SAND--96-1431

Distribution
Category UC-704**SAND REPORT**
SAND96-1431 UC-704
Unlimited Release
Printed June 1996**RECEIVED**

JUL 22 1996

OSTI

Final Report: High Temperature Solder Alloys for Underhood Applications

**J. A. Kern, M. W. Weiser, C. A. Drewien, F. G. Yost,
and S. Sackinger**

Prepared by Sandia National Laboratories
Albuquerque, NM 87185 and Livermore, CA 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000.

Approved for public release. Distribution is unlimited.

SF2900Q(8-81)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *BS***MASTER**

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: 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, nor any of their contractors, subcontractors, or their employees, makes 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, any agency thereof or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831

Prices available from (615) 576-8401, FTS 626-8401

Available to the public from
National Technical Information Service
US Department of Commerce
5285 Port Royal Rd
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

SAND 96-1431
Unlimited Release
Printed June 1996

Final Report: High Temperature Solder Alloys for Underhood Applications

J. A. Kern
Department of Mechanical Engineering
University of New Mexico
Albuquerque, NM 87131

C. A. Drewien, F. G. Yost, S. Sackinger
Materials and Process Sciences Center
Sandia National Laboratories
Albuquerque, NM 87185

M. W. Weiser
Johnson-Mathey Electronics Corp.
Spokane, WA 99216

Abstract

In this continued study, the microstructural evolution and peel strength as a function of thermal aging were evaluated for four Sn-Ag solders deposited on double layered Ag-Pt metallization. Additionally, activation energies for intermetallic growth over the temperature range of 134 to 190 °C were obtained through thickness measurements of the Ag-Sn intermetallic that formed at the solder-metallization interface. It was found that Bi-containing solders yielded higher activation energies for the intermetallic growth, leading to thicker intermetallic layers at 175 and 190 °C for times of 542 and 20.5 hrs, respectively, than the solders free of Bi. Complete reaction of the solder with the metallization occurred and lower peel strengths were measured on the Bi-containing solders. In all solder systems, a Ag-Sn intermetallic thickness of greater than ~7 µm contributed to lower peel strength values. The Ag-Sn binary eutectic composition and the Ag-Sn-Cu ternary eutectic composition solders yielded lower activation energies for intermetallic formation, less microstructural change with time, and higher peel strengths; these solder systems were resilient to the effects of temperatures up to 175 °C.

Accelerated isothermal aging studies provide useful criteria for recommendation of materials systems. The Sn-Ag and Sn-Ag-Cu eutectic compositions should be considered for future service life and reliability studies based upon their performance in this study.

1.0 INTRODUCTION

This study was a continuation of a cooperative research and development agreement (CRADA) with General Motors Corporation, in which Sn-Ag based solder systems including flux, metallization, and solder were screened for performance in a high temperature, under the hood application. The emphasis upon the Ag-Sn system is derived from the environmental issues surrounding the use of Pb and from the higher melting point of this system as compared to the classical Pb-Sn system. In typical operations for an under the hood environment, solder joints must survive temperatures greater than 80°C. Based upon reports in the literature,^[1-4] it is believed that solder alloys in the Ag-Sn system can fulfill this role because of the higher melting point of the Ag-Sn eutectic as compared to the Pb-Sn eutectic, higher creep resistance, higher tensile strength and ductility, better low cycle fatigue resistance, and higher impact resistance.

This present report summarizes the effects of thermal aging upon microstructural evolution and peel strength of the solder joint for the solder systems chosen through the screening study in an effort to recommend systems for service life and reliability testing. The initial study^[5] provided a screening mechanism for establishing which systems should be considered for subsequent thermal aging studies based upon processing and microstructural issues alone. Six Sn-rich solders, five Ag-rich metallizations, and four commercially available fluxing agents were screened in an experimental matrix whereby every combination was used to make sessile drops utilizing standard thermal processing techniques. The systems that allowed formation of sessile drops with contact angles of less than 30 degrees while exhibiting a fine, uniform microstructure without evidence of degradation in a humid, chlorine and sulfur containing environment were chosen for subsequent testing. In the event that the fluxing agents did not influence the sessile drop, environmentally conscious (no volatile organics or remaining debris) fluxes were chosen. Table I shows the solder systems tested and the systems selected for thermal aging studies.

TABLE I. Solder systems considered for high temperature, under the hood application.

SOLDER ALLOY	METALLIZATION	FLUXING AGENT
*Sn-Ag-Cu (SAC)	*5081/5082	RMA
*Sn-Ag-Cu-Bi (SACB)	6160	Water Soluble
*Sn-Ag-Bi (SAB)	6175	Citric
*Sn-Ag (121)	6277	*No Clean
Sn-Ag-Bi-Sb (SABSb)	7484	
Castin		
*Solder Alloys Chosen for Thermal Aging Studies	*Metallization Chosen for Thermal Aging Studies	*Fluxing Agent Chosen for Use

Based upon desirable sessile drop formation utilizing standard processing procedures, the four solders were formed on the Ag-Pt 5081/5082 metallization using a no clean flux. Isothermal aging studies were performed, and the effects of time and temperature upon the microstructure and strength of the solder system were investigated. Ultimately, the strength of the solder joint determines its usefulness, and the solder joint strength depends upon the solder and the solder/metallization joint microstructure. Microstructural changes are expected to occur as a function of time and temperature through diffusional processes between solder constituents and metallization, so the solder joint strength is also expected to change. Thus, mechanical tests to determine the influence of the thermal treatment upon the peel strength were performed. Accelerated aging tests such as isothermal aging cannot duplicate the service life of a solder joint. However, they provide one method of screening solder systems that potentially will provide the desired service life and reliability needed.

The purpose of this study was to examine the mechanical integrity of four Pb-free, Ag-rich solder systems on a Ag-Pt metallization for possible use in under the hood applications. This analysis focused on the kinetic growth rate of the intermetallic layers that formed in these systems and how the strength was ultimately affected. The parameters involved isothermally aging the systems from 134°C to 190°C.

2.0 BACKGROUND

2.1 Intermetallics

Analysis of the solder joint microstructure is important for determining the factors that lead to failure. One such entity that has the propensity of existing, changing over time, and influencing the integrity of the solder joint is the growth of intermetallic layers.

The presence of an intermetallic layer is not a strict requirement for wetting to occur, but most solders containing Sn do form intermetallics with Ag. From previous documentation in a Sn-based solder, Sn is the active component, contributing to the formation of intermetallics that act as an association between the metallization and the solder.^[6] Sn is known to have a high affinity for dissolving Cu or Ag into itself. Therefore, a system containing Sn, Cu and/or Ag will have a high probability of containing Cu-Sn and Ag-Sn intermetallics.

During soldering of Cu substrates using Sn-based solders, an intermetallic layer of Cu_6Sn_5 forms at the solder/metallization interface.^[7] Based on the Cu-Sn equilibrium phase diagram,^[8] Cu_3Sn (ϵ) should also form. However, this intermetallic has not been visible at annealing temperatures below 135°C .^[7, 9, 10] This has led researchers to conclude that Cu_3Sn is observed following high temperature annealing, only.

Similar behavior has been documented in the Ag-Sn system.^[11] In viewing a Ag-Sn equilibrium phase diagram,^[8] both the ϵ and the ζ (composition) phases should form when Sn and Ag interact. However, only the reaction phase Ag_3Sn (ϵ) is observed, even after annealing temperatures between 20°C and 170°C . Therefore, in the assessment of possible intermetallics that would appear in Sn, Ag, and Cu containing solder alloys, the Ag_3Sn , the Cu_6Sn_5 , and the Cu_3Sn intermetallics exhibit a high propensity to form.

The growth of intermetallic compounds by a diffusion controlled process is illustrated in Figure 1. The Sn must diffuse through a continuously increasing thickness of the intermetallic layer and then react with the Ag; the Ag must diffuse through the intermetallic layer to react with the Sn. The growth, therefore is limited by diffusion through the intermetallic layer.

FIGURE 1. A schematic of a diffusion controlled process with a Sn-rich solder on a Ag-rich metallization.

2.2 Joint Strength

A soldered joint is required to provide bonds sufficiently strong and durable in meeting the design life of an assembly.^[1] Microstructural analysis to detect the presence of brittle layers and/or voids in the microstructure provide important information on joint integrity. Kirkendall voids form as a result of different diffusion fluxes.^[12, 13] Other factors that result in voids are contaminants in the metallization, gas becoming trapped when the metals are molten, or shrinkage of the constituents due to solidification as the system cools.

Through mechanical testing, the influence that voids, along with microstructural coarsening, and intermetallic formation have on the mechanical properties of the solder joint are exposed. There are many forms of mechanical testing and they are all designed in attempts to simplify the actual conditions that exist during the service life of a device. Tensile strength,^[14-16] and thermal shock,^[14] tests have been documented. However, shear testing appears to be a popular means of measuring the solder joint's strength.^[17-20] The ring and plug shear,^[17, 21, 22] the double-lap shear,^[18, 22, 23] and the single-lap shear^[22, 24] are among the different ways that shear testing is performed. Shearing involves stresses that act parallel to the surfaces. It is imposed on a joint that is under thermal cycling conditions where the solder bonds of two materials with different coefficients of thermal expansion exist. When one side is heated, the joint expands more than the other; upon cooling, it contracts further than the other resulting in shear strain in the solder. This shear strain results in heterogeneous coarsening of the microstructure, where cracks form resulting in joint failure.

Some solder joints in electronic systems also experience strains that act to tear or peel them apart. Since the scope of this study is not thermal cycling, the peel test which is important in exposing a brittle interface has been chosen. There are many different geometric configuration of peel tests,^[20] but the peel tests that were explored for this study had to give strength values that were representative of a wire bonded to a solder/metallization system. DuPont^[25] defined an in-board peel test that appeared to appropriately measure the strength of a wire/solder system. It is quick and easy to perform and produces a reasonable set of results.^[26] The only concern was that the wire could be weaker than the joint, producing measured stress in breaking the wire instead of a straight forward response of a failure load as applied to the joint.^[6] Fortunately this was not the case in this study.

3.0 EXPERIMENTAL PROCEDURE

The four different Pb-free solder alloys and a single, two layer Ag-Pt metallization, 5081/5082, selected from a preliminary study^[5] were used in this project. The solders are shown in Table II, along with their varying weight percent in Sn, Ag, Cu, and Bi. These solder/metallization systems were exposed to isothermal aging after which a microstructural analysis of the intermetallic growth was completed and an in-board peel test was performed. These tests gave necessary information in determining the individual mechanical integrity of the solder/metallization systems.

TABLE II. The Sn-Ag solder alloys used in this experiment. They will be denoted by the notation in the parenthesis, hereafter.

