

Effect of Thermal Conditions and Durations on Reaction Kinetics and Phase Transformations within SAC 305 Solder

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Abstract

As technology becomes increasingly reliant on electronics, understanding the longevity of lead-free solder also becomes imperative. This research project focused on phase transformation kinetics within SAC 305 lead free solder during thermal aging processes. Today in the electronics industry, it is the most widely used solder, making it a high priority to understand its long-term stability and performance in a variety of service conditions. Reaction kinetics during thermal aging has been studied to parallel a previous research project concerning the activation energy to form Cu_3Sn_1 . Results from the previous project will be included for the purpose of comparison.

The previous research project was designed to determine which application parameters will immediately cause the growth of the detrimental Cu_3Sn_1 layer. The data was useful in predicting the amount of growth within this layer during soldering. The current research has analyzed the effect of various aging temperatures on the initial growth of Cu_3Sn_1 .

Introduction

In 2002, the European Union initiated the Restriction of Hazardous Substances Directive (RoHS) that would eliminate the use of hazardous substances in industry^[5]. Several hazardous materials, including lead, were restricted during manufacturing of electronic equipment. Since then, electronic manufacturers have spent time and resources shifting from lead solders to lead-free solders. The addition of lead in solder was important to the durability of the solder and it prevented tin whisker formations while being used in electrical components. Although lead has been removed from solder for most electronic manufacturing, high importance applications, such as space and military applications have remained temporarily exempt from these restrictions^[8]. As lead solders become more difficult to produce and purchase, the United States space and military agencies will need to verify the reliability and life expectancy of the alternative lead-free solders. Eventually, lead solders will be replaced entirely with lead-free solders. As lead-free solders are used for prolonged periods of time, subsequent service problems have been observed^[8-9]. Researchers continue to address reliability issues that could prevent equipment from meeting critical performance objectives.

Copper dissolution is considered one of the main concerns of lead-free solder research^[13]. Copper dissolution is the term used to describe elemental interaction at the solder-copper interface. The copper pad on the printed circuit board (PCB) is dissolved by the molten solder that is placed on the copper pad during the solder application process. This problem was not a major concern with lead-tin solders because over several decades an alloy composition was developed and implemented that reduced diffusion rates within the solder-copper system (63Sn and 37Pb.) However, methods to control copper dissolution in lead-free solders are currently being evaluated, and until more is understood about lead-free solder alloys, copper dissolution will continue to be a concern.

As molten solder comes into contact with the copper substrate, copper dissolution begins and continues until the solder solidifies or until the copper is fully diffused into the solder. After solidification, copper atoms will continue to diffuse into the solder at a reduced rate by means of solid state diffusion. Copper diffuses into pure tin at a higher rate than if alloyed with other elements, so numerous solder alloys have been created to reduce the amount of copper dissolution and intermetallic formation from the diffused copper in tin^[4]. Copper diffusion rates for the liquid solder depend on three main parameters: the chemical composition of the solder, the reflow temperature, and the time that solder is held above the liquidus temperature^[9]. The reflow temperature is the temperature of the liquid phase solder which is usually several degrees above the melting point. Manufacturers typically use a reflow temperature near 235°C and a time above the liquidus temperature of less than 90 seconds. Once the solder has solidified, continued diffusion is dependent on component

temperature. In order to remain cost effective and reduce diffusion rates, SAC 305 solder is commonly used. This solder is 96.5 % Sn, by weight, alloyed with 3% Ag and 0.5% Cu, and its melting point is 217°C.

The diffusion of copper atoms from the substrate pad into the tin solder will contribute to the formation of two different intermetallic compounds, as shown in the Cu-Sn phase diagram in Figure 1. The first intermetallic compound to form is Cu_6Sn_5 (η phase). This first layer is desirable, as it forms a strong durable interface bond between the copper and the solder. The second intermetallic compound that forms is Cu_3Sn_1 (ϵ phase). This second layer forms between the copper pad and the Cu_6Sn_5 intermetallic layer. Its brittle characteristics cause it to weaken the metallic bond at the interface between solder and copper. The presence of Cu_3Sn_1 intermetallic compound is a concern to electrical components that undergo prolonged use at high temperatures and vibrational shock loading ^[10].

