Role of Tin Content in the Wetting of Cu and Au by Tin-Bismuth Solders

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This study describes tests in which solder composition, substrate metallization, temperature, and dwell time were combined in a factorially designed experiment to determine the effect of those factors on solder spread area. Measure of spread area, reflowed solder shape, solder microstructure, and solder and interface chemistry were taken in order to provide insight about the wetting mechanism(s). The reactivity of Au vs Cu metallization with solder was found to be a major factor in increasing spread area. The role of increasing tin content is to increase spread and spread rate. A similar effect is seen by increasing temperature. Time allowed for spread is a minor contributor to the spread area. Segregation of the tin and bismuth solder components during the wetting process was observed which indicated the role of bismuth as a carrier species. Analysis of variance methods based on the statistically designed experiments[1a, 1b] were used to show how to generate a model which estimates the spread area as a function of the tested factors.

Key words: Metallization, solders, tin content, wetting

INTRODUCTION

Considerable work has been done by industry and universities[2–5,7,9,10,12–14] on solder compositions for various component assembly operations.

One driver in developing new solder compositions is the need to eliminate lead in electronic assemblies due to environmental reasons. The Sn-Bi solder system is particularly attractive since it provides for lead elimination, a lower eutectic temperature than Sn-Pb for easier assembly processes and relatively high strength (although only moderate results in shear.[5,7,8,11]

The purpose of this study was to look at the wetting properties of several Sn-Bi compositions and to use designed experiments to model the wetting behavior. One measure of wetting is the amount of solder spread on a clean gold or copper surface at a controlled temperature and uniform dwell time. Specifically, this study was to look at the spread of 0.508 mm (20 mil) Sn-Bi solder balls on 0.1016 mm (4 mil) thick copper coupons both with and without electroplated gold (0.635 μm [25 microinches]). The solders tested included the Sn-Bi eutectic and two noneutectic compositions of increased Sn content (42/58 SnBi, 50/50 SnBi, 60/40 SnBi, all in mass percent).

The study employed a factorially designed 2^4 test matrix to investigate the significance of test factors and their interactions. Other reports of factorial experiments of wettability[9b] have raised important issues about the significance of process and material variables studied here. The report by Melton[9b] listed solder composition, metallization, and atmosphere as significant as well as some of their interactions. However, in statistical evaluations significance is an assignable quantity which must be stated in terms of level of significance. Furthermore, as we will show,

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Table I. Solder Spread Area (Gold Substrate)

Temp. °C	43/57 Sn/Bi mm^2	50/50 Sn/Bi mm^2	60/40 Sn/Bi mm^2
200, 1 min Dwell	0.44	1.40	1.65
200, 4 min Dwell	0.65	1.60	1.89
250, 1 min Dwell	1.05	2.05	2.65
250, 4 min Dwell	2.28	3.11	5.22

factorially designed experiments can be used in developing models for prediction of behavior in order, for example, to estimate the role of each tested process factor on such outcomes as change in spread area.

METHOD

Solder balls with the compositions listed below were reflowed on a heating stage in a chamber with a flowing nitrogen environment. The ball diameters were 0.508 mm ± 0.0304 mm (20 mil ± 1.2mil).

42/58 Tin-Bismuth—melting point 138°C (eutectic)
50/50 Tin-Bismuth—melting range 138–153°C
60/40 Tin-Bismuth—melting range 138–167°C

The coupons were 0.1016 mm (4 mil) copper that had been cut into approximately 12.7 × 12.7 mm (1/2 × 1/2 inches). These copper coupons were dipped in 15% hydrochloric acid to insure a clean copper surface and rinsed in isopropyl alcohol. This was done just prior to reflow. Clean coupons were exposed to air for minimal time prior to being placed on the heating stage.

The gold samples were 0.1016 mm (4 mil) copper electroplated with 2.54 microns (100 microinches) of nickel and then, plated with 0.635 microns (25 microinches) of gold.

The experiments were performed on a heating stage enclosed to allow atmosphere control and setup with microscope and video observation access. The 76.2 × 76.2 mm (3 × 3 inch) heating stage had a thermocouple embedded in it and a digital temperature readout on the base. The video camera on top of the stage magnified the image to 50X to allow both video taping of the experiment and in-situ observation of the reflow process on the monitor.

