Experimental Wetting Dynamics Study of Eutectic and Lead-Free Solders Varying Flux, Temperature and Surface Finish Metallization

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Abstract

Demands on solder bump interconnects have increased in modern electronics this is characterized by high density, small size and fine pitch devices. In solder bump interconnects, solder wetting onto bond pads is the key factor that determines the interconnect process yield and the solder joint reliability. Solder wetting involves various physical phenomena such as a surface tension imbalance, viscous dissipation, molecular kinetic motion, chemical reactions and diffusion. In this paper, an experimental study on solder wetting dynamics will be presented along with an analytical predicting solder ball wetting. The effects of solder reflow process parameters and bonding materials will be discussed, as they relate to the physics of solder wetting and ultimately the interconnect process yield and solder joint reliability. The experimental setup consists of a high-speed image acquisition system and a temperature chamber which were used to measure the time dependent behavior of molten solder spheres onto bond pads under an isothermal condition. The solder materials investigated are eutectic tin-lead solder and lead-free 95.5Sn-4.0Ag-0.5Cu solder. The wetting dynamics of the solder materials were investigated on Cu, Cu/OSP, and Cu/Ni/Au bond pads, with several different flux systems, at different environmental temperatures and with various solder sphere sizes. The experimental observations indicate that the wetting dynamics clearly depend on temperature, solder materials and substrate metallization but do not depend significantly on the flux system or the solder sphere size.

Moreover, this research develops an analytic methodology based on solder wetting dynamics, that can be used to predict solder interconnect formation during electronics assembly. The major benefit of such an advanced process model is that it enables process design and process parameter optimization through simulation. The model also reveals the cause of wetting problems that may occur during the assembly process and provides a solution. Low cost assembly process will be achieved via optimizing an assembly process time and reducing a interconnect failure rate. This work will lead to a fundamental basis for better understanding the complex phenomenon of solder wetting during electronics assembly.

Introduction

Flip chip solder bump interconnect technology provides greater I/O density and a shorter electrical path with less propagation delay than traditional wirebond packages [1]. In addition, a variety of packages such as ball grid array (BGA) and chip scale package (CSP) are using solder bump interconnect technology as opposed to conventional lead frame technology.

One of the most critical processes in flip chip assembly is the reflow operation. During reflow solder becomes liquidous, it wets to the substrate bond pads, and the chip collapses. It has been observed that the interconnect process yield and the solder joint reliability are highly dependent on the conditions in reflow [2]. For example, a short time above liquidus and/or a low peak temperature may lead to incomplete melting of the solder spheres which would negatively impact the solder wetting dynamics, or potentially a cold joint could form. If the time above liquidus is too long and the peak temperature is too high, an excessive amount of intermetallic compound may be formed, resulting in an unreliable, brittle solder joint.

Therefore, from a processing standpoint, the dynamics of solder wetting are important in optimizing the reflow temperature profile in terms of the interconnect process yield and solder joint reliability. However, the complexity of the solder wetting dynamics resulting from the simultaneous occurrence of various physical phenomena such as a surface tension imbalance, viscous dissipation, molecular kinetic motion, chemical reaction and diffusion, have been studied by only a few researchers.

Boettinger *et al.* introduced the physical processes involved in the wetting of molten solder on a metal substrate and surveyed the current status of solder wetting studies [3]. Braun *et al.* analyzed reactive wetting by modeling the Marangoni effect, which is due to a temperature gradient and the changing concentration of Sn produced the near the substrate [4]. Yost *et al.* discussed the energetics and kinetics

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of the dissolutive wetting process assuming that substrate dissolution controls the wetting kinetics [5]. This model begins with a relationship for the increase in entropy associated with the wetting process and is applied to the system with the Bi-Sn droplet on the Sn substrate. Gao *et al.* modeled the solder profile evolution and triple point line motion driven by surface tensions and the gravity field, assuming that the velocity of the interface (wetting kinetics) was a linear function of the driving force [6]. However, the results have not been experimentally verified. Peebles *et al.* constructed an ultrahigh vacuum in situ surface analysis and wetting system experimental setup [7] and measured isothermal spreading of Sn solder on the Cu substrate without a fluxing agent [8]. The experimental work presented in this paper shows that temperature plays a key role in determining the solder wetting rate. The impact of the surface chemistry on the spreading rate of solder was studied with various substrate metallizations.

The objective of this research was to experimentally study the solder wetting dynamics under various process and material conditions. The solder materials investigated in this research are eutectic tin-lead solder and lead-free 95.5Sn-4.0Ag-0.5Cu solder. The wetting dynamics of the solder materials were investigated on pure Cu pads and Cu/Ni/Au pads, with several different flux systems, at several different environment temperatures and with several solder sphere sizes. The experimental results presented here provide valuable information for the modeling of solder wetting dynamics.

In addition, this research develops an analytic methodology based on solder wetting dynamics, that can be used to predict solder interconnect formation during electronics assembly. The major benefit of such an advanced process model is that it enables process design and process parameter optimization through simulation. The model also reveals the cause of wetting problems that may occur during the assembly process and provides a solution. Low cost assembly process will be achieved via optimizing an assembly process time and reducing a interconnect failure rate. This work will lead to a fundamental basis for better understanding the complex phenomenon of solder wetting during electronics assembly.

Experimental Setup

The authors of this paper developed a system to conduct solder wetting experiments that monitor the dynamic wetting behavior of solder in a high temperature environment. The experimental setup consisted of a thermal chamber, a high-speed video system, and a solder sphere delivery mechanism. A schematic of the experimental setup is shown in Figure 1.

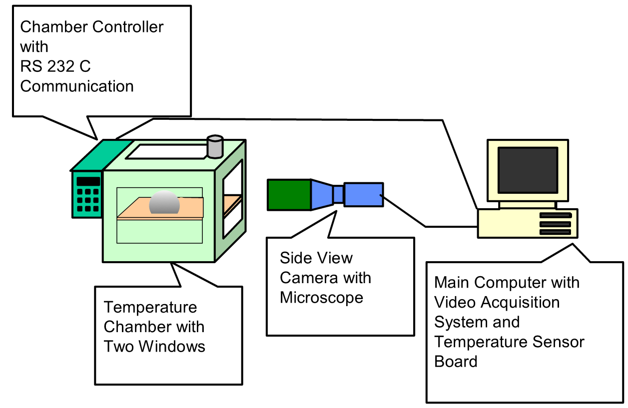


Figure 1 Schematic diagram of experimental setup

The thermal chamber was fitted with two insulated double-pane windows to permit external monitoring of solder wetting. The chamber can provide high ramp rates, which are up to 100^{o}C per minute and a maximum temperature capacitance of 350^{o}C. Isothermal conditions are maintained during solder wetting so the effect of environmental temperature on solder wetting can be investigated. A gas inlet port was provided such that the atmosphere inside the chamber could be modified, the conditions used in the experimentation were an inert nitrogen environment as well as an air environment.

The monitoring system used a high-speed camera and a video acquisition system. A 7× microscopic lens was attached to the camera to magnify the small solder sphere throughout the wetting process.

A solder sphere delivery system was added to the original thermal chamber. The delivery system consisted of a micrometer, an aluminum rod, a non-wettable delivery surface (a glass slide), and a holder (a glass slide holder) as shown in Figure 2.