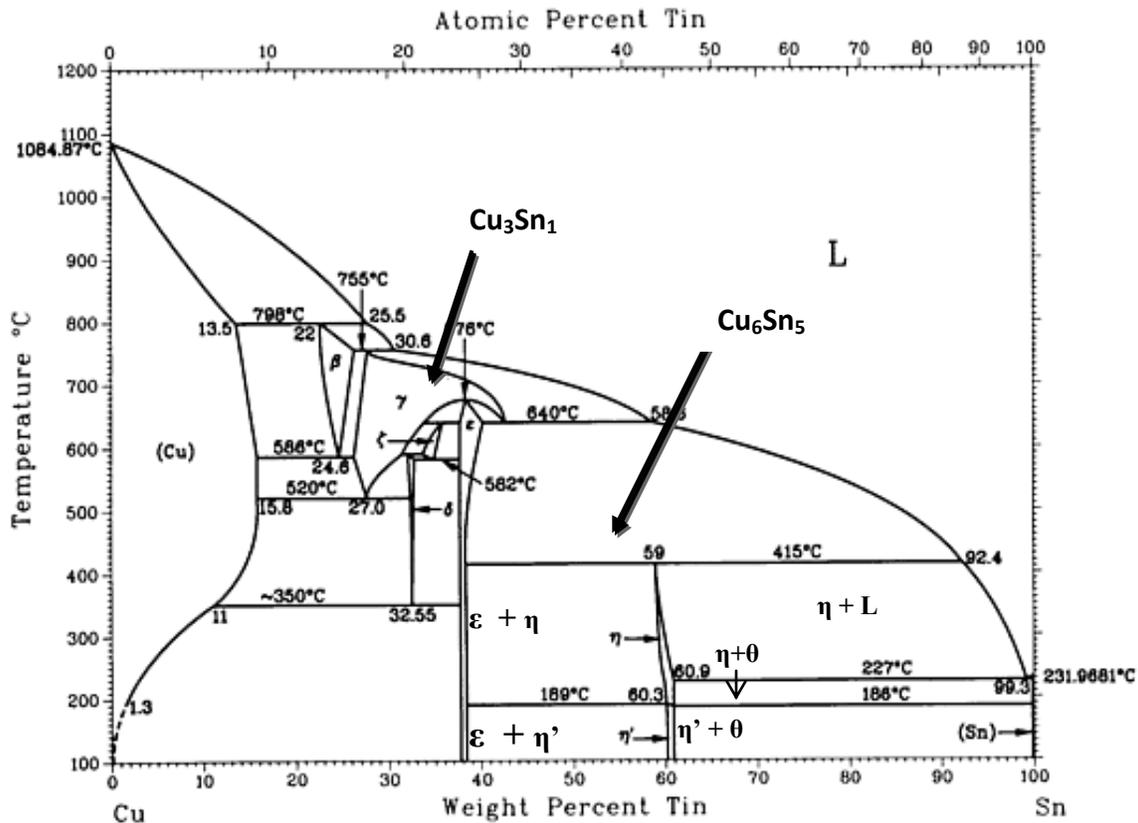


Figure 1 The Cu-Sn phase diagram shows the temperature range where the intermetallic phases are stable. The two intermetallics of interest are labeled. ^[11]

These two intermetallic compounds have different property characteristics, as well as a different appearance. The Cu_6Sn_5 layer has a columnar and irregular formation ^[6]. Its growth takes place during the initial solidification process. Cu_3Sn_1 grows at a slower rate and will form as a thin intermetallic layer that is darker in appearance and more uniform than the first layer intermetallic (Cu_6Sn_5). As copper concentration increases from 39.1% (Cu_6Sn_1) to 61.6% (Cu_3Sn_1), the metastable $\epsilon + \eta'$ phase becomes evident ^[12]. The boundary between Cu_6Sn_5 and Cu_3Sn_1 is indistinguishable until the Cu_3Sn_1 thickness reaches 200 nanometers. Thicknesses below 200 nanometers are not considered a stable Cu_3Sn_1 layer. In Figure 2, both stable intermetallic layers are visible. Again, the beneficial first layer will form immediately during the application of solder on the copper substrate. The second layer may visibly form after thermal aging or under extreme application temperatures and times. In order to extend the service life and increase the reliability of electronic components, studies are being conducted to understand the kinetics and the formation processes of Cu_3Sn_1 .

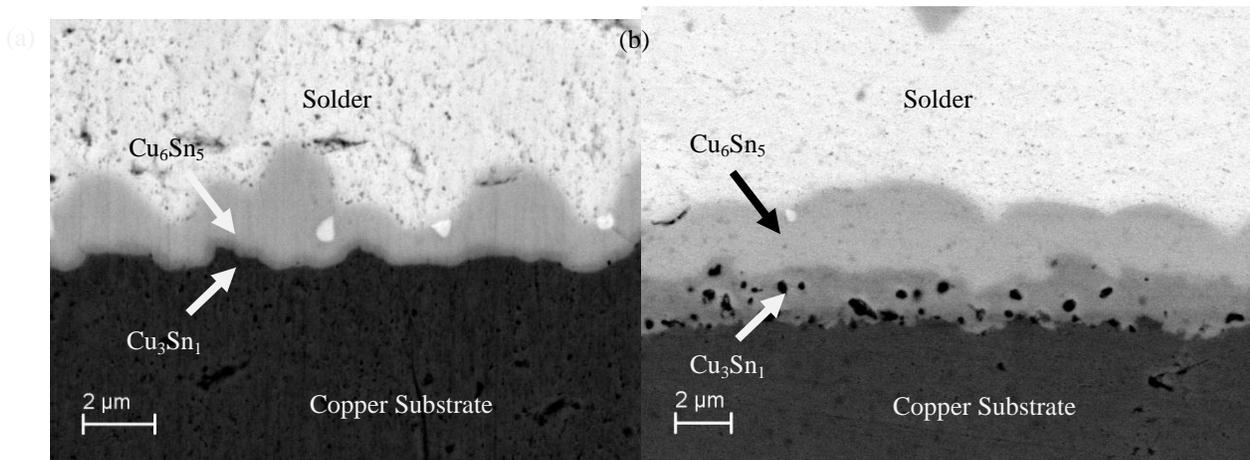


Figure 2 First and second layer intermetallics. (a) Sample was manufactured at a reflow temperature of 223°C and held above liquidus for 105 seconds. (b) Solid state diffusion sample thermally aged at 125°C for 3300 hours.

Several copper dissolution research projects have been conducted and the findings have led to a study to find the activation energy for Cu_3Sn_1 formation [2-4]. Projects were designed to determine the effect of reflow temperature and time above liquidus during the solder application process. It was concluded that the second layer intermetallic is affected more by reflow temperature than by time above liquidus [4]. Additionally, it was assumed that thermal aging promoted the formation of the Cu_3Sn_1 phase. In order to further verify this assumption, a previous research project was designed to monitor thermal aging affects [4]. Samples were produced at a reflow temperature of 235°C and a time above liquidus 50-60 seconds. The parameters were established to simulate standard solder application processing typically used in industry and the thermal aging temperature was chosen to replicate aging of an electronic component in a computer for an extended period of time. Results concluded that the second layer intermetallic did not grow to a measurable thickness after 6500 hours of thermal aging at 50°C. It was concluded that the low reflow temperature and time above liquidus did not breach the activation energy for the Cu_3Sn_1 formation. In order to quantify the activation energy for Cu_3Sn_1 formation, another series of tests were developed.

Experimental Procedure

In order to determine the environmental conditions in which the Cu_3Sn_1 layer becomes detrimental, research projects were developed to determine the activation energy for Cu_3Sn_1 formation during application and thermal aging processes. Although analysis and preparation procedures were similar for both experiments, samples were produced differently. Prior to discussing the procedure, several terms used in this analysis should be clarified. The time above liquidus (TAL) is defined as the length of time (seconds) the solder is heated above the melting temperature of the solder alloy. The reflow temperature is the temperature (°C) that the solder is held above liquidus or melting point. Another important term to understand is activation energy. Activation energy refers to the energy (J/mol) required to initiate or continue a chemical reaction. This may also refer to the distortional energy needed to produce atomic phase changes in an alloy [7].

