MASTER

AN INVESTIGATION OF THE CONTACT ANGLES BETWEEN VARIOUS
MOLTEN METALS AND SUBSTRATES OF NIOBIUM AND ZIRCONIUM

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ABSTRACT

The sessile drop technique was utilized for the determination of the contact angles between droplets of liquid tin, indium, and gallium; and substrates of niobium, and zirconium. Contact angles, θ , were measured for various substrate surface roughness and over the temperature range 30-650°C. Values of θ for all of these systems were found to be greater than 90° i.e., constituting a case of nonwetting between the liquid metals and the substrates. Three characteristic regions of the temperature dependence of contact angles were observed. A steady-state region in which the contact angle is relatively independent of temperature was preceded and followed by regions in which θ decreased rapidly with increasing temperature. For the steady-state or second region, contact angles were found to be independent of time whereas in the third region contact angles showed a decreasing trend with time at constant temperature. In accordance with theoretical predictions for $\theta > 90^\circ$, increasing roughness of the substrate caused a corresponding increase in θ . Electron microprobe analyses showed that only the Ga-Zr system exhibited evidence of diffusion at the interface. Photographs of the sessile drop of this system over a period of time indicated that the drop had spread over a greater area thus supporting the possibility of a surface diffusion mass-transport process.

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INTRODUCTION

Contact angle studies of various liquid-solid systems have been the focus of interest of numerous investigators over the past few decades. Such an interest has been generated, in part, by the importance of this parameter in the determination of wettability of solid surfaces by liquids. Considerations in such practical matters as adhesion,¹ ceramic to metal bonding,² ohmic contact in electronic devices,³ and the selection of a suitable liquid metal as a coolant for laser fusion reactors,⁴ are a few of those examples in which knowledge of the wettability of a substrate by a metal or alloy is of primary importance.

The original contributions of Laplace have been modified by Young so as to describe the interaction between a liquid drop and a solid substrate.^{1,5,6,7} The contact angle shown in Figure 1 defines the following equilibrium relationship between interfacial energies involved:

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

In this equation γ_{SV} , γ_{SL} , and γ_{LV} represent, respectively, the energies of the solid-vapor, solid-liquid, and liquid-vapor interfaces. Complete wetting is described as the condition at which $\theta=0^\circ$. A value of 90° has been arbitrarily selected as the boundary between partial wetting and nonwetting.¹

Bangham and Razouk⁸ have modified the Young-Dupre' equations to account for the influence of adsorbed gases on the contact angle between a liquid and a solid. The relationship between θ and the modified interfacial energies is

$$\gamma_{SV^0} = \gamma_{SL} + \gamma_{LV^0} \cos \theta \quad (2)$$

where γ_{SV^0} and γ_{LV^0} are the energies at the interfaces when the condensed phase is saturated with adsorbed vapor.

The validity of the fundamental equations derived by Young and others is based on the premise that the vertical component of γ_{LV} is small and does not deform the solid at the contact periphery. Although this is acceptable since most solids are rigid, yet the proof is not exact. The main shortcoming of the equation derived is that it demands a knowledge of the surface energies. It is possible to estimate γ_{SV} from bond energies between neighboring atoms in a given crystalline plane.⁹ However, for nonclose packed structures e.g., body-centered cubic, next, and subsequent neighbors will have to be considered in order to obtain a more realistic estimate of γ_{SV} . With regards to liquid-solid surface energies, γ_{LS} , estimation methods are made more complicated by the lack of long-range order in liquids. Details of the exact nature of the atomic bonding at the solid-liquid interface is not well understood, thus making the task of estimation of interfacial energies somewhat speculative.

Observations of the influence of temperature on the contact angle have been well documented. On the basis of observations on systems of liquid metal on ceramic substrates Rhee¹⁰ has proposed the following relation between temperature and contact angle, θ ,

$$\cos \theta = 1 + B(T - T_C) \quad (3)$$

Here T is the absolute temperature, T_C is the temperature at which complete wetting takes place, and B is a constant. Studies on the wetting of sapphire by liquid aluminum¹¹ and of GaAs by gold-germanium and gold-tin alloys¹² have demonstrated a temperature dependence which falls into three characteristic regions. The observations by Zee and Munir¹² on gallium arsenide have provided evidence for extensive mass transport across the liquid-solid interface during the third region. In contrast,

it was shown that diffusional processes in the second region were essentially absent.

During early investigations it was observed that for the same combination of liquid-solid materials significantly different contact angles could result for a given temperature. The apparent anomaly was clarified by Wenzel¹³ who developed a relation between surface roughness and the contact angle. He defined a roughness factor r as the ratio of the cosines of the apparent and real contact angles i.e.,

$$r = \cos \theta' / \cos \theta \quad (4)$$

Kashkooli, Munir, and Williams¹⁴ investigated the influence of substrate characteristics on the wettability of a solid by a liquid. Their observations are in accordance with the predictions of Wenzel. According to Equation (4) r is a decreasing function of θ for values of θ less than 90° , and conversely it is an increasing function of θ for θ greater than 90° .