A tacky flux holds the solder sphere in place on the glass delivery slide as it is lowered to the wettable substrate, when the solder sphere contacts the wettable substrate it wets to the substrate. The delivery system prevents the solder sphere from reaching the wettable surface of the substrate prior to when the desired thermal and environmental conditions are reached in the chamber. Three conditions must be reached before solder wetting can take place and these conditions must be maintained throughout the wetting process. First, a solder sphere must be in the molten state in the absence of the solid phase. Second, the surfaces of the solder sphere and a substrate must be oxide-free. Third, the atmosphere must reach a uniform isothermal condition. The delivery system keeps the solder sphere away from the wettable substrate while the sphere melts, the flux is activated and removes the oxides from the surfaces of the solder sphere and the substrate, and the environmental temperature is increased to a specific set point.

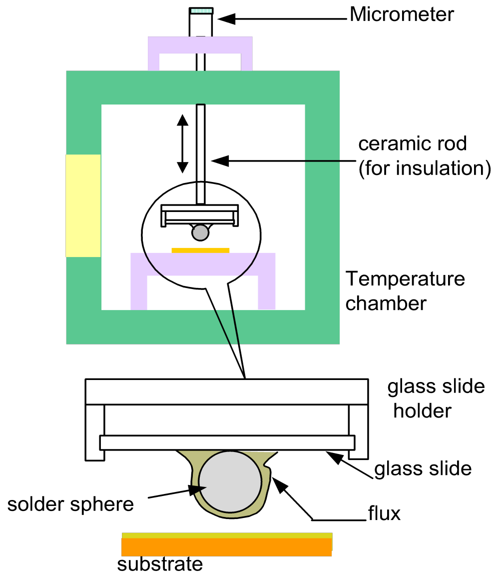


Figure 2 Schematic illustration of the solder delivery system

Experiment procedure

A series of experiments were performed to measure the motion of solder wetting between solder and a substrate under isothermal conditions. The experiment started by preparing the various materials for solder wetting. The Cu substrates were cleaned with a 10% Hydrochloric acid solution, rinsed in deionized water and then dried with purified air from an air gun. The Cu/OSP and Cu/Ni/Au substrates were not cleaned with HCl prior to running the wetting experiments. Next, the wettable substrate was loaded into the thermal chamber. A small amount of flux was applied on the glass slide with a syringe and needle, and a solder sphere was then carefully placed in the flux deposit. One of the functions of the flux in this situation was to hold the solder sphere on the glass slide when the glass slide was flipped and loaded into the slide holder. The temperature of the chamber was then increased to a specified temperature set point. Once the temperature had stabilized at the specified set point and the oxide free solder sphere was liquidous, the solder sphere was positioned to contact the surface of the wettable substrate. A high-speed camera recorded the time-dependent motion of the solder sphere wetting to the substrate.

Two K-type thermocouples were placed near the solder sphere to obtain an accurate temperature reading. One thermocouple was attached to the surface of the substrate, and the other was positioned in the air near the substrate. The accuracy of the temperature measurement device was tested before the experiments by reading temperature of boiling water and an ice slush. The temperature was 100.0 ± 0.1°C in the boiling water and 0.00 ± 0.1°C in the ice slush. This was acceptable for the purposes of this experiment.

A calibration block that consisted of three sapphire balls embedded in an aluminum holder with the contact angle of 90.0 ± 1.0° was used to adjust the camera angle prior to the experimentation (Figure 3). To verify the accuracy of the angle in the calibration standard, the height and the base diameter of the sapphire balls were measured using a micrometer. The contact angles obtained confirmed the accuracy of the calibration standard.

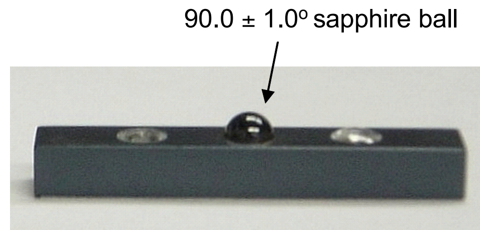


Figure 3 Calibration standard

The image processing software, Optimas™ was employed to obtain the shape information from the recorded images. The analysis of the solder drop images started with the detection of the edge of the liquid/gas interface, this was the edge of the molten solder droplet. The Minimum Variance method (Otsu's method), which was provided in Optimas™ as one of the automatic threshold selection methods, was used to detect precise liquid/gas interface information from the solder wetting images. Once the liquid/gas interface was obtained, a reference line that was parallel to the surface of the substrate was needed before a contact angle could be calculated. The coordinates for the reference line were determined either by automatic edge detection or by picking two points manually on the image.

The overall shape of a solder droplet was approximated as a truncated sphere, which was the shape that corresponds to the minimum surface energy. If the surface tension in the liquid solder/flux interface was the dominant force over gravity and viscous dissipation, it was acceptable to approximate the shape of the solder as a truncated sphere. A small Bond number (Bo) that represents the gravity force to surface tension ratio and a small Capillary number (Ca), which represented the viscous dissipation to surface tension ratio, justified this approximation.

$$Bo = \frac{g(\rho_L - \rho_V)d^2}{\gamma} = 0.02 \qquad (1)$$

where the gravitational acceleration is g, the density of liquid solder is ρ_l=8400kg/m^3, the density of air is ρ_v=0.70kg/m^3, the liquid solder surface tension with flux, surface tension, γ = 400mN/m, and the characteristic length, d = 317.5μm. If we consider the density of the flux instead of the density of the air, the Bond number becomes less than 0.02.

$$Ca = \frac{\mu v}{\gamma} = 6.25 \times 10^{-6} \qquad (2)$$

when the viscosity of liquid solder, μ =2.5mPa·s [9], velocity of the triple contact line was assumed to be v=1,000 μm/s, and the liquid solder surface tension with flux, γ =400mN/m. The truncated sphere approximation was also verified by the visual inspection of solder wetting images in Figure 4.

With this approximation, a circle fitting was performed using the edge information extracted from the images. A nonlinear least square subroutine (LMDIF) in the nonlinear fitting solver (MINPACK), which was developed by Argonne

National Laboratory, was modified and implemented in Optimas™ as a dynamic linked library for curve fitting. A horizontal center, a vertical center, and a radius of a circle were obtained by circle fitting. The average coefficient of determination resulting from the circle fit of measured images was larger than 0.99 for most of the clear images.

Materials Properties

Eutectic Pb/Sn and 95.5Sn-4.0Ag-0.5Cu solder spheres manufactured by Cookson Semiconductor were employed as test solder materials. Table 1 summarizes the properties of the solder materials used for the analysis.

The surface tension (γ) of eutectic Pb/Sn solder versus absolute temperature (T) was estimated by the empirical model in [10] and the surface tension of 95.5Sn-4.0Ag-0.5Cu solder was assumed as 431mN/m based on the surface tension of Sn-3.5Ag alloy [11].