The heating stage enclosure had the ability to flow nitrogen through the chamber. The nitrogen line provided 99.8% pure nitrogen and was run onto the stage at 18 cfm.

The experiments were run at two temperatures for the gold. Those temperatures were 200 and 250°C. The heating stage reached the tin-bismuth eutectic melting point in 1 min 35 s (±7 s) and reached 200°C in 3 min 5 s (±10 s). It took 4 min 55 s (±10 s) to reach 250°C. Three samples were run at each temperature.

The solder spread area was measured on a VIDAS imaging system (trademark Carl Zeiss) with a personal computer printout. A comparator was used at 50X magnification to translate the solder spread shape on to a transparency. This shape was then traced on the VIDAS to record the spread area. Three measurements were taken of each sample on the VIDAS and the average of these was reported.

RESULTS AND DISCUSSION—GOLD SUBSTRATES

The results of the solder spread on gold (Table I) consistently indicate an increase in solder spread area with increasing tin content of the solder. This occurred at all temperatures tested. The increase in the spread area with tin content was greater at the lower reflow temperatures which was an unanticipated result since the higher tin content solders also have a higher liquidus temperature and larger range of reflow temperature. The 60/40 Sn/Bi spread area was 3 to 4X greater than the eutectic at the lower temperature.

As the temperature was increased to 250°C, the average difference in solder spread area was >2X for the 60/40 compared to the eutectic and about 60% greater for the 60/40 vs 50/50 solder.

The edges of the reflowed eutectic solder were relatively smooth and uniform. The noneutectic SnBi solder compositions were more irregular in shape. A reason for this variation in reflow shape could be the eutectic solidification where the 42/58 Sn/Bi eutectic solder would solidify uniformly at 138°C. The noneutectic compositions on the other hand, melt and solidify over a range of temperatures thus producing a more jagged edge as some proeutectic (Sn-rich composition) forms. This nonuniform solidification also yielded a grainer surface texture with the noneutectic solders.

The other result was, as expected, that the wetting area increased with increasing temperature. Viscosity and surface tension both decrease with increasing temperatures and the solder-metallization reactivity increases which should improve wetting.

As anticipated, the solder area increases with dwell time. This effect is less pronounced at the lower temperature (10–50% increase) but is greater with increasing temperature (100–200% at 250°C). It should be noted from this set of tests that the 50/50 Sn/Bi solder appears to have significantly increased spread areas at 200°C compared to the 42/58 Sn/Bi.

DATA ANALYSIS

A statistical analysis of the results of this factorially designed experiment can be done using an analysis of variance (ANOVA) on the data. The advantage[1a,b] of the designed experiment format for these tests is that in addition to providing a determination of significance of the effects of each factor tested, this design can also give results in terms of the interaction between factors. As noted later, this experiment shows that there are significant interactions between factors such as solder tin content and temperature. In this particular experimental design, we have tested four factors (metallization type, solder tin content, temperature, and spread time) each at two levels in a simple 2^4 full factorial design. From the

$2^4 = 16$ tests required we can determine the significance of the effect of each separate factor as well as the six two factor interactions, (e.g., solder tin content*temperature), the three interactions between three factors, e.g., (solder tin content*temperature*time) and the single four factor interaction.[1a,b]

The results of our ANOVA analysis show that there is a significant ($\alpha = 0.05$) increase in the amount of solder spread due to increased Sn content. The increase in temperature also produced a significant ($\alpha = 0.05$) increase in the solder spread. The interaction between composition and temperature was also significant although at a statistically lower level ($\alpha = 0.1$).

The interaction effect shows that different Sn/Bi solder compositions had different responses to the temperature changes. This can be seen by examining the changes in wetting area with composition from 200 to 250°C. Both the eutectic and the 50/50 Sn/Bi solder wetting area increases by about 3X as the temperature increases from 200 to 250°C while the 60/40 Sn/Bi solder area increases by less than 2X.

COPPER SUBSTRATES

The variation in solder spread area due to variations in solder composition and/or reflow temperature was greatly reduced on the copper substrates (Table II). In addition, the solder spread does not increase for the 60/40 Sn/Bi compared to the 50/50 Sn/Bi solder at 200°C.

