

Effect of Soldering Parameters on Reaction Kinetics and Phase Transformations of SAC 305 Solder

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Abstract

As technology becomes increasingly reliant on electronics, understanding the reliability of lead-free solder also becomes increasingly important. This research project focused on phase transformation kinetics with the lead-free solder SAC 305. Today in the electronics industry, SAC 305 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. Recent evidence has shifted the focus from thermal aging to reflow temperature and time above liquidus values during initial solder melting.

Previous research projects were designed to record the initial growth of Cu_6Sn_5 and monitor the development of Cu_3Sn_1 ^{[1][2][3]}. These studies analyzed thermally-aged samples prepared at various reflow temperatures and times above liquidus temperatures. The initial growth of Cu_6Sn_5 developed as expected, but the Cu_3Sn_1 layer did not precipitate as anticipated. The detrimental second layer (Cu_3Sn_1) exhibited limited or no growth during this study.

Introduction

For the past five years, electronic manufacturers have spent time and resources shifting from lead solders to tin alloy solders. In 2002, the European Union initiated a directive that would eliminate the use of hazardous substances in industry^[4]. Several hazardous materials, including lead, were restricted during manufacturing. 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^[7]. As lead solders become more difficult to produce and purchase, the United States space and military technology 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 become a concern. 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. 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. Pure tin diffuses at a higher rate than if alloyed with other elements, so numerous solder alloys have been created to reduce the amount of copper dissolution. The addition of alloying elements results in the reduction of copper dissolution due to decreased copper diffusion in the alloy and the intermetallic compounds formed from the alloying elements and the tin^[3]. Copper diffusion rates for the solder alloys 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^[8]. 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. In order to remain cost effective and reduce diffusion rates, SAC 305 solder is commonly used. This solder is predominantly tin with an addition of 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, because 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^[9].