$$\gamma = 442.3 - 0.047(T-273.15) \text{ (mN/m)} \quad (3)$$

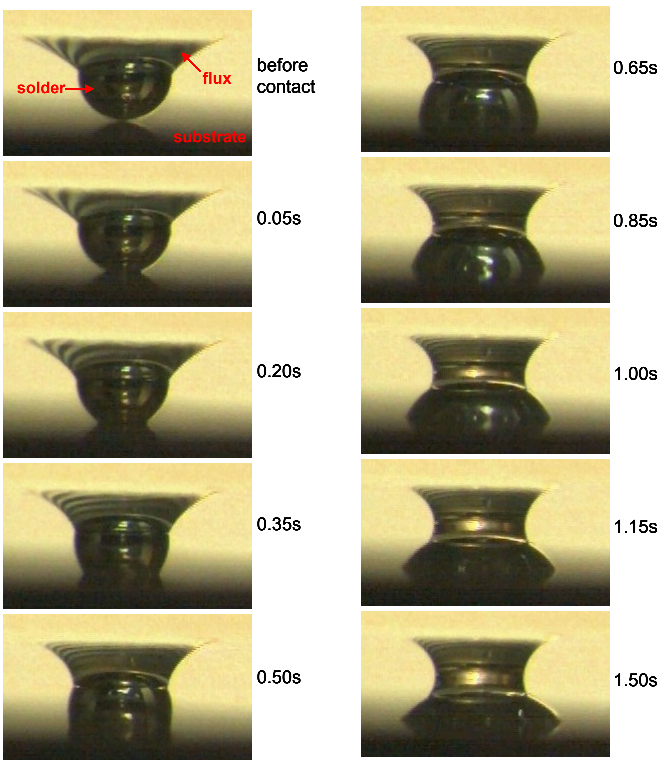


Figure 4 Images of a eutectic tin-lead solder on a Cu/Ni/Au substrate, where the diameter of solder sphere is 635μm, and the ambient temperature is 190^{o}C

The liquid density of eutectic tin-lead solder was assumed as 8.4 g/cm^3 [10] regardless of temperature variation because the liquid density of solder materials changes only slightly with temperature. The liquid density of 95.5Sn-4.0Ag-0.5Cu solder was estimated as 7.5g/cm^3 based on the liquid density of Sn, Ag, and Cu.

The viscosity of molten Pb/Sn solder and molten 95.5Sn-4.0Ag-0.5Cu solder was assumed as 2.5mPa·s and 2.0mPa·s, respectively, based on empirical data [9]. It was assumed that the viscosity of molten 95.5Sn-4.0Ag-0.5Cu solder is the same with that of pure Sn.

A Cu, Cu/OSP, and Cu/ENIG (which was also referred to as Cu/Ni/Au in this paper) substrates were chosen for the solder wetting experiments. The top layer of gold in a Cu/ENIG substrate prevents oxidization before and during wetting as does the organic OSP coating. Therefore, the surface of the substrate can be kept oxide-free during wetting experiments. The nickel layer is a solderable diffusion barrier to prevent a rapid reaction between copper and the solder. The thickness of gold layer ranges from 0.1 to 1.0μm and the thickness of nickel layer from 5 to 10μm. The equilibrium contact angles of the two solder materials were measured on each of the substrates (Table 1).

Table 1 Material Properties of Solders

Properties	**Sn/Pb (37/63)**	**95.5Sn/4.0Ag/0.5Cu**
density ($\aleph_s$)	8,400 kg/m^3	7,500 kg/m^3
melting temperature	183 ^{o}C	217~218 ^{o}C
($\aleph$)	442.3–0.047T* mN/m	431.0 mN/m
viscosity ($\aleph$)	2.5 mPa·s	2.0 mPa·s
Cu/Ni/Au ($\aleph_{eq}$)	7 degrees	27 degrees
Cu($\aleph_{eq}$)	10 degrees	30 degrees

Results and Analysis

Eutectic Pb/Sn Solder on Cu/Ni/Au Substrates

Figure 5 shows the time-dependent contact angle variation of a eutectic-tin lead solder sphere on a Cu/Ni/Au substrate at 210^{o}C in three different experimental trials under the same environmental conditions. Each shape of scattered symbols in the graph represents an independent trial run. A no clean, tacky, ROL0 classification flux (Kester TSF-6522) was applied to the solder sphere to remove oxides on the surface of the solder sphere. Consistent wetting behavior was observed in the different experiments under the same environmental conditions. The maximum deviation of the contact angles was less than 6^{o}. This result showed that the experimental methods were repeatable in measuring the contact angles.

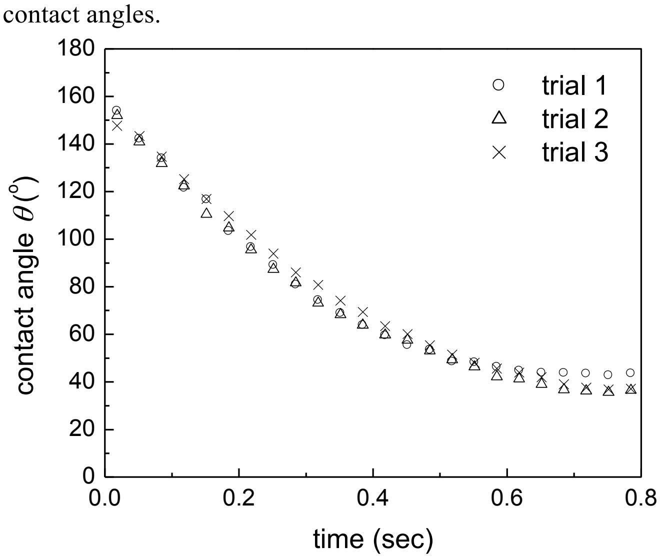


Figure 5 Time-dependent contact angle variation of a eutectic-tin lead solder sphere on a Cu/Ni/Au substrate at 210°C in three different experiments

The effect of flux types on the dynamics of solder wetting was studied by comparing the contact angle relaxation over time with different types of flux under the same environmental conditions. It was obvious that the type or the activity of the flux influenced the wetting rate and wetting force when the solder wetting and oxide removal processes occurred simultaneously [12,13]. However, this study focused on the wetting behavior of a single liquid solder sphere onto a metal substrate without any oxidation on the surface of the solder or on the substrate bond pads. Therefore, if the experimental methodology could successfully create the conditions in which flux activated and removed oxides before wetting began, very similar wetting behavior would be expected with different types of flux. Five different types of flux were tested; their characteristics are summarized in Table 2.

Table 2 Summary of Fluxes

Fluxes	Manufacturer (Part #)	Flux classification (Standard J-STD-004)	Description
Flux A	Kester TSF-6522	ROL0	No clean, tacky
Flux B	Kester 1544	ROM1	Activated Rosin, liquid
Flux C	Kester TSF-6805	ORH0	Water soluble, tacky
Flux D	Alphametals 9171L	ORM0	No clean, liquid
Flux E	Alphametals Rosin	ROL0	Rosin mildly activated, liquid

The comparisons of contact angle relaxation over time with three different flux types are shown in Figure 6.

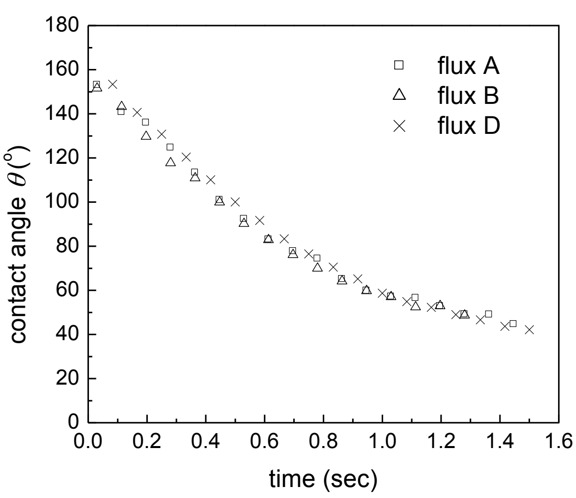


Figure 6 Time-dependent contact angle variation of a eutectic-tin lead solder sphere on a Cu/Ni/Au substrate with different types of flux at 190°C

They were all measured at 190°C. Each data point was the average value of more than three measurements of contact angle relaxations with the same flux and same environmental conditions. It was shown that the use of different fluxes created no significant difference in the wetting motion at either temperature.

