

WETTABILITY OF LOW SN SOLDERS ON
INTEGRATED CIRCUIT PACKAGE METALLIZATIONS

by

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ABSTRACT

Sessile drop experiments were performed on six types of substrates (bulk Cu, bulk Ni, bulk Au, evaporated layers of CrCu and CrCuAu on silicon wafers, and plated layers of NiAu on screened Mo frit) with 9 Pb-Sn solder compositions ranging from 0 to 5%Sn. Samples were held in nitrogen for 2 minutes 30 seconds above 315°C, with a peak temperature of 345° 5°C. Area of spread and contact angle measurements were made to determine wettability. Statistical analysis of the data confirmed the observations that wettability is affected by Sn content, substrate material, and an interaction effect of the two. A general trend of increasing wettability with increasing Sn content was seen on all substrates. Cu, CrCu, and CrCuAu were relatively insensitive to changes in Sn content as compared to the other substrates. The MoNiAu structure wet to a greater extent and showed a greater sensitivity to changes in Sn content than any of the other substrates tested. The effects of surface preparation and Au surface concentration were studied as possible causes of this high wettability.

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INTRODUCTION

In industry there are numerous methods for attaching an integrated circuit chip to a ceramic substrate. One such method is through the use of a solder connection between terminal metals on the chip and substrate.

The substrate materials evaluated in this study were chosen for their similarity to actual metallizations which are soldered at IBM. Six types were used: bulk Cu, bulk Ni, bulk Au, blanket evaporated layers of CrCu and CrCuAu on silicon wafers, and blanket plated layers of NiAu on alumina screened with molybdenum frit. The solder pellet compositions were chosen as follows: 0%Sn, 0.1%Sn, 0.5%Sn, 1.0%Sn, 1.5%Sn, 2.5%Sn, 3.5%Sn, 4.5%Sn, 5.0%Sn, and balance Pb. This range of compositions was chosen based on current product use of 5.0%Sn.

In an effort to explain some of the results, four follow-up experiments were performed. First, large scatter in the MoNiAu results and the normalization factor used to make those results comparable were studied. Wettability tests were made with small size pellets of 2.5%Sn on CrCuAu substrates since these substrates showed the least scatter.

Experiments concentrating on surface conditions were also run. Alumina substrates with screened molybdenum frit were both Ni plated and Ni plated followed by immersion Au plating with no Ni/Au diffusion. Tests using 2.5% Sn were run on these parts so that bulk and plated Ni results could

be compared along with the effect of Au on wettability. Finally, the effect of cleaning Cu with 10% HCl, as opposed to 10% HNO₃, was observed using 2.5%Sn and 5.0%Sn.

BACKGROUNDSYSTEM DEFINITION

Wettability is a phenomenon that has been extensively studied since the early 1800's. Unfortunately, work on the subject is clouded in confusion due to a lack of universally agreed upon definitions and terms applied to wetting and its conditions. Also, much of the initial work performed on actual systems is invalid since the purity and cleanliness of the metals, surfaces, and atmospheres were not carefully controlled.⁽¹⁾

The conditions of wetting can be described mechanistically by Young's equation:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

where θ is the contact angle between the solid surface and the tangent to the liquid surface at the contact point.⁽²⁾

Wetting is usually defined in terms of this angle θ :

"wetting" or "partial wetting" at $\theta < 90^\circ$, "nonwetting" at $\theta > 90^\circ$, and "complete wetting" or "spreading" for $\theta = 0^\circ$.⁽³⁾

There is much dispute in the literature as to a definition of the " γ " terms in Young's equation that is both mechanistically and thermodynamically consistent. Johnson reviewed the literature and concluded that γ is a surface tension, not a surface free energy, although the two can be related.⁽⁴⁾ Therefore, in equation 1, γ_{LV} , γ_{LS} , and γ_{SV}

are defined as surface tensions of the liquid/vapor, liquid/solid and solid/vapor interfaces.

Gibbs derived Young's equation for the case of a drop of liquid small enough to neglect gravitational effects.⁽⁵⁾ In the 1950's Johnson defined Young's equation, the effect of the gravitational field, and the effect of curvature on pressure as necessary conditions to be considered for total mechanical equilibrium.⁽⁴⁾ The action of the pressure can be seen in the curved liquid surface at the line of contact with the solid.⁽⁶⁾

It should be noted that for chemical equilibrium the total free energy, not merely the free surface energy, of the system must be at a minimum.⁽⁴⁾ Since the liquid is mobile, it will always contract to form a spherical drop which has a minimum of surface free energy. The surface layers, however, will also rearrange themselves to minimize internal bond energy.⁽⁶⁾ Milner writes that the constituent which has the lowest surface free energy in the pure state will segregate to the surface of the mixture. Thus, the addition of a lower surface energy liquid to a higher one should markedly lower the latter's energy. This effect can be seen in many systems including Pb-Sn, Zn-Al, Mg-Al and Mg-Zn.^(6,1)

The major use of equation 1 is to help predict wetting behavior between a solid and a liquid. Another term commonly used for this purpose is the spreading coefficient

S_v , where S_v is the difference between the work of adhesion, W_A , and the work of cohesion, W_C :^(1,7,3)

$$W_C = 2\gamma_L \quad (2)$$

$$W_A = \gamma_S + \gamma_L - \gamma_{LS} \quad (3)$$

$$S_{VS} = \gamma_S + \gamma_L - \gamma_{LS} \quad (4)$$

The W_A term must be negative for wetting to take place spontaneously and S_{VS} must be positive for spreading to occur.^(8,9)

The aforementioned treatments of wetting assume that the solid and liquid are nonreactive and there is no mass transport across the smooth, planar interface. In this case the free energy changes driving the wetting are only associated with changes in interfacial area.⁽¹⁰⁾ If reactions do occur, such as formation of solid solutions or intermetallic compounds, then chemical reactivity, and the changing nature of the bonding surface, including the loss of planarity, must also be taken into account.⁽¹¹⁾

Although there is a reaction between the solid and the liquid, at the first instant of formation of an interface, it behaves like the nonreactive systems. That is, the decrease in the free energy of the system is attributed to the decrease in the free energy of the interfacial areas.⁽¹⁰⁾ When the solid is undersaturated with some component of the liquid, as in the formation of a compound at the interface, the change in free energy depends on the rate of reaction.⁽¹²⁾ If the driving force for wetting exceeds the surface energy of the liquid, spreading will

occur.⁽¹²⁾ When the liquid is undersaturated relative to a component in the solid, spreading does not occur and θ will change as γ_{LV} changes.⁽¹²⁾

Bailey and Watkins write that alloying is essential for wetting to occur, although alloying energy is not the driving force of the wetting reaction.⁽¹¹⁾ The alloying can take place on a very small scale, such as a few atom layers adjacent to the base metals.⁽⁶⁾ Thus, even a very low solubility between the liquid and solid should allow for some wetting.

The importance of the various interfacial tensions on wetting can be seen from equations 1 and 4 and much effort has been spent on their accurate determinations. Both experimental and theoretical approaches have been used, with the theoretical methods attempting to relate known physical or thermodynamic properties to surface tension and energies.

Although there are no universal techniques for finding γ_{LV} of all materials, the sessile and pendant drop methods are accurate over a wide range of temperatures for liquid metals and alloys.⁽¹³⁾ Weyl found for pure metals in general γ_{LV} decreases as the atomic radius increases within a given group of the Periodic Table, and within corresponding groups of metal derivatives.⁽¹⁾ Data by Hoar and Medford were consistent with a modified form of the classical regular solution model which relates the surface tension of a binary mixture to the surface tension of the pure components and the heat of mixing.⁽¹⁴⁾

Both γ_{SV} and γ_{LS} are difficult to determine by either experiment or calculation. Many methods have been devised to measure γ_{SV} ; however, they have been plagued by faulty logic, mathematical errors, and narrow conditions of applicability.⁽¹³⁾ Calculations of γ_{SV} based on atomic bonding energies are only approximate, such as Wassink's derivations of the relation:

$$\gamma_{SV} = \Delta H_V / 4 \text{ (molar surface area)} \quad (5)$$

where ΔH_V is the heat of vaporization.⁽¹⁵⁾ Jones reviewed experimental and theoretical methods for finding γ_{SL} between a crystal and its melt.⁽¹⁶⁾ Measuring of the dihedral angles at grain boundaries can only be used if the values of γ_{SV} and γ_{LV} are known. An approximate value of γ_{SL} can be calculated from values of the heat of alloying.⁽¹⁵⁾

The three interfacial energies are not independent of each other and thus their effects on wettability cannot be studied singly. For example, as discussed previously, additions of Pb to Sn will decrease γ_{LV} . Equations 1 and 4 show that as γ_{LV} increases, wettability should decrease; instead it increases. Harvey describes his work with Pb-Sn alloys on iron and found that in alloys up to 62.5% Sn, the decrease in γ_{SL} is controlling as opposed to high Sn alloys where the effect of lower γ_{SL} is overshadowed by higher γ_{LV} .⁽⁸⁾ The magnitude of γ_{SL} is dependent on the degree of chemical bonding.⁽¹⁰⁾ As the amount of the reactive component of the alloy increases, γ_{SL} decreases and approaches either γ_{SV} or γ_{LV} , whichever is lower.⁽¹⁰⁾

Thus, mixing of second components into a liquid can effect its wetting ability by changing surface tension, interfacial free energy, or both.⁽¹⁾

SURFACE CLEANLINESS AND FLUXES

Surface cleanliness is a critical determinant of wetting behavior. Hawkins and Feldman concluded that all liquids should spread spontaneously on completely clean metal and other solids with high surface free energies.⁽¹⁷⁾ The behavior of Pb on Fe illustrates this point: Pb will not wet on iron in air but will wet iron that has been scratched in vacuo, even though Pb and Fe are immiscible.⁽⁹⁾

Surface oxides and adsorbed gas layers on the solid will prevent or hinder wetting by lowering the solid surface tension and increasing the liquid/solid interface tension.^(1,9) This effect is often not complete and permanent, however, due to diffusion of the liquid into or through the metal-oxide interface.⁽¹⁾ The presence of an adsorbed surface layer will not prevent wetting completely if there is any interaction between the two unlike metals.⁽⁹⁾

Three methods are used to remove oxide films and adsorbed gases: heating in a reducing atmosphere, heating in a vacuum, or fluxing the system.⁽⁶⁾ The maximum cleaning effect is often found with fluxes, whose primary purpose is to promote contact between the molten metal and solid surface by removing the metal oxide film and preventing reoxidation.⁽¹⁸⁾

Fluxes are classified by the nature of their residues: corrosive, intermediate, and noncorrosive.⁽¹⁹⁾ Corrosive

or acid fluxes are composed of inorganic acids and salts, such as zinc chloride. Intermediate fluxes consist of mild organic acids and bases and certain of their derivatives. Noncorrosive fluxes are generally white water resin dissolved in an organic solvent. They contain abietic acid and become activated resin fluxes on the addition of small amounts of organic halides. Due to their fluxing power and low risk of corrosion, activated resin fluxes are used in electronic work.⁽¹⁹⁾

In addition to using acids to dissolve oxides, fluxes influence wetting behavior by altering surface tensions. Studies on Pb-Sn alloys show that both corrosive and noncorrosive fluxes reduce the surface tension of liquid solder to below that in its own vapor or in the presence of hydrogen.⁽¹⁴⁾ This effect may be due to the absorption of a component of the flux at the liquid-liquid interface.⁽¹⁴⁾

Lowering the liquid surface tension should reduce the contact angle if the other two surface tensions remain unaltered. On the addition of a flux, however, the solid/vapor interface no longer exists since the flux layer covers the metal. Also, resin based fluxes oxidize at soldering temperatures, which would affect all metal-flux interfacial tensions during heating.⁽²⁰⁾

Besides direct contact, the fluxing agent can modify surface tension by "pretinning". The solder-flux-metal system can form a galvanic cell when fused fluxes containing

molten salts are used, as was first demonstrated by Latin on a solder-chloride flux-copper system.^(9,21) Local cell formation has also been found with tin-flux-iron systems.⁽⁹⁾ Tin may be deposited by electrolytic action in front of the advancing solder, which will ensure a high substrate/flux interfacial tension and improve wetting.⁽¹¹⁾

The use of flux for removal of oxides and absorbed layers, and for lowering the surface tensions through direct contact, and pretinning: all increase wetting. Clearly, the appearance and strength of these phenomena are dependent on the fluxing agent chosen (corrosive, intermediate, or noncorrosive) and the degree of contamination or oxidation.