The ANOVA of solder reflow area data on copper shows a significant ($\alpha = 0.05$) effect of composition and of temperature. A less significant ($\alpha = 0.1$) interaction between temperature and composition is also seen.

It was interesting to note that the dwell time effect appeared to vary with composition and temperature. At 200°C, no change in solder spread area was noted in the eutectic solder and the increase in area for the 50/50 and 60/40 Sn/Bi solders were similar. At 250°C, the area increased for all compositions with increasing time, but increased more in the higher Sn content solder.

FLUX EFFECT

An additional experimental matrix was run on the copper samples to look at the effect of solder reflow with flux. Kester 3331 water soluble RMA flux was applied to the substrates prior to reflow. The results are shown in Table III. The use of flux improves the wetting area of all the Sn/Bi solders on copper, especially at 200°C but, only results in a maximum wetting area of about 1.2 mm² at any temperature. That

Table II. Solder Spread Area (Copper Substrate)

Temp. °C	43/57 Sn/Bi mm²	50/50 Sn/Bi mm²	60/40 6Sn/Bi mm²
200, 1 min Dwell	0.64	0.65	0.68
200, 4 min Dwell	0.64	0.80	0.82
250, 1 min Dwell	0.65	0.77	0.82
250, 4 min Dwell	0.75	0.94	1.12

Table III. Solder Spread Area with Flux (Copper Substrate)

Temp °C	43/57 Sn/Bi mm²	50/50 Sn/Bi mm²	60/40 Sn/Bi mm²
200	1.09	1.20	1.04
250	1.16	0.99	1.09

Table IV. Results of Yates Algorithm Calculation

Avg. S_{obs} (mm²)	Factor* t	M	T	A	Effects	
0.64	—	—	—	—	21.95	Mean (S_o)
0.64	+	—	—	—	4.79	t
0.44	—	+	—	—	9.71	M
0.65	+	+	—	—	3.71	t*M
0.65	—	—	+	—	7.13	T
0.75	+	—	+	—	3.61	t*T
1.05	—	+	+	—	6.01	M*T
2.28	+	+	+	—	3.09	t*M*T
0.68	—	—	—	+	7.75	A
0.82	+	—	—	+	1.71	t*A
1.65	—	+	—	+	6.23	MxA
1.89	+	+	—	+	1.03	t*M*A
0.82	—	—	+	+	2.41	T*A
1.12	+	—	+	+	1.37	t*T*A
2.65	—	+	+	+	1.77	M*T*A
5.22	+	+	+	+	1.25	t*M*T*A

*Factors: t = time; M = Metallization; T = temperature; A = solder alloy.
Factor levels: (–) = 1 min, Cu, 200°C, 42Sn; (+) = 4 min, Au, 250°C, 60Sn.
Estimation Model: $S_{est.}$ $S_o + t(X_t) + M(X_M) + T(X_T) + A(X_A) + M*A(X_M*X_A) + M*T(X_M*X_T)$ + error.
e.g. for $X_t = X_M = X_T = X_A$ (+); $S_{est.} = 6.57 \pm 0.067$; $S_{obs} = 5.22$; for $X_t = X_M$ = (+); $X_T = X_A$ = (–); $S_{est.} = -0.21 \pm 0.067$; $S_{obs} = 0.65$.

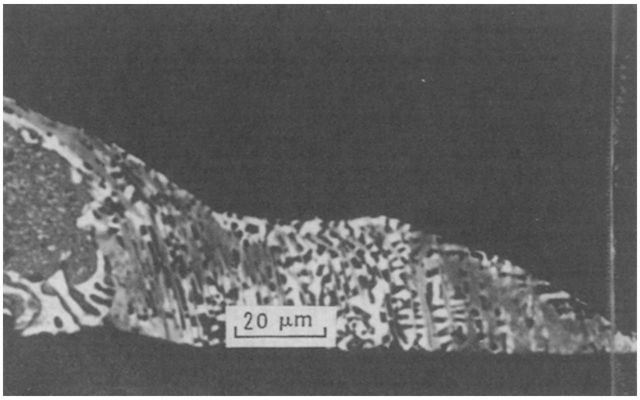

Fig. 1. Backscattered electron SEM image of 60Sn-40Bi on Au at 200°C. Sn-rich areas are lightest contrast. Folded vertical layers appear near the spreading front.

is still significantly less spread than attained on gold without flux for all but the worst case condition, i. e., shortest time, with the lowest tin alloy at 200°C.