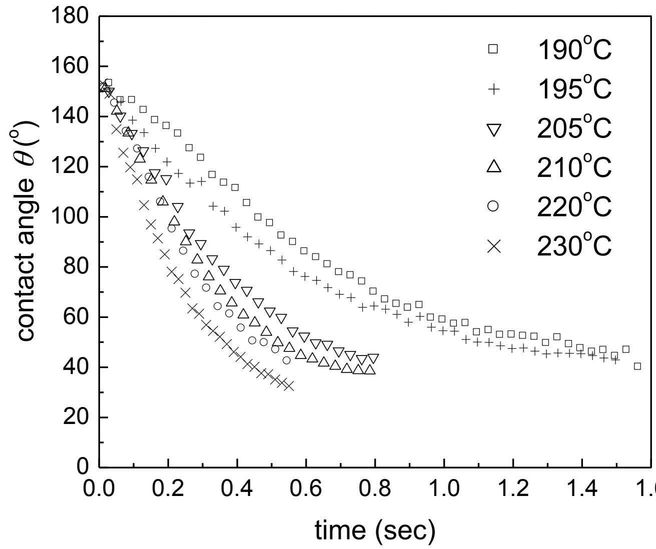


Figure 7 Time-dependent contact angle variation at various temperatures.

Figure 7 shows the time-dependent contact angle variation at three different temperatures: 195°C, 210°C, and 230°C. In all three measurements at different temperatures, the contact angle decreased more slowly with time. In other words, the velocity of the triple contact line was very high initially in the high contact angle region and then decreased gradually with the decrease in contact angle. This trend can be observed more clearly in Figure 8, which shows that the dependence of the triple contact line velocity on the instantaneous contact angle at three different temperatures.

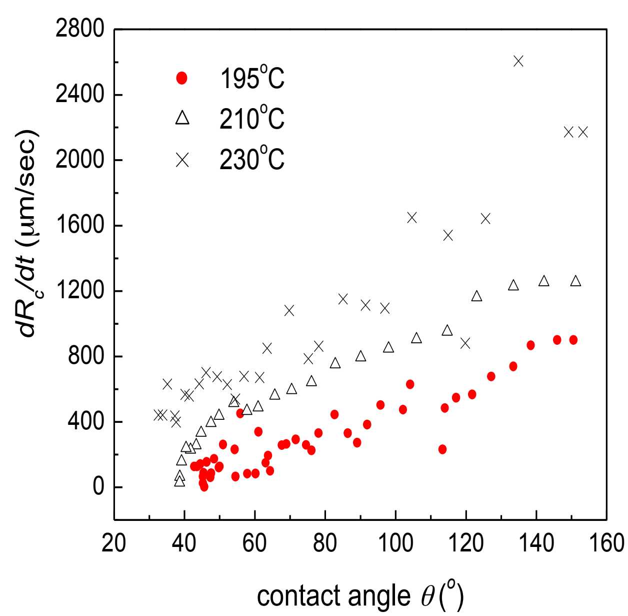


Figure 8 Variation of the velocity of the triple contact line over the contact angle at three temperatures

The rate at which the contact angle is decreasing and the velocity of the triple contact line are the first order derivatives of the data in Figure 7. The first order derivatives of the data set were calculated based on performing a local linear regression around each point (two points to the left and two points to the right). Although there were some fluctuations that occurred when measuring the discrete data and differentiating them, the trends showed that the rate at which the contact angle decreased and the velocity of the triple contact line clearly depended on time and temperature.

It was also observed that an increase in temperature accelerated the contact angle reduction rate and thus the velocity of the triple contact line significantly. At higher temperatures, the reactivity between the solder and the substrate material became higher, the diffusion process inside the solder alloy became more active, the viscosity of the molten solder became lower, the surface tension of the molten solder decreased, and the movement of the molecules near the triple contact line became more dynamic. All of the changes in physical properties associated with an increase in temperature inside the molten solder, near the triple contact line, and on the surface of the molten solder and substrate worked favorably to accelerate the velocity of the triple contact line.

To quantitatively investigate the wetting rate change with reflow process parameters, duration time (t_d) was defined as the time required for the contact angle to evolve from 140^o to 50^o. The inverse of t_d represented an average reduction rate of the contact angle from 140^o to 50^o. There were several advantages in limiting the contact angle range from 140^o to 50^o. The evolution of the contact angle could be measured more accurately and consistently in this range during the solder wetting experiment. The contact angle from 180^o to 140^o was very sensitive to the position of the reference line, such that a slight error in determining the position of the reference line leads to a significant error in the measured contact angle. If the contact angle was smaller than 40^o, the contact angle evolved to the equilibrium contact angle very slowly. The flux burn-off could occur in this range which made it difficult to obtain clear continuous images of solder wetting. The duration time for the evolution of the contact angle from 180^o to 140^o was shorter than from 140^o to 50^o by more than a factor of 10. Therefore, the wetting time from 180^o on 140^o could be neglected when it was compared to the wetting time from 140^o to 50^o.

The variation of the duration time, t_d, with an increase in temperature is shown in Figure 9. The duration time depended inversely on the increase in temperature. The duration time decreased nearly 70% from 190^{o}C to 230^{o}C.

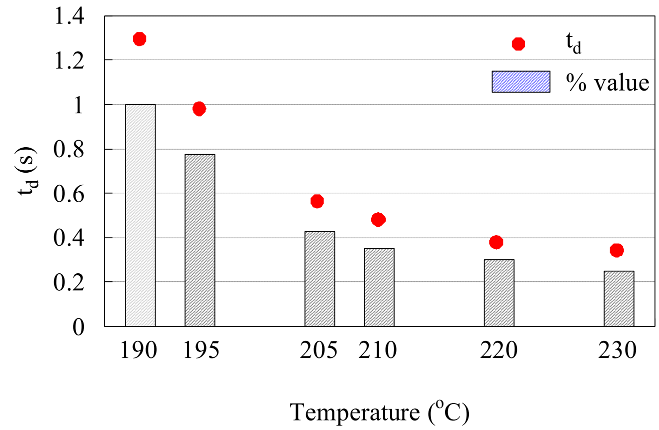


Figure 9 Comparison of the wetting duration times (t_d) versus isothermal wetting temperatures

The effect of solder sphere size on solder wetting was also studied by comparing the rate of contact angle relaxation under the same environmental conditions with three different sizes of solder spheres: 200μm, 305μm, and 635μm. An isothermal wetting temperature of 205^{o}C was maintained throughout the experiment. Figure 10 shows that the contact angle for a small solder sphere decreased much more rapidly than the contact angle for a large solder sphere. The same change in radius of the contact area lead to a larger change in the contact angle for a smaller solder sphere than for a large solder sphere. However, the velocity of the triple contact line did not clearly depend on the size of a solder sphere.