SURFACE INHOMOGENEITIES

Surface inhomogeneities due to energetic and physical causes have a distinct effect on wettability.⁽²²⁾ In general, these are not independent properties of real surfaces. If any reaction occurs between the liquid and solid, not only is the chemical nature altered but also the physical orientation of the surface is changed.

The first treatment of the effects of surface roughness, commonly called Wenzel's equation, was made in 1936. Wenzel stated that:

$$r(S_S - S_{SL}) = S_L \cos \theta \quad (6)$$

where S_S , S_{SL} , and S_L are surface tension values and r is the ratio of the area of the actual surface to that of a smooth surface having the same geometric size and shape.⁽²³⁾

This equation implies that behavior on a rough surface is increased over that on a smooth one.⁽⁶⁾ It is important to note, though, that the slopes and angles of the surface asperities determine " r ", not the heights of corrugations. Wenzel cites experimental work showing no change in wetting with a 100x change in asperity height.⁽²⁴⁾ Thus, r cannot be measured by surface profiles.

Wenzel's equation does not account for contact angle hysteresis, i.e. the angle of the liquid, as it spreads

outwards, exceeds the angle of the liquid as it retracts.

In 1948, Cassie extended Wenzel's equation to :

$$\cos \phi = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 \quad (7)$$

where ϕ is the contact angle of a heterogeneous surface and σ_1 and σ_2 are fractions of the surface having the intrinsic contact angles θ_1 and θ_2 respectively.⁽²⁵⁾ In this case, hysteresis is explained by changes in σ_1 and σ_2 as the liquid advances and recedes.

Shuttleworth and Bailey showed that Wenzel's equation is only applicable to cases of general roughness and not to a surface consisting of parallel grooves.⁽²⁶⁾ Grooved systems have been the emphasis of recent work since equilibrium can be obtained at a number of positions and may be a reason for contact angle hysteresis.⁽¹⁷⁾ Thus, the effect of surface heterogeneities can only be measured by studying very specific geometries and not on samples representing typical industrial surfaces.

PREVIOUS STUDIES

Much previous work has been performed on the specific solder-base metal systems discussed in this thesis. The following is a review of the results of other research. The topics covered include results of area of spread tests, immersion or flooding tests, capillary penetration tests, and surface tension measurements.

All of these tests offer some measure of wettability. The area of spread and contact angle measurements are described in detail in the Measurement Methods section of this thesis. Immersion or flooding tests consist of immersing a specimen in solder for a given time using a tilting furnace.⁽¹¹⁾ Capillary penetration tests measure a penetration coefficient of solder which flows between prefluxed and preheated flat horizontal plates. The general trends found using these methods, however, often contradict each other since different surface tension properties are being measured. For example, area of spread tests measure θ while capillary flow tests measure $\gamma_{LV} \cos \theta$.⁽²⁷⁾

In addition to studying composition variables, work has also been done on other experimental variables; accordingly, results of some studies of the effects of time and temperature on wettability will be covered.

It should be noted that reports of nonwetting in the older data should not always be accepted. This behavior may be due to experimental artifacts such as surface films and contaminants.

Nickel and Gold Plated Nickel

Bailey and Watkins performed immersion tests of Ni into pure Pb. Pure Pb showed no wetting (i.e. $\theta > 0^\circ$) or initial spreading on Ni in hydrogen at temperatures lower than 358°C .⁽¹¹⁾ From 358°C - 700°C , Pb forms a solid solution with Ni and will wet it. The effects of time (0-25 minutes) and temperature (300°C - 500°C) of immersion on the wetting of Ni by Pb are plotted to show what ranges of time and temperature are needed to produce a stable Pb coating on Ni. An extreme case of contact angle hysteresis was found at 500°C , where on immersion of Ni into Pb, the contact angle exceeded 90° but was 0° upon withdrawal. Also at this temperature, tin-lead alloys showed contact angles of 30° .

Experiments have also been reported on the wettability of pure Sn on Ni. Bailey and Watkins found good wetting at temperatures above 400°C in hydrogen.⁽¹¹⁾ Tammann and Ruhenbeck also performed tests in hydrogen and found no wetting at temperatures lower than 340°C and good wetting above 358°C .⁽¹⁾

In a more recent study, Feldstein and Thomas in 1979 reported contact angle measurements of 60/40 solder onto electroless Ni-B and Ni-P deposits with and without flux.⁽²⁸⁾ Contact angles of 32 - 56° were found on fluxed Ni deposits. In addition, tests on nickel sheet showed angles of 45° .

Harding and Pressly reviewed some work on soldering to Au plating over Ni and its alloys.⁽²⁹⁾ He theorized the cause to be due to the poor solderability of the base metal.⁽²⁹⁾ Many other researchers, however, found that if Ni and its alloys were properly cleaned before plating, they were readily soldered.⁽²⁹⁾

Copper

There is an extreme amount of variability of results found in the literature on copper soldering. For example, four independent measurements of a 60/40 alloy on clean copper with pure resin flux reported the contact angle to be 11°-13°, 15°, 24°, and 56°.⁽²⁰⁾ Therefore, it is more productive to examine trends and ranges of wetting behavior rather than absolute numbers.

In 1948 using capillary penetrations tests, Latin measured penetration coefficients of tin-lead alloys on copper.⁽²¹⁾ His results show the lowest coefficients with low Sn contents and the highest coefficients with pure Sn. He also found that the penetration coefficients were little affected by changes in flux but increased linearly with increasing amounts of superheat. From these results, it could be predicted that of the Pb-Sn alloys, pure Sn should wet the most on copper, and this wetting should increase as the superheat increases. Contradictory results are found, however, in area of spread tests.

Bailey and Watkins measured the effect of Sn concentration on the spreading of Sn-Pb alloys on copper in hydrogen at 250°C, 300°C, 350°C, and 400°C.⁽¹¹⁾ In general, the wettability is seen to increase to some maximum value at intermediate values of Sn, and then steadily decrease. These peaks in area of spread occur at higher tin contents as the temperature increases. The 400°C curve shows only a slight change in area changing Sn content, while the 250°C curve shows dramatic changes.

Unfortunately, testing all alloys at the same temperature may present misleading trends. Since the liquidus temperatures of the alloys vary with Sn content, the superheat and therefore the fluidity also vary. Since the variable of fluidity is uncontrolled, no conclusions about the effect of any variable can be made.

Bailey and Watkins also present work done on the spreading of Sn-Pb alloys on copper in a zinc ammonium chloride flux for superheats of 60°C, 100°C, and 150°C.⁽¹¹⁾ Similar behavior is seen here: the area of spread increases to a maximum at the intermediate range of Sn contents and then decreases. The maximum spreading in this case is found at around 50% Sn, as opposed to maxima in the range of 35%-65% Sn in the previous case. A general trend of decreasing wettability with increasing superheat can be readily seen in this example.

Besides the effects of temperature and superheat, Bailey and Watkins also studied the variable of time in the

solder-copper-hydrogen system.⁽¹¹⁾ Drops of solder alloys of less than 30% or greater than 70%Sn showed little or no change of shape after 30 minutes at temperature. From 30-70%Sn, however, an increase of drop diameter was observed. The strength of the effect was very dependent on the composition of the solder alloy 40-50 %Sn alloys at a 60°C superheat and observed no significant change in area over a 1/2 to 4 minute time period.⁽¹⁸⁾

In all of the above studies a contact angle greater than 0° and less than 90° was found. This is interesting in light of surface tension and solubility data. By measurements of grain boundary grooving, Bailey and Watkins reported the surface tension of solid Cu to be 1800 dynes/cm at 800-900°C. In the presence of Pb vapor, the solid Cu surface tension drops to 780 dynes/cm.⁽³⁰⁾ Fisher and Dunn also reported a value of 760 dynes/cm for Cu in the presence of Pb vapor.⁽³¹⁾ A value of 420 dynes/cm can be calculated for Cu in the presences of Pb vapor at 350°C.⁽³¹⁾ This value is nearly identical to the surface tension of liquid Pb under the same conditions.⁽³¹⁾ These low results suggest that under the selected test conditions, a complete monolayer of Pb atoms was deposited on the Cu.⁽³¹⁾

Bailey and Watkins also measured a solid metal/liquid metal surface tension of 340 dynes/cm for a Cu-Pb-hydrogen system at 800-900°C.⁽³⁰⁾ Given the surface tension

values of solid Cu in vacuum and the solid/liquid interfacial tension, the Pb should spread completely.⁽¹¹⁾

Thirty to forty degree contact angles of Pb on Cu have been measured though, and may be accounted for by an absorbed layer of Pb. In this case, however, poor adhesion might be expected. Bailey and Watkins observed that although pure Pb failed to wet Cu or Fe in a smooth continuous layer, the adhesion was strong when it was allowed to solidify in contact with either.⁽¹¹⁾ Although the solubility of Pb in Cu is very low, Howes and Saperstein did measure a reduction in the thickness of a piece of Cu immersed in pure Pb at 360°C for 300 seconds.⁽³²⁾ A balance of surface tensions and solubility may account for the reported contact angle of pure Pb on Cu.

EXPERIMENTAL PROCEDUREMATERIALSPellets

Solder pellets were obtained from Indium Corporation of America, Utica, NY. The vendor processing consisted of making a chill cast ingot of the solder alloy, rolling the ingot into a sheet, and punching pellets from the sheet. Table I lists the compositions requested and some measured compositions.