Contact angles are often measured at the contact periphery of a liquid sessile drop on a flat substrate. The influence of drop dimensions on the contact angle of a gallium-gallium arsenide system has been investigated.¹⁴ It was observed that the size of the drop has a significant effect on contact angle for drops of diameter in the range 1.0 to 2.0 mm. Thus any experiments conducted to study the effect of other parameters should be on drops of uniform diameter or should be conducted in a drop-size independent region.¹⁴

It has been well documented that contact angles in many liquid-solid systems vary with time at a constant temperature.^{11,12,15,16} A time study on the gallium-gallium arsenide system¹² indicated that the variation of contact angle with time is dependent on the temperature at which the experiment is conducted. For instance in the steady-state region the contact angle

was observed to be constant over a prolonged period of time regardless of temperature. At specific temperatures selected from the third (high temperature) range, contact angles were observed to decrease with time. Other investigators^{11,15,16} have noted that although contact angles initially change, they tend to assume a steady-state value over a period of time.

Numerous techniques for contact angle measurement are reported in the literature. These could be basically divided into two general groups. The prerequisite for the first general group is the availability of accurate surface tension data. Determination of contact angle by a capillary rise is one such method. The relationship θ and the height of the capillary rise is expressed as:

$$\cos \theta = g\rho ha / 2\gamma \quad (5)$$

where h is the height of the capillary, ρ and γ are the density and surface tension of the liquid, a is the radius of the capillary, and g is the acceleration due to gravity. Another technique which is based on surface tension data is the capillary pull method.⁷ The weight of a flat plate when in air, W_0 , and when partially immersed in a liquid, W , are related to the contact angle as follows:

$$W - W_0 = 2[1 + \delta] \gamma \cos \theta - \ell g z \delta \rho \quad (6)$$

Here z is the depth to which the plate is immersed, ρ and γ are the density and surface tension of the liquid, and ℓ and δ are the width and thickness of the plate, respectively. Reliable values of surface tension must be available for the liquid under investigation to estimate contact angles with any degree of accuracy.

Langmuir and Schaefer¹⁷ observed that at a particular elevation the reflection of a light source off a sessile drop could be made to appear and disappear for small changes in height when viewed at the same level

as the source. The principle of this phenomenon is illustrated in Figure 2. Based on this idea, Fort and Patterson¹⁸ developed an instrument to measure contact angles. This proved to be successful for angles of θ less than 90° .

The level surface method⁷ is another method that does not require knowledge of surface tension of the liquid. A flat plate is partially immersed in a liquid and rotated about an axis parallel to the surface of the liquid until the liquid and the plate form a continuous surface. At this point the inclination of the plate to the surface of the fluid is the desired contact angle. The methods described so far either require large amounts of fluid, or demand a knowledge of the surface tension of the fluid. Other direct techniques that do not suffer from these shortcomings have become popular in the recent past.

The contact angle between a sessile drop and a flat substrate as depicted in Figure 1 can be measured by using a cathetometer equipped with a goniometer.^{11,12,19} As discussed earlier, where there is significant mass-transport across the interface, values of θ become a strong function of time especially at relatively high temperatures. Thus direct measurements can suffer from this advantage in that it takes a finite period of time to complete one observation. To overcome this disadvantage, photographing the sessile drop with subsequent measurement of the angle from the enlarged print has been adopted.^{15,16} The sessile drop is illuminated through a window at the rear end of the chamber, while photographs are taken through a front window, using a camera equipped with a telephoto lens. This back lighting arrangement provides a high contrast on the print and thus improves the accuracy of the measurement. This type of illumination is called a "shadow technique" and can be used in collaboration with a telescope and goniometer for direct observations. White²⁰ has stated that

Figure 1 A schematic diagram of a sessile drop of molten metal on a flat substrate.

Figure 2 Principle of the Reflection Goniometer.

- (a) If light from a point source A strikes the drop B at too low an angle, no reflection is seen at the view point C.
- (b) As the angle is increased a bright spot of light appears at the edge.
- (c) If the angle is too high light is reflected to the view point not from the edge.
- (d) At the angle where the reflected light just appears or disappears, the angle of displacement θ of the point source and view point (A,C) from the vertical equals the contact angle.

the most accurate surface tension data available are those obtained by Zeizing,²¹ and Smolders and Duyvis,²² using the sessile drop method and shadow technique. An obvious advantage of the photography method is that it is an instantaneous mode of recording and hence can be used with greater confidence in kinetic studies where variation in contact angle with time is to be investigated. Furthermore, contact angles could be measured from the print by several methods. For example, direct measurement of the angle from the print could be carried out using a protractor. Bashforth and Adams²³ have derived the following equation relating the coordinates of the meridional profile of the liquid sessile drop:

$$\frac{d^2y}{dx^2} = (2 + \beta y) \left(1 + \left(\frac{dy}{dx} \right)^2 \right)^{\frac{3}{2}} - \frac{1}{x} \frac{dy}{dx} \left(1 + \left(\frac{dy}{dx} \right)^2 \right) \quad (7)$$

where x and y are the coordinates of points on the meridional profile of the drop. The parameter β is a constant which is defined by:

$$\beta = g\rho b^2/\gamma \quad (8)$$

where g is the acceleration due to gravity, ρ and γ are the density and surface tension of the liquid, and b is the constant. Numerical solutions of this equation are available in the literature. Staicopolus,²⁴⁻²⁶ Larkins,²⁷ and Ehrlich²⁸ have solved the above equation using a digital computer to obtain values of contact angles from drop dimensions.