Specimens for this project were prepared by the Rosebud Electronic Integration Corporation (REI Corp) in Mission, South Dakota. Sample production was completed using an industry standard automated production line to simulate industrial produced components. The solder used was commercially available lead-free solder, SAC 305. During the solder process, the reflow temperature and time above liquidus values were controlled in a Heller 1800 EXL Reflow Oven. Specimens that required thermally aged were placed in multiple Lindberg Blue M Ovens in ambient air.

The differences in sample production are separated into two parts desired below:

Experiment 1

Reflow temperature and time above liquidus provide the solder alloy with the thermal energy that is necessary to initiate intermetallic formation. This project was designed to assess the amount of activation energy necessary to form the Cu_3Sn_1 phase. The samples were prepared at reflow temperatures ranging from 223 – 243°C and TALs ranging from 30 seconds to 360 seconds. Intervals of 3°C and of 15 seconds were used during this study. The sample layout is shown in Table 1. This study only included samples #26 to #146. Specimens numbered 1-25 were prepared at a reflow temperature of 220°C.

However, with a melting point of 217°C, the solder did not fully reach the liquidus temperature and were excluded from this analysis.

Table 1 Sample numbers are included in the columns that are categorized by reflow temperature and time above liquidus.

TAL (sec)	Reflow Temperature (deg C)						
	223	227	230	233	236	240	243
30	#26	#51	#72	#91	#108	#123	#135
45	27	52	73	92	109	124	136
60	28	53	74	93	110	125	137
75	29	54	75	94	111	126	138
90	30	55	76	95	112	127	139
105	31	56	77	96	113	128	140
120	32	57	78	97	114	129	141
135	33	58	79	98	115	130	142
150	34	59	80	99	116	131	143
165	35	60	81	100	117	132	144
170	36	61	82	101	118	133	145
175	37	62	83	102	119	#134	#146
180	38	63	84	103	120	-----	-----
195	39	64	85	104	121	-----	-----
210	40	65	86	105	#122	-----	-----
225	41	66	87	106	-----	-----	-----
240	42	67	88	#107	-----	-----	-----
255	43	68	89	-----	-----	-----	-----
270	44	69	#90	-----	-----	-----	-----
285	45	70	-----	-----	-----	-----	-----
300	46	#71	-----	-----	-----	-----	-----
315	47	-----	-----	-----	-----	-----	-----
330	48	-----	-----	-----	-----	-----	-----
345	49	-----	-----	-----	-----	-----	-----
360	#50	-----	-----	-----	-----	-----	-----

Experiment 2

Samples were produced at a reflow temperature of 235°C and remained at liquidus temperature for 50 seconds. These parameters are widely used as commercial standards. Samples were then thermally aged at various temperatures and were retrieved after a certain time interval. Specimens were analyzed to provide information about the rate of formation of Cu₃Sn₁. Experiment 1 analyzed intermetallic growth during solidification, but this project will assess the effect of time and temperature on growth and formation of Cu₃Sn₁ after solidification.

Thermally aged samples would have the thermal energy that is necessary to initiate intermetallic formation stored in the solder. This project was designed to assess the amount of activation energy necessary to form the Cu₃Sn₁ phase. All the samples were prepared with the same soldering parameters and then thermally aged at temperatures ranging from 60°C to 125°C and from 100 hours to 1000 hours. Intervals of 10°C and of 100 hours were used during this study for most samples. Additional samples were prepared at a temperature of 125°C and others at smaller time intervals between 100 and 300 hours. The sample layout is shown in Table 2. It is apparent that samples thermally aged at 60°C were not included in the table. At this temperature, the amount of thermal aging time was not adequate for producing the Cu₃Sn₁ intermetallic.

Table 2 The layout below depicts thermal aging conditions that were tested. Thermal aging temperatures are included in columns and aging times are in rows. The gray cells record the conditions of specimens prepared. The values included are measured thicknesses of the intermetallic growth. The gray regions without values represent areas that a Cu_3Sn_1 layer was not observed.

Aging Time (hr)	Thermal Aging Temperature (Deg C)				
	70	80	90	100	125
100					0.35
125	-----	-----	-----	0.29	-----
150	-----	-----	-----	0.25	-----
175	-----	-----	-----	0.29	-----
200				0.32	0.49
225	-----	-----		-----	-----
250	-----	-----		-----	-----
275	-----	-----	0.23	-----	-----
300			0.30	0.42	0.70
400			0.30	0.45	0.61
500	-----	0.21	-----	-----	-----
600		0.22	-----	-----	-----
700	0.22	0.26	-----	-----	-----
800	0.25	0.26	-----	-----	-----
900	0.25	0.27	-----	-----	-----
1000	0.29	0.29	0.47	0.64	1.25

KEY:	
Samples Created	
Not Analyzed	-----

For both experiments, an individual sample consists of a single solder ball, which is approximately the size of a pencil eraser, on a printed circuit board. Each solder ball was cross-sectioned using the Buehler IsoMet 1000 precision saw with a diamond blade, which allows controlled cutting at lower speeds. One half of each sample was archived, and the other half is mounted. The cross-sectional view of the sample was placed face down into a sample mount and then cold mounted using epoxy. Epoxy mounting was preferred to hot pressure mounting to prevent board delamination and alterations to the intermetallic region. After samples are mounted, grinding and polishing procedures are completed to allow viewing of the intermetallic phases. The grinding process begins with 400 grit paper and continues to 800 and 1200 grit paper. As the 400 grit grinding wheel rotates, the sample is placed on the wheel with the solder ball is against the grinding wheel rotation. Scratches will be perpendicular to the copper pad, and the wheel should first move across the solder and then to the copper pad. On the next wheel, the sample will then be rotated a quarter turn clockwise so the solder ball facing the center of the wheel. As the sample is moved from each wheel, it will be rotated between those two orientations. These orientations minimize smearing of the intermetallic layers during grinding. After finishing the 1200 grit, the samples are polished using 9.0 micron, 3.0 micron and 0.05 micron polishing stations. The 9.0 and 3.0 micron wheels use diamond suspension solutions with a Leco-Nylon polishing pads. The 0.05 micron solution is an alumina solution that is applied to a micro-fiber cloth. Although all the grinding wheels use water, the polishing wheels only use their respective solutions. The specimens were thoroughly cleaned with soap and water between each step to prevent any cross contamination from the previous the grinding/polishing steps.