Based on a 90 sample lot, 10 pellets of each composition, the average weight per pellets was found to be 0.3105 gram (0.011 ounce) with a standard deviation of 0.0034 gram (0.00012 ounce). This uniformity of weight was then assumed for all pellets used.

Substrates

Ten mil (0.0254 cm) thick strips of 99.999% pure Cu, Ni, and Au were obtained from Research Organic/Inorganic of Belleville, NJ. Layered substrates of CrCu, CrCuAu, and MoNiAu were manufactured by IBM/East Fishkill. Table II lists the methods of metal deposition for these substrates.

The CrCu and CrCuAu substrates see no further processing after metal deposition. The MoNiAu substrates, however, go through one Mo/Ni diffusion and one Ni/Au

diffusion step. The thickness of the plated metals is often uneven and will cause the alloy composition and depth to vary from sample to sample and within one sample.

TABLE I: PELLETT ANALYSIS

Nominal %Sn	Titration*	ICAP**	DSC***	
			Run #1	Run#2
0.0		<0.0001	0.10	0.13
0.1	0.08	0.15	0.13	0.38
0.5	0.56	0.40	0.54	0.58
1.0	1.12	0.53	0.72	0.72
1.5	1.14		1.53	1.50
2.5	2.44		2.80	2.80
3.5	3.48	3.7	4.18	4.18
4.5	4.27		4.99	4.99
5.0	5.41		6.66	6.66

* Titration was performed by the vendor on approximately 8 gram samples with 0.3% accuracy.

** ICAP (Ion Coupled Argon Plasma) spectrometric technique used 0.01 gram samples with an accuracy of 2%.

*** DSC (Differential Scanning Calorimetry) used actual pellets with an accuracy of $\pm 0.5\%$ Sn.

TABLE II: LAYERED SUBSTRATE COMPOSITION

Base Substrate	Metallization	Metal	Deposition Method
Silicon Wafer	CrCu	Cr	evaporation
		Cu	evaporation
Silicon Wafer	CrCuAu	Cr	evaporation
		Cu	evaporation
		Au	evaporation
Alumina ceramic	MoNiAu	Mo	electroless plating
		Ni	electroless plating
		Au	immersion plating

SAMPLE PREPARATION

Pellets

The as received pellets were used on all substrates except for MoNiAu. On these surfaces the standard solder volume (0.3105 gram) spread until constrained by the edge of the sample. These tests are invalid since the tests did not allow for the full spreading of the solder. Smaller pellets that did not spread as much were required. For use on MoNiAu substrates, discs of 0.058-0.060 gram (0.00204-0.00211 ounce) and 0.040-0.041 gram (0.00141-0.00144 ounce) per pellet were punched from flattened standard size pellets of 0 to 4.5% Sn and 5.0% Sn respectively.

Substrates

The standard size substrate was approximately 1/2" x 3/4" (1.27 cm x 1.90 cm). Variations in the size were tolerated as long as the piece could accommodate all of the solder spread. Cu and Ni parts were cut with scissors from a strip of foil. CrCu and CrCuAu parts were made by scribing the surface of the metallized silicon wafer and snapping off the pieces. MoNiAu parts were cut to size with a diamond saw.

CLEANING PROCEDURES

Pellets

Solder pellets were cleaned ultrasonically in xylene for two minutes to remove grease and loose dirt, rinsed with isopropyl alcohol, and air dried.

Substrates

The following steps were used to clean the substrates.

Cu, Ni

1. Acid Clean
 - a. Cu - 10% Nitric acid for two minutes
 - b. Ni - 2:1 solution of Glacial Acetic acid: Nitric acid for 30 seconds.
2. Deionized (DI) water rinse
3. Blown with dry nitrogen
4. Cleaned ultrasonically for two minutes in xylene
5. Isopropyl alcohol rinse
6. Blown with dry nitrogen

Au, CrCuAu, MoNiAu

1. Steps 4 through 6 for the Cu, Ni procedure

CrCu

1. Xylene rinse (Samples could not be ultrasonically cleaned due to a delamination of the Cu)
2. Isopropyl alcohol rinse
3. Blown dry with nitrogen

After cleaning, the substrates were covered with a mixture of 2/3Jα-102 flux--1/3 isopropyl alcohol. A flux sprayer was used to ensure each substrate received the same surface coverage of flux. The flux was dried in a box furnace for 10 minutes at 100±5°C in nitrogen.

APPARATUS

The controlled atmosphere hot stage used for the sessile drop experiments is shown schematically in Figure 1. A tantalum strip was heated from below by a dumbbell shaped element. The hot zone was not isothermal, so a graphite specimen boat was placed on the strip for a more even distribution of heat. A metal cover over the nitrogen inlet port dissipated the gas and prevented uneven cooling of the boat.

Five holes were drilled into the lid of the graphite boat, three for gas passage and two for placement of thermocouples. One thermocouple was connected to a Houston Instrument Superscribe chart recorder, the other thermocouple led to the control portion of the equipment. A function diagram of the apparatus is shown in Figure 2.

The temperature controller used was an Omega Engineering Company Model 4602-KC. The powerstat was a variable autotransformer type 3PN116B made by the Superior Electric Company. The time delay relay was a Midtex/AEMCO Model 615-31T400, and the power relay was an Arrow Hart Model ACC230V20.

A photo of the entire apparatus is shown in Figure 3.

The control loop was started when the powerstat was manually turned on. The temperature controller's two set points were connected to the time delay relay and the power relay. When the controller read 315°C, the time delay

relay was activated. The second set point turned the powerstat on and off to reach but not overshoot the peak temperature. After approximately 90 seconds, the time delay relay turned off the power relay and therefore the powerstat. The powerstat was manually turned off before cooling to 315°C to prevent the cycle from starting again.

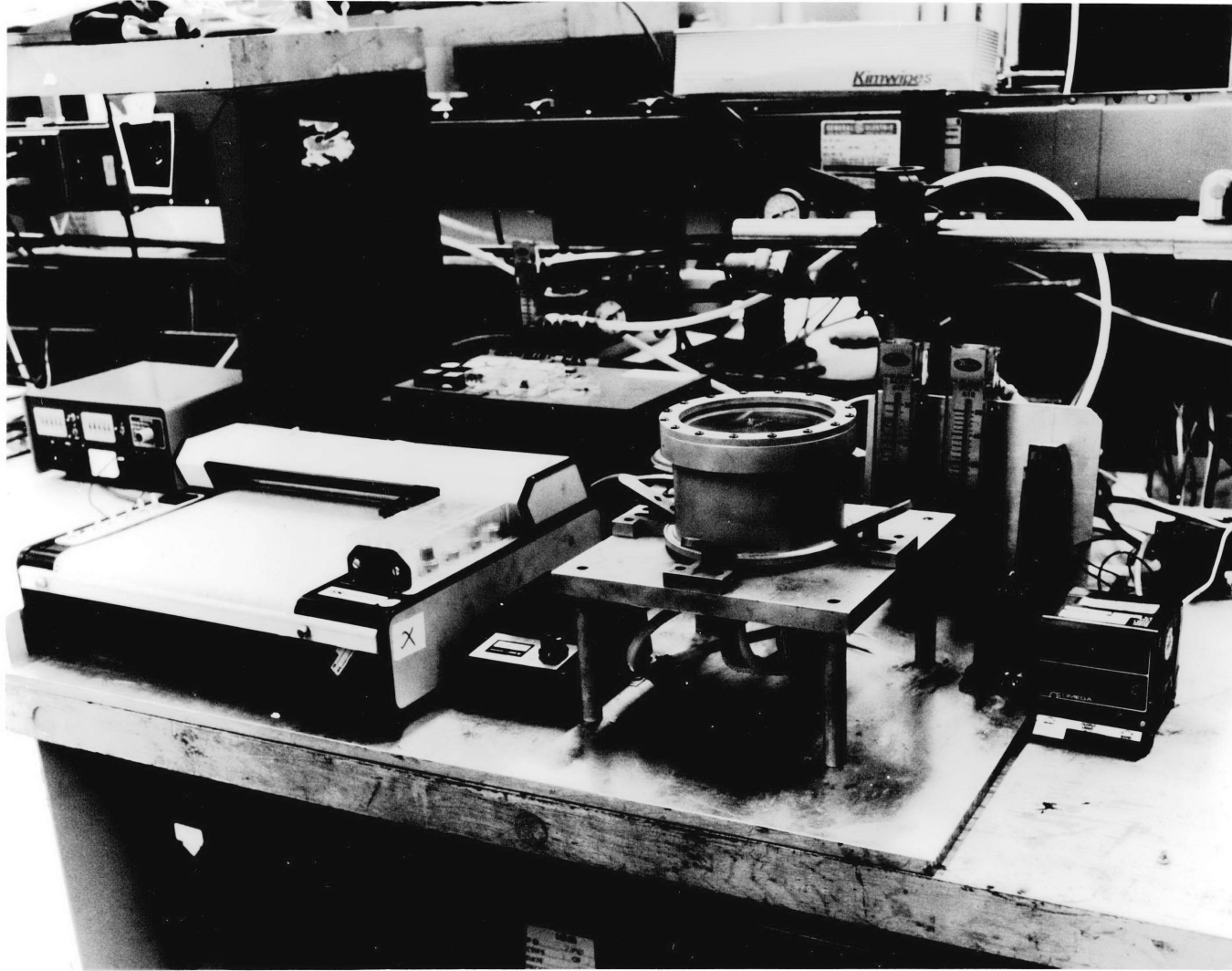
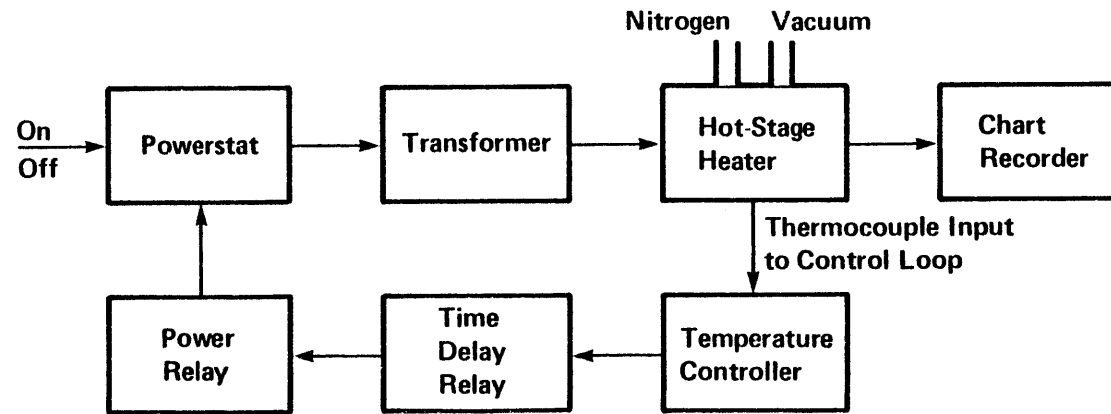