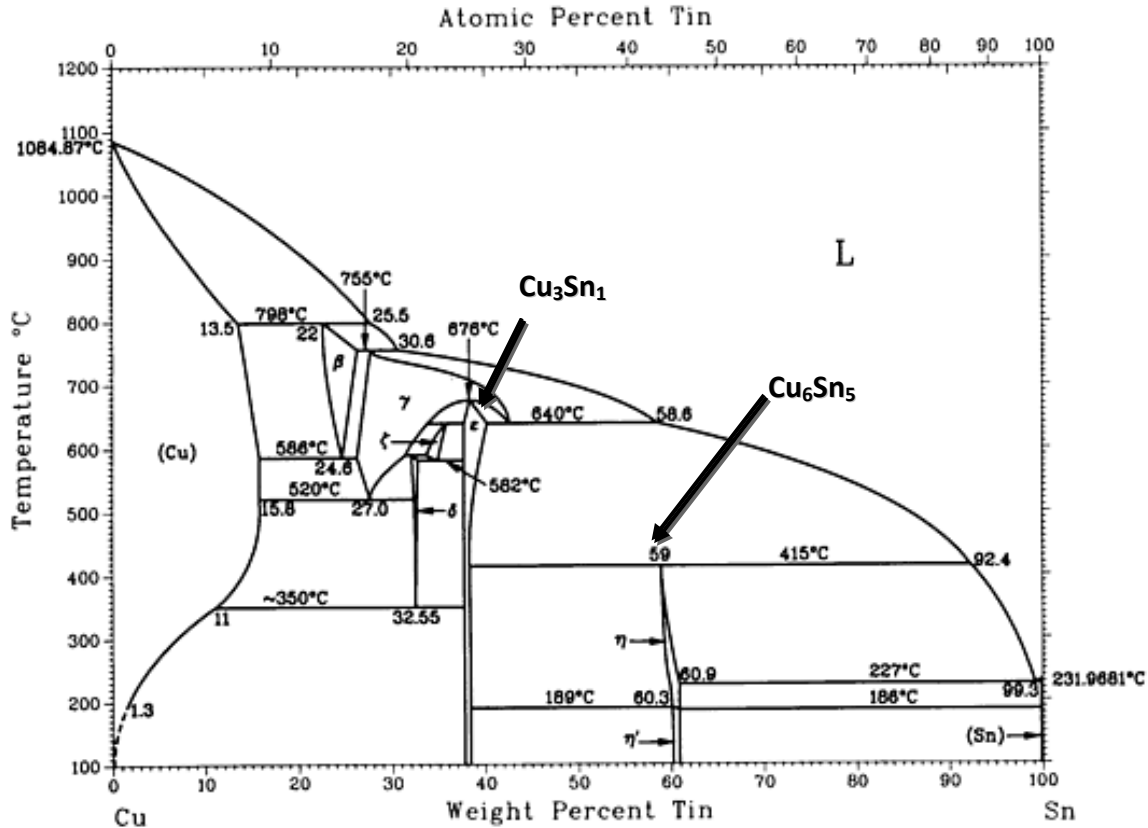


Figure 1 The Cu-Sn phase diagram shows the temperature range where the intermetallic phases are stable. The two intermetallics of interest are labeled.^[10]

These two intermetallic compounds have different property characteristics, as well as a different appearance. The Cu₆Sn₅ layer has a columnar and irregular formation^[5]. Its growth takes place during the time that the solder is above liquidus temperature. Cu₃Sn₁ grows at a slower rate and will appear as a thin intermetallic layer that is darker and more uniform than the first layer intermetallic (Cu₆Sn₅). In Figure 2, both 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 process of Cu₃Sn₁ formation.

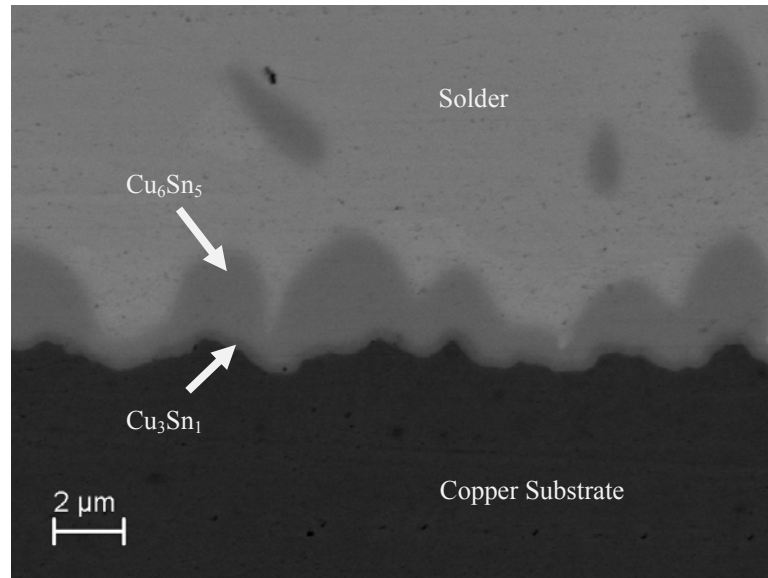


Figure 2 First and second layer intermetallics are present in this sample that was manufactured at a reflow temperature of 223°C and held above liquidus for 105 seconds.

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 ^{[1][2][3]}. Projects were designed to determine the affect 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 ^[3]. 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 ^[3]. 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 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 identify the environmental conditions required for the Cu_3Sn_1 layer formation, a research project was developed to determine the activation energy for Cu_3Sn_1 formation. Samples were prepared with a range reflow temperatures and times above liquidus with no post-soldering thermal aging cycle. The samples were analyzed to provide information about the rate of formation of Cu_3Sn_1 . Past research had shown that the reflow temperature parameter influenced the growth of intermetallic compounds more than the time above liquidus (TAL).

Several terms are used that should be clarified. The time above liquidus 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. These two parameters are the controlled variables during this investigation. For this project, activation energy will be another important term. 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 [6].

Specimens for this project were prepared by the Rosebud Electronic Integration Corporation (REIC) 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.