SOLDER ALLOYS	COMPOSITION (wt%)
Sn-Ag (121)	96.5 Sn, 3.5 Ag
Sn-Ag-Cu (SAC)	93.6 Sn, 4.64 Ag, 1.76 Cu
Sn-Ag-Bi (SAB)	91.9 Sn, 3.33 Ag, 4.8 Bi
Sn-Ag-Cu-Bi (SACB)	88.9 Sn, 4.5 Ag, 1.6 Cu, 5.0 Bi

3.1 Metallization

The E.I. DuPont metallization 5081/5082, comprised of two different metallizations (weight percents of 75 Ag-7 Pt, and 79 Ag-6 Pt, respectively^[5] and will be referred to by this numerical identification, hereafter), was in the form of pastes or thick-film conductor inks. These pastes were printed onto a ceramic substrate using a patterned wire screen (325 openings per inch). Initially this mesh screen was covered with a 4 to 12 mil thick photosensitive emulsion. Using an Instant Mercury Printer this system was then exposed to a pattern via ultraviolet light. The emulsion not exposed to light was then washed off with water, leaving behind a pattern on the screen. A Presco thick film screen printer was then used to apply the thick-film ink metallization, through this patterned screen onto an alumina substrate. Squeegee blade pressure on the Presco screen printer was controlled to produce a consistent thickness of the thick-film ink while printing.

The 5081/5082 was applied as a two stage process. First metallization 5081 was screened printed, dried in a 150°C oven for 10 minutes, and fired. To bond the metallic conductor to the ceramic surface, this system was fired in a furnace, ramping the temperature for one hour to a peak temperature of 850°C for ten minutes. The same procedure was repeated again for the application of metallization 5082. When the firing had been completed on the two different metallization patterns, the substrates were stored in a container with an inert atmosphere. This prevented oxidation and sulfidation of their surfaces.

This two stage process occurred for the two different test patterns; one pattern for the specimens that would be used for the cross sectional analysis and the other pattern to be used for the in-board peel test, shown in Figure 2 and Figure 3, respectively. Figure 2 illustrates a pattern of 16 one cm squares where laser scribed lines were applied around the perimeter and through the center of each pad on the non-printed side of the substrate. These scribe marks allowed easy separation of pads to form individual aging samples. Figure 3 shows the in-board peel test pattern that consisted of 21 two mm square metallization pads; 3 pads in 7 rows. Pad sizes of two mm square were chosen to enable the wires to be kept vertical during the testing.^[26] Fourteen small markers, located at each end of a row, were used to align the wires, insuring that the wires were centered on the test pads. The center strip of pads served as a buffer when the peel test was performed, since the middle pad absorbed the tensile shock when the bond broke keeping the opposite outer pad from being affected.

FIGURE 2. The pattern used to make the aging samples. The lines designate the lines that were laser scribed onto the back of the alumina substrate used for separating the pads individually and in half.

FIGURE 3. The screen print design used for the in-board peel test. Approximately 170 ceramic boards were printed with this design to allow for testing of the four solder alloys in each time and temperature increment.

3.2 Solder

The solder, which was in the form of a paste, was comprised of solder particles and a no clean flux binder. This no clean flux was chosen because it is commonly used in industry. The 121 solder paste was purchased from Indium Corporation of America and the SAB paste was purchased from AIM (American Iron and Metal Company). The SACB and the SAC solder pastes were processed from AMES laboratory.

Aging specimens were formed with 20 ± 1 mg of solder paste individually placed onto the one cm square metallization pad. Beforehand, these solder quantities were weighed out, placed on plastic sheets, and placed in air permeable containers. Until they were ready to be used, these quantities were stored in a refrigerator at 3.3°C (38°F) to prevent the solder paste degradation by reaction of the flux with the solder. Thermal treatment to form the aging samples is described below.

For the mechanical testing samples, the solder paste was screen printed to a thickness of approximately $150\text{ }\mu\text{m}$ (6 mils) on the 2 mm square metallization pads (see Figure 3). Standard Sn-plated, 20 gauge (0.8 mm diameter) Cu wire was cleaned and hand placed across three pads as shown in Figure 4. This procedure does not follow the preparation parameters defined by DuPont, where solder baths were used to coat the metallizations. Instead, screen printing of the solder was chosen, because it offered a consistent thermal processing of the system, and a constant volume application of the solder, i.e., a volume that did not depend on the straightness of the wire. It was anticipated that the stress distribution in the wire/solder/metallization assembly would be quite reproducible, due to the constant thickness of solder and controlled thermal history.

FIGURE 4. Placement of the Cu-Sn wire on the metallization pads.

3.3 Reflow Heat Treatment

A Heller 988C reflow oven was used to reflow all samples. This oven consisted of four inert atmosphere convection heated zones and two infrared panels where the temperatures could be programmed for a desired profile. Compressed nitrogen, stored in cylinders, was used to keep the atmosphere inside the oven inert, the infrared panels clean, and to reduce the effects of oxidation of the molten solder. A motor/gear driven conveyor belt moved the samples through the heated zones of the reflow oven at designated speeds.

The cooling rate determines the initial solder microstructure. The faster cooling rate allows less time for diffusion to occur, resulting in a finer microstructure. The preliminary study^[5] showed that microstructural differences existed between the two heat treatments; the hot plate microstructure versus the reflow oven microstructure. The hot plate produced a finer eutectic microstructure of Ag_3Sn and Sn. It was clear that the finer microstructure was a result of the rapid cooling rate experienced by the solder during the thermal processing.

To achieve a finer microstructure a faster cooling rate temperature profile was made for the reflow oven. This involved increasing the belt speed from 25 cm per minute to 35 cm per minute while keeping the time above the liquidus temperature of the 121 solder alloy (221°C), at 68 seconds. This new temperature profile is shown in Figure 5. Performing this change in the profile proved to be a success. This can be seen when comparing microstructures resulting from the old temperature profile shown in Figure 6, and the new temperature profile used in the reflow oven, shown in Figure 7. Here the microstructure is seen to be fine and homogenous. Both of these figures show the 121 reflowed on metallization, 5081/5082.

FIGURE 5. Temperature profile for the Heller reflow oven. The saturation time (SAT) denotes the time that the solder/metallization system was above 221°C.

To reduce the variation in the sample preparation, the preceding temperature profile was used, to reflow both the aging samples and the in-board peel test samples for all four alloys.

FIGURE 6. The 121 has been reflowed on the 5081/5082 metallization using the reflow oven resulting in a coarse microstructure.

FIGURE 7. The fine, homogeneous microstructure of Indalloy 121 is indicative of a faster cooling rate.

3.4 Isothermal Aging

Accelerated aging tests were constructed to simulate a period of natural aging in an under the hood environment. These tests consisted of five different temperatures with eight different time intervals. The parameters were selected based on previous data and the Arrhenius equation, shown in equation (1)

$$x(t, T) = x_o + At^n e^{-Q/RT} \quad (1)$$

where t is the time, T is the temperature (Kelvin), A is a constant, Q is the activation energy, and n is the empirical power-law constant. Previous aging of intermetallics has been performed on Sn-Ag (100% Sn and 100% Ag) systems,^[27] using equation (1). This study covered a temperature range from 20°C to 170°C, using a multivariable regression to determine the values of A , n , and Q . In order to effectively examine the growth process at both high and low temperatures in accelerated isothermal aging conditions, these values were used to design this experiment. These parameters are shown in Table III for Sn-plated on Ag.

TABLE III. Values that were used in equation (1), to design the isothermal aging experiment.^[27]

Parameters		Units
A	8.62×10^3	$\mu\text{m}/t^n$ (time in days)
n	0.416	dimensionless
Q	28.31	KJ/mol

Since the under hood temperatures in automobiles range from 150 to 180°C, a median temperature of 160°C was chosen. A maximum time of 1,000 hours with the minimum time of 2 hours (which equated to 0.2% of the maximum time), was selected using the temperature of 160°C. Rearranging equation (1) to give equation (2) gave a growth formula that could be applied to other temperatures giving corresponding maximum aging times.

$$\frac{x - x_o}{A} = t^n e^{-Q/RT} \quad (2)$$

Four other aging temperatures, 134°C, 146°C, 175°C, and 190°C were chosen so that they were distributed evenly in terms of $1/T$ (Kelvin). The annealing time periods are distributed uniformly in terms of $\ln(t)$ and are listed for all of the temperatures in Table IV ranging from .6 hour to 3,401 hours.

TABLE IV. Different aging temperatures and their corresponding time intervals. There are five different temperatures, each with eight time intervals.

TEMPERATURE	134 °C	146 °C	160 °C	175 °C	190 °C
TIME	Hours	Hours	Hours	Hours	Hours
1	6.8	3.7	2	1.1	.6
2	16.5	9	4.9	2.6	1.4
3	40.2	21.8	11.8	6.4	3.5
4	97.6	53	28.7	15.6	8.4
5	237	128.6	69.7	37.8	20.5
6	576	312.4	169.4	91.9	49.8
7	1400	759	411.6	223.2	121
8	3401	1844	1000	542.2	294

Three different ovens were used to perform the accelerated isothermal aging: a Hot Pack, a Blue M, and a Lindberg. The latter two were computer controlled which allowed the ovens to be programmed to a desired profile; however, only one temperature could be obtained for the oven compartment at any given time. The Hot Pack and Blue M ovens were of the forced convection type while the Lindberg was natural convection.

The Hot Pack, which was not computer controlled, was used for the 134°C temperature tests. The 146°C and 190°C temperatures were performed in the Blue M, while the other aging temperatures, 160°C and 175°C, were achieved in the Lindberg. To ensure that the temperatures were calibrated to within $\pm 3^\circ\text{C}$ between the three ovens, a portable thermocouple was used.

During both aging cycles, the 134°C and the 146°C temperature intervals, power failure occurred in the ovens, using the Hot Pack and the Blue M, respectively. The Hot Pack, operating at 134°C lost its power due to a blown fuse. This occurred after the sixth time increment (576 hours) for approximately one to three days; the exact duration is unknown. The Blue M operating at 146°C lost its power due to a power outage in the building. This happened approximately 75 hours into the fifth time interval of 128.5

hours. The duration of power loss was approximately four hours. However, the percentage of time lost in either oven was small when compared to the total time at the aging temperature: two percent lost time in the Hot Pack and less than one percent lost time in the Blue M. Therefore, these interruptions should have minimal effect on the results.

4.5 In-board Peel Test

The mechanical testing was performed using a modification of the in-board peel test specified by DuPont,^[25] which is believed to represent a realistic failure mode that is similar to failures occurring in hybrid microcircuits.^[28]

The test apparatus consisted of two sections: grips that maintained the position of the wire and a slotted holder that maintained the stability of the alumina substrate during the peel test. Both items were made out of 3031 aluminum and 1040 steel. These dimensions are shown the Appendix. The section that held the wire during a peel test was mounted to a Interface load cell (Model #: SM-50; 50 pound maximum load) and the slotted holder was positioned onto an actuator situated in a computer controlled MTS load frame (closed loop system for mechanical testing of materials and structures, MTS Systems Corp., Model #: 661.234-01). The vertical displacement of the actuator was measured by an LVDT (linear-variable differential transformer). This setup is shown in Figure 8.