Figure 1: Controlled Atmosphere Hot Stage

Figure 2: Function Diagram for Closed Loop Hot-Stage Heating Apparatus



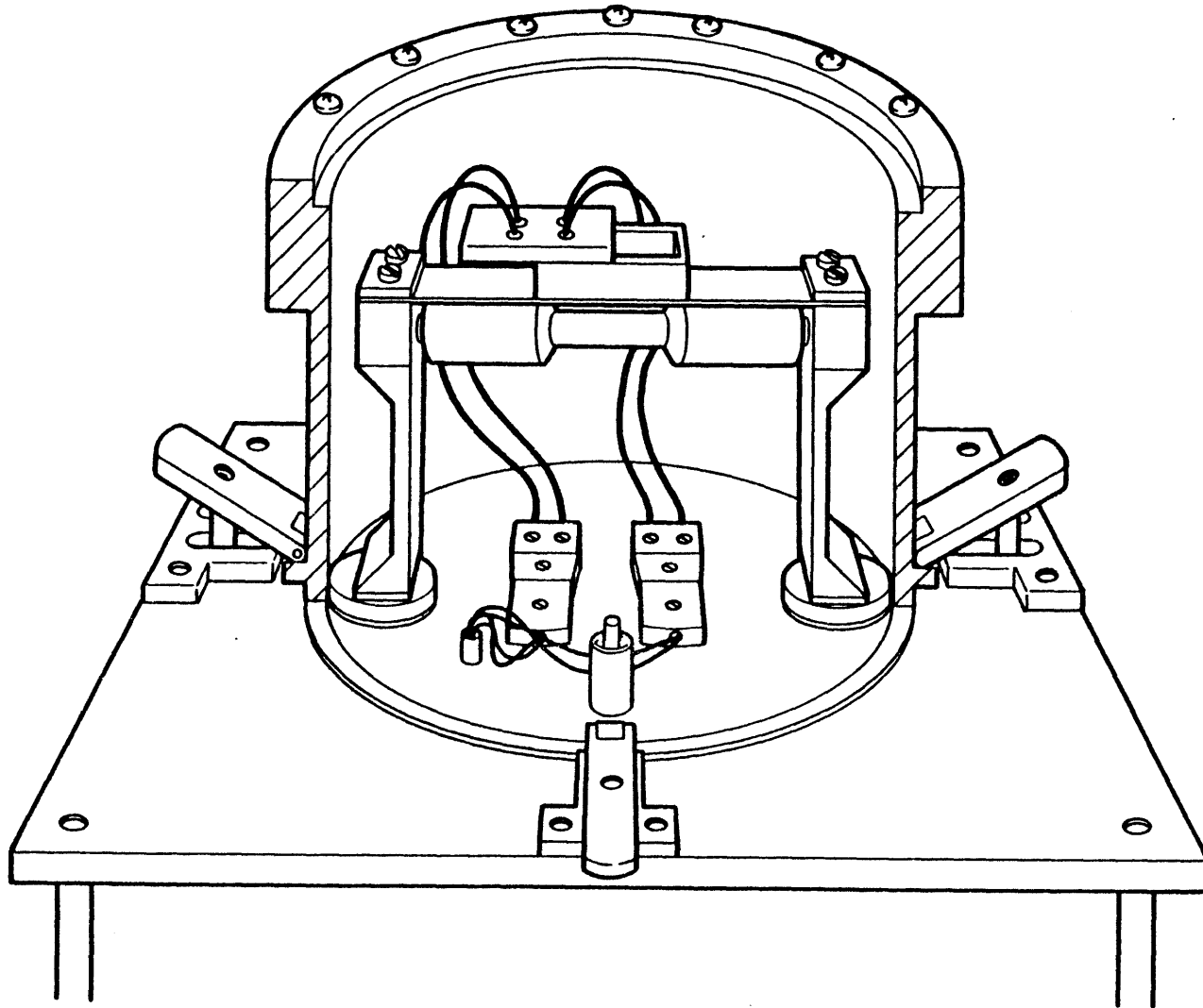


Figure 3: Area of Spread Testing Apparatus

TEST PROCEDURE

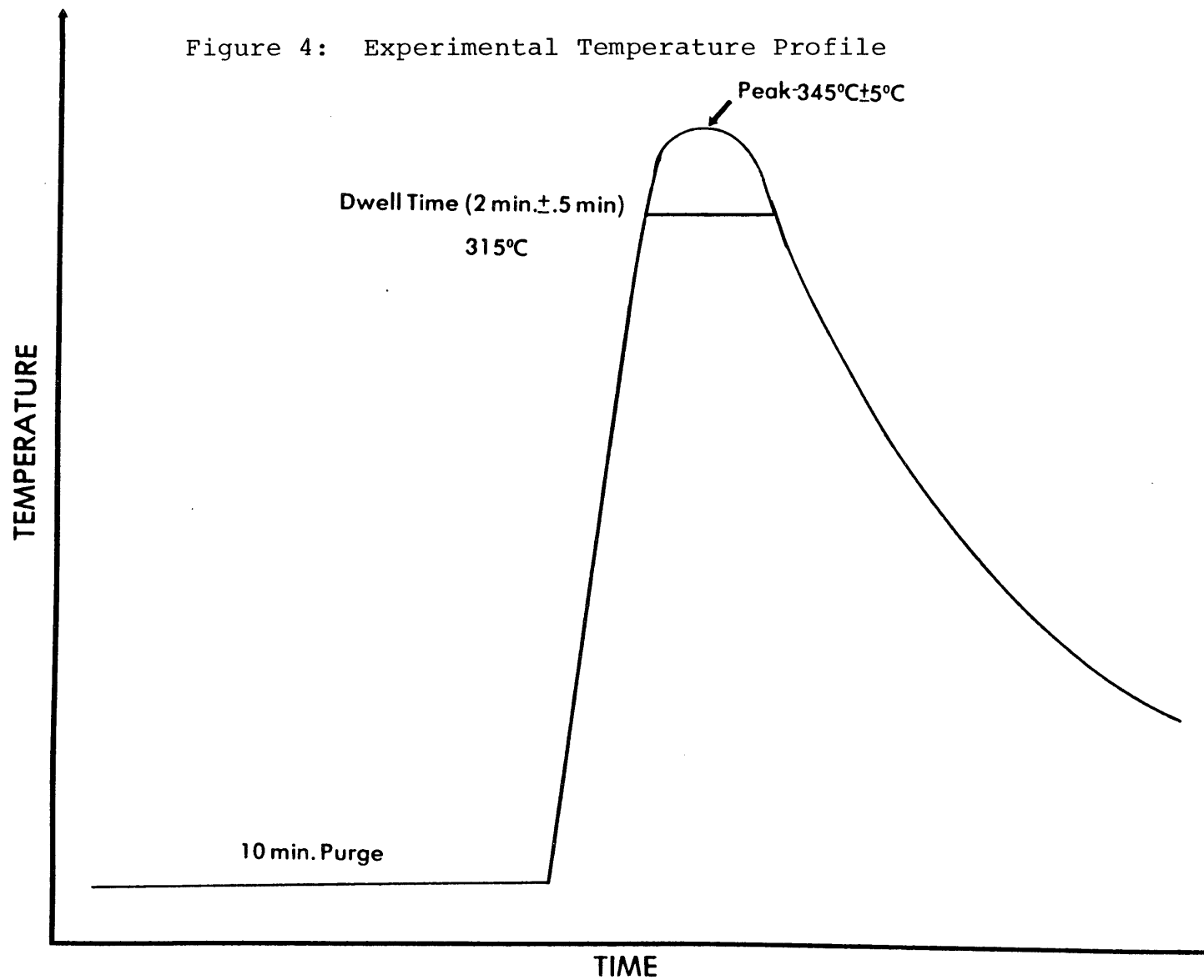
The following procedure was used for the wetting experiments after the substrates and solder pellets were prepared as described previously.

1. Temperature controller and chart recorder turned on
2. Chart recorder calibrated daily with Eurotherm Model 239 millivolt source.
3. Graphite boat centered on strip.
4. Substrate placed in boat.
5. Solder pellet placed on substrate.
6. Lid placed on graphite boat.
7. Lid placed over strip heater.
8. Gas regulators set to: vacuum - 20 to 21 SCFH, nitrogen - 19 to 20 SCFH. These settings were held throughout the experiment.
9. System swept with nitrogen for 10 minutes.
10. Powerstat manually turned on.
11. Powerstat turned off between peak temperature and 315°C.
12. Strip heater cover removed when boat temperature is 100°C.
13. Chart recorder stopped and dwell time checked.
14. Nitrogen and vacuum turned off.
15. Sample removed.
16. Graphite boat cooled to 35°C before next experiment.
17. Sample flux cleaned ultrasonically in xylene.

The temperature profile generated by the heating and controlling apparatus is shown in Figure 4.

This procedure was used for three samples in each cell of the 9 (solder compositions) x 5 (substrate types) matrix of experiments and for follow-up experiments.

Figure 4: Experimental Temperature Profile



MEASUREMENT METHODS

Contact angle

A drop of liquid will assume a shape with a minimum surface free energy, i.e. a sphere. Liquid solder on a solid substrate will also try to minimize its surface free energy, but its shape will be a spherical cap. The contact angle between the liquid and the solid is one measure of wettability. The lower the contact angle, the greater the wettability. A 0° angle indicates complete spreading, while an angle greater than 90° indicates no wetting or dewetting.

There are many sources of error in using this measurement on sessile drop experiments. Spherical geometry of the solder spread is assumed, but this assumption may not be valid for many reasons. First, the solder volume must be small enough that gravitational effects can be ignored. Second, the substrate must have no directional roughness. For example, any grooves in a surface, due to scratches or a rolling direction, would cause the solder shape to be ellipsoid, rather than spherical.

Another source of error is the assumption of equilibrium. Whether or not the liquid solder has reached a final equilibrium shape and spread, the measurement is made after the solid has solidified. The growth of dendrites during the crystallization of the solder leaves the interface edge rough. Determination of the angle exactly at

the point of contact is extremely difficult due to this cooling effect.

Besides the errors inherent in the sample itself, there are numerous sources of error in the actual act of making the measurement. Samples must be cross sectioned and finely polished, which is not feasible for large numbers of samples. The angle should be measured from the plane intersecting the highest point on the spherical section. Determining the center of a sample is not a clear-cut problem, and cross sectioning to that plane is not easily done. Once a picture of the sample is taken, determination of where the angle should be measured from is very subjective.

Therefore, although the contact angle is volume independent and representative of the balance of solder and substrate forces, it is not a precise measure of wettability.

Area of Spread

The area of spread test of wettability involves placing a fixed volume of solder on the surface of a substrate and heating the sample for a fixed time and temperature. The test is usually run at some level of superheat to ensure the fluidity of the solder. The greater the spread of the solder, the higher the wettability. The objective of this test is to measure an extent of wetting only; rates of wetting are not taken into account.

A commonly used test of wettability (ASTM), the area of spread measurement is often chosen for both technical and practical reasons. Since the sample is viewed from above, there is no need for an assumption of sphericity. The sample as a whole, not just a section is measured. Variables affecting the spread can be straight forwardly manipulated in the laboratory. Running the tests and taking the measurements can be easily done on large numbers of samples.