The reflow temperature and time above liquidus provided 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 Cu₃Sn₁ 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	-----	-----	-----	-----	-----	-----

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 is archived, and the other half is mounted. The cross-sectional view of the sample is placed face down into a sample mount and then cold mounted using epoxy. Epoxy mounting is 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 320 grit paper and continues to 400, 600, 800 and 1200 grit paper. As the 320 grit grinding wheel rotates, the sample is placed on the wheel with the solder ball facing the center of the wheel. Scratches will be parallel to the copper pad. On the next wheel, the sample will then be rotated a quarter turn counter-clockwise so the solder ball is against the grinding wheel direction. 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 3.0 micron and 0.05 micron polishing stations. The 3.0 micron solution uses a diamond suspension solution 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 prevent the specimen from becoming conductive. 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 10,000 to 15,000 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. From each region, four measurements are taken. 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. 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

The results in Table 2 show the reflow temperatures and time above liquidus values as the second layer became observable. White cells in the table indicate samples that did not form a distinct second layer intermetallic (no layer). The dark cells indicate values for Cu_3Sn_1 intermetallic thicknesses that were observed. For dark cells with intermetallic thickness data, rates of diffusion were calculated. Based on steady-state diffusion calculations, the rate of growth should remain constant for a specific temperature. For the purposes of this study, an average growth rate was calculated using the different thicknesses assessed at their respective time above liquidus values. Reaction rates are related to activation energy through an Arrhenius equation. This equation is used in various rate applications, including diffusion. The data below were used to solve the necessary activation energy of the Cu_3Sn_1 phase formation. The information includes reflow temperatures and TALs that are recorded during the application of the solder onto the copper pad.

Table 2 Samples were analyzed to determine a threshold at which a Cu_3Sn_1 layer becomes a visible layer. The dark cells have Cu_3Sn_1 layer intermetallic thickness values in microns. The white cells (NL) indicate that samples showed no Cu_3Sn_1 layer.

TAL (sec)	Reflow Temperature (deg C)						
	223	227	230	233	236	240	243
30	NL	NL	NL	NL	NL	NL	0.242
45	NL	NL	NL	NL	NL	NL	0.290
60	NL	NL	NL	NL	NL	0.231	0.305
75	NL	NL	NL	0.177	0.233	0.235	0.251
90	NL	0.278	0.219	0.272	0.315	0.258	-----
105	0.244	0.260	0.237	-----	0.281	-----	-----
120	-----	0.282	0.291	0.265	-----	-----	-----
135	-----	-----	-----	0.327	-----	-----	-----
150	0.275	-----	-----	-----	-----	-----	-----
165	-----	-----	-----	-----	-----	-----	-----
170	0.316	-----	-----	-----	-----	-----	-----
175	-----	-----	-----	-----	-----	-----	-----
180	-----	-----	-----	-----	-----		
195	-----	-----	-----	-----	-----		
210	-----	-----	-----	-----	-----		
225	-----	-----	-----	-----			
240	-----	-----	-----	-----			
255	-----	-----	-----				
270	-----	-----	-----				
285	-----	-----					
300	-----	-----					
315	-----						
330	-----						
345	0.341						
360	0.339						

No 2nd Layer (NL)

2nd Layer

No Data Collected -----

The following equations were used to calculate second layer intermetallic growth rates and activation energy for the Cu_3Sn_1 intermetallic formation. Equation 1 was used to calculate the growth rate (ϵ) for the Cu_3Sn_1 , where dg refers to the change in thickness, or growth, and dt refers to the change in time (TAL). The units on growth rate were nm/sec.

$$\text{growth rate}(\epsilon) = \left(\frac{dg}{dt} \right) \quad (1)$$

After the growth rate was determined, the Arrhenius equation could be used to correlate the affect 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 equation for the growth rate (ϵ) is as follows:

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

where A is the frequency factor (nm/sec), and R is the ideal gas constant (J/mol K.)