After the specific aging had been performed on a sample, the wires on the mechanical testing boards were bent up 90° using a fixture to control the location of the bend, as shown in Figure 9. The substrate was then inserted into the slot of the substrate holder, shown in Figure 8. This holder was critical in supplying support for the substrate so that the substrate itself did not fracture during the in-board peel test. Each wire was individually pulled at a rate of 3.81 cm per minute, in a direction normal to the plane of the substrate (see Figure 10). The in-board peel test program was set to acquire data every second. When a distance of 0.3 cm had been reached, the LVDT stopped the peel test. This distance guaranteed failure of the bond between the wire and the solder pad, since the diameter of the wire was 0.8 mm and the approximate thickness of the solder was 150 μ m. The actuator then held that position for 10 seconds, while the

FIGURE 8. Schematic set up of the in-board peel test using a MTS loading frame.

wire was manually released. The actuator then returned to its original starting position, which insured that the end of the wires were gripped at exactly the same point every time to prevent any deviation in the length of the moment arm.^[28] A total of fourteen load failure values were obtained from each solder/metallization system for each time at a given aging temperature unless some of the joints had failed during isothermal aging.

FIGURE 9. The apparatus used for controlling the location of the 90° bend on the wires.

FIGURE 10. A schematic drawing of the in-board peel test on one 2 mm square metallization pad. Redrawn from the DuPont test document.^[25]

3.6 Measurement of Intermetallic Growth

The measurement of the intermetallic growth was performed on a micrograph containing a cross sectional view of the solder/metallization system. This view was obtained by the sectioning of the aged solder/metallization systems along the laser scribed line on the alumina substrate into two segments. Each of the segments were cold mounted in alumina (Al_2O_3) filled Castolite epoxy and polished on a $20\mu\text{m}$ fixed diamond wheel. They were then polished with $6\mu\text{m}$ and $1\mu\text{m}$ Metadi diamond paste using Buehler's Metadi extender on a nylon cloth. Secondary and back-scattered electron images were obtained on the polished surface using a JEOL 6400 scanning electron microscope (SEM).

From these micrographs, the intermetallic thickness in the image was measured in mm with a resolution of 0.5 mm and converted into the actual thickness in μm based upon the magnification of the micrograph. A total of thirty measurements were taken at random locations along the interface for each sample at each time and temperature increment. Using the method of least-squares^[29] a multivariable regression analysis was performed on this data using equation (1). A general model of this regression is shown in equation (3)

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \quad (3)$$

where Y is the dependent variable (intermetallic growth), β_0 is the intercept, x_1 and x_2 are the independent variables (temperature and time), β_1 and β_2 are the unknown coefficients, and ϵ is the random error term that is added to allow for deviation between the dependent and independent part of the model.

Due to the computational difficulty of fitting data to a multivariable regression model, a computer package worksheet, EXCEL^[30] was used. This enabled the ease in determining the values of the unknown coefficients A , n , and Q ; the intercept and values of β_1 and β_2 , respectively. Prediction of the intermetallic growth rate of each solder alloy was then possible once these parameters were calculated.

4.0 RESULTS

4.1 Intermetallic Growth

In conducting the isothermal aging only four of the eight time increment samples from the five temperatures were examined due to limited financial resources. In the temperatures 134°C, 160°C, and 190°C, the odd numbered time increments (times 1, 3, 5, and 7) were analyzed. For the remaining temperatures, 146°C and 175°C, the even numbered time increments (times 2, 4, 6, and 8) were analyzed.

While examining the micrographs obtained from the cross sectional views of the solder/metallization systems, an intermetallic layer was visible for all of the different temperature and time conditions. This layer was also apparent in the as-soldered condition, where no isothermal aging had been performed. Figure 11 is a schematic of the typical behavior that was exhibited as a solder/metallization system isothermally aged; from the initial as-soldered state (without aging) to the final aged state. The intermetallic and the metallization systems have a jagged interface that runs parallel to the substrate. As the aging time and temperature increased, this intermetallic layer observed to increase in thickness. In severe cases, the complete reaction of the solder with the metallization occurred leaving behind only an intermetallic layer where the metallization originally existed.

FIGURE 11. A typical progression of intermetallic growth from a) the as-soldered condition, $t = 0$, showing precipitates, voids, and an intermetallic layer, b) the solder/metallization after exposure to some time and temperature duration, $t > 0$, showing the coarsening of the voids and increase of intermetallic growth, and c) the solder/metallization having been exposed to a long time and temperature condition, $t \gg 0$, showing a significant increase of the intermetallic thickness.

Voids apparent at the interfacial regions of the intermetallic layer and metallization were assumed to be Kirkendall vacancies. Other voids could be seen in the as-soldered condition throughout the metallization and the intermetallic/metallization interface. As the aging continued on any one solder/metallization system, these voids appeared to grow and coarsen. Small colonies of precipitates could also be seen in the solder itself with varying composition of elements that were dependent on the type of solder used.

In the following four sections, the microstructure of the four solder alloys will be discussed. Note that this analysis did not cover the compositional study of the microstructure of the sessile drop or the intermetallics that formed. Therefore, the constituents of the solder microstructure and intermetallics are identified based upon

limited compositional studies. This is justified by the limited number of phases and relatively unique backscattered images that they produce.

4.1.1. Sn-Ag (121)

The 121 solder, shown in Figure 12, alloy had a fine-grained microstructure. Grains of Sn are surrounded by Ag_3Sn near the metallization. Voids are apparent at the intermetallic/metallization interface and throughout the metallization. The intermetallic layer that was measured is assumed to be comprised of Ag_3Sn .

Previously, a Pt-Sn phase containing traces of Ag was observed in this system.^[5] The compositional analysis of this phase indicated a stoichiometry near PtSn_7 . In the binary equilibrium Pt-Sn phase diagram, no such phase has been identified; so this phase may be metastable. No attempt was made to determine the presence of this phase in the as-deposited or aged microstructures.

Upon examination of the metallization over all the time and temperature increments, the metallization was still identifiable even at the highest temperature, 190°C . This is shown in Figure 13 and Figure 14, where the metallization is visible after one hour and 121 hours of aging at 190°C , respectively. From the observations of the aged samples, there appeared to be no visible coarsening of the microstructure or voids.

4.1.2 Sn-Ag-Cu (SAC)

The SAC solder alloy also exhibited a fine grained microstructure. In Figure 15, large primary Ag_3Sn , coarse eutectic Sn (light gray), and Cu_6Sn_5 (dark structures) can be seen. A layer of large grains of Ag_3Sn is present on top of the metallization. Voids throughout and along the interface of the metallization are also seen and they are observed to coarsen over time at a given temperature.

FIGURE 12. A cross sectional view of the 121 solder alloy in the as-soldered condition.

FIGURE 13. A micrograph showing the cross sectional view of the 121 solder alloy isothermally aged for one hour at 190°C.

FIGURE 14. A micrograph showing the cross sectional view of the 121 isothermally aged for 121 hours at 190°C. The metallization is still apparent.

FIGURE 15. A cross sectional view of the SAC solder alloy in the as-soldered condition.

The average intermetallic thickness ranged from 3.4 to 25.1 μm , where the latter value was obtained in the 190°C temperature at 121 hours. In this sample, the metallization had been completely consumed by the intermetallic growth. This is shown in Figure 16.

4.1.3 Sn-Ag-Bi (SAB)

The microstructure of the SAB shows small round white regions that are essentially pure Bi, as seen in Figure 17. It is believed that during cooling, this Bi precipitated in the solder matrix. The Sn-Ag eutectic is surrounded by primary Sn and Bi phases. Close to the metallization, large grains of Ag_3Sn form a continuous layer over the metallization. Voids in the metallization and its interface with the intermetallic layer are visible and appear to coarsen as time and temperature increase.

The SAB caused a total reaction of the metallization in the 175°C temperature cycle, unlike the SAC where a total reaction of the metallization by the intermetallic growth occurred in the 190°C temperature cycle. Figure 18 shows the SAB after 2.6 hours at 175°C where the metallization is visible. Figure 19 shows the SAB at the end of the 175°C aging temperature, 542 hours, where the metallization is no longer apparent and only the intermetallic layer can be seen. Again, as seen with the SAC after high temperatures and extended time, the SAB microstructure coarsened.

4.1.4 Sn-Ag-Cu-Bi (SACB)

The microstructure of the SACB, shown in Figure 20, is similar to the microstructure of the SAB solder alloy where the same small round white regions of Bi can be seen. The large dark regions in the microstructure are primary Cu_6Sn_5 . Below the Sn-rich region there is a layer of large Ag_3Sn grains near the remaining metallization. Voids are visible in the intermetallic layer, intermetallic/metallization interface, and solder matrix. These voids and the solder microstructure appear to coarsen with time and temperature.

Total reaction of the metallization into the intermetallic growth also occurred in the 175°C temperature range, which was similar behavior to the other solder alloy containing Bi, SAB. Figures 21 and 22 show the observation of the visible metallization after 92 hours at 175°C and then the total reaction of the metallization into intermetallic growth, 450 hours later at 175°C, respectively. Visible in Figure 22, is a dark region at the interface of the solder matrix and the intermetallic layer. This formation is assumed to be the Cu_6Sn_5 intermetallic.

FIGURE 16. The metallization in the cross sectional view of the SAC was fully consumed. This sample was aged for 121 hours at 190°C.

FIGURE 17. A cross sectional view of the SAB solder alloy in the as-soldered condition.

FIGURE 18. A micrograph showing the cross sectional view of the SAB isothermally aged for 2.6 hours at 175°C.

FIGURE 19. A micrograph of the SAB aged for 542 hours at 175°C. Complete dissolution of the metallization has occurred and only the intermetallic layer is present.

FIGURE 20. A micrograph showing the cross sectional view of the SACB solder alloy in the as-soldered condition.

FIGURE 21. A cross sectional view of the SACB solder alloy aged at 175°C for 92 hours. The metallization is still visible beneath the intermetallic layer.

FIGURE 22. A micrograph showing the cross section of the SACB solder alloy aged at 175°C for 542 hours. The metallization is no longer visible and only the intermetallic layer, Ag_3Sn , is seen.

4.1.5 Intermetallic Growth Discussion

The interface of the intermetallic between the solder matrix and the metallization was rough and non-uniform; therefore, measuring the intermetallic thickness was not a straight forward process. Large voids were visible at the interface of the intermetallic and metallization with smaller voids, in comparison, throughout the microstructure. When measuring the intermetallic layer, these small voids were included, but the voids present at the interface were not and an effort was made to avoid these areas. It was assumed that a variety of intermetallics existed, but a compositional analysis was not performed to confirm this. However, it was assumed that most of the intermetallic layer was comprised of the Ag_3Sn intermetallic. Cu_6Sn_5 intermetallics were also present if the solder alloy contained Cu; therefore, the Cu-based intermetallic was included in these measurements and not viewed as a separate entity. The data appears in Table V. The measured values where total reaction of the metallization occurred are denoted by shading. The x_0 values, also shown in Table V, are the averages calculated the as-soldered states of the four solder alloys.