THE ANOVA BASED WETTING ESTIMATE

Our data provides the opportunity to model the factor effects into a prediction relation by which it is possible to estimate the contribution of each factor on the change of spread area. From our 2^4 design, for example, using a simple Yates Algorithm,[1a,b] we can construct a model of the spread which includes the significant effects as factors. Such a model is represented as follows:

Factors:

t = time; M = metallization; T = temperature; A = solder alloy; factor levels: (–) = 1 min, Cu, 200°C, 42Sn; (+) = 4 min, Au, 250°C, 60Sn

Estimation Model:

$$S_{est.}\ S_o + t(X_t) + M(X_M) + T(X_T) + A(X_A) + M{*}A(X_M{*}X_A) + M{*}T(X_M{*}X_T) + \text{error}$$

From the ANOVA, it is possible to estimate increases (mm^2) in spread area due to the significant factors to be:

Au vs Cu metallization	→ 1.20 mm^2
60%Sn vs 42%Sn	→ 0.97 mm^2
250 vs 200°C	→ 0.89 mm^2
Au*60Sn vs Cu*42Sn	→ 0.78 mm^2
Au*250°C vs Cu*200°C	→ 0.75 mm^2
4 min vs 1 min	→ 0.60 mm^2

Thus, at each of the $2^4 = 16$ test conditions, we could estimate the area of spread from the model equation by employing the significant factors with the appropriate sign for level of the factors[1a,b], e.g.,

$$\text{for } X_t = X_M = X_T = X_A\ (+);\quad S_{est} = 6.57 \pm 0.067;\ S_{obs} = 5.22$$
$$\text{for } X_t = X_M = (+);\ X_T = X_A = (-)\quad S_{est} = -0.21 \pm 0.067;\ S_{obs} = 0.65$$

The error associated with these factors can be estimated from the remaining interactions of the 2^4 design.[1a,b] Such data yields a very large error estimate of approximately 2.4 mm^2. However, the error term can be more accurately estimated in this case since each test was replicated three times. Using data from replicates, the error term is almost two orders of magnitude less, i.e.. 0.067 mm^2. This difference between the 2.4 and 0.067 implies that some of the other terms obtained by the Yates calculation may also be important in the estimation model. The complete listing of the results of the Yates calculation is given in Table IV under the column heading Effects. No further estimation based on this model is, however, worth pursuing at this point since as the 50% Sn alloy data clearly show the effects are nonlinear yet the two-level factorial model can only predict in a linear fashion. A more sophisticated experimental design, e.g., a central composite design should be used to estimate the nonlinear behavior. Nonetheless, this two-level screening design has identified the significance of the roles of the factors tested.

Clearly, the metallization effect appears to be strongest with time (dwell time) being only half as effective. However, increase of Sn content and increase in process temperature are also likely to be useful process control factors. Of the factors listed, Sn content appears to be the most economically interesting factor since it can be more easily controlled at a lower overall expense.

WETTING PROPERTIES & MICROSTRUCTURAL ANALYSIS

In viewing the solder wetting process on the video monitor, it appeared that the wetting mechanism for copper and gold were different. The solder balls melted on the copper and quickly collapsed to spread as a circular bump on the substrate (see Fig. 3). Little spread after collapse was observed in most cases especially at the lower temperature.

On gold, the solder ball would reflow and sit on the substrate for a while. Solder would then spread out from under the bottom of the ball and become visible on the top camera (see Fig. 1 and Fig. 2). This would occur sometime between 170 to 205°C for the various solders (around 2-1/2 to just over 3 min). The solders continue to slowly spread out with increasing temperature and time.