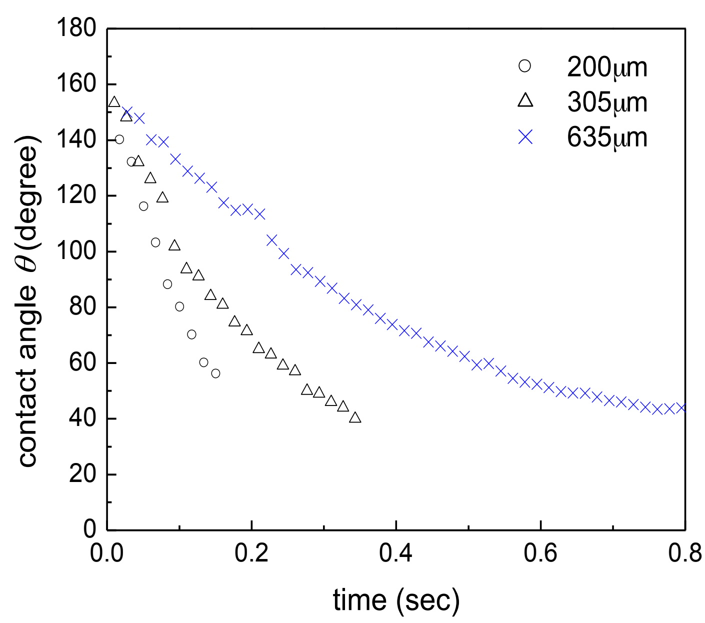


Figure 10 Wetting dynamics versus solder sphere size at 205^{o}C with three different sizes of solder spheres, 200μm, 305μm, and 635μm

The velocity of the triple contact line over the contact angle showed a relatively similar trend and it magnified with the variation of the solder sphere sizes. From studying for the effect of solder size, we may conclude that the size of the solder sphere had a significant effect on the contact angle reduction rate and on the wetting time but an insignificant effect on the velocity of the triple contact line, at least for the range of solder sphere diameters that were tested - 200μm to 625μm. This result may lead to the conclusion that the physical processes like viscous dissipation that were occurring inside the bulk of the molten solder and were highly affected by the volume of the liquid solder were not very important in determining the velocity of the triple contact line during solder wetting for the solder ball dimensions of interest.

Eutectic Pb-Sn Solder on Cu Substrates

To study the effect of the substrate material on the dynamics of solder wetting, contact angle measurements were gathered with eutectic Pb/Sn solder on a Cu substrate, and the measured results were compared with the wetting of a eutectic Pb/Sn solder on a Cu/Ni/Au substrate. The isothermal experiments were performed at two different temperatures, 195°C and 230°C. It was found that the contact angle decreased faster at 230°C than at 195°C (Figure12); the same trend was shown with a eutectic Pb/Sn solder on a Cu/Ni/Au substrate. In addition, the wetting time with a eutectic Pb/Sn solder on a Cu substrate was noticeably shorter than on a Cu/Ni/Au substrate (Figure13). The duration time, t_d was 0.0323sec for a Cu substrate and 1.011sec for a Cu/Ni/Au substrate. A difference in t_d of more than ten times was found between the two substrate materials.

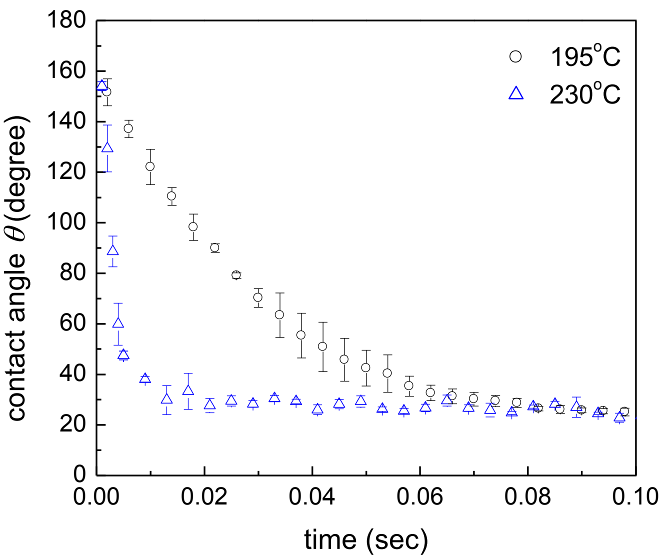


Figure 11 Variations of contact angle over time for a eutectic tin-lead solder on a Cu substrate at different temperatures

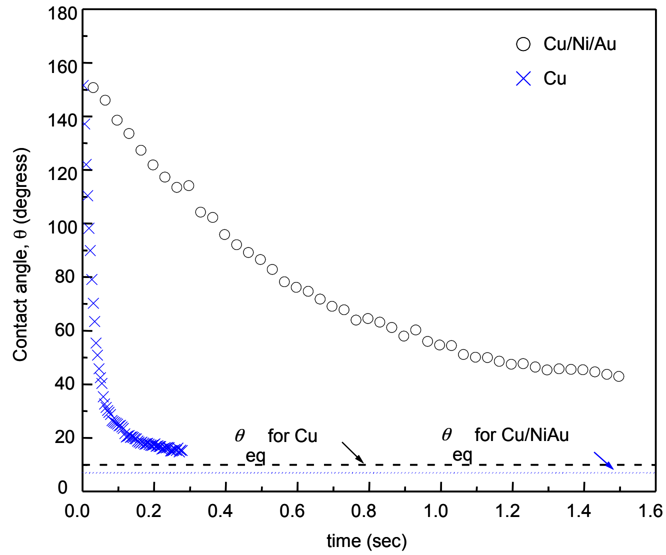


Figure 12 Comparison of wetting behavior of a eutectic tin-lead solder on a Cu substrate and on a Cu/Ni/Au substrate at 195°C

The possible sources of the difference in the velocity of the triple contact line between Cu substrate and a Cu/Ni/Au substrate were differences in the surface tension imbalance, reaction rate between solder and substrate materials, and dissolution of substrate into molten solder near the triple contact line. Surface tension imbalance depends on the surface tension of molten solder and the equilibrium contact angle. Since the equilibrium contact angle of eutectic Pb/Sn solder on Cu was less than on Cu/Ni/Au, the surface tension imbalance on Cu was less than on Cu/Ni/Au. This result was the opposite of the experimental results. The difference in the triple contact line velocity between a Cu/Ni/Au surface and a Cu surface cannot be explained in terms of a surface tension imbalance.

The difference of the reaction rate between eutectic Pb/Sn solder on Cu and on Cu/Ni/Au can be deduced based on the dissolution rate or the intermetallic compound formation rate. The study of Au, Cu, and Ni dissolution in the 40Pb/60Sn solder [14] shows that the order of the dissolution rate is $O(1\mu m)$, $O(10^{-1}\mu m)$, and $O(10^{-3}\mu m)$, respectively, for Au, Cu and Ni in the temperature range from 190°C to 240°C. The thickness of an Au layer in the Cu/Ni/Au substrate is less than 0.3?m. Au may dissolve in the eutectic Pb/Sn solder less than 0.3sec in the experiment. The dissolution rate of Ni is slower than Cu by more than an order of magnitude. After instantaneous dissolution of Au, a Ni layer under an Au layer may cause the solder wetting to slow down. The intermetallic compound formation rate of Cu and Ni with a molten Pb/Sn solder also shows that the intermetallic compound formation rate on Cu is faster than on Ni by more than an order of magnitude [15,16]. Based on previous studies, we may explain that the slow solder wetting rate on a Cu/Ni/Au substrate is caused by the slow reaction between a Ni layer and a molten solder.

Lead-free 95.5Sn-4.0Ag-0.5Cu Solder on Cu/Ni/Au and Cu Substrates

Figure 13 shows the time-dependent contact angle variation of 95.5Sn-4.0Ag-0.5Cu solder on a Cu/Ni/Au substrate and a Cu substrate at 230°C. 95.5Sn-4.0Ag-0.5Cu solder shows wetting behavior similar to that observed with eutectic Pb/Sn solder. Figure 14 compares the variation of the contact angle over time with four sets of material systems at 230°C. Very similar magnitudes and trends of the contact angle variation over time were observed with both solder materials.