This report gives the results of an investigation of the contact angles between liquid Sn, In, and Ga, and substrates of niobium and zirconium. Tin, indium, and gallium were selected because of their low melting points: 231.9°, 156.2°, and 29.78°C, respectively. Furthermore, these materials have low vapor pressures²⁹ in the temperature range investigated (Sn $\sim 10^{-9}$, In $\sim 10^{-8}$, Ga $\sim 10^{-11}$ torr). The selection of the substrate materials has been made on the basis of their suggested use as structural

members in controlled thermonuclear fusion reactors.³⁰ A knowledge of the ability of various liquid metals to wet these solid surfaces is essential for the selection of suitable coolants.

EXPERIMENTAL MATERIALS AND PROCEDURE

A schematic view of the apparatus used to determine contact angles by the sessile drop technique is shown in Figure 3. It consists of a stainless steel tube surrounded by a resistance heating furnace. The furnace was manufactured by Hevi-Duty Electric Company specified as type 70-T, has fine and coarse temperature controls, and is capable of attaining a maximum temperature of 1000°C. Two lenses of optical quality are attached to the ends of the tube furnace thus providing viewing windows. The windows at one end can be easily removed without disturbing the main system and thus providing for an easy access to the sample. The furnace tube is connected by means of a T-joint to a vacuum system which has a working background pressure of 10^{-7} torr. In the lower portion of the furnace tube a mild steel plate 3.175mm thick was situated to serve as a platform for the niobium and zirconium substrates. This plate extends from one end of the tube to the other and is supported by the inner walls of the tube furnace. Substrate temperatures were measured by means of a chromel-alumel thermocouple. The thermocouple was located such that its hot junction lay directly under the middle portion of the substrate. The thermocouple was calibrated by observing the melting points of tin, indium, and gallium.

The stainless steel joints of the vacuum system were made by helium-arc welding and those which were coupled to brass or copper were silver soldered. Varnish and scale from soldered parts were removed with concentrated hydrochloric acid, and more successfully with a nitric acid solution

Figure 3. Layout of Apparatus to Measure Contact Angle

consisting of 40% nitric acid, 30% sulfuric acid, 0.5% hydrochloric acid, and 29.5% water by volume. The acid bath was followed by a distilled water rinse. The basic parts of the entire system were cleaned in dilute hydrochloric acid solution and rinsed sequentially in acetone, trichloroethylene, and Freon 12 solution. Apart from the standard use for contact angle measurements this apparatus also has the facility to handle materials which require special atmospheres. A glove box compartment can be easily coupled to the flange provided at the front end of the tube.

The horizontal tube which is surrounded by the resistance heater is first leveled by means of a spirit level. The substrate holder which is a long rectangular bar was machined such that its cross section is a perfect rectangle along its length. This is then inserted into the tube furnace and by virtue of its shape assumes a perfectly horizontal position if the tube is accurately leveled. This was further ascertained by the use of a cathetometer. Each time a new substrate was loaded the telescope of the cathetometer, which carried horizontal crosshairs, was focused on the sharp edge of the substrate and the substrate was then rotated until it lay perfectly horizontal.

Substrates 0.5mm thick and rectangular in shape were cut from sheets of niobium of 99.995% purity, and zirconium of 99.9% purity. Each specimen was 25mm in width and about 50mm in length. Mechanical polishing of these substrates was then carried out on emery paper and diamond paste. Emery paper ranging in grit dimensions from 204 mesh to 600 mesh; and diamond paste of 6, 1, and $\frac{1}{2}$ μ m size were used to attain a mirror-like finish. After polishing, the substrates were washed in dilute soap solution and rinsed in distilled water and acetone. Before the insertion of each substrate into the tube furnace it was washed in dilute

hydrochloric acid solution and rinsed once more with distilled water and acetone.

The surface roughness, defined as the root-mean-square of the average height of the peaks, was determined by a "Surf-Indicator" which has a reported accuracy of 1.25×10^{-2} μm . The probe of the surf-indicator was traversed on the surface of the substrate along four arbitrary directions, and the average of the four readings was taken as the surface roughness of the specimen. As the sharp spike on the surf-indicator probe would damage the surface, roughness measurements were carried out after the completion of the contact angle experiments.

Nearly spherical pellets of tin, indium, and gallium approximately 2mm in diameter were used for the sessile drop experiments. Tin and indium samples of 99.999% purity were supplied by the Electronic Space Products, Inc., of Los Angeles. The Atomergic Chemetal Company of New York supplied gallium of the same purity. These pellets were washed with dilute hydrochloric acid and rinsed in distilled water and acetone just before insertion into the tube furnace for contact angle measurements. This treatment was carried out to remove any adherent surface oxide layer.