At the onset of any one aging cycle, the intermetallic layers x_0 measured between 2.2 to 3.1 μm thick. In the higher temperatures, 175°C and 190°C, towards the end of these aging cycles, it was found that in most of the Pb-free solders (except for the Indalloy 121), the metallization had completely reacted. Occurring at a faster rate as the temperature increased, this complete reaction gave a 21.6 to 26 μm thick layer of intermetallic.

The data that were obtained on the samples that involved total reaction of the metallization were included in the multivariable regression analysis. These data points held statistical significance for the constants used in predicting the growth rate of the overall system. Using the t statistic it was found that all the coefficients determined were highly significant (94.6% and greater).

In performing the multivariable regression analysis, values for the unknown coefficients of equation (1) were found for each of the solder alloys the 121, SAC, SAB, and SACB: the pre-exponential constant, A, the time exponent, n, and the apparent activation energy, Q, ranging from 0.7×10^8 to $1.9 \times 10^8 \mu\text{m}/\text{t}^n$ (time in hours), 0.26 to 0.48, and 27.6 to 88.5 kJ/mol, respectively. The multiple correlation coefficient, R^2 was used to determine the adequacy of the regression model; a perfect fit occurring when R^2 equals 1.0. For this analysis the R^2 values ranged from 0.72 to 0.84. The value of the unknown constants found through regression, their t-statistics, and the values calculated for R^2 are summarized in Table VI.

TABLE V. Average thickness values of the 30 total intermetallic thickness measurements that were obtained for each solder alloy after the accelerated isothermal aging. The shaded values denote the situation involving complete reaction of the metallization. Average thickness values determined from the as-soldered conditions of each solder alloy is noted by x_0 .

TEMP (°C)	TIME (hrs)	121	SAC	SAB	SACB
		MEAN THICKNESS			
		(μm)			
x_0	0	2.2 ± 0.8	3.0 ± 1.2	2.2 ± 1.1	3.1 ± 1.8
134	6.8	2.8 ± 0.8	3.4 ± 1.3	2.6 ± 0.9	3.3 ± 1.5
	40.2	6.3 ± 0.9	4.5 ± 1.8	4.5 ± 0.9	5.4 ± 1.1
	237.1	4.7 ± 1.1	5.5 ± 2	4.4 ± 0.8	5.4 ± 1.9
	1400	7.1 ± 1.4	6.7 ± 1.6	6.9 ± 1.1	7.3 ± 1.7
146	8.9	4.4 ± 1.1	4.6 ± 1.7	4.5 ± 1.1	3.8 ± 1.9
	52.9	4.4 ± 1.3	5.3 ± 1.4	5.3 ± 1.1	4.5 ± 1
	312.4	6.1 ± 1.4	5.9 ± 1.4	6.2 ± 0.9	6.7 ± 1.3
	1844	9.6 ± 1.8	8.6 ± 1.6	10.8 ± 2.5	9.9 ± 1.6
160	2.0	3.5 ± 1.4	4.3 ± 1.1	4 ± 1.3	3.9 ± 2.4
	11.8	3.9 ± 0.9	3.8 ± 0.9	4.9 ± 1.2	4.8 ± 1
	69.7	5.2 ± 1.3	5.3 ± 1.5	5.9 ± 1.2	4.9 ± 1.3
	411.6	5.6 ± 1.8	5.3 ± 1.5	7 ± 1.4	7.5 ± 1.5
175	2.6	4.3 ± 1.4	4 ± 1.7	3.9 ± 1.2	4.5 ± 1.5
	15.6	4.9 ± 1.7	5.7 ± 1.9	5.5 ± 1.4	6.1 ± 1.8
	91.8	5.7 ± 1.5	7.4 ± 6.8	8.6 ± 3.4	8 ± 2
	542.2	7.2 ± 2.3	7.8 ± 2.4	25.2 ± 3.3	23.5 ± 2.5
190	1.0	3 ± 1.2	4.5 ± 1.6	3.9 ± 1.3	4.5 ± 2.1
	3.5	4.3 ± 0.8	5.2 ± 1.4	6.6 ± 1.5	6.5 ± 1.8
	20.5	6.7 ± 1	6.9 ± 1.7	21.6 ± 2.9	24.7 ± 1.6
	121	15.3 ± 2.2	25.1 ± 2.7	23.8 ± 3.6	26.3 ± 3

TABLE VI. Values that were obtained for A, n, and Q in a regression analysis performed on the data obtained from the four solder alloys during the accelerated aging environment.

Constants	121	t statistic	SAC	t statistic
A ($\times 10^8 \mu\text{m}/\text{t}^n$)	0.6 ± 0.2	96.5%	1.2 ± 0.2	95.2%
n	0.26 ± 0.04	93.4%	0.31 ± 0.05	95.0%
Q(kJ/mol)	27.6 ± 8.3	96.7%	52.3 ± 10.8	94.1%
R ²	0.73		0.72	
Constants	SAB	t statistic	SACB	t statistic
A ($\times 10^8 \mu\text{m}/\text{t}^n$)	1.7 ± 0.2	92.2%	1.9 ± 0.3	93.5%
n	0.36 ± 0.04	92.0%	0.48 ± 0.08	94.5%
Q(kJ/mol)	71.0 ± 9.4	92.4%	88.5 ± 13.6	93.5%
R ²	0.84		0.84	

These values were then substituted into equation (1) to obtain a model predicting the kinetic growth rate of the intermetallic layer. A trend was seen with the four solder alloys when the average raw data values were compared to the predicted values from the regression analysis. This is shown on a log-log plot in Figure 23 with the SAC solder. Deviation can be seen in the higher temperature 160°C, 175°C, and especially at 190°C.

FIGURE 23. A log-log plot of SAC, showing the intermetallic growth, in μm , at the five different aging temperatures. The symbols represent the average of the raw data obtained and the lines show the predicted regression model.

The values in Table VI found from the regression corresponded well to the growth behavior that was evident at the 160°C temperatures for each solder alloy. The solder alloys containing Bi, had higher values of A, n, and Q and were characterized by the high growth rate of intermetallics. In comparison to the other alloys, the SAC solder had a slower growth rate mechanism, while SACB had a faster intermetallic growth rate. This behavior is portrayed in Figure 24, where a comparison is made between the four solder alloys' raw values obtained in measuring the growth intermetallics for the 160°C temperature.

Upon further observation at this temperature at 160°C, the SAB, the SAC, and the 121 show a subparabolic growth. Without more data measurements, it is impossible to determine, based on one data point, why the SACB did not exhibit subparabolic growth at this temperature. Perhaps a different mechanism was present, or there was experimental error, because this behavior of the SACB was not apparent in the other temperatures.

FIGURE 24. A comparison of intermetallic growth, in μm , is shown between the four solder alloys in the 160°C temperature cycle using the raw measurement values.

In analyzing solid-state growth (intermetallic), three types can be identified, based on the values that are found through regression for the time exponent, n: i) linear growth kinetics where $n = 1$, ii) parabolic growth kinetics where $n = 0.5$, and iii) subparabolic growth where $n < 0.5$. Parabolic growth kinetics are a result of bulk diffusion, while subparabolic growth has an inclination of exhibiting formation of more than one intermetallic compound.^[27]

The intermetallic growth proved to be non-linear from the n values obtained from the regression model. These values indicated subparabolic controlled kinetics growth ($n < 0.5$), where the growth is assumed to be composed of more than one intermetallic compound growing in solid state. In the two alloys containing Cu, SAC and SACB, the possible intermetallics could be Cu_6Sn_5 , Ag_3Sn , or Cu_3Sn . The Cu-Bi phase equilibrium diagram^[8] shows that an intermetallic phase does not exist between the Bi and the Cu. However, a metastable compound Cu_5Bi_2 has been reported.^[31] In SAB and the 121 it is uncertain at this time, other than the Ag_3Sn intermetallic compound, what other intermetallics exist; it was not determined if another intermetallic phase was present. Nevertheless, recalling from the preliminary study, a non-equilibrium phase of PtSn_7 was found in this Sn-Ag solder alloy joined to a Ag-Pt metallization.

The regression model produced activation energies that varied by a factor of 3.2 between the four different solder alloys. This type of difference is fully expected to result in a change in the growth rate as the temperature increases. In general the alloys with a high activation energy would be expected to grow slower at low temperatures and faster at high temperatures compared to those with a low activation energy. This trend is shown in Figure 25, where the 121 solder having a low activation energy value exhibits a faster growth rate at lower temperatures while the SACB, having a high activation energy value is seen to have a slow rate of intermetallic growth at the lower temperatures. These activation energies were plotted using the Arrhenius equation while keeping time constant at 100 hours.

FIGURE 25. A comparison of activation energies (kJ/mol), is shown between the four solder alloys keeping the time constant at 100 hours.

In performing the regression analysis, 121 yielded an activation energy of 27.6 kJ/mol. This agrees with another study reporting an activation energy of 28.3 kJ/mol in which Sn-Ag was annealed on Cu substrates and aged in an air furnace at constant temperatures.^[32]

For the SAC solder alloy the regression analysis yielded an activation energy of 52.3 kJ/mol. This value corresponds with a similar study where the combined activation energy for the Ag-Sn-Cu-interfacial intermetallics was 59 kJ/mol.^[10] The isothermal aging was performed in air furnaces with temperatures ranging from 70°C to 205°C. Both the Cu_6Sn_5 and Ag_3Sn intermetallics were present, but the Cu_3Sn was only observed at annealing temperatures above 170°C.

A literature review was performed to find documentation on activation energies involving the SAB, and SACB solder alloys, annealed in a similar fashion, but was unsuccessful. In comparison to the 121 and the SAC solder alloys that did not contain Bi, the SAB and the SACB solders yielded the highest activation energy. Why does the addition of Bi appear to boost the activation energy? At present, intermetallics that contain Bi have not been identified and there is belief that Bi will not readily combine to form compounds, because it seems to precipitate out of the solder matrix. An answer arises from the fact that the Bi lowers the melting point of a system, increasing the activation energy. Activation energy is defined as the minimum energy needed to form products from the reactants. Perhaps in exploring this further it can be determined that the Bi works as a catalyst in the formation of the intermetallic compounds. With this increase of energy added to the system, the fraction of atomic mobility collisions increase leading to more reactions that form the intermetallics.