After the samples are polished, each mounted sample is examined using the Nikon Epiphot 200 Optical Microscope. It is then determined if the intermetallic region is fully visible. The success of the polishing techniques is pivotal to the analysis process, so great attention is taken using light microscopy. Samples are then prepared for scanning electron microscopy (SEM). Carbon paint is applied around the sample to make it conductive and prevent charging during SEM evaluation. This

step will limit the amount of drifting and charging that may occur while using the SEM. A Zeiss Supra 40VP SEM was used to examine the samples. The intermetallic region was viewed at 15,000 to 20,000 times in magnification, which allows measurements to be taken at the nanometer scale. The thickness of the Cu_3Sn_1 intermetallic layer is obtained by SEM measurement tools while using a backscatter imaging detector. Measurements were taken from three different regions on each sample, with six measurements taken from each region. After the intermetallic thicknesses are recorded, an average thickness was calculated.

An accelerating voltage of 15 keV was used with a field aperture of 60 microns in high current mode. Typically, a depth of field of 8 microns was used. Adjustments in brightness and contrast are optimized using a line scan feature on the SEM. Both secondary electron detector and the backscatter electron detector were used to evaluate the intermetallic regions on each sample.

Experimental Results and Discussion

For both experiments, the objective was to determine the rate of Cu_3Sn_1 formation, whether during solidification or after solidification. Different mathematical approaches were taken to predict the growth rate of the detrimental intermetallic.

Experiment 1

In order to determine the required energy for intermetallic formation, Equation 1 below was considered. Further calculations were completed and described in a previous paper ^[1].

$$\varepsilon = A * e^{(-\frac{Q}{R}) * (\frac{1}{T})} \quad (1)$$

The Arrhenius equation above may be used to correlate the effect of temperature to the growth rate. Based on the relationship between these parameters, the activation energy (Q) of the system was calculated. The units for the activation energy are J/mol, or kJ/mol. The growth rate refers to the change in thickness, or growth, with respect to the change in time (TAL). Reflow temperature (T) was used to understand the thermal environment of the system. In the equation, A is the frequency factor (nm/sec), and R is the ideal gas constant (J/mol K.).

During sample analysis, intermetallic thicknesses were measured and used to determine an average growth rate at each reflow temperature (See Table 1). The natural log of Equation 1 results in the linear relationship between $\ln(\varepsilon)$ and $(\frac{1}{T})$, as shown in Equations 2 and 3.

$$\ln(\varepsilon) = \left(-\frac{Q}{R}\right) * \left(\frac{1}{T}\right) + \ln(A) \quad (2)$$

$$y = m * x + b \quad (3)$$

Solving for the slope $(-\frac{Q}{R})$, yields Equation 4.

$$\left(-\frac{Q}{R}\right) = \left(\frac{\ln[(\varepsilon_2)] - \ln[(\varepsilon_1)]}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right) \quad (4)$$

Finally, by rearranging Equation 5, it is possible to calculate Q, as shown in Equation 5.

$$Q = \left(\frac{R * \ln\left(\frac{\varepsilon_1}{\varepsilon_2}\right)}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right) \quad (5)$$

To obtain Q and A, information about growth rate and reflow temperature were used to create an Arrhenius plot. Rate (ε) is temperature dependent. Theoretically, at a constant reflow temperature the growth rate will remain the same as TAL varies. For this reason, an average growth rate for each reflow temperature was used to calculate the Arrhenius plot shown in Figure 3.

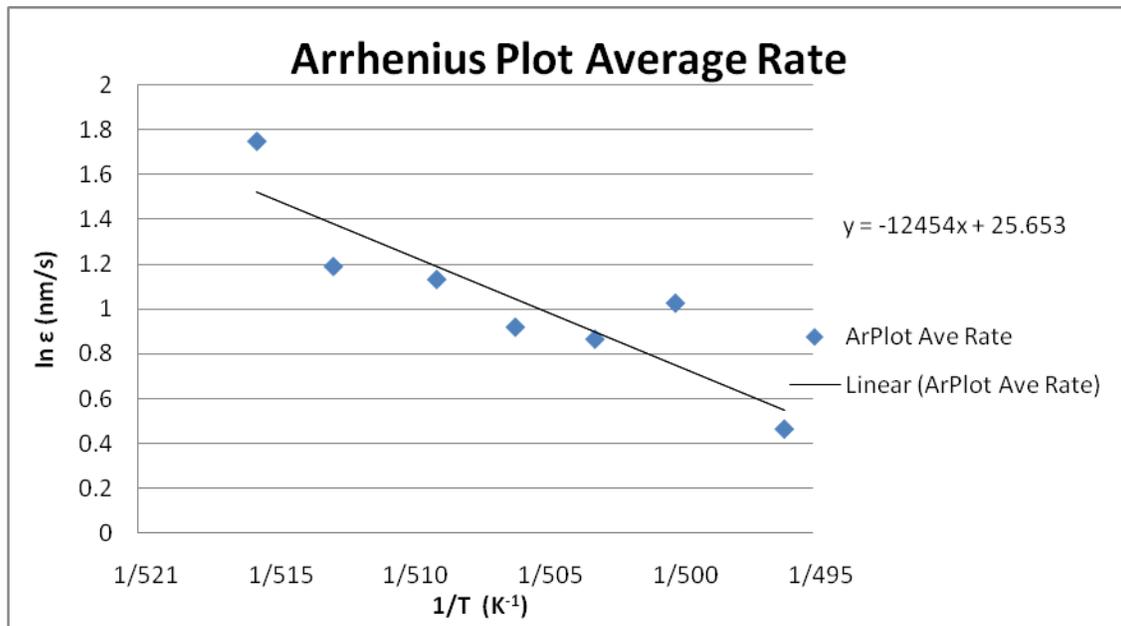


Figure 3 The Arrhenius plot was derived from average growth rate data. The equation to the right follows slope-intercept form. The slope (m) would be activation energy over the negative gas constant $\left(-\frac{Q}{R}\right)$ and the y-intercept (b) would be the frequency factor (ln A).