Metallographic analysis and scanning electron microscopy/energy dispersive x-ray (SEM/EDX) were also used to further analyze the wetting process differences between the copper and gold coupons. Scanning electron microscopy observations of the wetting front morphology for a eutectic Sn/Bi solder at 250°C on both copper and gold showed differences in the wetting. The eutectic on the copper had a dendritic surface texture down to the substrate surface. A small area, or wetting film, appeared protruding from under the bulk of the reflowed solder.

On the gold, the surface of the bulk of the solder was much smoother with just a hint of the texture or dendritic shapes occurring. The wetting front was an area of irregular, spherical-like protrusions that were largest on the edge of the bulk solder and became smaller closest to the edge of the wetting front.

This difference in wetting mechanism can also be inferred by EDX compositional peak analysis from the SEM. The two eutectic samples were analyzed using the no standards analysis (NOSTD) program on the SEM data. Compositional analysis was performed across the sample. Three analyses were performed: one on the bare substrate, one at the wetting front, and one in the center of the reflowed solder.

From the EDX analysis of the eutectic on copper, it was evident that the solder composition changes only slightly from the wetting front to the center of the sample. The weight percent ratio (Sn/Bi/Cu) was estimated at 39/40/21 at the wetting front and 41/47/12 in the center of the sample. There appears to be a slightly higher Sn/Bi ratio at the wetting front.

The results of the EDX on the gold substrate show a very significant skew in the Sn content from the wetting front to the center of the sample. The EDX detected no bismuth present at the wetting front on the gold sample and about 50% bismuth in the center of the sample. The wetting front of the eutectic solder on the gold was Sn mixed with the gold, nickel and copper.

Figures 1–3 are examples of SEM micrographs obtained in this study. Figure 1 is a backscattered image at 15kV from the test of 60Sn on Au at 200°C. The lighter areas are Sn-rich. A vertically folded, layered morphology as seen beginning at the spreading front was observed in several of the 60Sn samples. Figure 2 is a backscattered image from the test of the eutectic alloy on Au at 200°C. Two notable features are observed in this micrograph: first, the profile indicating the difficulty of spreading for the bulk of the solder ball, and second, is the observed polygonal intermetallic phase particles of uniform gray contrast. These particular polygons were found to contain the following weight percent ratio of Au, Bi and Sn, respectively, 13/18/54.

Figure 3 is a secondary electron image of the eutectic alloy on Cu at 250°C. Notable in this micrograph is a rather higher apparent contact angle. A related EDX analysis of this sample shows the copper-tin intermetallic at the interface and also shows a slight enrichment in tin on the outer surface of the solder.

CONCLUSIONS

The results of this study show that the solder spread area of various Sn/Bi solders was affected by the substrate material used, i. e., gold vs copper. Gold provides a far superior wetting surface vs clean copper for temperatures >200°C when soldering without flux in an inert environment. The use of flux on copper increases the solder spread area but, only to a point. However, the use of flux does decrease variability. While the wetting area of all but the highest Sn content solder was larger for the copper coupons with flux, it still was one half to one quarter the wetting area of the gold substrates at 250°C.

The segregation of the elements of the Sn/Bi solder appear evident in this study, especially on the gold surface. From these results, it is apparent that tin's higher affinity for gold than copper controls the spread process. The EDX analysis showed that Sn is the dominant wetting agent in the reflow process on gold. The presence of the wetting front, or precursor film similar to that reported by Singler and Clum,[12] was observed with the SEM. Increasing the tin content of the Sn/Bi solder on gold significantly increased the solder spread area. The role of Bi is to act primarily as a carrier species for the reactive Sn.

Additionally, the study showed that increasing the amount of tin present in the Sn/Bi solder would improve the wetting of the solder on gold more at lower temperatures (around 200°C).

Consequently, the solder wetting and solder spread area of Sn/B solders on gold can be most effectively improved by increasing the tin content of the solder. Further work is needed to understand why increases in the Sn content improved the relative wetting at lower reflow temperatures on gold.

The use of designed experiments provides a means of quantifying and defining the robustness of the process factor effects. In this simple 2^4 factorial design case the main effects of metallization, alloy Sn content, temperature, and dwell time were able to be quantifiably related to changes in solder spread area.