The natural log of Equation 2 results in the linear relationship between $\ln(\varepsilon)$ and $\left(\frac{1}{T}\right)$, as shown in Equations 3 and 4.

$$\ln(\varepsilon) = \left(-\frac{Q}{R}\right) * \left(\frac{1}{T}\right) + \ln(A) \quad (3)$$

$$y = m * x + b \quad (4)$$

Solving for the slope $\left(-\frac{Q}{R}\right)$, yields Equation 5.

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

Finally, by rearranging Equation 5, it is possible to calculate Q, as shown in Equation 6.

$$Q = \left(\frac{R * \ln\left(\frac{\varepsilon_1}{\varepsilon_2}\right)}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right) \quad (6)$$

To obtain Q and A, the data in Table 3 were used to create an Arrhenius plot. Specimens analyzed were organized by sample number (column A) and reflow temperature (columns F and G). As shown in Equation 1, the rate (column D) was calculated by dividing growth (column C) by TAL (column B).

Table 3 Collected data and calculations for Arrhenius plot. Data is grouped by reflow temperature. Highlighted columns represent the x and y axes.

Sample	TAL (s)	Growth (nm)	Rate (nm/s)	In R	Temp C	Temp K	1/T (1/K)
31	105	244.34	2.327	0.845	223	496.1	0.002016
34	150	274.99	1.833	0.606	223	496.1	0.002016
36	170	315.51	1.856	0.618	223	496.1	0.002016
49	345	341.35	0.989	-0.011	223	496.1	0.002016
50	360	338.58	0.941	-0.061	223	496.1	0.002016
54	75	241.86	3.225	1.171	227	500.1	0.002
55	90	278.38	3.093	1.129	227	500.1	0.002
56	105	259.78	2.474	0.906	227	500.1	0.002
57	120	282.25	2.352	0.855	227	500.1	0.002
76	90	218.73	2.430	0.888	230	503.1	0.001988
77	105	237.22	2.259	0.815	230	503.1	0.001988
78	120	291.37	2.428	0.887	230	503.1	0.001988
94	75	176.73	2.356	0.857	233	506.1	0.001976
95	90	272.24	3.025	1.107	233	506.1	0.001976
97	120	265.00	2.208	0.792	233	506.1	0.001976
98	135	327.34	2.425	0.886	233	506.1	0.001976
111	75	233.30	3.111	1.135	236	509.1	0.001964
112	90	315.49	3.505	1.254	236	509.1	0.001964
113	105	280.81	2.674	0.984	236	509.1	0.001964
125	60	230.87	3.848	1.347	240	513.1	0.001949
126	75	234.90	3.132	1.142	240	513.1	0.001949
127	90	257.67	2.863	1.052	240	513.1	0.001949
135	30	242.02	8.067	2.088	243	516.1	0.001938
136	45	289.87	6.441	1.863	243	516.1	0.001938
137	60	304.63	5.077	1.625	243	516.1	0.001938
138	75	250.51	3.340	1.206	243	516.1	0.001938

Rate (ϵ) is temperature dependent. Theoretically, at a constant reflow temperature the growth rate will remain the same as TAL varies. As these variations were observed, an average growth rate for each reflow temperature was used to calculate the Arrhenius plot shown in Figure 3.