The activation energy is weakly temperature dependent;^[33] lower melting temperatures induce higher activation energies (in an extreme case an activation energy of zero indicates that the process is independent of temperature). Therefore, the activation energy can be varied when different alloys, melting at different temperatures, are combined. This dependence between the melting point and the activation energy was apparent in these four solder alloys. The 121 solder had a melting point at 221°C, the highest out of the four solders, and yielded the lowest activation energy. Likewise the SACB and the SAB, with melting points at 208°C and 211°C, respectively, had the highest activation energies, the SACB yielding the highest value.

In summary, the activation energies obtained through the regression analysis clearly demonstrate that solder alloy composition contributes to the apparent intermetallic growth rate. The 121 solder, consisting of only Ag and Sn, had the propensity to only form the Ag_3Sn intermetallic. Due to the limited solubility of Ag into Sn,^[10] the apparent growth rate of this intermetallic was lower when compared to solders containing Cu and/or Bi. It is evident that the Cu and especially the Bi that was added to the solder matrix increased the sensitivity of the intermetallic growth rate.

4.2 In-board Peel Test

Failure of the solder joint was achieved when the initial separation of the wire from the solder/metallization pad occurred. In assessing the collected values from each peel test, the maximum strength value (also known as the point of maximum stress or ultimate strength of the joint) obtained in a run was used as defining the system inoperable. This value represented the force that was required to completely detach a wire from the solder/metallization pad. Subsequent lower strength values from that maximum value signified the pulling on a wire that was no longer attached to the system.

A typical peel test is shown in Figure 26 performed on SAB aged for 128 hours at 145°C. An observation was made that the joint was weaker than the wire, because there was no deformation of the wire as the peel test was performed; therefore, the data collected described the properties of the joint and not the wire.

FIGURE 26. A typical peel test that was obtained on all the four solder alloys. This represents the data that was obtained on SAB aged for 128 hours at 145°C.

Different properties existed between the solder, the intermetallic layer, the Cu-Sn wire, and the metallization; therefore, an assumption was made that the failure occurred by joint fracture along or through the intermetallic layer interface at the metallization or solder matrix. However, this was not verified. Failure could also have occurred along the surface area of the wire where intermetallic layers could have formed. There is documentation stating that failure results from the formation of shrinkage voids, which divert the fracture path away from the intermetallic/solder interface and into the solder itself.^[34] Other studies have indicated that if the intermetallic layer is thin, fracturing will occur through the solder.^[35]

At the onset of the in-board peel test, it was anticipated that a total of 14 failure values would be obtained for each solder/metallization system from each time in a given temperature; however this was not the case. Factors that contributed to lost data were: i) improperly bending the wire at 90°, causing the wire to crumple, ii) improper insertion of the alumina substrate into the holder, causing the substrate to fracture, iii) human error in operating the load frame, and iv) degeneration of the solder/metallization joint, resulting in the wires detaching from the solder pad. Except for the Indalloy 121 solder, all the other Pb-free solder pads did not maintain the adhesion of their wires in the 190°C increment. The two solders that contained Bi had lost most of their wires after 50 hours (the wires were no longer attached to the solder pads), and lost all their wires after 294 hours. This would indicate that the metallization was completely dissolved resulting in a nonexistent bond between the wire and the board. Table VII summarizes the average strength value for a set of data for each solder alloy at a time and temperature increment. The actual number of data points that were obtained from the anticipated 14 values is denoted by the italicized font located in the shaded columns.

Although the in-board peel tests were well controlled, much deviation in the measured values existed. Some of these deviations could be explained by the uneven solder thickness when it was screen printed due to the consistency of the solder paste, or the alignment of the wire not being centered on the pad. Other factors to consider were the apparent jagged and uneven thickness of the intermetallic layer, and voids that were possibly present at the interfacial regions of the solder and/or the metallization.

Nonetheless, there were obvious trends that were observed with the solder alloys, except for the 121. The average values calculated from the 121's data sets obtained from the in-board peel test at each temperature and time cycle ranged from 23.1 to 26.3 N. A decreased strength was seen in the 190°C temperature, 17.3 N. However, since complete reaction of the metallization did not occur with the 121 solder and coarsening of the microstructure was not visible, the reason for this lower strength is not apparent.

At the end of an aging cycle at 134°C, 146°C, and 175°C, the SAC maintained a constant strength value of approximately 20.5 N. However, at the end of the 190°C temperature cycle a 40% decrease in strength, from the initial strength of 20.3 N, was seen. This decreased strength would appear to be dependent on the total reaction of the metallization that was evident at this temperature.

The Bi-containing solders exhibited a similar strength degradation behavior. The SAB and the SACB kept a constant strength of approximately $18.6 \text{ N} \pm 1.4 \text{ N}$ and $16.1 \text{ N} \pm 1.1 \text{ N}$, respectively, for the 134°C, the 146°C, and the 160°C temperatures. However, by the end of the aging cycle of 190°C, the strengths of the SAB and the SACB decreased to $3.6 \text{ N} \pm 1.6$ and $2.1 \pm 2.4 \text{ N}$, respectively. This behavior is illustrated in Figure 27, where comparison is made on SAB between the 160°C and the 190°C temperatures. The

extreme decrease in strength at 190°C is characteristic of two different stages of strength degradation occurring.

In comparison between the four solder alloys, a repeating behavior was seen at any given temperature, over the eight different time intervals. A representative example of this trend is shown in Figure 28, where the SAB and the SACB produced lower values of strength when compared to the other solder alloys, SAC and 121, for the 146°C temperature. Between the average strengths of the SAB and the SACB, the SAB was 13% stronger; between the SAC and the 121, the 121 was 14% stronger.

TABLE VII. The average values calculated from data sets obtained from the in-board peel test on the four solder alloys are summarized below. The number of data points in each set is denoted by the italicized font in the shaded columns (*).

TEMP (°C)	TIME (hrs)	AVERAGE STRENGTH (NEWTONS)							
		*	121	*	SAC	*	SAB	*	SACB
	0.0	<i>14</i>	22.1 ± 2.3	<i>14</i>	20.3 ± 1.8	<i>13</i>	17.7 ± 2.1	<i>14</i>	15.6 ± 0.9
134	6.8	<i>14</i>	24.5 ± 3.9	<i>14</i>	20.1 ± 3.6	<i>11</i>	20.2 ± 2.1	<i>14</i>	15.9 ± 2.2
	16.5	<i>14</i>	21.3 ± 3.3	<i>13</i>	22.3 ± 4.3	<i>14</i>	18.2 ± 2.6	<i>14</i>	15.9 ± 1.9
	40.2	<i>14</i>	23.7 ± 3.8	<i>14</i>	22.1 ± 2.8	<i>14</i>	17.9 ± 1.9	<i>14</i>	16.1 ± 1.0
	97.6	<i>14</i>	25.6 ± 3.6	<i>14</i>	26.1 ± 2.9	<i>14</i>	17.6 ± 2.1	<i>14</i>	17.4 ± 2.2
	237.1	<i>14</i>	25.2 ± 4.9	<i>14</i>	23.5 ± 2.6	<i>14</i>	17.0 ± 2.7	<i>14</i>	16.1 ± 2.9
	576.1	<i>14</i>	29.0 ± 6.2	<i>14</i>	22.8 ± 2.3	<i>14</i>	18.8 ± 2.5	<i>14</i>	15.6 ± 1.9
	1400	<i>14</i>	24.7 ± 3.3	<i>14</i>	21.9 ± 2.1	0		<i>14</i>	16.7 ± 2.3
	3401	<i>14</i>	24.8 ± 2.9	<i>14</i>	20.6 ± 2.0	<i>14</i>	19.4 ± 4.3	<i>14</i>	15.7 ± 2.6
146	3.7	<i>14</i>	24.6 ± 6.3	<i>12</i>	19.9 ± 2.3	<i>14</i>	17.8 ± 2.5	<i>14</i>	15.3 ± 1.9
	8.9	<i>14</i>	24.2 ± 4.2	<i>14</i>	21.7 ± 2.1	<i>14</i>	20.0 ± 3.1	<i>14</i>	16.0 ± 3.5
	21.8	<i>14</i>	23.8 ± 5.9	<i>14</i>	23.4 ± 1.3	<i>14</i>	18.4 ± 1.9	<i>13</i>	17.1 ± 1.0
	52.9	<i>14</i>	24.5 ± 3.7	<i>14</i>	22.1 ± 2.8	<i>14</i>	17.8 ± 1.5	<i>14</i>	17.0 ± 2.0
	128.6	<i>14</i>	27.1 ± 6.6	<i>14</i>	22.7 ± 4.8	<i>14</i>	18.8 ± 3.6	<i>13</i>	16.7 ± 1.0
	213.4	<i>14</i>	24.7 ± 1.7	<i>14</i>	23.6 ± 2.9	<i>14</i>	19.9 ± 4.9	<i>14</i>	15.3 ± 2.7
	759	<i>14</i>	26.3 ± 2.6	<i>14</i>	22.6 ± 2.1	<i>14</i>	18.1 ± 2.0	<i>12</i>	15.8 ± 2.4
	1844	<i>14</i>	23.1 ± 2.9	<i>14</i>	21.6 ± 3.5	<i>13</i>	18.1 ± 2.7	<i>14</i>	15.1 ± 2.7
160	2.0	<i>14</i>	25.8 ± 3.3	<i>14</i>	19.8 ± 1.9	<i>14</i>	20.6 ± 2.9	<i>14</i>	15.7 ± 1.6
	4.9	<i>14</i>	24.4 ± 2.1	<i>12</i>	22.8 ± 1.4	<i>14</i>	20.9 ± 3.3	<i>14</i>	17.0 ± 2.9
	11.8	<i>14</i>	24.7 ± 4.4	<i>14</i>	20.1 ± 2.3	<i>14</i>	18.5 ± 2.3	<i>14</i>	15.4 ± 1.2
	28.7	<i>14</i>	24.8 ± 3.2	<i>14</i>	24.6 ± 2.9	<i>14</i>	17.8 ± 3.5	<i>14</i>	15.8 ± 1.7
	69.7	<i>14</i>	25.8 ± 2.6	<i>14</i>	23.5 ± 3.2	<i>12</i>	20.7 ± 4.0	<i>14</i>	18.9 ± 2.8
	169.4	<i>14</i>	27.5 ± 4.0	<i>13</i>	23.1 ± 3.2	<i>14</i>	19.2 ± 2.4	<i>14</i>	17.8 ± 2.7
	411.6	<i>14</i>	24.9 ± 4.2	<i>14</i>	22.8 ± 1.3	<i>14</i>	17.4 ± 3.7	<i>14</i>	13.9 ± 3.3
	1000	<i>13</i>	24.8 ± 3.7	<i>13</i>	25.5 ± 2.5	<i>14</i>	15.1 ± 4.6	<i>14</i>	14.3 ± 2.2
175	1.1	<i>14</i>	25.2 ± 5.4	<i>14</i>	22.9 ± 1.9	<i>14</i>	18.9 ± 3.7	<i>14</i>	16.1 ± 1.6
	2.6	<i>14</i>	24.8 ± 4.2	<i>14</i>	22.2 ± 1.9	<i>14</i>	18.2 ± 3.6	<i>14</i>	16.1 ± 1.5
	6.4	<i>14</i>	25.1 ± 2.2	<i>14</i>	23.1 ± 2.2	<i>14</i>	18.6 ± 3.4	<i>14</i>	16.8 ± 3.1
	15.6	<i>14</i>	25.9 ± 5.2	<i>14</i>	23.2 ± 1.7	<i>14</i>	18.2 ± 2.8	<i>14</i>	16.8 ± 2.4
	37.8	<i>14</i>	24.9 ± 3.6	<i>14</i>	21.8 ± 2.6	<i>11</i>	21.0 ± 2.5	<i>14</i>	16.4 ± 2.1
	91.8	<i>12</i>	23.1 ± 3.4	<i>14</i>	22.1 ± 3.1	0		<i>14</i>	16.4 ± 2.6
	223.2	<i>14</i>	25.2 ± 3.4	<i>14</i>	23.8 ± 2.4	<i>14</i>	19.4 ± 2.6	<i>13</i>	16.7 ± 2.1
	542.3	<i>14</i>	26.3 ± 3.9	<i>14</i>	20.5 ± 1.5	<i>14</i>	16.9 ± 4.3	<i>14</i>	11.5 ± 4.0
190	1.0	<i>14</i>	26.7 ± 3.9	<i>14</i>	22.4 ± 2.2	<i>14</i>	19.4 ± 2.4	<i>14</i>	16.0 ± 1.6
	1.4	<i>14</i>	25.1 ± 2.0	<i>12</i>	23.3 ± 1.6	<i>14</i>	18.9 ± 2.2	<i>13</i>	16.6 ± 2.6
	3.5	<i>14</i>	25.7 ± 2.0	<i>14</i>	23 ± 2.8	<i>14</i>	20.9 ± 3.2	<i>13</i>	16.1 ± 2.5
	8.4	<i>14</i>	23.7 ± 3.6	<i>14</i>	24.3 ± 2.5	<i>12</i>	17.8 ± 3.2	<i>13</i>	15.8 ± 1.4
	20.5	<i>14</i>	25.3 ± 4.9	<i>14</i>	21.9 ± 3.5	<i>12</i>	9.9 ± 5.3	4	6.3 ± 5.4
	49.8	<i>14</i>	21.6 ± 4.5	<i>14</i>	21.1 ± 1.4	<i>13</i>	8.8 ± 2.3	5	6.5 ± 1.5
	121	<i>14</i>	17.1 ± 6.3	<i>14</i>	16.7 ± 2.1	4	3.6 ± 1.6	4	2.1 ± 2.4
	294	<i>14</i>	17.3 ± 5.7	<i>13</i>	12.2 ± 2.9	0		0