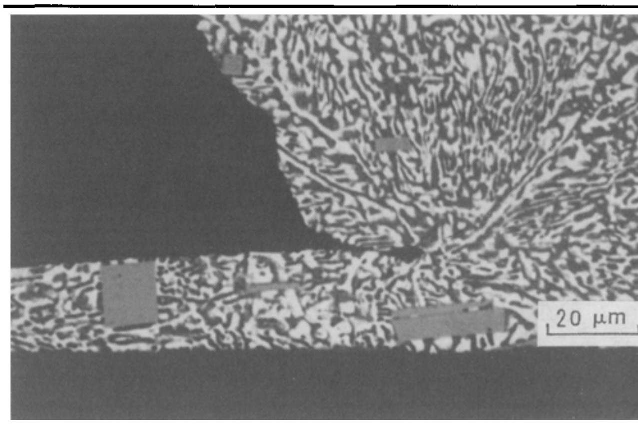

Fig. 2. Backscattered electron SEM image of eutectic Sn-Bi alloy on Au at 200°C. Morphology shows lack of complete spreading. Blocky phase particles are found to be a Sn-rich intermetallic of 54%Sn-13%Au-18%Bi, (wt %).

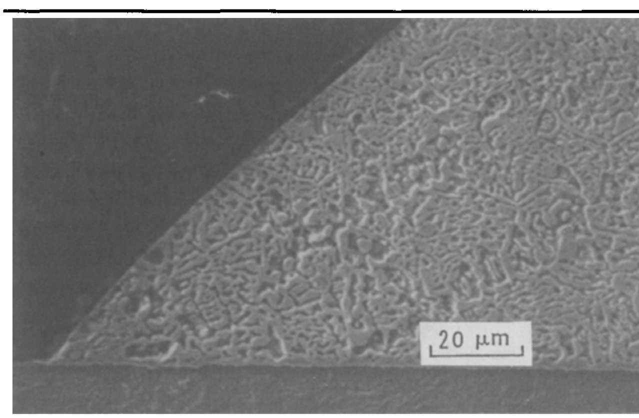

Fig. 3. Secondary electron SEM image of eutectic Sn-Bi alloy on Cu at 250°C. Apparent contact angle is larger than same alloy on Au.

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REFERENCES

1a. T. Barker, *Quality by Experimental Design,* (New York: Marcel Dekker, Inc., 1985).
1b. G.E.P. Box, W.G. Hunter and J.S. Hunter, *Statistics for Experimenters,* (New York: J. Wiley, 1978).
2. H. Betrabet, J. McKinlay and S. McGee, *J . Mater. Sci.* 27, 4009 (1992).
3. J. Cameron, J. Marshall, et al., *IEEE Trans.* 647 (1991).
4. Gordon Foster, *Embrittlement of Solder by Gold from Plated Surfaces* (Murray Hill, NJ: Bell Telephone Laboratories) source: unknown.
5. S. Fujiuchi, *Fundemental Study of Solder Paste for Fine Pitch Soldering* (Shiga-ken, Japan: IBM), source unknown.
6. Peter Haasen, *Physical Metallurgy,* (Cambridge, UK: Cambridge University Press, 1978).
7. J. Hwang and R. Vargas, *Proc. 1989 Intl. Symp. on Microelectronics,* (Intl. Soc. Hybrid Microelectronics, 1989), p. 513.
8. T. Massalski, *Binary Alloy Phase Diagrams* eds. J. Murray and L. Bennett, (Metals Park, OH: ASM, 1986).
9a. Z. Mei and J. Morris, *J. Electron. Mater.* 21, (6), 599 (1992).
9b. C. Melton, *JOM* 45, (7) 33 (1993).
10. J. Phillips and K. Stillahn, *Electronic Packaging & Production,* (2) 78 (1992).
11. J. Schey, *Introduction to Manufacturing Processes,* (New York: McGraw Hill, Inc., 1987).
12. T. Singler, J. Clum and E. Prack, *Trans, ASME* 114 (6) (1992).
13. P. Vianco, P. Hosking and F. Rejent, *Proc. National Packaging and Production Conf.*, Vol. 3, (Des Plaines, IL: Cahner Exposition Group, 1992), p. 1730.
14. R. Wild, *Nepcon Proc.* 1974, p. 105.