The shadow technique^{21,22} was used to obtain the drop image. A 35mm Asahi Pentax camera with a 135mm telephoto lens and extension tube was used to photograph the sessile drop. Back lighting was provided by a 600 watt "Colortran Mini-Pro" spot lamp. The intensity of illumination was determined by a built-in light meter. A shutter speed of 1/250th of a second, and an aperture of f/8 were used for all photographs. Fine-grained Kodak Panatomic-X film which has an ASA rating of 32 was used. The films were processed in Kodak developer D76 and Kodak fixer. An enlarger made by Simmon Omega carrying a Baltar MA 138, 50mm f/2.3 lens, was used to

project the drop image. The enlarged image was printed on Ilfobrom IB 4.1 K gloss paper, and processed in Bromophen developer and Kodak fixer. The paper and developer is manufactured by Ilford. Developing and fixing details prescribed by the manufacturers were followed. A total magnification of 14.5x was established as suitable for the final print of the image of the sessile drop.

The contact angle on the enlarged drop was measured by means of an Edscorp pocket optical comparator equipped with a protractor reticle. This instrument which was supplied by Edmund Corporation has a magnifying power of 6x, and an accuracy of $\frac{1}{2}^\circ$. To establish confidence in this technique faceted steel balls representing contact angles within the range of 90° to 180° were photographed and the drop images were printed. The contact angles from the prints were compared to the mathematically calculated values and were found to lie within $\pm 0.5^\circ$.

After loading each specimen the system was evacuated to a pressure of at least 2×10^{-6} torr before power was introduced to the heating element of the furnace. The rate of heating was maintained at around 2°C min^{-1} up to a temperature within 20°C of the melting point of each pellet, and then increased to about $10^\circ\text{C min}^{-1}$ beyond this range. For the Sn-Nb and Sn-Zr systems photographs were taken at the melting points and upwards at 50°C increments up to a maximum of 650°C . This procedure was repeated for the In-Nb, In-Zr, Ga-Nb, and Ga-Zr systems. The temperature ranges were $156\text{--}500^\circ\text{C}$ for the In-Nb and In-Zr systems, and $30\text{--}450^\circ\text{C}$ for the Ga-Nb and Ga-Zr systems. These experiments were repeated for different roughnesses of the substrates. Additional experiments were also conducted to establish the dependence of contact angles on time at constant temperatures. In such experiments photographs were taken at half hour intervals for a total time of ninety minutes.

This was performed on each combination of liquid-solid system, on a particular roughness at a selected temperature. The substrates used for the time study of contact angles were sectioned at the meridian of the base of the sessile drop and mounted in a resin. After undergoing a series of polishes ending with a $\frac{1}{4}$ μm diamond paste, they were etched in hydrochloric acid solution and rinsed in distilled water and acetone before performing a microprobe analysis. A simultaneous scan of the two metals of each system was carried out in steps of 1 μm across the interface of each of these systems.

RESULTS

Figures 4 and 5 demonstrate the variation of contact angles of tin on substrates of niobium and zirconium as a function of temperature. The four curves in each figure correspond to specific roughnesses of the substrate. Similarly, Figures 6 through 9 depict the temperature dependence of contact angles of indium and gallium on substrates of niobium and zirconium for different roughnesses. Most of these curves, notably those at higher roughnesses, show three characteristic regions. In the first, the relatively low temperature region, the contact angle is a decreasing function of temperature. The effect of temperature on the contact angle in the second region is comparatively negligible. This is followed by a region in which contact angles decrease with temperature. In the Sn-Zr, In-Zr, and Ga-Zr systems, the third characteristic region was absent within the temperature range investigated for the smoother substrates.

The dependence of contact angle on surface roughness is demonstrated by the curves in Figures 10, 11, and 12. The Sn-Nb and the Sn-Zr systems were investigated at 650°C, the In-Nb and the In-Zr systems were investigated at 500°C, and the Ga-Nb and Ga-Zr systems were studied at 450°C. The variation

Figure 4. Temperature Dependence of Contact Angles Between Sn and Nb Substrates.

Figure 5. Temperature Dependence of Contact Angles Between Sn and Zr Substrates.

Figure 6. Temperature Dependence of Contact Angles Between In and Nb Substrates.

Figure 7. Temperature Dependence of Contact Angles Between In and Zr Substrates.

Figure 8. Temperature Dependence of Contact Angles Between Ga and Nb Substrates.

Figure 9. Temperature Dependence of Contact Angles Between Ga and Zr Substrates.

Figure 10. The Influence of Surface Roughness on the Wettability of Sn on Substrates of Zr and Nb.

Figure 11. The Influence of Surface Roughness on the Wettability of In on Substrates of Nb and Zr.

Figure 12. The Influence of Surface Roughness on the Wettability of Ga on Substrates of Zr and Nb.

of contact angles with surface roughness at other temperatures for these systems could be determined from Figures 4 through 9, which are plots of contact angles as a function of temperature for different roughnesses. The curves of contact angle versus roughness thus obtained, will resemble Figures 10, 11, and 12 in most cases. However for the In-Nb system the curve corresponding to a roughness of 12.5 μ inches (0.31 μ m), Figure 6, displays an unusual low temperature behavior with the result that below about 210°C contact angle versus surface roughness variation does not conform to the general pattern of the curves in Figures 10, 11, and 12. A similar unusual pattern of behavior is observed in the Sn-Zr system for the 7.25 μ inch (0.18 μ m) roughness curve below 300°C.