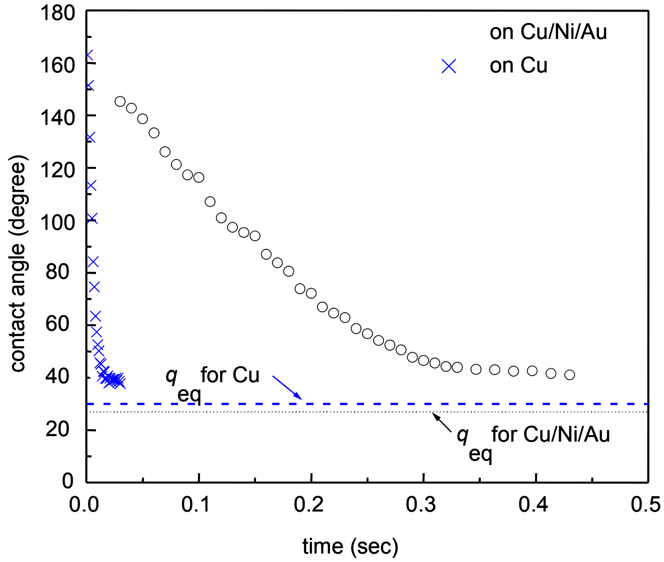


Figure 13 The comparison of wetting behavior of a 95.5Sn-4.0Ag-0.5Cu solder on a Cu substrate and on a Cu/Ni/Au substrate at 230°C

Figures 15 and 16 show the wetting behavior of 95.5 5Sn-4.0Ag-0.5Cu solder onto Cu/Ni/Au and Cu/OSP substrates, respectively. The Cu/OSP substrates appear to be more sensitive to the isothermal temperature in the chamber than did the Cu/Ni/Au substrates. In addition, the velocity of the triple contact line seemed to vary more with temperature for the Cu/OSP substrate metallization than it did with the Cu/Ni/Au substrate metallization.

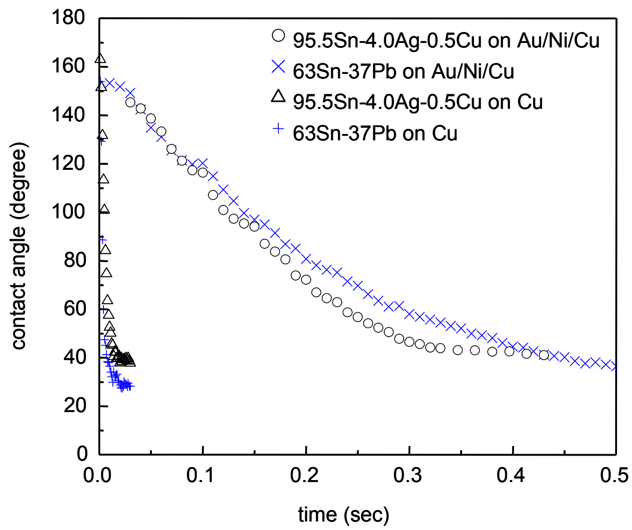


Figure 14 The comparison of wetting behavior between four different sets of solder and substrate materials at 230°C

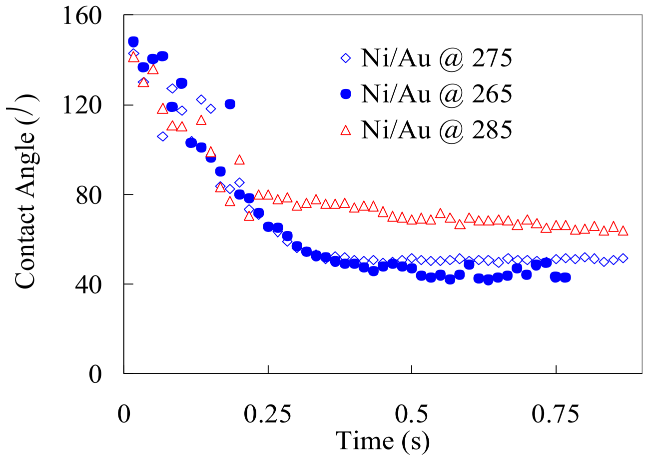


Figure 15 Contact angle versus time for 95.5Sn-4.0Ag-0.5Cu solder on Cu/Ni/Au substrates

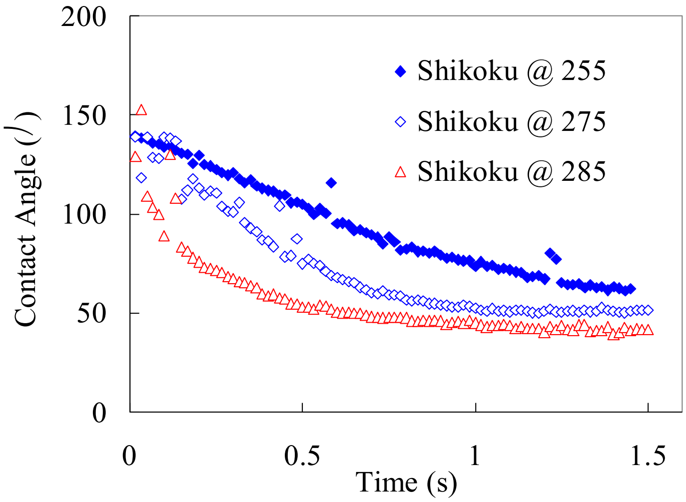


Figure 16 Contact angle versus time for 95.5Sn-4.0Ag-0.5Cu solder on Cu/OSP substrates

Proposed wetting dynamics model

For practical purposes, the closed form wetting dynamics model should predict the wetting behavior of solder with various material properties, temperature profiles, and geometries of solder and substrate. Therefore, a constitutive equation that includes the effects of surface tension imbalance, chemical reaction or diffusion was proposed based on experimental observation and evaluation of the theoretical models.

To include in the wetting dynamics model the complex effects of chemical reaction or diffusion, a mobility coefficient, M_t, is introduced. Originally, mobility was introduced by Gao et al. as a phenomenological parameter of the wetting model and was determined by comparing model predictions with experimental observations [Gao et al., 2000]. He assumed that a mobility coefficient is uniform and isotropic; it is a material constant for the kinetic model. However, the physical meaning of mobility was not clearly investigated, and no attempt was made to relate mobility to a chemical reaction or to the effects of wetting parameters such as temperature, substrate types and solder types, etc.

Therefore, this research redefines a mobility coefficient, M_t, in the following form by adopting an Arrhenius type representation that is employed for the molecular-kinetic modeling, chemical reaction kinetics, and a diffusion coefficient.

$$M_t = M_o \exp(\frac{\Delta G_W^*}{N k_B T}) \tag{4}$$

where, k_B is the Boltzmann constant, ΔG_W^* is a molar activation free energy of wetting, N is the Avogadro number, and M_o is a material constant determined by the material properties of solder and substrate based on experimental curve fitting. The new definition of mobility enables it to be related to the effect of temperature and chemical reaction on the velocity of triple contact line.

Assuming the velocity of the triple contact line is linearly proportional to the driving force exerted by the surface tension imbalance (F_d) and the mobility coefficient (M_t), the constitutive equation for the wetting rate or the velocity of triple contact line is proposed as

$$v = M_t \cdot \gamma(\cos\theta_{eq} - \cos\theta) \tag{5}$$

where M_t is given by equation (4).

