.41	-71%
Center	87.66	-44%	39.19	-39%	234.05	-46%	39.19	-39%	36.77	-55%
Lower Left	84.06	-60%	40.98	-27%	234.28	-43%	40.98	-27%	40.38	-31%
Lower Right	87.38	-45%	39.87	-34%	233.01	-60%	39.87	-34%	38.63	-42%
Delta	7.36		2.07		1.73		2.07		5.98	

Process Window:

Solder Paste: SAC 405 Copper Blank

Statistic Name	Low Limit	High Limit	Units
Preheat Time 23-150C	75	120	Seconds
Preheat Time 150-175C-(2)	30	60	Seconds
Time Above Reflow - 217C	30	60	Seconds
Peak Temperature	230	245	Degrees Celsius
Total Time Above - 217C	30	60	Seconds

Description:

Verify 405 Lead-free recipe 4 x 6 Copper Blank.

KIC Thermal Profiling
San Diego, CA USA

Profiled Using KIC 2000 Technology
Tel: +1 858 673 6050
Fax: +1 858 673 0085

www.kicthermal.com
tech@kicmail.com

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. R034 Date: 01/30/2009
Copper Dissolution # 5 SAC 405

Scope of work:

Previous work on copper dissolution has concentrated on use with the SAC 305 alloy. SDSM&T has requested that we begin expanding the research to other alloys in order to understand how alloy changes will affect the intermetallics formation under the same parameters used for the SAC 305. The effort here is to understand how changing alloys may help or hinder copper dissolution in search of potential new non-hazardous alloys that will slow or prevent formation of the brittle secondary intermetallic layer

To begin this project you will need to acquire samples of the SAC 405 from any major supplier. Match flux and solder ball size to that of SAC 305 samples used previously. 4 each copper clad coupons that have been milled into 96 small copper squares will be provided. Place a drop of liquid flux and a dollop of SAC 405 roughly the size of a pencil eraser on each pad prior to reflowing in the Heller or DRS-22 as instructed.

Two coupons should be reflowed per the solder manufacturer's recommended profile for SAC 405 using the Heller reflow oven. Note* verify the profile as it may be somewhat different than SAC305. This is designed to replicate a standard manufacturing process. Section the completed boards into individual copper squares and place on a tray in the Blue M oven at 50^0 C. Remove one sample every 50 hours for shipment to SDSM&T.

The other 2 coupons will be reflowed at different TAL's and times using the Air Vac Engineering DRS-22. Refer to the attached chart for TAL and temperatures for each square. Meticulously track and record the exact TAL and reflow temp for each square on the samples. When complete place one board in the Blue M oven at 50^0 C for 500 hours and package the other for immediate shipment to SDSM&T

Relevant Research Documents or Websites:

Reference Research Projects #'s 31, 27, and 24 if needed
List studies, websites, or attach documents to aid in researching this project if such studies are available

Special Requirements:

Please list known special or unique test equipment, parts, or precautions to be observed while performing this work order
Projected Completion Date is 02-27-09

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.