The results of the time studies carried out at points corresponding to the temperatures in the different regions of the curves in Figures 4 through 9 are indicative of the kinetic control of each of these regions. A temperature of 650°C for tin on a substrate of niobium of roughness 4.25 μ inches (0.11 μ m) corresponds to the third region of the T vs θ curve. A time study of this system at this temperature is depicted in Figure 13. Over a ninety minute period the contact angle decreased with time. The behavior of the In-Zr and In-Nb systems at a temperature of 500°C (which is in the third region for the two systems) is depicted in Figure 14. The decrease in contact angle over the ninety minute period is qualitatively similar to that observed for the Sn-Nb system described above, but somewhat less in magnitude.

For molten tin on a substrate of zirconium of roughness 5.75 μ inches (0.14 μ m), a temperature of 650°C corresponds to a point in the second region of the temperature-contact angle curve. A ninety minute time study of the system at this temperature revealed that the contact angle remains

Figure 13. Time Dependence of the Contact Angles Between Sn and Substrates of Nb and Zr at Constant Temperatures.

Figure 14. Time Dependence of the Contact Angles Between In and Substrates of Nb and Zr at Constant Temperatures.

constant as seen in Figure 13. The contact angle also was constant over a ninety minute period for the Sn-Nb system for a substrate of roughness 4.25 μ inches (0.11 μ m) at 500°C (Figure 13). Similar results were obtained from time studies at 300°C for indium on a substrate of zirconium of roughness 12.75 μ inches (0.32 μ m), Figure 14; and also at 450°C for gallium on a substrate of niobium of roughness 15.5 μ inches (0.39 μ m), Figure 15. The temperatures at which all these time studies were carried out corresponded to points in the second i.e., constant θ region of the temperature-contact angle curves. The results indicate that in this region contact angles are not a function of time within the limits of the present observations.

The time dependence of contact angles for the Ga-Zr system was difficult to interpret because of the formation of a eutectic phase. The photographs of the drop image demonstrated the existence of two angles at each contact surface as shown in Figure 16. A microprobe analysis of this substrate further confirmed the formation of a nondistinct interface, and thus one could conclude that inter-diffusion had taken place. The photographs of the cathode ray oscilloscope traces of this region are shown in Figures 17(a) and (b).

Microprobe analysis of the substrates used in the time studies of the other systems was conducted in steps of 1 μ . However this analysis did not yield any useful information other than confirming the absence of significant diffusion of one species into the other.

DISCUSSION

The variation of the contact angle with temperature reveals a general pattern of behavior for the systems investigated. In all cases the contact angle was observed to either decrease with increasing temperature or remain

Figure 15. Time Dependence of the Contact Angles Between Ga and a Substrate of Nb at 450°C.

(a)

(b)

Figure 16 Sessile drop of liquid Ga on a substrate of Zr at 450°C.

(a) After 30 minutes, and (b) After 90 minutes.

(a)

(b)

Figure 17 Electron microprobe oscilloscope traces of cross sections of Ga with Zr after 90 minutes at 450°C. (a) Zr radiation and (b) Ga radiation.

constant over an interval. These results are in agreement with the patterns observed in other systems. The work of Zee and Munir¹² on the interfacial properties between gold-germanium and gold-tin alloys and gallium arsenide substrates provides an example of such patterns. For the systems studied in this work the temperature-contact angle curves exhibited three distinct regions in most cases. However it was observed that for the Sn-Zr, In-Zr, and Ga-Zr systems when smoother substrates were utilized the third characteristic region was absent in the temperature range of investigation. Furthermore, there is preliminary evidence to indicate that the temperature marking the commencement and end of the constant contact angle region is dependent on roughness of the substrate. However a definite functional dependence cannot be derived from the present data. The first region of the contact angle versus temperature plots could be regarded as a period in which equilibration of contact angle occurs.¹² The second region is obviously one in which temperature has negligible effect on contact angle. A time study of contact angle over a period of ninety minutes at a temperature in this region indicated that contact angle did not change with time. One could conclude then, that diffusional processes are either absent, or are occurring at an extremely slow rate during this region. Time studies in the third region gave evidence for significant mass-transport across the interface. Zee and Munir,¹² who observed a similar characteristic region for gold-germanium and gold-tin alloys on gallium arsenide, conducted microstructural and electron microprobe observations on the substrate in the third region. Based on their findings they concluded that diffusional processes did occur in this last region. In most of these studies, however, only bulk diffusion across the interface has been investigated. Of the systems studied in this work, the Ga-Zr system was

the only one that exhibited any form of bulk diffusion. A microprobe analysis of the substrates confirmed the formation of a new phase. Figures 17(a) and (b) show evidence for the diffusion of gallium into the zirconium substrate across the initial interface. Another interesting phenomenon is the surface diffusion of gallium along the substrate of zirconium. This is clearly demonstrated in Figures 16(a) and (b). The gallium is observed to have diffused over a greater area with time as seen in Figure 16(b). This strongly suggests that surface diffusion is a significant process in the high temperature region of this system.