Much of the subjectiveness and difficulty in execution inherent in the contact angle measurement is by-passed by the area of spread test. Assuming a spherical geometry, there is a simple relationship between contact angle and area of spread:⁽³³⁾

$$\text{Area} = 3.7 \left(\frac{\text{Volume}}{\theta \text{ (rads)}} \right)^{2/3} \quad (8)$$

MEASUREMENT PROCEDURE

Due to the ease and precision possible in the technique, area of spread was chosen as the major measurement of wettability for this study. Area of spread measurements were made using a Zeiss Omicron T.A.S. (Texture Analysis System). Each sample was scanned by a television camera and displayed on a CRT screen. The instrument electronically counted the number of picture dots in the designated area and, given a magnification constant, converted these values into square inches. With no change in lighting parameters, the instrument would read the areas with 100% precision.

Due to their high reflectivity, the samples themselves could not be used to directly measure the areas. Therefore, measurements were made from photographs, viewing the samples from overhead. The lighting was adjusted to show as sharp a contrast as possible between the solder and the substrate.

On all MoNiAu substrates, and some samples of the other substrate types, the picture contrast was very poor. In these cases, a contour of the solder was drawn with a light pencil, and the area within the contour measured. The contouring was repeated three times for each ambiguous specimen. An average of these readings was taken as representative for the sample.

Since contact angle is the classic measure of wettability, this method was used to a limited extent. One

sample from each cell of the original test matrix was cross sectioned. Pictures of both sides of the solder/substrate edge were taken at x380 magnification. A base and a slope line were drawn on the photo. The angle was read from these constructions with a protractor.

It was often unclear where to place the base and slope lines. In these cases, another set of lines was drawn and additional measurements were made. If, on one side of a sample, the angles varied by more than 10° , the measurement differing the most from the opposite side was discarded. The angular values from both sides of the specimen were averaged and converted into areas of spread using equation 8.

RESULTS AND ANALYSIS

RESULTS

Preliminary tests performed on pure Au substrates showed that solder dissolved through the foil rather than spreading. No measurements were taken and experiments on the Au were discontinued.

Figures 5 through 9 show both the measured and calculated areas of spread of 0-5%Sn solders on Cu, Ni, CrCu, CrCuAu and MoNiAu substrate types, respectively. Tables III through VII list the measured areas of spread that are plotted in Figures 5 through 9 for the five substrate types. The measured contact angles and the calculated areas of spread based on these angles are listed in Table VIII.

Since smaller pellets were used on the MoNiAu substrates, a normalization factor was needed in order for these areas to be comparable to results using standard size pellets. The following relation, which assumes a spherical geometry, was used to calculate this factor:

$$(V_1/V_2)^{2/3} = (A_1/A_2) \quad (7)$$

Table VII lists both the measured and normalized areas for wetting on MoNiAu.

Tables IX through XI show the results of the follow-up experiments. Listed in Table IX are the areas of spread measured for 2.5% and 5.0%Sn alloys on Cu cleaned with two different acid solutions, i.e. 10% hydrochloric acid and 10% nitric acid. The areas of spread on CrCuAu for 0.0580-

0.060 gram pellets and standard size pellets of 2.5%Sn are shown in Table X. Table XI lists the areas of spread of 2.5%Sn on bulk Ni, electroless plated Ni, and electroless plated Ni with nondiffused immersion Au. Solder pellets of 0.058-0.060 gram size were used on the Au plated samples. The values listed for this surface were normalized to be comparable to standard size solder pellets.