By fitting a regression line to the data, the activation energy (Q) and the frequency factor (A) are calculated. The y-intercept is ln(A) or 25.7 and the slope of the line is $\left(-\frac{Q}{R}\right)$ or -12,454.0. The frequency factor (A) is $e^{26.39}$, and Q is the product of the slope and -R, where R equals 8.314 J/mol*K. The activation energy (Q) was calculated to be 103,548.8 J/mol or 103.6 kJ/mol. The y-intercept is the natural log of A, which was determined to be 1.38×10^{11} nm/sec.

The values for Q and A are applied to Equation 6 below:

$$\varepsilon = 1.38 \times 10^{11} * e^{\left(\left(-\frac{103,549}{8.314}\right) * \left(\frac{1}{T}\right)\right)} \quad (6)$$

Where T represents reflow temperature and ε represents thickness with respect to time (TAL), values for thickness and T may be used to determine an advisable or maximum time to remain above liquidus.

$$\frac{2 \times 10^{-7}}{TAL} = 1.38 \times 10^{11} * e^{\left(\left(-\frac{103,549}{8.314}\right) * \left(\frac{1}{508}\right)\right)} \quad (7)$$

Equation 6 correlates test parameters of reflow temperature and TAL to estimate growth of the second layer intermetallic (Cu_3Sn_1). This research suggests that manufacturers using SAC305 solder should not exceed a Cu_3Sn_1 intermetallic thickness of 200 nm. As previously stated, a Cu_3Sn_1 thickness less than 200 nanometers is not considered stable. If a reflow temperature of 235 °C (T=508K) is used in Equation 7 and a thickness of 200 nanometers (2×10^{-7} meters) is used as intermetallic thickness, the time above liquidus (TAL) can be determined. Based on the calculation, it would be advisable not to remain above liquidus temperature for more than 55 to 60 seconds.

Experiment 2

In order to understand the reaction kinetics that occur after solidification, Equation 8 was used. This equation was used to determine the rate of diffusion for the system.

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \text{erf}\left(\frac{x}{2 * \sqrt{D * t}}\right) \quad (8)$$

C_s , C_x , C_o are the known concentrations of copper in the copper substrate, Cu_3Sn_1 intermetallic region, and SAC solder ball, respectively. The thickness, x, is the observed intermetallic thickness. D refers to the diffusion coefficient, which is the

unknown. And t is the value of time for thermal aging. An average diffusion coefficient was calculated for each temperature using the equation.

$$D = D_0 * e^{\left(\frac{-Q_d}{RT}\right)} \quad (9)$$

Using Equation 8, a $\ln D$ vs $1/T$ plot was generated to solve for the activation energy for diffusion (Q_d). By fitting a regression line to the data, the activation energy (Q) and the diffusion coefficient that is independent of temperature (D_0) are found. The y-intercept is $\ln(D_0)$ or -26.003 and the slope of the line is $\left(-\frac{Q}{R}\right)$ or -6390.3. The frequency factor (A) is $e^{-26.003}$, and Q is the product of the slope and $-R$, where R is the ideal gas constant which equals 8.314 J/mol*K. The activation energy (Q) was calculated to be 53,129.0 J/mol or 53.13 kJ/mol. The y-intercept is the natural log of D_0 , which was determined to be 5.09×10^{-12} m²/sec.

Using Equations 8 and 9, predictions were made for Cu_3Sn_1 thickness at varying times and temperatures, and were compared to our previous observations. At higher temperatures and shorter times the calculations were accurate, however at lower temperatures the observed thicknesses was consistently less than predicted. This discrepancy was attributed to the energy required for Cu_3Sn_1 formation being greater than the energy required for diffusion to occur. Further analysis is in progress, which will take into consideration the required energy of formation.

Conclusion

The reaction kinetics for the formation of Cu_3Sn_1 was studied in Experiment 1 and 2 to assess the activation energy during solidification and after solidification, respectively. Several parameters, such as reflow temperature, time above liquidus (TAL), and thermal aging time and temperature are important factors when assessing the reliability of electrical components. In Experiment 1, the research showed that the formation of this detrimental Cu_3Sn_1 layer may occur upon applying molten solder to a copper substrate. An initial activation energy value must be reached to observe an established Cu_3Sn_1 layer. Using an Arrhenius equation, the activation energy (Q) and the frequency factor (A) were determined to be 103.55 kJ/mol and 1.38×10^{11} nm/sec, respectively. To prevent the formation of a stable Cu_3Sn_1 intermetallic layer with a thickness of 200 nm, manufacturers should not exceed a TAL of 55 to 60 seconds while using a reflow temperature of 235°C. These results are relevant to the kinetics of liquid solder on a solid copper substrate. Experiment 2 was designed to determine the growth rate of Cu_3Sn_1 after solidification. The rate of diffusion was determined; however, the rate of formation must be addressed to provide an accurate estimation at lower aging temperatures and longer times. Further analysis will be completed to compare solid state diffusion mechanisms with the rate of intermetallic formation. Future research will inform consumers about the reliability and maintenance requirements for electronics designed with lead-free solder during and after solidification. In addition, information pertaining to intermetallic growth will be correlated to mechanical properties.

References

- [1] T. Ryno, A. Kelley, D. Medlin, C. Voyles Effect of Soldering Parameters on Reaction Kinetics and Phase Transformations of SAC-305 Solder MS&T Proceedings, Houston, TX, October 2010.
- [2] L. Nielsen, C. Voyles, S. Richards, D. Medlin, Effect of Thermal Treatments on Copper Dissolution of SAC-305 Solder TMS Conference and Exposition, San Francisco, CA, February 15-18, 2009.
- [3] T. Ryno, L. Nielsen, C. Voyles, S. Richards, D. Medlin, Effect of Thermal Treatments on Copper Dissolution of SAC-305 Solder MS&T Proceedings, Pittsburgh, PA, September 2009.
- [4] L. Nielsen, Effect of Thermal Treatments on Copper Dissolution of SAC-305 Solder. MS Thesis. Rapid City, SD: South Dakota School of Mines and Technology, 2008.
- [5] Committee, Economical and Social. "Directive 2002/95/EC of the European Parliament and of the Council." Official Journal of European Union (2003): L37/19-L37/23.
- [6] C. Hamilton, P. Snugovsky and M. Kelly. Have High Cu Dissolution Rates of SAC305/405 Alloys Forced a Change in the Lead Free Alloy Used During PTH Processes? Toronto, ON, Canada: Celestica Inc, IBM Corporation, 2007.