It is interesting to compare at this point a sessile drop on a flat substrate to a solid sphere onto a flat plate in sintering experiments. Figures 18 and 19 represent the two systems, respectively. In sintering studies it has been demonstrated that transport of matter from the particle to the neck region occurs by one or a combination of the following processes: evaporation-condensation, volume diffusion, grain-boundary diffusion, viscous flow, and surface diffusion.³² The driving force for the evaporation-condensation process is the difference in pressures at the surface of the sphere and the neck regions arising from the difference in radii of curvature.³³ Such a pressure differential is related to the radii of curvature by:

$$RT \ln [p_1/p_0] = [\gamma M/d] (1/\rho - 1/x) \quad (9)$$

where p_1 is the vapor pressure over the region with the small radius of curvature ρ , p_0 is the vapor pressure over the sphere of radius x , γ is the surface free energy, d is the density of the sphere, M is the molecular weight, R is the gas constant, and T is the absolute temperature. This equation was obtained by the application of Kelvins equation³⁴ to the system in Figure 18. Regardless of mechanism, differences in the

thermodynamic activities between the two regions would be the driving force for the surface and bulk diffusion processes. Thus it appears likely that either all or a combination of these processes can play a role in a sessile drop-substrate system. Although there is no conclusive evidence to this effect, several observations indicate that an evaporation-condensation mechanism could be the dominant mass transport process in the higher temperature regions. During preliminary contact angle studies on the Zn-Nb system at 500°C the contact angle was observed to change rapidly from an obtuse to an acute angle. This phenomenon was coupled with a rise in vapor pressure of the liquid as judged by the increased deposition rate of Zn on the view post. At 500°C the vapor pressure of Zn is ~ 2 torr.²⁹ Based on Kelvins equation and the Langmuir equation it is possible to estimate a value for the mass transported to the neck region by evaporation-condensation (cf. Appendix C). For the Zn-Nb system at 500°C a flux of 1.43×10^{-7} gm/cm²-sec is calculated. It is possible that in certain regions evaporation-condensation is a dominant mass-transport process leading to rapid changes in contact angles. Carefully controlled experimentation in a suitably designed apparatus is necessary to substantiate these preliminary observations.

In the past many theories have been proposed which view the phenomenon of wetting as a balance of three forces. A statistical interpretation of wetting as given by Young's equation¹ would thus be misleading as there now exists evidence that the wetting phenomenon is a kinetic process strongly influenced by temperature.^{11,12,15,16} Refinements of the earlier theories are necessary in order to make realistic predictions based on theoretical models.

There is preliminary evidence from the present investigation and from the results of other workers in this field¹² that roughness not only

Figure 18 A schematic diagram of a sessile drop of molten metal on a flat substrate.

Figure 19 A schematic diagram of a spherical particle sintered to a flat plate.

influences the value of contact angle but also has an effect on the temperature of transition from the first region to the second, and from the second to the third. Thus, for a particular combination of materials, knowledge of temperature alone is not sufficient to predict whether a system is in a dynamic or a steady-state region. The variation of contact angle with surface roughness is in accordance with Wenzel's equation¹³ i.e., contact angles were observed to increase with roughness. Similar observations have been reported by Kashkooli, Munir, and Williams.¹⁴

The electron microprobe analysis of the substrates of the Sn-Nb, Sn-Zr, In-Nb, In-Zr, and Ga-Nb systems used in the time dependence study of contact angles at a constant temperature did not yield any conclusive information. However it can be concluded that a significant amount of bulk diffusion across the interface is unlikely. It is possible that diffusion to depths of a few atomic layers could have taken place without being detected by the microprobe scan. The smallest step scan of the electron microprobe is $1\text{ }\mu\text{m}$ or $10^4\text{ }\text{\AA}$. This value corresponds roughly to a region of 3000 monolayers. Hence the resolution of this instrument is insufficient to detect diffusion depths within the first few thousand atomic layers.

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APPENDIX A

Tables of experimental Results

TABLE 1: Contact angles of Sn on substrates of Hb of varying surface roughnesses at different temperatures.

Temperature °C	Contact angle θ , degrees			
	4.25 μ inch	6.25 μ inch	11.88 μ inch	15.50 μ inch
250	-	167.00	-	171.00
300	162.50	163.50	166.00	170.00
350	159.00	159.50	161.75	166.00
400	156.00	157.00	159.00	163.50
450	153.00	156.50	157.50	163.50
500	153.50	156.50	157.25	163.25
550	153.00	154.00	157.50	155.50
600	148.00	150.00	155.50	155.50
650	143.00	147.50	150.00	153.25

TABLE 2: Contact angles of Sn on substrates of Zr of varying surface roughnesses at different temperatures.

Temperature °C	Contact angle θ , degrees			
	5.75 μ inch	6.25 μ inch	7.25 μ inch	8.00 μ inch
250	154.75	160.00	157.50	172.00
300	148.00	156.00	156.50	166.25
350	144.50	156.50	155.75	164.00
400	143.50	154.50	157.00	164.25
450	142.75	154.25	156.50	164.00
500	141.50	154.75	155.50	163.25
550	142.00	149.50	156.75	158.25
600	141.50	149.00	154.50	155.25
650	141.50	142.50	150.00	153.25

TABLE 3: Contact angles of In on substrates of Nb of varying surface roughnesses at different temperatures.