Figure 5: Wettability as a Function of Percent Tin

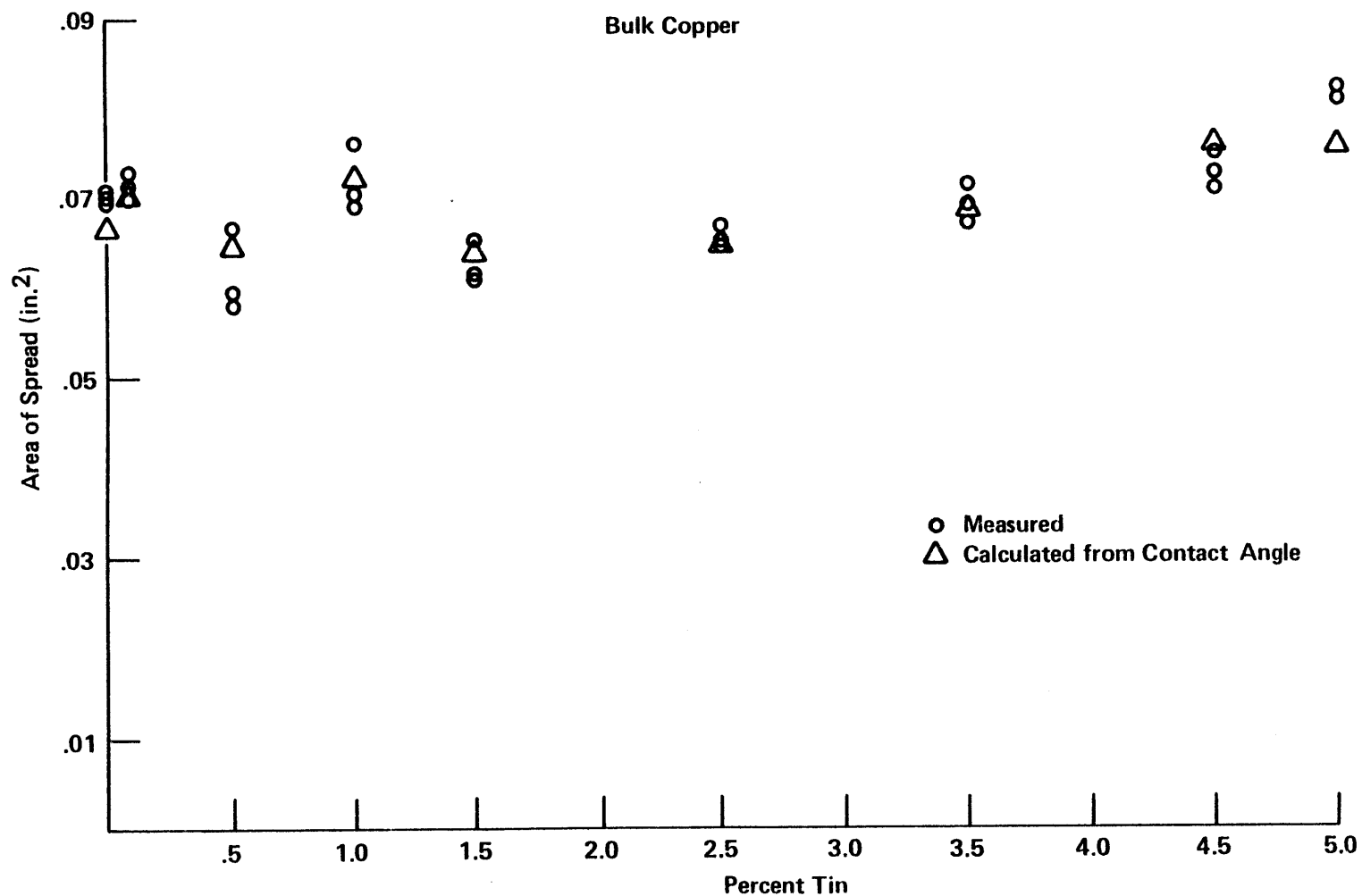


Figure 6: Wettability as a Function of Percent Tin

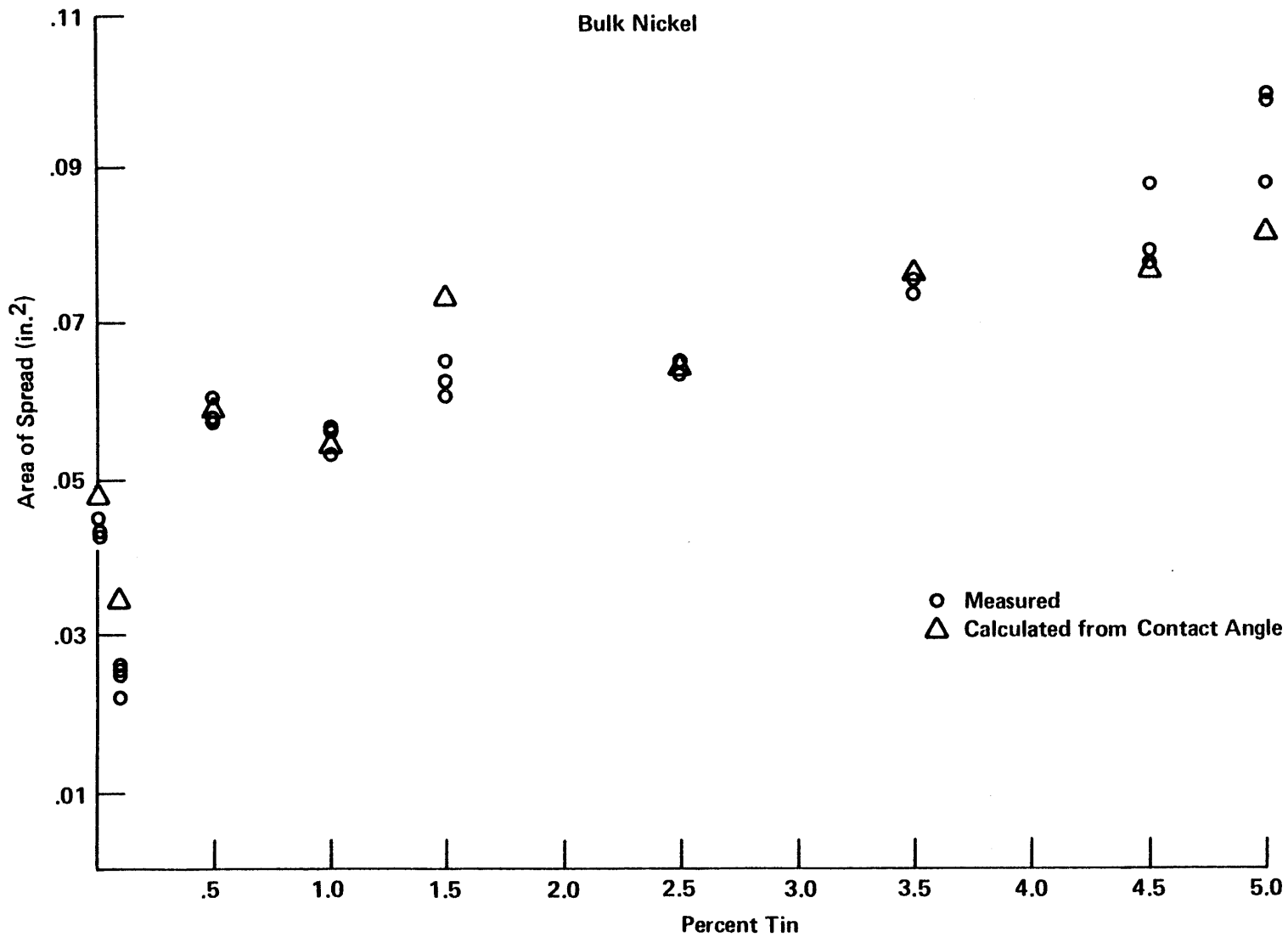


Figure 7: Wettability as a Function of Percent Tin

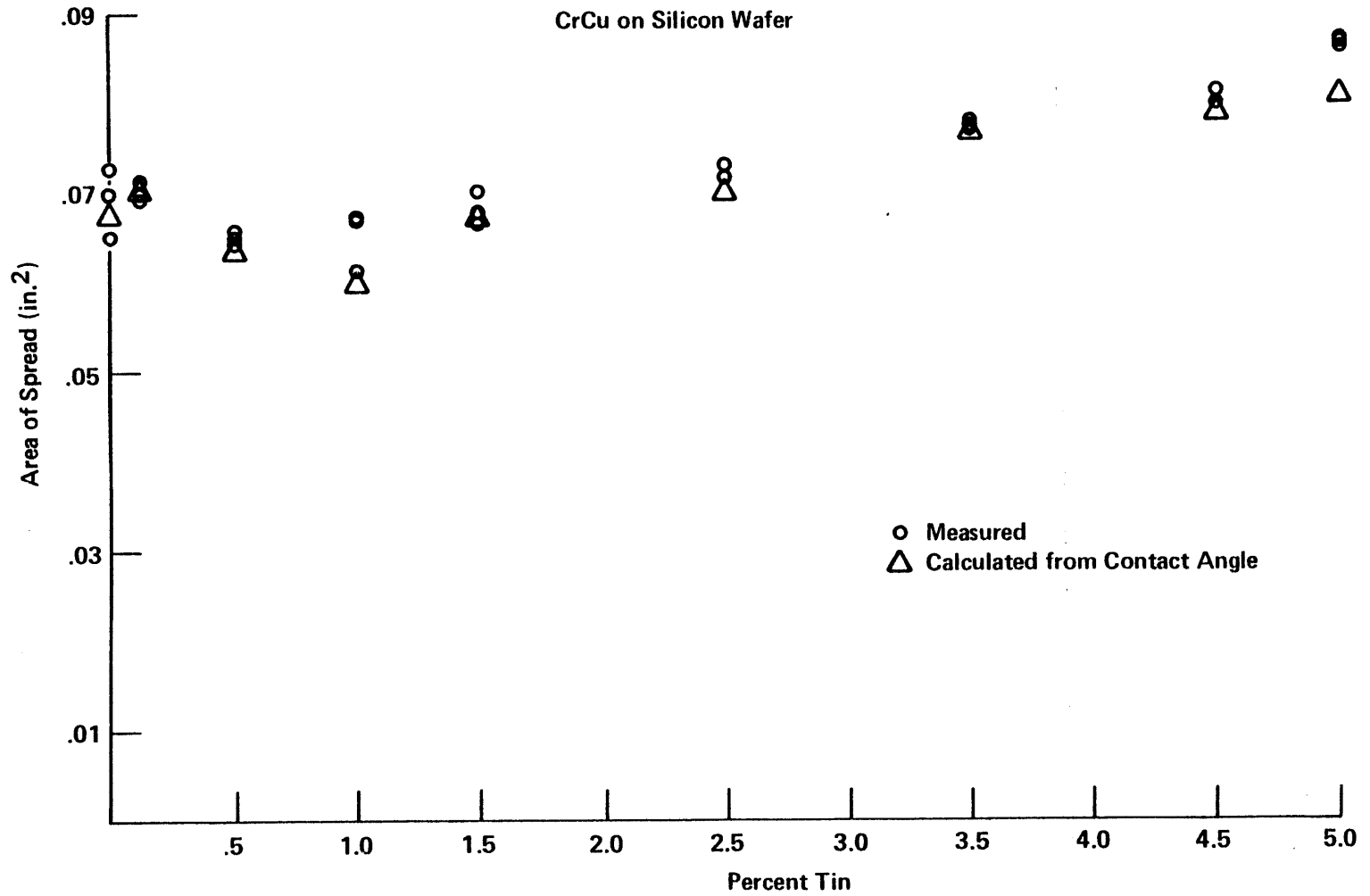


Figure 8: Wettability as a Function of Percent Tin

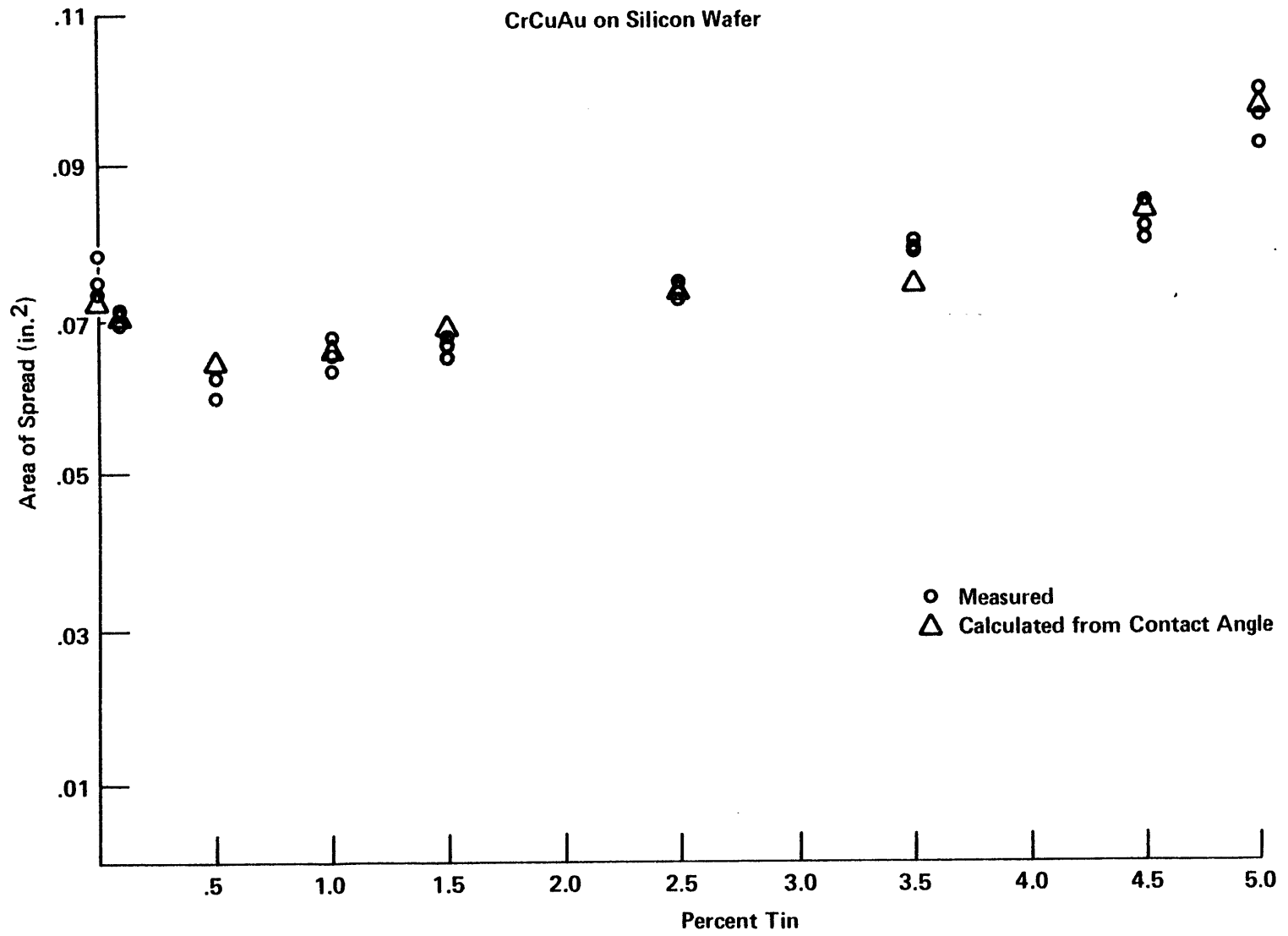


Figure 9: Wettability as a Function of Percent Tin

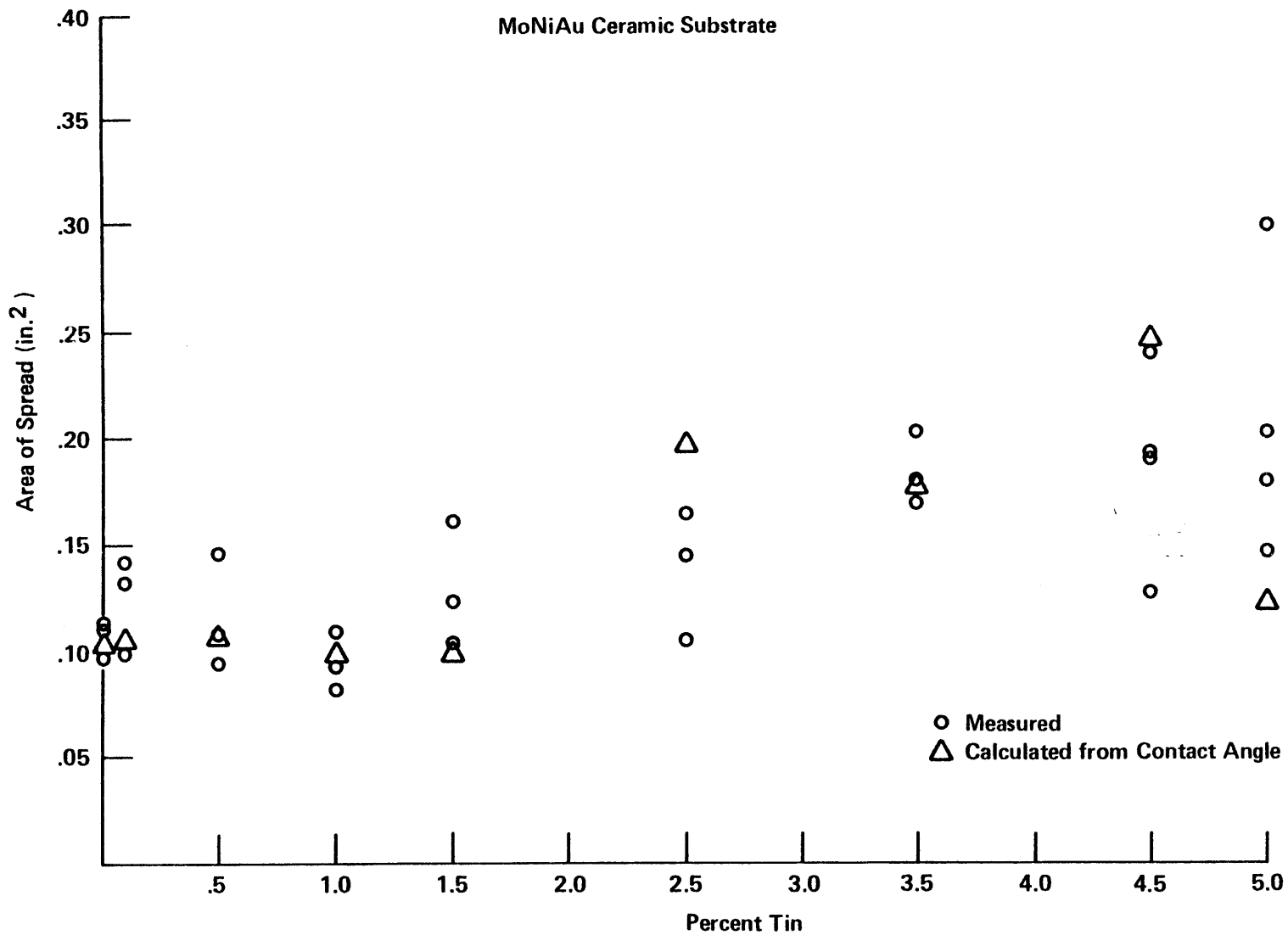


TABLE III: AREA OF SPREAD ON COPPER (in²)