- [7] J.G. Henderson, Metallurgical Dictionary. New York: Reinhold Publishing Corp, 1953.
- [8] J. Jenkins, Lead-Free Electronics Pose Reliability Problems for Navy Aircrafts. Patuxent River, MD: United States Naval Air Systems Command, 2007.
- [9] H. Lee, et al. A Study of Reliability between Solder Alloy and Pad Materials. Conference Proceeding. Chicago, IL: IPC Midwest Conference and Exhibition, 2008.
- [10] J. Madeni, et al. Intermetallics Formation and Growth at the Interface of Tin-Based Solder Alloys and Copper Substrates. Conference Proceeding. San Diego, CA: 2nd Annual Brazing and Soldering Conference (ISBC), 2003.
- [11] N. Saunders and A. Miodownik. Cu-Sn Binary Phase Diagrams. ASM Handbooks. ASM International, 2007.
- [12] Smith, William F. Structure and Properties of Engineering Alloys. New York: McGraw Hill Inc, 1993.
- [13] Universal Instruments Corporation. "Fragility of Pb-free Solder Joints." 2004.

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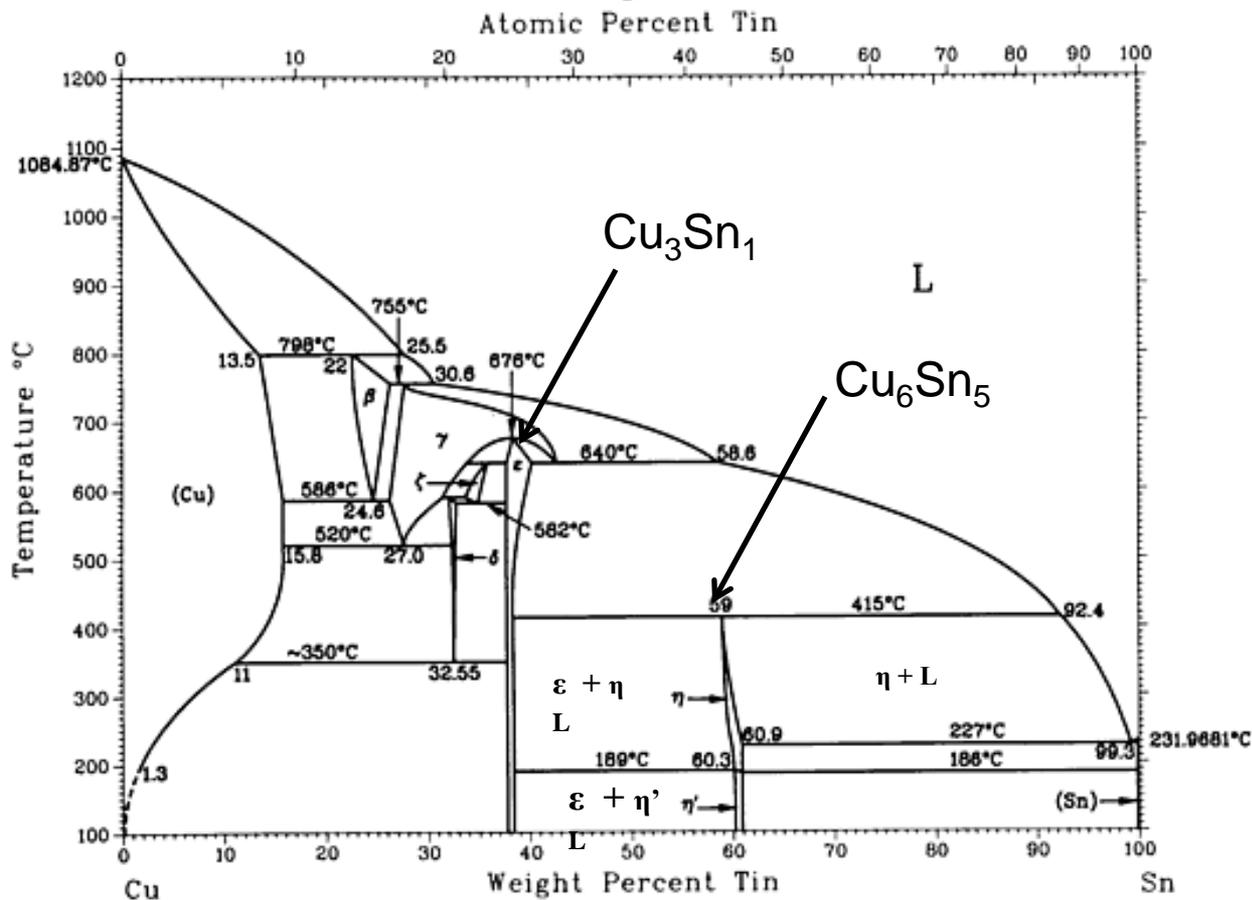