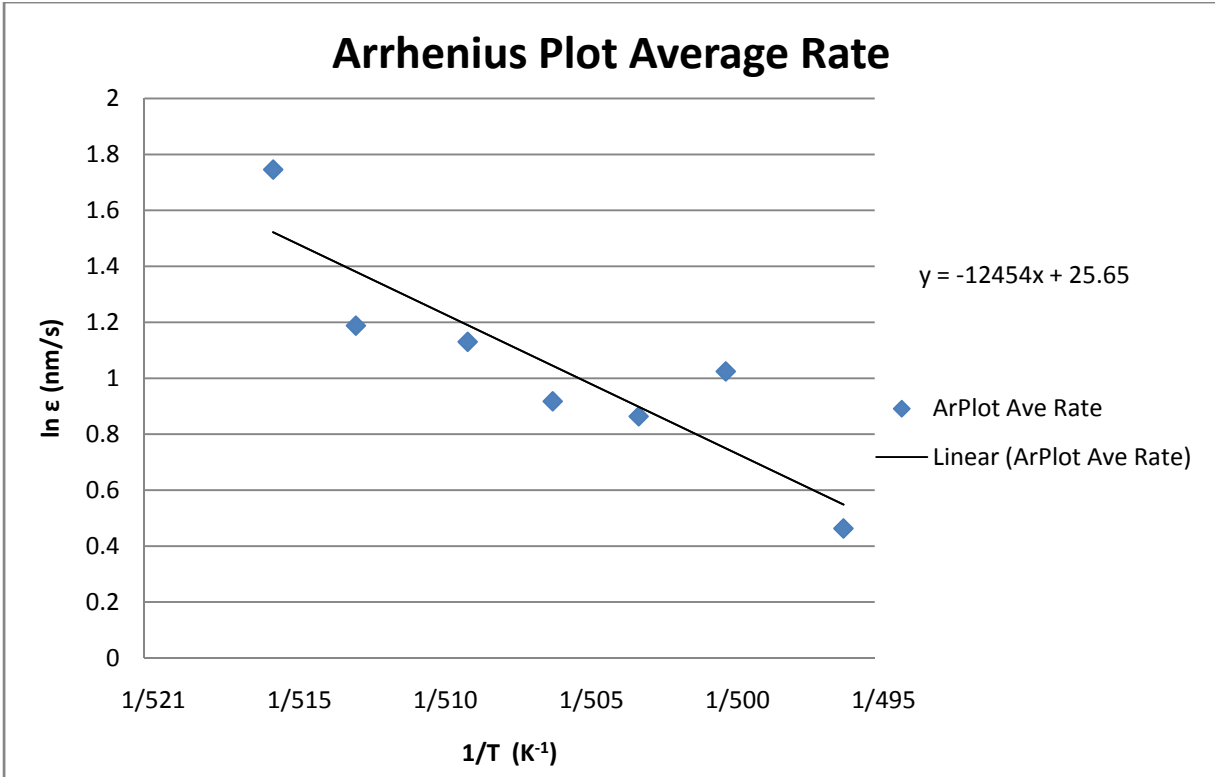


Figure 3 The Arrhenius plot was derived using data in Table 2. The equation to the right follows slope-intercept form. The slope (m) would be activation energy over the negative gas constant $\left(-\frac{Q}{R}\right)$ and the y-intercept (b) would be the frequency factor ($\ln A$).

By fitting a regression line to the data, the activation energy (Q) and the frequency factor (A) are found. 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 5 below:

$$\varepsilon = 1.38 \times 10^{11} * e^{\left(\left(-\frac{103,549}{8.314}\right) * \left(\frac{1}{T}\right)\right)} \quad (5)$$

Equation 5 correlates test parameters of reflow temperature and TAL to an estimated growth of the second layer intermetallic (Cu_3Sn_1). This research suggests that manufacturers using SAC305 solder do not exceed an intermetallic thickness of 200 nm. If a reflow temperature of 235 °C is used, it would be advisable not to remain above liquidus temperature for more than 55 to 60 seconds. This equation can only be used to approximate the intermetallic thickness that forms during solder application.

The required energy to form an intermetallic compound will be different when the solder is in a liquid phase than it is in a solid phase. Future research will determine the activation energy values necessary after solidification to form Cu_3Sn_1 when the solder is thermally aged in the solid state.

Conclusion

Several parameters, such as reflow temperature and time above liquidus (TAL,) are important factors when soldering electrical components. It was concluded that the formation of Cu_3Sn_1 phase is not independent on thermal aging. The formation of this detrimental second 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 the Arrhenius equation, the activation energy (Q) and the frequency factor (A) were determined to be 103.55 kJ/mol and A was 1.38×10^{11} nm/sec, respectively. It was determined that at a reflow temperature of 235°C manufacturers should not exceed a TAL of 55 to 60 seconds. This data pertains to the kinetics of liquidus solder on a solid copper substrate. Future studies will determine the growth rate of Cu_3Sn_1 under thermally aged solid state conditions.

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