FIGURE 27. A comparison is shown of the strengths at the 190°C and the 160°C temperature increment of the SAB. These values are the averages obtained from the in-board peel test.

FIGURE 28. Comparison of bond strength of the four different solder alloys at 146°C. The Bi-containing solders, SAB and SACB, can be seen as having lower strengths than the other two solder alloys, SAC and 121.

When comparing the overall strengths between the 121 and the SAC and between the SAB and the SACB there appeared to be a correlation that the solder alloys containing Cu, SAC and SACB presented a lower strength when compared to their counterpart, i.e., the SAC was weaker in strength to the 121. Similarly the SACB was weaker in strength compared to the SAB. In viewing the micrographs of the Cu containing solders, SAC and SACB, and the solders that did not contain Cu, 121 and SAB, a comparison was made to see if the intermetallic layer revealed a different microstructure. However, no apparent differences, i.e., difference in voids or coarsening, were noted from these visual inspections. Nonetheless, throughout the solder matrix and along the interfacial region of the intermetallic layer in the Cu containing alloys dark somewhat elongated grain formations were visible in these microstructures (see Figure 15 and Figure 20, respectively). Their size was substantial in giving the structure a nonhomogeneous appearance. It is believed that these formations are Cu_6Sn_5 particles and that they weakened the systems. Analysis was not performed to substantiate this, but documentation shows that Cu_6Sn_5 are hollow hexagonal rods and under testing conditions, the formation of these brittle rods appear to expedite the failure of the joint.^[16, 36] Voids which also have the bias to weaken a system were also compared between the SAC and SACB solders and the 121 and SAB solders. There appeared to be voids throughout all the microstructures of the four solders and it was not apparent if the Cu-containing solders had a larger number of voids. Without further analysis it was not apparent if the voids found in the Cu-containing solders were larger in size when compared to the voids in the other two solders, not containing Cu. In addition to the voids, solid solution and precise image analysis for size and shape of microstructural constituents must also be considered.

In the same manner, when the strengths of the Bi solders, SAB and SACB, were compared to SAC and 121, the Bi appeared to lower the overall strength. Despite the potential solid solution strengthening provided by the Bi in the Sn, it is believed that these lower strengths are the result of the Bi that precipitated out into the microstructure. The Bi occurred in the microstructure as large white grains resulting in a nonhomogeneous microstructure. Another factor that needs consideration is the Bi also appeared to increase the kinetic growth rate of the intermetallic layer in these Bi-containing solders. A fast growing brittle compound in a solder system would have the tendency to challenge the integrity of the joint.

To better understand the influence that temperature and time had on the solder alloys' strength, Analysis of Variance (ANOVA)^[37] was performed on the strength values that were acquired from the in-board peel test. This was not a straightforward analysis due to missing data points (sometimes as much as twelve values) from a fourteen set replication. An alternative method was chosen to create a simulated data set based on the mean and standard deviation of the existing data.

Random values of probability between 0 and 1 were selected and converted into standardized values, z-scores that are based on a normal distribution. Using the mean and standard deviation of the present data these z-scores were used to fabricate strength values. These dummy values could then be used to fill a deficient data set with the same number of data points as an average data set. This method was performed using EXCEL, a software spreadsheet, for data sets that had less than nine values.

In performing the ANOVA, the average data set size (nine to twelve values) was used instead of a full fourteen value set that may or may not contain simulated data. Data sets that contained fourteen values were reduced to the average data set size by randomly dropping strength values from the set. Using full size data sets would over estimate the true significance of the factors. It was believed that by using the average data set size a reasonable estimate of the significance would be obtained.

A summary of the ANOVA tables calculated for each of the four alloys is shown in Table VIII where SS is the sum of the squares, df is the degrees of freedom, MS is the mean square equal to SS/df , and F calc is the Fisher F statistic that is calculated for each factor. F crit is the value obtained from statistical tables^[38] based on the df of the system and the level of desired significance of 95%. If F calc is greater than F crit then the factor and/or interaction does have a significant effect on the bond strength. The p-value, also shown in Table VIII indicates that the probability of achieving the same results due to random variation is very low.

TABLE VIII. An ANOVA Table for time, temperature, and time-temperature interactions influencing intermetallic growth of the four solder alloys.

	<i>Source</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F calc</i>	<i>F crit*</i>	<i>P-value</i>
Alloy 121							
	TIME	179.5	7	25.64	1.43	2.03	0.19
	TEMP	350.1	4	87.53	4.89	2.39	7.32E-04
	TIME*TEMP	1324.5	28	47.30	2.64	1.5	1.8E-05
	ERROR	7155.2	400	17.89			
	Total	9009.3	439				
SAB	TIME	1375.6	7	196.43	21.24	2.03	2.44E-24
	TEMP	2727.72	4	681.93	73.73	2.39	9.1E-47
	TIME*TEMP	4219.37	28	150.69	16.3	1.5	4.79E-50
	ERROR	3699.58	400	9.24			
	Total	12021.732					
SAC	TIME	612.76	7	87.54	13.9	2.03	2.3E-16
	TEMP	311.27	4	77.82	12.4	2.39	1.45E-09
	TIME*TEMP	1642.1	28	58.64	9.34	1.5	5.2E-30
	ERROR	2760.92	440	6.27			
	Total	5327.06	479				
SACB	TIME	1417.1	7	202.44	38.35	2.03	6.07E-42
	TEMP	2684.1	4	671.0	127.14	2.39	4.82E-72
	TIME*TEMP	3079.01	28	109.96	20.84	1.5	1.08E-63
	ERROR	2322.3	440	5.28			
	Total	9502.42	479				

*This is based on using a 95% confidence interval.

From Table VIII, all factors except time for the 121 were significant for the solder alloys. This is demonstrated by the *F calc* being greater than the *F crit* indicating the significant effect time, temperature, and time-temperature had on the strength. However, there was greater significance in these variables for some alloys than for others. This is illustrated in Figure 29, where the *F crit* values are compared to the *F calc* values for each of the two factors and their interaction.

FIGURE 29. Comparison of F crit to F calc values obtained in an ANOVA.

The value of significance given for all the factors appear to support the hierarchy of strength that was exhibited by the four solder alloys. From the ANOVA the weakest strength alloy, SACB appeared to have low resistance to the effects of time, temperature, and time-temperature interaction while the strongest alloy, 121, appeared to be only slightly affected by the factors.

In viewing the significance that time and temperature had on 121, it can be seen that time was irrelevant. When compared to the other three alloys, 121 appeared to maintain a lesser significance in the temperature and time-temperature interaction. This supports the data obtained on the 121, where its strength sustained a fairly average constant strength of 25 N up until the 190°C temperature.

Time and temperature had more significance on the bond strength with the solder alloys containing Bi (SAB and SACB). This was reflected in the overall lower strengths of these solders. Both solder alloys had a lesser significance in time than temperature but this significance proportionally increased for the temperature factor. For the time-temperature interaction, the F calc was greater than the F crit, but it was not as significant as the individual factors.

Overall, the significance was similar for all the factors on the SAC. There was only 1.5 units difference of significance between the time and temperature; time being more, and 3 units difference between the temperature and time-temperature interaction. In comparison to the other alloys, the SAC showed lesser significance in time and temperature when compared to the SAB and the SACB but when compared to the 121, the factors contributed more to the SAC.

The most significant effects the time and temperature factors had on the bond strength of the solder alloys containing Bi was that they may not be strong candidates in replacing the Pb-Sn systems. The results indicate they were not resistant to isothermal aging and may not have mechanical strengths required for under the hood applications.

5.3 Comparison of Intermetallic Layer Growth versus Strength

A comparison, among the four solder alloys, was made between the strengths and their corresponding growth rate of intermetallics. It is believed that the continuous Ag_3Sn formation along the interface may have influenced the integrity of the joint because this intermetallic is brittle. For the most part, the anticipation that the solder alloy strength would decrease as the growth rate increased was proven correct at the higher temperature. However, finding a behavioral pattern became impossible in the 134°C , the 146°C , and the 160°C temperatures for all the alloys. The difference in the thickness of intermetallic appeared to have little or no affect on the strength. This was especially prominent with 121 where there seemed to little correlation of how thick the intermetallic was in regards to the strength in all the temperatures.