Temperature °C	Contact angle θ , degrees			
	7.25 μ inch	8.75 μ inch	12.50 μ inch	15.25 μ inch
156.2	149.50	159.00	146.50	166.00
175	144.00	152.00	147.00	165.50
200	130.25	143.00	147.00	163.50
250	128.00	132.50	147.00	164.00
300	126.75	130.50	148.00	164.00
350	122.00	129.00	145.75	164.50
400	122.00	130.00	143.25	162.50
450	121.75	125.50	139.00	160.00
500	119.75	123.00	134.00	158.50

TABLE 4: Contact angles of In on substrates of Zr of varying
surface roughnesses at different temperatures

Temperature °C	Contact angle θ , degrees			
	9.00 μ inch	9.25 μ inch	12.75 μ inch	14.75 μ inch
156.2	-	145.50	150.00	-
175	118.00	143.00	147.50	162.00
200	116.00	136.00	142.20	156.50
250	115.00	136.00	141.00	156.00
300	114.50	134.00	135.50	156.00
350	113.25	132.00	138.00	156.00
400	113.50	127.25	136.00	154.00
450	113.50	124.50	136.00	151.50
500	113.50	119.00	135.50	150.00

TABLE 5: Contact angles of Ga on substrates of Nb of varying surface roughnesses at different temperatures.

Temperature °C	Contact angle θ , degrees			
	10.00 μ inch	12.75 μ inch	15.50 μ inch	19.95 μ inch
30	-	125.00	-	-
50	-	112.00	-	-
100	-	110.00	-	-
150	-	106.00	-	166.50
200	-	104.50	-	165.00
250	100.00	105.00	130.00	164.75
300	98.00	104.50	123.00	164.00
350	97.50	102.00	125.00	164.00
400	96.50	99.00	124.00	164.00
450	92.00	94.75	124.00	161.75

TABLE 6: Contact angles of Ga on substrates of Zr of varying
surface roughnesses at different temperatures,

Temperature °C	Contact angle θ , degrees			
	6.50 μ inch	12.10 μ inch	13.00 μ inch	13.10 μ inch
50	140.00	142.00	-	-
100	122.00	126.50	154.00	-
150	110.00	122.00	144.50	155.00
200	107.00	116.00	138.50	143.75
250	105.50	113.00	134.50	137.00
300	106.00	112.00	130.50	136.00
350	105.00	112.50	132.00	134.50
400	106.00	112.00	127.50	134.75
450	105.00	112.00	125.00	130.00

TABLE 7: The variation of contact angle of Sn on a substrate
of lb of roughness 4.25μ inch, with time at 650°C .

Time, minutes	Contact angle θ , degrees
0	143.00
30	137.50
60	136.00
90	134.50

TABLE 8: The variation of contact angle of Sn on a substrate
of Zr of roughness 5.75μ inch, with time at 650°C .

Time, minutes	Contact angle θ , degrees
0	141.50
30	141.75
60	141.50
90	142.00

TABLE 9: The variation of contact angle of In on a substrate
of Nb of roughness 12.50 μ inch, with time at 500°C.

Time, minutes	Contact angle θ , degrees
0	134.00
30	134.00
60	133.75
90	133.50

TABLE 10: The variation of contact angle of In on a substrate
of Zr of roughness 12.75 μ inch, with time at 500°C.

Time, minutes	Contact angle θ , degrees
0	135.50
30	134.50
60	131.50
90	129.50

TABLE 11: The variation of contact angle of Ga on a substrate
of Nb of roughness 15.5μ inch, with time at 450°C .

Time, minutes	Contact angle θ , degrees
0	124.00
30	123.75
60	123.25
90	123.50

TABLE 12: The variation of contact angle of Sn on a substrate
of Nb of roughness 4.25μ inch, with time at 500°C .

Time, minutes	Contact angle θ , degrees
0	153.50
30	154.00
60	153.50
90	153.75

TABLE 13: The variation of contact angle of In on a substrate
of Zr of roughness 12.75μ inch, with time at 300°C .

Time, minutes	Contact angle θ , degrees
0	138.00
30	137.50
60	137.50
90	138.00

TABLE 14: The variation of contact angles of Sn at specific temperatures, with substrates of Nb of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	350°C	450°C	550°C	650°C
4.25	159.00	153.00	153.00	143.00
6.25	161.75	157.50	157.50	150.00
11.88	159.50	156.50	154.00	147.50
15.50	166.00	163.50	163.50	153.25

TABLE 15: The variation of contact angles of Sn at specific temperatures, with substrates of Zr of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	350°C	450°C	550°C	650°C
5.75	144.50	142.75	142.00	141.50
6.25	156.50	154.25	149.50	142.50
7.25	155.75	156.50	156.75	150.00
8.00	164.00	164.00	158.25	153.25

TABLE 16: The variation of contact angle of In at specific temperatures, with substrates of Nb of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	200°C	300°C	400°C	500°C
7.25	130.25	126.75	122.00	119.75
8.75	143.00	130.50	130.00	123.00
12.50	147.00	148.00	143.25	134.00
15.25	163.50	164.00	162.50	158.50

TABLE 17: The variation of contact angle of In at specific temperatures, with substrates of Zr of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	200°C	300°C	400°C	500°C
9.00	116.00	114.50	113.50	113.50
9.25	136.00	134.00	127.25	119.00
12.75	142.25	135.50	136.00	135.50
14.75	156.50	156.00	154.00	150.00

TABLE 18: The variation of contact angle of Ga at specific temperatures, with substrates of Nb of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	150°C	250°C	350°C	450°C
10.00	-	100.00	97.50	92.00
12.75	106.00	105.00	102.00	94.75
15.50	-	130.00	125.00	124.00
19.95	166.50	164.75	164.00	161.75

TABLE 19: The variation of contact angle of Ga at specific temperatures, with substrates of Zr of different roughnesses.