Sample	% Sn								
	0.0	0.1	0.5	1.0	1.5	2.5	3.5	4.5	5.0
A	0.0696	0.0721	0.0590	0.0690	0.0605	0.0649	0.0673	0.0710	0.0809
B	0.0706	0.0699	0.0578	0.0755	0.0666	0.0645	0.0693	0.0748	0.0819
C	0.0698	0.0711	0.0668	0.0702	0.0613	0.0664	0.0714	0.0725	0.0806

TABLE IV: AREA OF SPREAD ON NICKEL (in²)

Sample	% Sn								
	0.0	0.1	0.5	1.0	1.5	2.5	3.5	4.5	5.0
A	0.0432	0.0224	0.0576	0.0560	0.0606	0.0638	0.0759	0.0779	0.1002
B	0.0436	0.0253	0.0580	0.0566	0.0625	0.0637	0.0756	0.0880	0.0994
C	0.0452	0.0261	0.0602	0.0534	0.0652	0.0654	0.0736	0.0795	0.0882

TABLE V: AREA OF SPREAD ON CrCu (in²)

Sample	% Sn								
	0.0	0.1	0.5	1.0	1.5	2.5	3.5	4.5	5.0
A	0.0694	0.0688	0.0641	0.0673	0.0695	0.0726	0.0766	0.0809	0.0860
B	0.0722	0.0696	0.0650	0.0685	0.0672	0.0714	0.0772	0.0807	0.0866
C	0.0651	0.0707	0.0645	0.0668	0.0660	0.0728	0.0774	0.0796	0.0860

TABLE VI: AREA OF SPREAD ON CrCuAu (in²)

Sample	% Sn								
	0.0	0.1	0.5	1.0	1.5	2.5	3.5	4.5	5.0
A	0.0780	0.0691	0.0597	0.0651	0.0665	0.0730	0.0798	0.0817	0.1000
B	0.0734	0.0694	0.0622	0.0631	0.0677	0.0745	0.0789	0.0851	0.0976
C	0.0748	0.0711	0.0621	0.0674	0.0650	0.0722	0.0784	0.0798	0.0928

TABLE VII: AREA OF SPREAD ON MoNiAu (in²)*

Sample	0.0	0.1	0.5	1.0	% Sn 1.5	2.5	3.5	4.5	5.0**
A	0.0325 (0.0972)	0.0326 (0.0988)	0.0482 (0.1458)	0.0274 (0.0829)	0.0530 (0.1605)	0.0342 (0.1035)	0.0668 (0.2021)	0.0791 (0.2395)	0.0461 (0.1791)
B	0.0368 (0.1114)	0.0439 (0.1328)	0.0353 (0.1069)	0.0308 (0.0932)	0.0344 (0.1042)	0.0541 (0.1636)	0.0563 (0.1705)	0.0626 (0.1895)	0.0374 (0.1456)
C	0.0363 (0.1097)	0.0468 (0.1412)	0.0325 (0.0983)	0.0364 (0.1103)	0.0405 (0.1227)	0.0479 (0.1449)	0.0593 (0.1794)	0.0635 (0.1921)	0.0543 (0.1937)

* Numbers in parentheses are areas normalized for 0.3105 gm pellets.

** One additional point was measured: 0.0876
(0.3046)

TABLE VIII: MEASURED CONTACT ANGLE ($M, ^\circ$) AND CALCULATED AREA OF SPREAD (C, in^2)

Substrate		%Sn								
		0.0	0.1	0.5	1.0	1.5	2.5	3.4	4.5	5.0
COPPER	M	38.0	36.8	40.0	34.5	41.2	40.0	35.8	32.5	33.0
	C	0.0678	0.0694	0.0656	0.0724	0.0642	0.0656	0.0706	0.0753	0.0745
NICKEL	M	62.8	100	46.2	54.0	33.5	40.8	31.8	31	27.2
	C	0.0486	0.0356	0.0595	0.0537	0.0738	0.0648	0.0764	0.0777	0.0846
CrCu	M	38.2	37.5	42.1	45.6	39.0	36.2	33.2	32.2	31
	C	0.0675	0.0685	0.0634	0.0600	0.0667	0.0699	0.0742	0.0760	0.0777
CrCuAu	M	34.8	35.8	40.5	39.8	36.8	33.8	33.2	28.2	23.0
	C	0.0720	0.0706	0.0650	0.0658	0.0694	0.0734	0.0742	0.0827	0.0949
MoNiAu	M	18.3	18.0	17.5	19.8	20.0	7.8	9.0	5.5	18.5
	C	0.1105	0.1117	0.1139	0.1049	0.1041	0.1961	0.1773	0.2461	0.1096

TABLE IX: AREA OF SPREAD ON Cu CLEANED
WITH HCl AND HNO₃ (in²).

SAMPLE	% Sn			
	2.5		5.0	
	10% HCl	10% HNO ₃	10% HCl	10% HNO ₃
A	0.0672	0.0649	0.0805	0.0809
B	0.0688	0.0645	0.0791	0.0819
C	0.0655	0.0664	0.0820	0.0806

TABLE X: AREA OF SPREAD OF 2.5% Sn SMALL PELLETS
AND 2.5% Sn STANDARD SIZE PELLETS ON CrCuAu

SAMPLE	PELLET SIZE	
	SMALL PELLETS (Normalized)	STANDARD PELLETS
A	0.0787	0.0730
B	0.0773	0.0745
C	0.0797	0.0722
D	0.0786	

TABLE XI: AREA OF SPREAD OF 2.5% Sn ON BULK Ni,
PLATED Ni AND PLATED Ni WITH NON-DIFFUSED
IMMERSION Au (in²)

SAMPLE	SURFACE		PLATED Ni IMMERSION Au NO DIFFUSION
	BULK Ni	PLATED Ni	
A	0.0638	0.0679	0.1083
B	0.0637	0.0646	0.1105
C	0.0654	0.0666	0.1076

STATISTICAL ANALYSIS

All area measurements of the main test matrix were submitted for statistical analysis. Using substrate type and %Sn as the variables, a two way analysis of variance was performed. The following combinations of surface types were tested: all five substrate types, all substrate types except for MoNiAu, and all copper containing substrates. The results of this analysis (see Tables XII and XIII) indicated that variations in the data are due to surface type, %Sn, and an interaction effect between these two factors. Thus, although the area values for all substrate types except MoNiAu are within the same range, 0.06-0.80 in², there is a statistically significant change of wettability with substrate type.

In addition to analysis of variance, regression analysis was used on the data to determine wettability as a function of Sn content. Data on bulk Ni, CrCuAu, and CrCu were fairly consistent and mathematical models with high correlation to the actual data were calculated. Due to the high degree of scatter of area values on bulk Cu and MoNiAu substrate types, satisfactory models to fit all the data were not obtained.

Some of the significant regression models are listed in Table XIII. The insensitivity of the Cu substrates to changes in Sn content can be seen by the regression model based on means. In this case the model calling for area of

spread to equal a constant has a fairly high multiple correlation coefficient. The extremely low scatter in the CrCuAu substrate data can be seen by the calculation of exactly the same fourth order model with very similar multiple correlation coefficients, regardless whether the model is based on all area values or on their means. The opposite property is seen for the MoNiAu substrates. Although almost the same first order model is found based on all values or on means, the multiple correlation coefficient improves almost 50% when the means are used.

TABLE XII: ANALYSIS OF VARIANCE RESULTS

Source A refers to %Sn, source B refers to substrate type and source AB refers to an interaction effect. An F calculation greater than $F_{.975}$ indicates that variation in the data is due to the sources.

- 1] Based on 9 different tin contents, 5 different substrate types:

Source	F Calculation	$F_{.975}$	Probability
A	8.5	3.75	1.0000
B	58.9	8.34	1.0000
AB	2.0	1.90	0.9949

- 2] Based on 9 different tin contents, 4 different substrate types (MoNiAu eliminated):

Source	F Calculation	$F_{.975}$	Probability
A	207.9	3.77	1.0000
B	125.8	13.98	1.0000
AB	41.9	2.07	1.0000

- 3] Based on 9 different tin contents, 3 different substrate types (bulk Cu, CrCuAu, and CrCu):

Source	F Calculation	$F_{.975}$	Probability
A	124.3	3.79	1.0000
B	41.3	39.48	1.0000
AB	9.9	2.48	1.0000

TABLE XIII: SIGNIFICANT REGRESSION MODELS

y = Area of Spread, x = %Sn. The closer the multiple correlation coefficient is to 1, the better the degree of fit.

SUBSTRATE TYPE	MODEL	MULTIPLE CORRELATION COEFFICIENT
Cu	$y = .0017x + .0059$	0.523
	$y = .0016x^2 - .0058x + .0700$	0.781
	$y = .0697$	0.828*
Ni	$y = .0101x + .0417$	0.906
	$y = .0015x^4 - .0012x^3 + .0316x + .0359$	0.934
	$y = .0377x + .0352$	0.943*
CrCu	$y = .0035x + .0651$	0.888
	$y = .0010x^2 - .0013x + .0677$	0.944
	$y = -.0004x^4 - .0038x^3 + .0140x^2 - .0153x + .0698$	0.996*
CrCuAu	$y = .0046x + .0649$	0.801
	$y = .0020x^2 - .0052x + .0701$	0.916
	$y = .0009x^4 - .0092x^3 + .0312x^2 - .0343x + .0740$	0.975
	$y = .0009x^4 - .0092x^3 + .0312x^2 - .0343x + .0740$	0.988*
MoNiAu	$y = .0257x + .0977$	0.619
	$y = .0257x + .0990$	0.899*
	$y = -.033x^3 + .0271x^2 - .301x + .1137$	0.927*

* Based on Means

SOURCES OF ERROR

Scatter in the wettability data is due to a combination of pellet, substrate, and process parameters. Variations in the volume and composition of the pellets will effect area values. Given a spread of 3 standard deviations, the weight of the standard pellets would be 0.3105 ± 0.051 gram. Although the pellets are very uniform in weight, any difference would effect the area of spread. Slight variations in Sn content of the pellets would also cause some error.