This trend can easily be seen with the SACB solder alloy, shown in Figure 30, where the average intermetallic thickness is compared to the average strength obtained from the in-board peel test performed at the last time cycle of each aging temperature. At the 134°C , the 146°C , and the 160°C temperatures, the intermetallic growth does not correlate with the strength, i.e., the smaller growth seen should indicate a higher strength. However, the association between the intermetallic thickness and strength becomes significant at 190°C . At this temperature the strength decreased approximately 17 N, as a noticeable increase in the intermetallic layer occurred.

FIGURE 30. Comparison of the average intermetallic growth, in μm , and the average strength, in Newton, that the SACB solder alloy exhibited at the last time increment for isothermal aging temperatures.

It was of interest to analyze the 190°C temperature further. In performing the peel test eight values were obtained from each of the eight time intervals. However, as discussed earlier, only four time intervals were examined for the measurements of the intermetallic growth. To compensate for the lack of thickness data, the coefficients determined from the multivariable regression were used to simulate the nonexistent data, using equation (1). This calculation gave an intermetallic thickness value for each strength value. In plotting the strength versus the intermetallic growth a correlation between the intermetallic thickness and the strength became apparent after the thickness had exceeded 7.3 (ln 1.9) μm . This behavior is illustrated with SAC and SAB in Figure 31. Nonetheless, it was observed that at the smaller aging times there appeared to be a wide variation of intermetallic thickness, resulting in little effect on the strength. It appears that a linear correlation can be used to fit the dependence of the peel strength on intermetallic thickness of 7.3 μm or greater.

FIGURE 31. Comparison of SAB and SAC and how their intermetallic growth affects their strength at 190°C.

The total reaction of the metallization that was observed at higher temperatures left behind a brittle intermetallic compound phase, perhaps disabling the adhesion of the wires to the solder/metallization system and causing the wires to become detached. However, there are other considerations to investigate when determining the reasons for the lower strength values that were obtained. One possibility is that there was degradation of the Cu-Sn wire. This degeneration would result in formation of Cu-Sn brittle intermetallics and/or the reduction of the cross-sectional area of the wire causing an increase in the sensitivity of forces that act on the joint. If the difference in the diffusional fluxes are significant between the wire and the solder/metallization system, Kirkendall voids form resulting in a severe reliability issue.^[27] Without further investigation it is not known at this time if perhaps this difference in flux existed between the elements present in the solder/metallization system and the wire.

Even though there appeared to be a correlation between the intermetallic thickness and strength at higher temperatures, the voids that were visible throughout the microstructures of the solders should not be overlooked. These voids that were visible throughout the solder matrix, intermetallic layer, and metallization appeared to coarsen at longer times and higher temperatures. Not only do these voids give the microstructure a nonhomogeneous entity, but they have the potential to initiate failure. A dependence of the solder joint strength may also exist between the size and amounts of voids.

5.0 SUMMARY AND CONCLUSION

For high temperature applications for under the hood components, four Pb-free solders comprised of varying weights of Sn, Ag, Cu, and Bi were chosen based upon previous screening of low contact angles and desirable sessile drop appearances and microstructures. The four solders, Sn-Ag eutectic (Indalloy 121), Sn-Ag-Cu eutectic, Sn-3.33 Ag-4.8 Bi, and Sn-1.6 Cu-4.5 Ag-5.0 Bi, were reflowed using no clean flux onto a double-layer Ag-rich Pt metallization using a Heller reflow oven. The initial appearances, contact angles, and microstructure were analyzed. The samples were subjected to accelerated isothermal aging at five different temperatures. An analysis was performed to determine the mechanical integrity of these four solder alloys by examining the kinetic growth rates and strengths of the intermetallic layers that formed. The results are summarized as follows:

1. The constant thermal processing produced fine and homogeneous initial microstructures in the four solder alloys, even though the melting points were different in each system. For the initial processing and subsequent aging treatments that were used in this experiment, it was found that the increase in intermetallic thickness maintained a subparabolic growth rate ($n < 0.5$). As the aging temperature and time increased in any given cycle, voids and microstructure coarsening were observed in the solder alloys, except for the Indalloy 121.
2. From measurements of the intermetallic thickness as a function of time and temperature of aging, activation energies were obtained over the temperature range of 134 to 190°C. The activation energy for the binary eutectic Sn-Ag was found to be 27.6 kJ/mole. An increase in activation energy was found with the addition of alloying elements. The activation energies for the other solder systems were 52.3 kJ/mole, 71 kJ/mole, and 88.5 kJ/mole for the SAC, SAB, and SACB solders, respectively. The actual mechanism(s) contributing to the activation energies found here are not fully understood, but represent the overall interfacial behavior for the systems studied.
3. In correlation to the activation energies obtained, the increase in intermetallic layer thickness varied from solder to solder with greater intermetallic thickness observed in the systems with higher activation energies. The average joint strengths in the as-soldered condition, presumably of the solder system and substrate, as determined by the DuPont in-board peel test were about 22, 20, 18, and 16 N for the 121, SAC, SAB, and SACB systems, respectively. With aging, the values remained constant within the limit of experimental error unless an intermetallic layer thickness of 7.3 μm or greater had been reached. This correlation was observed in the solder alloys, SAC, SAB, and SACB, but due to limited data and slower growth of the intermetallic, it was not observed for 121.
4. An Analysis of Variance (ANOVA) demonstrated the relative influence that time, temperature, and time-temperature interactions from the aging experiments had on the peel strength. The analysis showed little influence of time, temperature, and time-

temperature interactions upon the peel strength of the 121 solder, which was substantiated by the limited growth of the intermetallic over the time and temperature aging regime investigated. The lack of influence by these variables upon the peel strength suggest that this solder system is resilient to these aging conditions and may prove useful as a reliable joint for under the hood applications.

5. For Bi containing solders, the following observations were made:

- i) Higher activation energies were obtained for these two solder alloys, when compared to SAC and 121. Fast growth of the intermetallic layer was observed. Perhaps the Bi acted as a catalyst in expediting the intermetallic growth.
- ii) Total reaction of the metallization occurred during aging at 175°C and 190°C. This resulted in wires becoming detached and/or low strength values obtained from the in-board peel test performed at these temperatures.
- iii) Bi was seen clearly in the microstructure, because it had precipitated out from the solder matrix. This left the microstructure as a nonhomogeneous entity.
- iv) Out of the four solder alloys, SAB and SACB provided the lowest strengths in the in-board peel test at all the temperatures; SACB had the lowest strength value.
- v) In performing the ANOVA, these solders exhibited significant sensitivity to time, temperature, and time-temperature interactions.
- vi) These solders do not appear to provide joints that would be mechanically reliable after aging.

6. For the solders without Bi, the following observations were made:

- i) Lower activation energies were obtained for 121 and SAC; the 121 having the lowest value.
- ii) Total reaction of the metallization only occurred with the SAC solder at 190°C.
- iii) The SAC and 121 solders demonstrated higher in-board peel strength; 121 yielded the highest average values in the initial and aged conditions.
- iv) In performing the ANOVA, the time, temperature, and time-temperature interactions had only a slight effect on SAC, while no significant effect was noted with the 121.

7. When comparing solders with Cu to those without Cu, it appears that Cu weakens the peel strength of the system. The SAC and the SACB, both containing Cu, exhibited lower strengths when compared to their non-Cu containing counterparts--121 and the SAB, respectively. Even though the 121 and the SAC gave higher strengths when compared to the SAB and the SACB, between the 121 and the SAC, the SAC was lower. Likewise with the SAB and the SACB, the lower strength solders, in comparison SACB was lower in strength. The influence of Cu upon the strength is not fully understood, however the microstructure revealed Cu_6Sn_5 intermetallics, which may have been present not only as large grains in the bulk of the solder but possibly also as a thin, continuous layer of intermetallic.

At the onset of this project there was belief that a strong correlation would exist between the increasing intermetallic thickness and the peel strength of the solder systems. However, based on the results this only holds true to an extent. Other methodologies were apparent such as coarsening of the microstructure, large formations of intermetallics existing in the solder matrix, voids that were visible throughout the microstructure, and possible reactions with the wire. The correlation only became evident between the intermetallic thickness and the peel strength when the intermetallic thickness had reached a certain thickness.

Nonetheless, from these results, the SAC and the 121 solder systems appear to show promising potential for use in high temperature, under the hood applications. They have low activation energies for intermetallic growth and consequently yielded thinner intermetallic layers. They were resilient to the effects of temperatures up to 175°C; the 121 showed little change in peel strength and microstructure even at 190°C. Through all the aging temperatures, the SAC and the 121 maintained higher strengths than the Bi-containing solders, even at the elevated temperature of 190°C.

6.0 FUTURE WORK

The isothermal aging that was used in this project is only the first step in giving a comparative test between solders. This accelerated isothermal aging should not be used to predict the service life but only as a relative reference in the reliability of solder joints. There are many questions where answers could be supplied if further investigations were performed.

After the regression analysis had been performed there appeared to be intermetallic growth of some of the solder alloys that did not fit the model well. For example, in the 160°C temperature the SACB initially did not exhibit a subparabolic growth curve. Further studies would include a larger collection of data points that would either lessen the deviation effect seen or discover an aging mechanism that SACB has at this temperature.

The kinetic rates that were obtained on the intermetallic growth for each solder were a general estimate in a given temperature range. Future work could include identifying the individual intermetallics and determining each of their activation energies and their contribution to the overall kinetic rates.

It is believed that the subparabolic growth rate that was apparent with the solder alloys was indicative of more than one intermetallic phase being present. In the Cu containing solders it would appear to be a straight forward assumption of what the second or third intermetallic constituent would be. However, with the 121 and the SAB solder, an

analysis could determine if the PtSn_7 compound that was identified in the preliminary study and the metastable compound, Cu_5Bi_2 that has been documented is actually present.

In the samples that exhibited total reaction of the metallization, a repeated accelerated aging test could be employed along with a rigorous compositional analysis to determine the cause of this event. It would be interesting to determine the outcome of this total dissolution had the time been extended at the 190°C temperature to see when cracks between the solder matrix and intermetallic layers began to appear.

In performing the in-board peel test, it was not clear where the actual failure of the joint occurred. Investigating the cross sectional view of these destroyed specimens may give insight into the failure mechanism, i.e., did the failure occur in the interfacial region between the intermetallic layer and metallization or propagate into the solder matrix or was there actual degradation of the wires themselves causing a faster failure rate? Thus, cross sectional analysis may also expose possible effects the voids that were present throughout the microstructure of the solder had on the ultimate strength of the joint.

If the failure had occurred in the solder matrix, hardness tests could be performed on the intermetallics that had been identified along the fracture path. For example, the Cu_6Sn_5 that was believed to be present, would it prove to be more ductile or brittle than the other intermetallics such as Ag_3Sn .