Background

- Terminology
 - RoHS
 - SAC 305
 - Reflow Temperature
 - Time Above liquidus (TAL)
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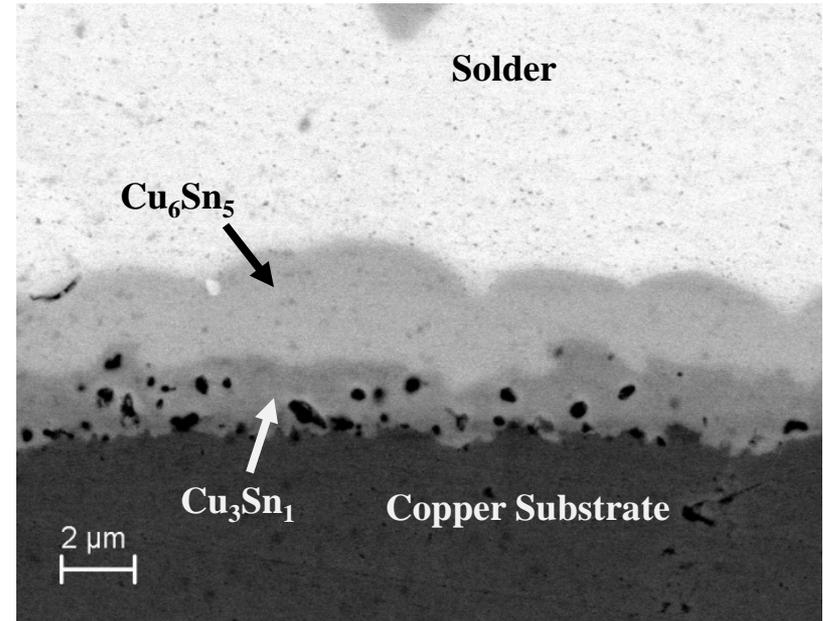
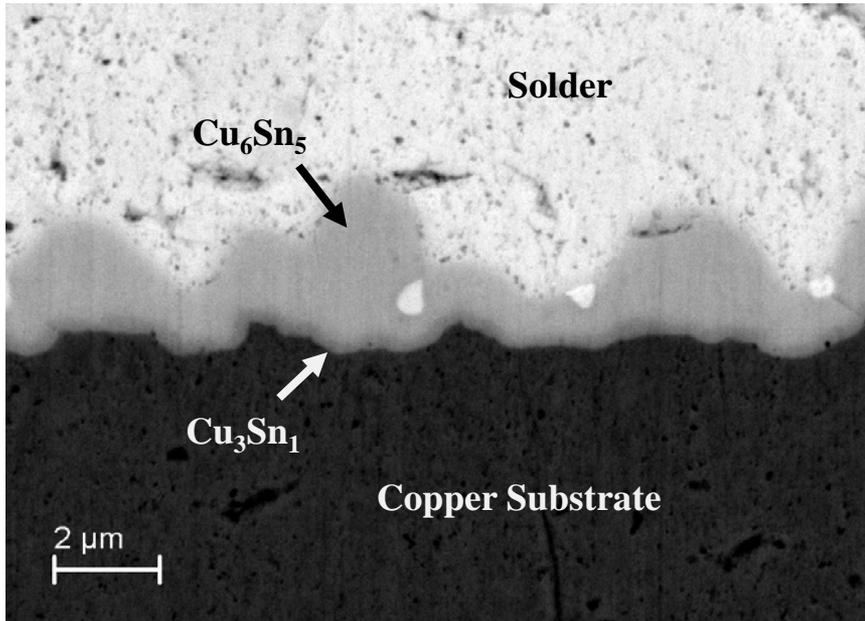


Background



Cu-Sn Phase Diagram

Background



Two scanning electron microscope (SEM) images from the two experiments presented. On the left side, an image from experiment shows Cu_3Sn_1 as it begins to form. On the right hand side, the detrimental intermetallic layer begins to visibly degrade through the formation of voids from diffusion.

Experimental Procedure

- Sample Production
 - Experiment 1

TAL (sec)	Reflow Temperature (deg C)						
	223	227	230	233	236	240	243
30	#26	#51	#72	#91	#108	#123	#135
45	27	52	73	92	109	124	136
60	28	53	74	93	110	125	137
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90	30	55	76	95	112	127	139
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120	32	57	78	97	114	129	141
135	33	58	79	98	115	130	142
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175	37	62	83	102	119	#134	#146
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195	39	64	85	104	121	-----	-----
210	40	65	86	105	#122	-----	-----
225	41	66	87	106	-----	-----	-----
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270	44	69	#90	-----	-----	-----	-----
285	45	70	-----	-----	-----	-----	-----
300	46	#71	-----	-----	-----	-----	-----
315	47	-----	-----	-----	-----	-----	-----
330	48	-----	-----	-----	-----	-----	-----
345	49	-----	-----	-----	-----	-----	-----
360	#50	-----	-----	-----	-----	-----	-----

The sample layout for experiment 1

Experimental Procedure

- Sample Production
– Experiment 2

Aging Time (hr)	Thermal Aging Temperature (Deg C)				
	70	80	90	100	125
100					0.35
125	----	----	----	0.29	----
150	----	----	----	0.25	----
175	----	----	----	0.29	----
200				0.32	0.49
225	----	----		----	----
250	----	----		----	----
275	----	----	0.23	----	----
300			0.30	0.42	0.70
400			0.30	0.45	0.61
500	----	0.21	----	----	----
600		0.22	----	----	----
700	0.22	0.26	----	----	----
800	0.25	0.26	----	----	----
900	0.25	0.27	----	----	----
1000	0.29	0.29	0.47	0.64	1.25

KEY:	
Samples Created	
Not Analyzed	----

The sample layout for experiment 2

Experimental Procedure

- Sample Preparation
 - Section & Mount



Epoxy used to mount sectioned samples

Experimental Procedure

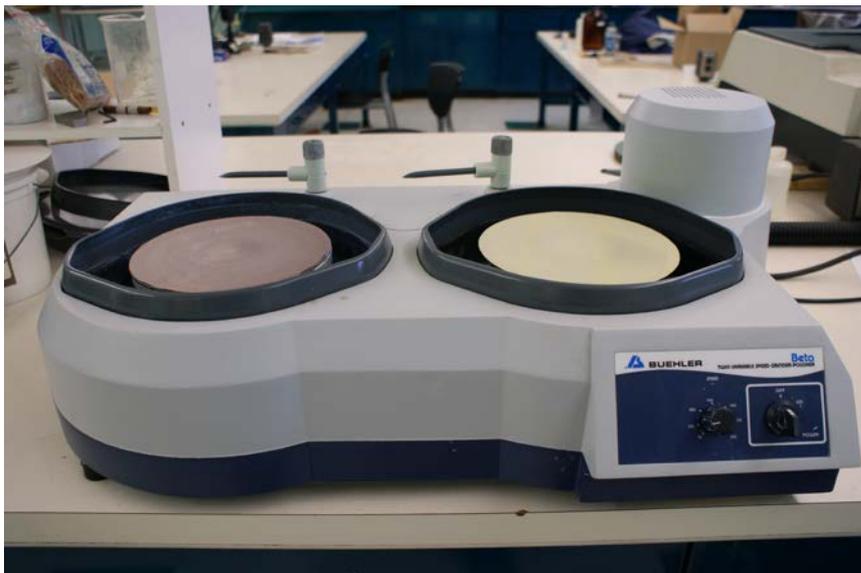
- Sample Preparation
 - Section & Mount
 - Grind