The volume of a truncated spherical can be expressed as a function of the radius of the contact area (R_c) and the contact angle (θ) as shown in Figure 1.

$$V(\text{volume}) = \text{constant} = \frac{\pi R_c^3}{3\sin^3\theta}\left(2 - 3\cos\theta + \cos^3\theta\right)$$
$$R_c = \left[\frac{3V\sin^3\theta}{\pi\left(2 - 3\cos\theta + \cos^3\theta\right)}\right]^{\frac{1}{3}} \tag{6}$$

Differentiating R_c with time (t), the velocity of the triple contact line during wetting is expressed as

$$v = \frac{dR_c}{dt} = \frac{dr}{d\theta}\frac{d\theta}{dt}$$
$$= -\frac{d\theta}{dt}\left(\frac{3V}{\pi}\right)^{1/3} \frac{1}{(2+\cos\theta)\left(2 - 3\cos\theta + \cos^3\theta\right)^{1/3}} \tag{7}$$

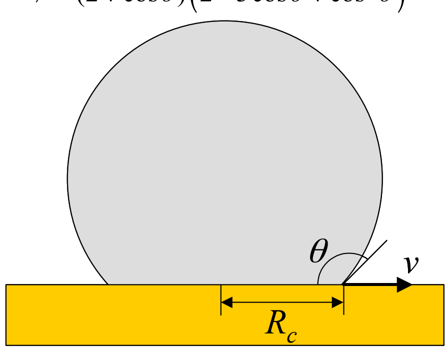


Figure17: Geometric parameters of a solder sphere on a flat substrate.

Evaluation of the proposed wetting dynamics model

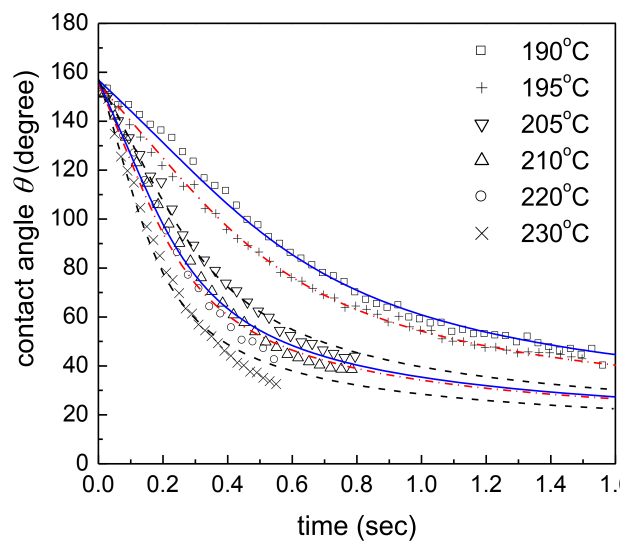
To evaluate the proposed wetting dynamics model with the experimental data of the time dependent contact angle variation, the following differential equation based on equation (5) and (7) was solved with a forth-order Runge-Kutta method and then fitted to the experimental data with a single fitting parameter of M_t.

$$\frac{d\theta}{dt} = -M_t\gamma(\cos\theta_{eq} - \cos\theta) \times \frac{(2+\cos\theta)\left(2 - 3\cos\theta + \cos^3\theta\right)^{1/3}}{\left(\frac{3V}{\pi}\right)^{1/3}} \tag{8}$$

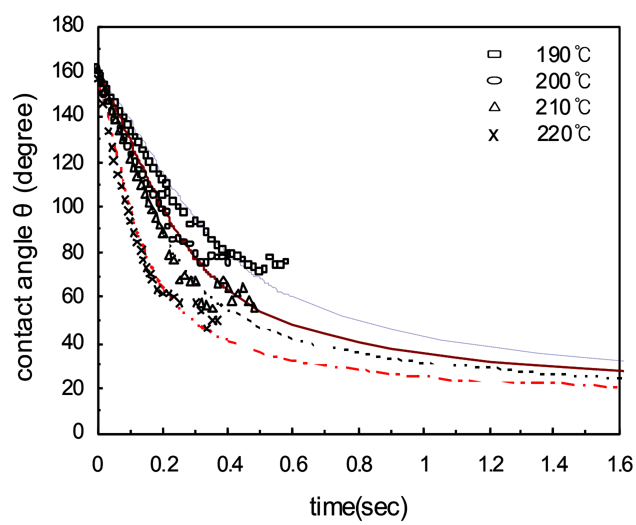
where V is volume of molten solder.

Comparisons the proposed model and the experimental results

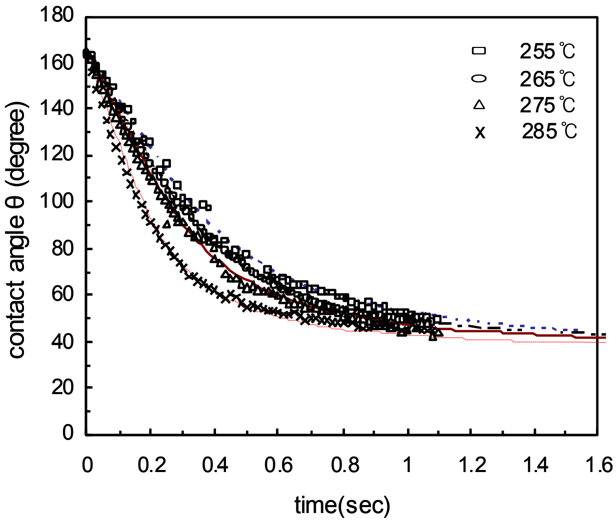
Experiment is executed with different solder and substrate to prove proposed valid in different solders and substrates. The first case is eutectic tin-lead solder on an Au/Ni/Cu substrate. The second is eutectic tin-lead solder on Cu/OSP substrate. The last is Sn/Ag/Cu solder on Cu/OSP substrate. Figure 1 (a, b, c) compares fitted curves and the experimental results of eutectic tin-lead solder at different temperatures.



(a) eutectic tin-lead solder on an Au/Ni/Cu

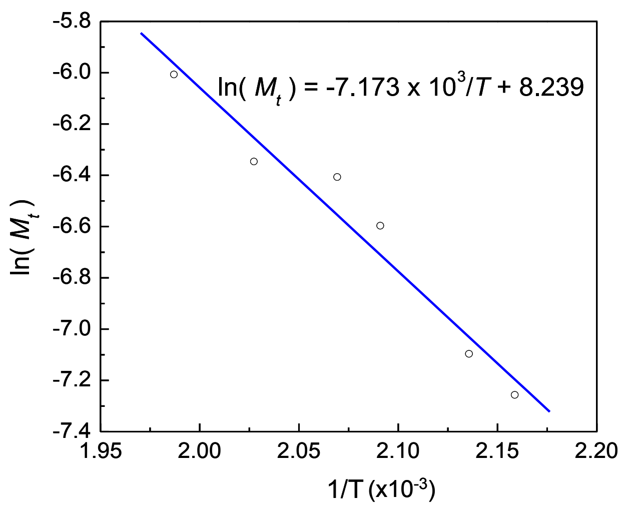


(b) eutectic tin-lead solder on a Cu/OSP substrate

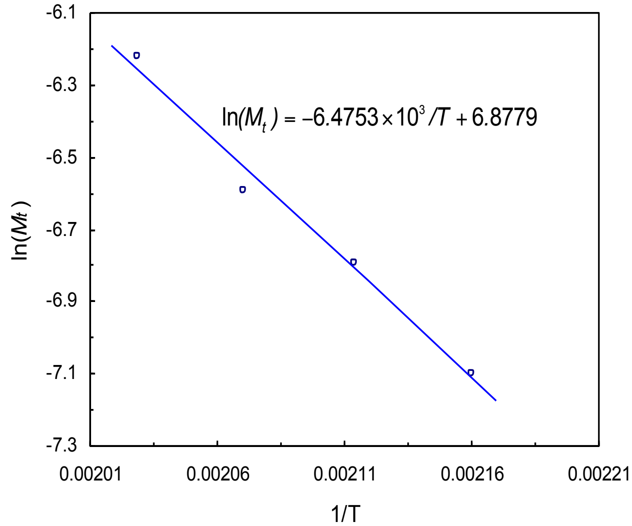


(c) Sn/Ag/Cu solder on a Cu/OSP substrate
Figure18: The comparisons between the proposed model and the experimental results at different temperatures.