On a more sensitive substrate such as MoNiAu, the pellet weight and composition effects would be stronger. This may help account for the high degree of scatter in the area data on these substrates. Another factor contributing to the high scatter is the uneven MoNiAu surface. After Au/Ni diffusion, the surface alloy composition and thickness of the alloyed layer will vary. Any change in alloy composition and depth will cause the wettability of the sample to vary.

On the MoNiAu substrates, smaller sized pellets were required for the wetting experiments. If the original pellets were inhomogeneous, there would be large variations in the Sn contents of the smaller pellets. In an effort to see how much scatter in the area data was due to these pellets, a follow-up experiment was performed using 2.5%Sn pellets of 0.058-0.060 gram weight on CrCuAu substrates (see

Table X). The CrCuAu substrate type was chosen since it showed the least amount of scatter in the data.

The results showed little scatter in the area values of the small pellets on CrCuAu substrates. Therefore, the pellet compositions must be relatively uniform and the high scatter must be due mainly to the unevenness and sensitivity of the MoNiAu surface.

The area values of the small pellets on CrCuAu also gave some idea of the error introduced by the MoNiAu normalization factor used to make MoNiAu substrate results comparable to the other substrate type results (see Table X). The results showed that the normalization factor biased the results to be slightly higher than actual. Although this effect may be small at 2.5%Sn, it is unclear whether the magnitude of this error is constant at all Sn contents.

In the thermal profile of the area of spread test, the peak temperature varies $\pm 5^{\circ}\text{C}$ and the dwell time varies ± 15 seconds. These changes will effect the kinetics of the wetting reactions and therefore the wettability. Slight variations in the quantity of flux on the samples may also have an effect on the results. No work was done to quantify the changes in wettability due to these factors.

Another procedural variable that may cause some error is the use of the same temperature profile in all of the tests for all compositions. Since the liquidus temperature changes from 327°C at 0%Sn to 315°C at 5%Sn, the superheat and therefore the fluidity of the molten solder will vary

for each composition. Although the difference is only 12°C, the magnitude of this variation could be measured.

In addition to errors inherent in the test materials and processes, errors are always introduced when taking measurements. These sources of error are discussed in the Measurements Methods section of this paper. It should be noted that a 10% error in θ will cause a 6-7% error in the calculated area of spread, based on equation 1.

DISCUSSION and CONCLUSION

From Figures 5 to 9 it can be seen that there is a general trend of increasing wettability with increasing Sn content. All substrates also showed some anomalous wetting behavior, i.e. unexpected dips and rises in the area of spread, at Sn contents lower than 1%. Especially meaningful was the use of 0.1% Sn on Ni substrates whereby the solder balled up rather than spreading. The wettability of solder on all Cu containing substrates was very similar. The wetting of MoNiAu surfaces was better and also had a higher increase of area of spread with increasing Sn content than any of the other substrates types tested. In comparison to the Ni and MoNiAu substrate types, the Cu containing substrates were relatively insensitive to changes in Sn content. All substrates showed wetting at 0% Sn (pure Pb).

The increase of wetting with increasing Sn content is an expected result. In terms of surface tensions, the wetting phenomenon can be mechanistically described by a modified form of equation 1 with flux in the system (see Figure 10):⁽³⁴⁾

$$\gamma_{SF} = \gamma_{SL} + \gamma_{LF} \cos \theta \quad (10)$$

where: γ_{SF} = surface tension of solid/flux interface

γ_{LF} = surface tension of liquid/flux interface, and

γ_{SL} = surface tension of solid/liquid interface.

The changes in surface tensions with increasing Sn content should increase the wettability, as was discussed in the background section of this paper.

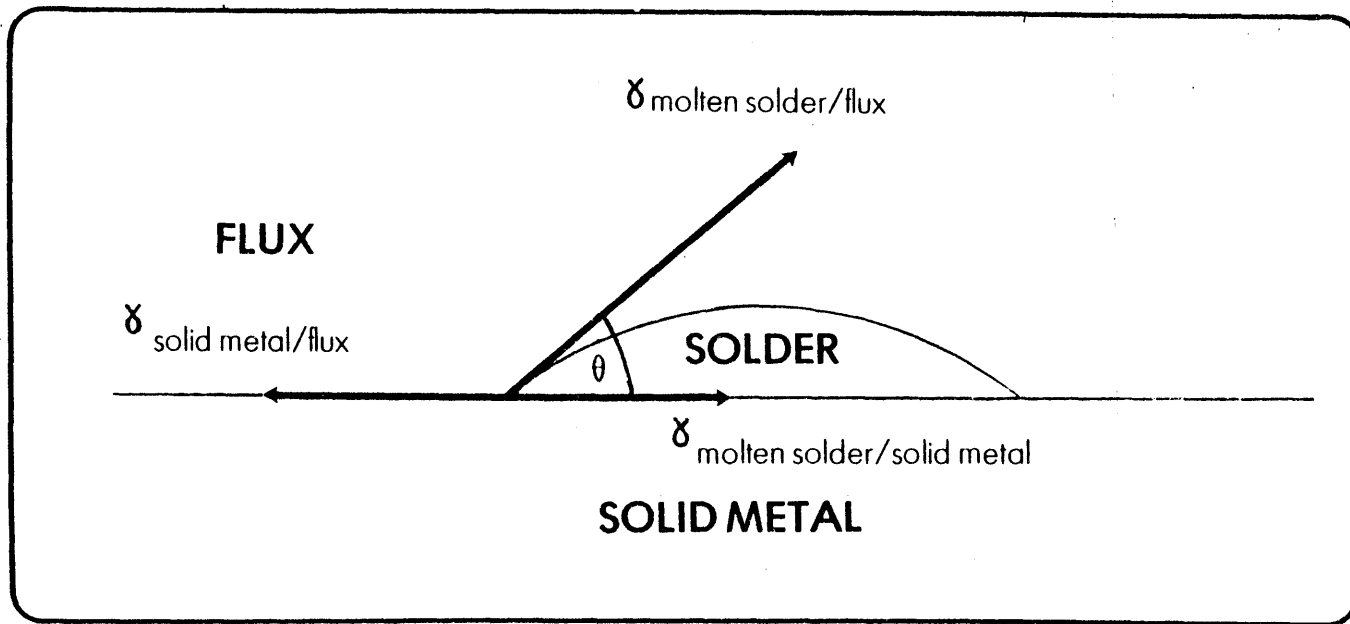


Figure 10: Diagrammatic Representation of Solder Pool on Fluxed Metal Surface

In the alloys containing Sn, intermetallics are formed at the interface. Some of the intermetallics likely to be formed during the experimental heating cycle include :

Cu_5Sn_6 , Cu_3Sn , Ni_3Sn_4 , AuSn , AuSn_4 , and AuSn_4 .⁽³⁵⁾ No compound identification was performed during the course of the study.

Once the Sn has started to react with the surface metallizations, both the roughness and composition of the solid surface change. Young's equation applies only to an unreacted solid and may therefore be used only as a guide and not a complete mechanistic description of, the wetting processes being viewed in these experiments.

That Au is extremely soluble in Pb and Sn was seen by the attempted wettability experiments where molten solder went through pure Au foil. The effect on wettability of Au on Cu and Ni appears to differ dramatically. The wettability of Cr and CrCuAu substrate types is very similar.

Bulk Ni and MoNiAu have extremely different wetting patterns. MoNiAu not only has a higher degree of spreading (0.10-0.30 in), it also has a higher rate of increase of spreading with Sn content. One possible explanation is the presence of different relative Au concentrations on the surface, however, there is another factor involved. The Ni on the MoNiAu substrates is electrolessly plated while the bulk Ni comes from a rolled sheet. (During diffusion of the

molybdenum and nickel, the codeposited agent necessary for Ni plating is totally removed.)

In an effort to separate the effects of surface condition and Au, follow-up experiments were performed with 2.5%Sn on Ni plated and Ni plated with nondiffused immersion Au substrates (see Table XI). The plated Ni surface shows only a slight, possibly insignificant, increase of wettability over the bulk Ni surface. Therefore the much higher wettability of the MoNiAu substrate must be due to the presence of Au and not the differences in plated and rolled Ni.

The nondiffused Au surface shows much better wettability than either of the pure Ni surfaces. The Au/Ni diffused substrates, however, have an even higher wettability. This effect may be understood in light of the pure Au results, where the solder did not spread but dissolved straight through the foil. If area of spread measurements were to be made on these samples, the results would show a non-wetting behavior since the spread area was not greater than the original area. Au, however, is wet by Pb-Sn solders.⁽³⁶⁾ In the case of the non-diffused surface, the thin Au layer did enhance the wettability of the Ni, but was eaten through before the solder could spread more. By alloying the Ni and Au, the Au is not free to be dissolved as quickly by the solder. Thus, the Au enhances the wetting without being totally dissolved into the solder.

From the preceding discussion it is obvious that the surface condition is extremely important in wetting phenomena. The cleaning procedures described in the experimental procedure were used consistently throughout the testing. On Cu surfaces, nitric acid may not only dissolve copper oxide but also copper itself. HCl should not dissolve the Cu, only the Cu oxides. Therefore, another cleaning procedures for Cu, namely 10% HCl solution for two minutes, was tried using 2.5% and 5.0%Sn (see Table IX). There is no apparent change in wettability caused by these different cleaning procedures.

FUTURE WORK

This paper describes the functional wettability of low Sn solders on some integrated circuit package metallizations. The results raise some questions that would be extremely useful to answer.

Some of the sources of error may be quantifiable with more testing to find the effects of process parameters, such as the $\pm 5^{\circ}\text{C}$ peak temperature and the ± 15 second dwell time. Tests should be run with carefully controlled temperature profiles. The change of wettability at the extreme superheat limits could be measured. This work would yield information that could also be useful in planning future experiments of time and temperature on wetting.

The accuracy of the normalization factor was studied to a slight extent. Tests using small size pellets of a range of Sn contents and substrates should be performed to determine whether the error inherent in the factor is systematic or not.

The fluxes and atmospheres chosen for this study are two more factors whose effects should be studied. They can have not only an oxide cleaning action, but can also alter the surface tensions of the solder and substrate. Both different types and quantities of fluxes, ambients (N_2 , N_2H_2 , and H_2) and combinations of these variables should be tested for their effects on the wettability of solders and surfaces.

Finally, the wetting of the low Sn solders directly onto intermetallics rather than pure metals should be studied. The results of tests on these substrate types would show the fundamental wettability of the intermetallics. In addition, if these results were then compared to the substrate types used in this study, the effect of the actual intermetallic formation during the wetting process could be seen.

With only minor changes, the apparatus and procedure described in this paper could be used to perform all of the above mentioned studies.

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