Grinding wheels for 400, 800 and 1200 grit

Experimental Procedure

- Sample Preparation
 - Section & Mount
 - Grind
 - Polish



Polishing wheels for 9 um, 3 um and 0.05 um

Experimental Procedure

- Sample Analysis
 - Scanning Electron Microscope
 - Intermetallic Thickness Measurements
 - Intermetallic Observations



Results and Discussion

- Experiment 1 – During Solidification

$$\varepsilon = A * e\left(\left(-\frac{Q}{R}\right) * \left(\frac{1}{T}\right)\right) \quad (1)$$

The natural log of Equation 1 results in the linear relationship between $\ln(\varepsilon)$ and $\left(\frac{1}{T}\right)$, as shown in Equations 2 and 3.

$$\ln(\varepsilon) = \left(-\frac{Q}{R}\right) * \left(\frac{1}{T}\right) + \ln(A) \quad (2)$$

$$y = m * x + b \quad (3)$$



Results and Discussion

Arrhenius Plot Average Rate

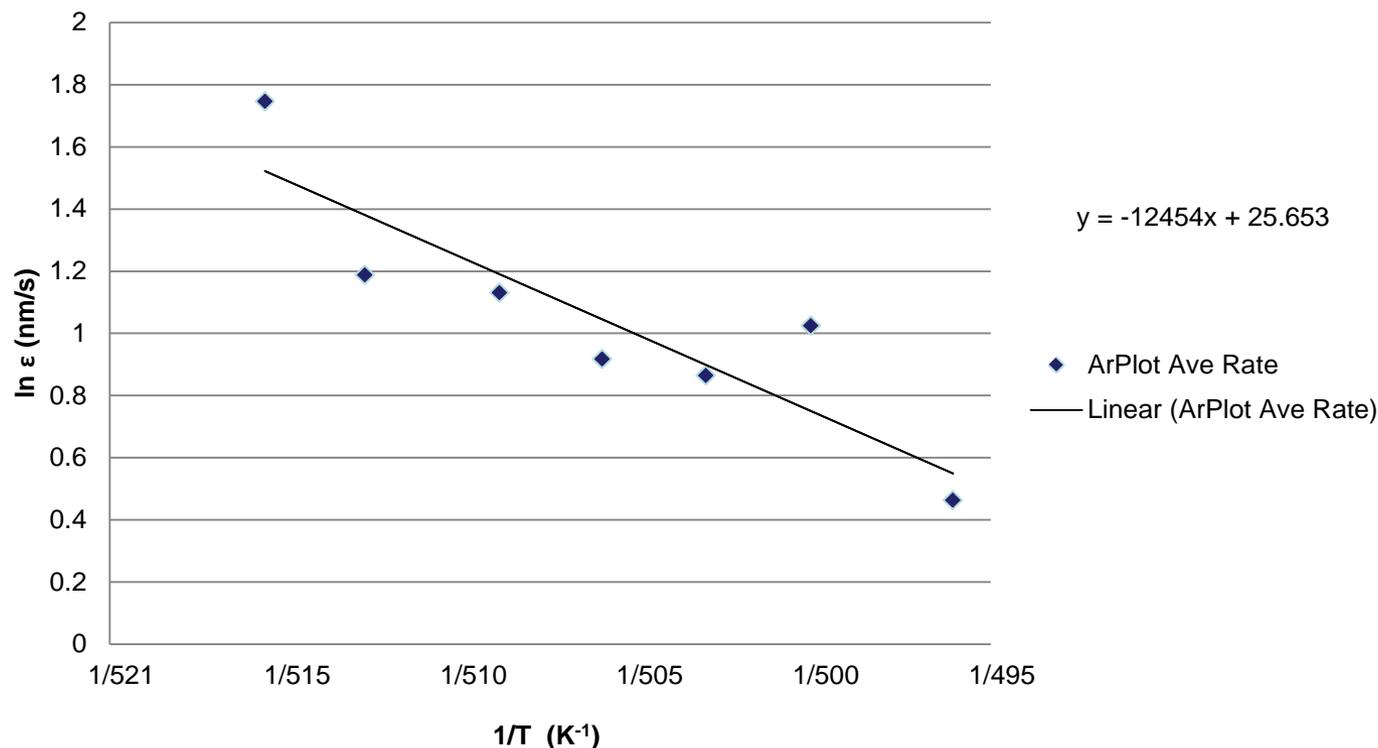


Figure 8: The slope of graph above is $\left(-\frac{Q}{R}\right)$. By solving for Q of the system, Equation 1 may be used to estimate the growth of Cu_3Sn_1 for a given time and temperature during solidification

Results and Discussion

- Experiment 1
 - During solidification, do not exceed a TAL of 55-60 seconds if a reflow temperature of 235 °C is used.
 - This information provides manufacturers with an understanding of the effects of soldering parameters.



Results and Discussion

- Experiment 2 – After solidification

$$\frac{C_x - C_o}{C_s - C_o} = 1 - \operatorname{erf}\left(\frac{x}{2 * \sqrt{D * t}}\right) \quad (4)$$

D was solved for by using the measured Cu_3Sn_1 thickness, x , and known Cu concentration.

$$D = D_o * e^{\left(\frac{-Q_d}{RT}\right)} \quad (5)$$

A plot of the natural log of Equation 5 gives a linear relationship between $\ln D$ and $1/T$. Q_d can then be solved from the slope.



Results and Discussion

- Experiment 2
 - Q_d was then used to estimate intermetallic growth at given times and temperatures and compared to observed measurements.
 - Estimates matched well at high temperatures, but diverged as temperature was decreased.



Results and Discussion

- Experiment 2
 - In order to estimate the thickness of the intermetallic after solidification, the activation energy of formation must be accounted for, in addition to activation energy of diffusion.
 - After further analysis is completed, manufacturers could determine the effects of thermal aging.



Future Work

- Research will continue to assess the affects of thermal aging and attempt to predict the growth of Cu_3Sn_1 after solidification.
- Mechanical property data and intermetallic thickness information will be correlated to determine a life expectancy for SAC 305.

Conclusions

- Experiment 1
 - Cu₃Sn₁ growth can be predicted for liquid solder application.
- Experiment 2
 - Energy of formation is limiting factor and must be considered.
- Future research
 - Relate data between intermetallic thickness and mechanical properties to quantify reliability of SAC 305 solder.

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Questions?