Performing these tests would enhance the knowledge that was obtained from this study. In turn, this information could lead to a more knowledgeable development of future Pb-free solders.

ACKNOWLEDGMENTS

The authors would like to thank the following people for their contributions to this study:
F. Uribe, G. Munson, B. McKenzie, A. Kilgo, G. Zender, P. Hlava, and J. Roberts.

REFERENCES

- 1] G. Humpston, D.M. Jacobson, Principles of Soldering and Brazing, (ASM International, OH, 1993).
- 2] J.S. Hwang, R.M. Vargas, *Soldering and Surface Mount Technology*, **5** (1990), p. 38.
- 3] H.D. Soloman, "Low Cycle Fatigue of Sn96 Solder with Reference to Eutectic Solder and a High Pb Solder", *Trans. ASME*, **113** (1991), p. 102.
- 4] R. L. Davies, "High Strength, Low Temperature Bonding with Silver-Tin Solders", *Welding Journal*, **55**, No. 10 (1976) p. 838.
- 5] C.A. Drewien, et al., "Progress Report: High Temperature Solder Alloys for Underhood Applications", *Sandia National Laboratory*, Report, #SAND95-0196 (1995).
- 6] C. Luchinger, et al., "Inside Solder Connections", *Advanced Packaging*, (1994), p. 14.
- 7] Yujing Wu, et al., "The Formation and Growth of Intermetallics in Composite Solder", *Journal of Electronic Materials*, **22**, No. 7 (1993), p. 769.
- 8] T.B. Massalski, Binary Alloy Phase Diagrams, 2nd Edition, (AMS International, OH, 1990), Vol. 1 - Vol. 2.
- 9] P.T. Vianco, P.F. Hlavà, A.C. Kilgo, "Intermetallic Compound Layer Formation Between Copper and Hot-Dipped 100In, 50In-50Sn, 100Sn, and 63Sn-37Pb Coatings", *Journal of Electronic Materials*, **23**, No. 7 (1994), p. 583.
- 10] P.T. Vianco, K.L. Erickson, P.L. Hopkins, "Solid State Intermetallic Compound Growth Between Copper and High Temperature, Tin-Rich Solders - Part I: Experimental Analysis", *Journal of Electronic Materials*, **23**, No. 8 (1994) p. 721.
- 11] B. Ozmat, *Proc. 40th Electr. Comp. & Techn. Conf.*, (Las Vegas, NV, 1990), pp. 959-972.
- 12] D.R. Frear, F.G. Yost, "Reliability of Solder Joints", *MRS Bulletin*, **18**, No. 12 (1993), p. 49.
- 13] W. Yang, R.W. Messler, "Microstructure Evolution of Eutectic Sn-Ag Solder Joints", *Journal of Electronic Materials*, **23**, No. 8 (1994), p. 765.
- 14] M. McCormack, S. Jin, "New, Lead-Free Solders", *Journal of Electronic Materials*, **23**, No. 7 (1994), p. 635.

- 15] G.B. Greeman, et al., "Intermetallic Embrittlement of Thin Unsupported Tin/Copper Specimens", *Journal of Electronic Materials*, **23**, No. 9 (1994), p. 919.
- 16] D.R. Frear, D. Grivas, J.W. Morris, "Thermal Fatigue in Solder Joints", *Journal of Metals*, **40**, No. 6 (1988), p. 18.
- 17] J.L. Goldstein, J.W. Morris, "Microstructural Development of Eutectic Bi-Sn and Eutectic In-Sn During High Temperature Deformation", *Journal of Electronic Materials*, **23**, No. 5 (1994), p. 477.
- 18] S.P.S. Sangha, G. Humpston, "Shear Strength of Diffusion Soldered Joints", *GEC Journal of Research*, **10**, No. 3 (1993), p. 174.
- 19] D. Tribula, et al., "Microstructural Observations of Thermomechanically Deformed Solder Joints", *Welding Journal*, **68**, No. 10 (1989), p. 404-s.
- 20] L. Chadwick, "Solder Alloy Data: Mechanical Properties of Solders and Soldered Joints", *International Tin Research Institute*, #ITRI 656 (undated).
- 21] D. Frear, et al., "Fatigue and Thermal Fatigue Testing of Pb-Sn Solder Joints", *Center for Advanced Materials, Berkeley, CA* (1983), p. 269.
- 22] J.J. Ramon, S.F. Dirnfeld, "A Practical Way to Measure the Strength of Small Soldered Joints", *Welding Journal*, **67**, No. 10 (1988), p. 19.
- 23] C.H. Raeder, et al., "The Effect of Aging on Microstructure, Room Temperature Deformation, and Fracture of Sn-Bi/Cu Solder Joints", *Journal of Electronic Materials*, **23**, No. 7 (1994), p. 611.
- 24] K. Shimizu, et al., "Solder Joint Reliability of Indium-Alloy Interconnection", *Journal of Electronic Materials*, **24**, No. 1 (1995), p. 39.
- 25] "Method of Test for Wire Peel Adhesion of Soldered Thick Film Conductors to Ceramic Substrates", *DuPont Electronic Materials Report #SS309297* (1992).
- 26] K.J. Williams, "Adhesion Test Methods for Solderable Thick Film Conductors", *Brazing & Soldering*, No. 15 (1988), p. 10.
- 27] D.R. Frear, W.B. Jones, K.R. Kinsman, Solder Mechanics: A State of the Art Assessment, (TMS, Warrendal, PA, 1991).
- 28] T.L. Crandell, J.E. Sergeant, "Some Aspects of the Measurement of the Adhesion of Thick Film Conductor Inks to Alumina Substrates", *Marshall Space Flight Center, Report #NAS8-31172* (undated).

- 29] R.L. Scheaffer, J.T. McClave, Probability and Statistics for Engineers, (Duxbury Press, Belmont, CA, 1995).
- 30] Microsoft Excel for Windows 95, Software Package System Version 7.0, Microsoft Corp. (1995).
- 31] Z. Mei, J.W. Morris, Jr., "Characterization of Eutectic Sn-Bi Solder Joints", *Journal of Electronic Materials*, **21**, No. 6 (1992), p. 599.
- 32] F.G. Yost, F.M. Hosking, D.R. Frear, The Mechanics of Solder Alloy Wetting and Spreading, (Van Nostrand Reinhold, NY, 1993).
- 33] P.W. Atkins, Physical Chemistry, 4th Edition, (W.H. Freeman and Company, NY, 1990).
- 34] W.J. Tomlinson, N.J. Bryan, "The Strength of Brass/Sn-Pb-Sb Solder Joints Containing 0 to 10% Sb", *Journal of Materials Science*, **21** (1986), pp. 103-109.
- 35] D.R. Frear, P.T. Vianco, "Intermetallic Growth and Mechanical Behavior of Low and High Melting Temperature Solder Alloys", *Metallurgical and Materials Transactions*, **25A** (1994), p. 1509.
- 36] D. Frear, D. Grivas, J.W. Morris, Jr., "The Effect of Cu_6Sn_5 Whisker Precipitates in Bulk 60Sn-40Pb Solder", *Journal of Electronic Materials*, **16**, No. 3 (1987), p. 181.
- 37] T.P. Ryan, Statistical Methods For Quality Improvement, (John Wiley & Sons, NY, 1989).
- 38] D.C. Montgomery, G.C. Runger, Applied Statistics and Probability For Engineers, (John Wiley & Sons, NY, 1994).

Appendix

	TOLERANCES ARE TO $\pm 1/16$ in UNLESS SPECIFIED	DIMENSIONS ARE IN inches	SCALE: 1 TO 1	DESIGNED BY: GEOFF MUNSON
			DATE: 4/10/95	CHECKED BY: MARTIN WEISER

TITLE Solder Tester	FIND NO. 1	PART NO. 1	QTY 1	DESCRIPTION	MATERIAL
DRAWING NUMBER 2				Bottom Mount	6061 - T6 Aluminum or Similar

	TOLERANCES ARE TO $\pm 1/16$ in UNLESS SPECIFIED	DIMENSIONS ARE IN inches	SCALE: 1 TO 1	DESIGNED BY: GEOFF MUNSON
			DATE: 4/10/95	CHECKED BY: MARTIN WEISER

TITLE Solder Tester	FIND NO.	PART NO.	QTY	DESCRIPTION	MATERIAL
DRAWING NUMBER 3	2	2	1	Bottom Retainer	304 Stainless Steel or Similar

	TOLERANCES ARE TO $\pm 1/16$ in UNLESS SPECIFIED	DIMENSIONS ARE IN inches	SCALE: 1 TO 1	DESIGNED BY: GEOFF MUNSON
			DATE: 4/10/95	CHECKED BY: MARTIN WEISER

Section A

TITLE Solder Tester	FIND NO.	PART NO.	QTY	DESCRIPTION	MATERIAL
DRAWING NUMBER 4	3	3	1	Top Mount	304 Stainless Steel or Similar

	TOLERANCES ARE TO $\pm 1/16$ in UNLESS SPECIFIED	DIMENSIONS ARE IN inches	SCALE: 1 TO 1	DESIGNED BY: GEOFF MUNSON
			DATE: 4/10/95	CHECKED BY: MARTIN WEISER

TITLE Solder Tester	FIND NO.	PART NO.	QTY	DESCRIPTION	MATERIAL
DRAWING NUMBER 5	4	4	1	Top Retainer	304 Stainless Steel or Similar

TOLERANCES
ARE TO
 $\pm 1/16$ in
UNLESS SPECIFIED

DIMENSIONS
ARE IN
inches

SCALE:
1 TO 1

DATE:
5/4/95

DESIGNED BY:
GEOFF MUNSON

CHECKED BY:
MARTIN WEISER

TITLE	FIND NO.	PART NO.	QTY	DESCRIPTION	MATERIAL
Solder Tester					
DRAWING NUMBER 6	N/A	N/A	1	Bend Fixture	304 Stainless Steel or Similar

Internal Distribution

1	MS 0161	M. Moss, 11510
5	MS 1405	C. A. Drewien, 1822
5	MS 1411	S. Sackinger, 1831
1	MS 1411	P. Vianco, 1831
1	MS 1411	D. Frear, 1831
15	MS 1411	F. Yost, 1831
2	MS 0619	Review and Approval Desk, 12630 for DOE/OSTI
5	MS 0899	Technical Library, 4414
5	MS 0957	F. Uribe, 1411
1	MS 1071	T. J. Allard, 2205
1	MS 9018	Central Technical Files, 8523-2

External Distribution

10	Martin Weiser Johnson-Mathey Corp. E 15128 Euclid Ave. Spokane, WA 99216
10	Julie Kern Department of Mechanical Engineering University of New Mexico Albuquerque, NM 87131
1	Larry Hocken AC Delco Systems Control Systems Engineering Department 32-18 1300 North Dort Highway Flint, MI 48556
1	Larry Hazelton AC Delco Systems Control Systems Engineering Department 32-18 1300 North Dort Highway Flint, MI 48556