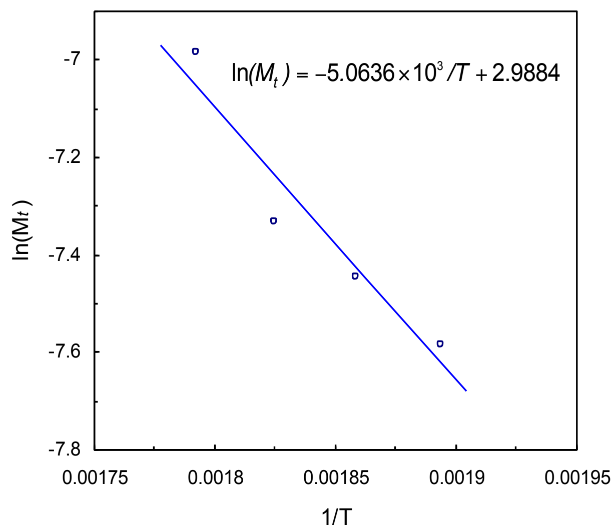
To obtain the quantitative representation for the effects of temperature on the dynamics of solder wetting, the fitting parameter (M_t) was plotted as an Arrhenius type representation in Figure 18(a, b, c).



(a) eutectic tin-lead solder on an Au/Ni/Cu



(b) eutectic tin-lead solder on a Cu/OSP substrate



(c) Sn/Ag/Cu solder on a Cu/OSP substrate
Figure19: An Arrhenius representation of mobility.

The proposed model shown in equation (5) was fitted to the experimental results in Figure 18. Very good agreement was observed between the fitted curves and experimental results in each case. The fitting parameter M_t was obtained in Table 3 from results of experiment with 95.5Sn-4.0Ag-0.5Cu solder on Cu/OSP is smaller than that of experiments with other cases.

Table3: Fitting parameter and the coefficient of determination for the proposed wetting dynamics model.

Solder	Substrate	Temperature (^{o}C)	R^2	M_t (m^3/Js)
Eutectic Pb-Sn	Au/Ni/Cu	190	0.9946	7.02×10^{-4}
		195	0.9979	8.23×10^{-4}
		205	0.9940	1.37×10^{-3}
		210	0.9921	1.65×10^{-3}
		220	0.9834	1.75×10^{-3}

		230	0.9870	2.46×10^{-3}
	Cu/OSP	190	0.9797	1.24×10^{-4}
		200	0.9728	1.71×10^{-3}
		210	0.9835	2.15×10^{-3}
		220	0.9837	3.31×10^{-3}
95.5Sn-4.0Ag-0.5Cu	Cu/OSP	255	0.9959	5.09×10^{-4}
		265	0.9989	5.85×10^{-4}
		275	0.9982	6.54×10^{-4}
		285	0.9937	9.27×10^{-4}

The numerical evaluation of M_0, and ΔG_W^* are obtained for there cases Table 4.

Table 4: The numerical evaluation of M_0, and ΔG_W^*

Solder	Substrate	M_0 (m^3/Js)	ΔG_W^* (m^3/Js)
Eutectic Pb-Sn	Au/Ni/Cu	4.21×10^3	5.98×10^4
Eutectic Pb-Sn	Cu/OSP	9.71×10^3	5.38×10^4
95.5Sn-4.0Ag-0.5Cu	Cu/OSP	0.20×10^3	4.66×10^4

Therefore, the wetting dynamics is proposed based on equations (4) and (7).

$$v = 4.21\times10^3 \exp\left(\frac{-5.98\ \times\ 10^4}{Nk_BT}\right)\cdot\gamma(\cos\theta_{eq}-\cos\theta) \qquad (9)$$

(m/sec)

where γ is given by Table 5.

Table 5: Summary of the parameters used in model evaluation

Properties	Unit	Eutectic Sn-Pb	95.5Sn-4.0Ag-0.5Cu
Density (ρ_s)	kg/m^3	8,400	7,500
Melting temperature	^{o}C	183	217-218
Surface tension with flux (γ)	mN/m	442.3 – 0.047T*	431
Viscosity (μ)	mPa ·s	2.5	2.0
Equilibrium contact angle on Au/Ni/Cu (θ_{eq})	degree	7	27
Equilibrium contact angle on Cu (θ_{eq})	degree	10	30
Equilibrium contact angle on Cu/OSP (θ_{eq})	degree	9	37

The dynamics of solder wetting on the metallic substrate is investigated based on the integration of the complex effects of chemical reaction, diffusion, temperature, solder types and substrate types. The model shows a good agreement with the experimental results. If the influence from flux model is considered, the proposed model will be more accurate.

Conclusions

To understand the dynamics of solder wetting with reflow parameters, contact angle measurements were gathered over time with a eutectic Pb/Sn solder and a 95.5Sn-4.0Ag-0.5Cu solder on a Cu/Ni/Au, Cu/OSP, and Cu substrates. The experiments were performed under conditions where solder retained its spherical shape during wetting and the wetting behavior of solder was consistent regardless of flux type once the flux was activated and had removed the contaminants on the surface of the solder and the substrate. The findings in the experiments are summarized as follows:

The velocity of the triple contact line was very rapid initially in the high contact angle region and then decreased gradually with the decrease in contact angle. Wetting velocity clearly depended on the instantaneous contact angle. An increase in temperature accelerated the wetting rate of eutectic tin-lead solder significantly on both substrate materials tested. At higher temperatures, the reactivity between solder and substrate material became higher, the diffusion of reactant in the solder alloy became more active, the viscosity of molten solder, on which the fluid motion negatively depends, became lower, the surface tension of the molten solder decreased, and the movement of molten solder molecules became more active. All of these changes in the physical processes and in the material properties associated with an increase in temperature work favorably to accelerate the velocity of the triple contact line. Wetting experiments with different sizes of solder spheres show that the smaller the size of the solder spheres, the faster the contact angle decreased. However, the velocity of the triple contact line over the contact angle does not clearly depend on the size of solder spheres.

The wetting time of a eutectic tin-lead solder on a Cu substrate was shorter than on a Cu/Ni/Au substrate by more than a factor of 10. The substrate material had a large effect on the dynamics of solder wetting. The experimental results of 95.5Sn-4.0Ag-0.5Cu solder wetting were very similar to the wetting behavior of a eutectic tin-lead solder except for the equilibrium contact angles.

A closed form model that predicts the dynamics of molten solder wetting on a metallic substrate is presented. This model fit the experimental results well for: eutectic solder on Au/Ni/Cu, on Cu, and on Cu/OSP. In addition, the model fit the experimental results well for 95.5Sn-4.0Ag-0.5Cu solder on Au/Ni/Cu, on Cu, and on Cu/OSP.

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