Surface Roughness μ inch	Contact angle θ , degrees			
	150°C	250°C	350°C	450°C
6.50	110.00	105.50	105.00	105.00
12.10	122.00	113.00	112.50	112.00
13.00	144.50	134.50	132.00	125.00
13.10	155.00	137.00	134.50	130.00

APPENDIX B

A sample set of photographs of the sessile drop of Sn on substrates of Nb of varying roughnesses, at different temperatures.

Roughness = 4.25μ inch, Temperature = 300°C , $\theta = 162.5^{\circ}$.

Roughness = 4.25μ inch, Temperature = 350°C , $\theta = 159.0^{\circ}$.

Roughness = 4.25μ inch, Temperature = 400°C , $\theta = 156.0^{\circ}$

Roughness = 4.25μ inch, Temperature = 450°C , $\theta = 153.0^{\circ}$

Roughness = 4.25 μ inch, Temperature = 500°C, θ = 153.50°.

Roughness = 4.25 μ inch, Temperature = 550°C, θ = 153.00°.

Roughness = 4.25μ inch, Temperature = 600°C , $\theta = 148.00^{\circ}$.

Roughness = 4.25μ inch, Temperature = 650°C , $\theta = 143.00^{\circ}$.

Roughness = 6.25μ inch, Temperature = 250°C , $\theta = 167.0^{\circ}$

Roughness = 6.25μ inch, Temperature = 300°C , $\theta = 163.5^{\circ}$.

Roughness = 6.25μ inch, Temperature = 350°C , $\theta = 159.5^{\circ}$.

Roughness = 6.25μ inch, Temperature = 400°C , $\theta = 157.0^{\circ}$.

Roughness = 6.25μ inch, Temperature = 450°C , $\theta = 156.5^{\circ}$

Roughness = 6.25μ inch, Temperature = 500°C , $\theta = 156.5^{\circ}$.

Roughness = 6.25μ inch, Temperature = 550°C , $\theta = 154.0^{\circ}$.

Roughness = 6.25μ inch, Temperature = 600°C , $\theta = 150.0^{\circ}$.

Roughness = 6.25 μ inch, Temperature = 650°C, $\theta = 147.5^\circ$.

Roughness = 11.88 μ inch, Temperature = 350°C, θ = 161.75°.

Roughness = 11.88 μ inch, Temperature = 300°C, θ = 166.0°

Roughness = 11.88 μ inch, Temperature = 400°C, θ = 159.0

Roughness = 11.88 μ inch, Temperature = 450°C, θ = 157.5°.

Roughness = 11.88μ inch, Temperature = 500°C , $\theta = 157.25^{\circ}$

Roughness = 11.88μ inch, Temperature = 550°C , $\theta = 157.5^{\circ}$.

Roughness = 11.88μ inch, Temperature = 600°C , $\theta = 155.5^{\circ}$.

Roughness = 11.88μ inch, Temperature = 650°C , $\theta = 150.0^{\circ}$.

Roughness = 15.50 μ inch, Temperature = 250°C, θ = 171.0°.

Roughness = 15.50 μ inch, Temperature = 300°C, θ = 170.0°.

Roughness = 15.50 μ inch, Temperature = 350°C, θ = 166.0°.

Roughness = 15.50 μ inch, Temperature = 400°C, θ = 163.5°.

Roughness = 15.50μ inch, Temperature = 450°C , $\theta = 163.50^{\circ}$.

Roughness = 15.50μ inch, Temperature = 500°C , $\theta = 163.25^{\circ}$.

Roughness = 15.50μ inch, Temperature = 550°C , $\theta = 163.5^{\circ}$.

Roughness = 15.50μ inch, Temperature = 600°C , $\theta = 155.5^{\circ}$.

Roughness = 15.50 μ inch, Temperature = 650°C, θ = 153.25°.

APPENDIX C

Calculation of the mass transported from a sessile drop of Zn by evaporation-condensation, to the neck area.

Calculation of the mass transported from a sessile drop of Zn to the neck region, between the drop and a substrate of Nb by evaporation-condensation.

Diameter of the sessile drop, $2r$	=	2.0 mm
Diameter of the neck of the drop, $2x$	=	1.5 mm
Surface tension, γ	=	761.0 dyne/cm
Molecular weight of Zn, M	=	65.37 gms/mole
Density of the drop, d	=	6.47 gms/cm ³
Temperature, T	=	500.0 °C
Vapor pressure over the sphere, p_0	=	2.0 torr.

For this system the following equations relate the parameters given above with the radius of curvature at the neck, ρ , the pressure difference between the surface of the sphere and the neck, Δp , and the flux transported from the sphere to the neck by evaporation-condensation, $\dot{m}$:

$$\rho = x^2/2r \quad (a)$$

$$\Delta p = \gamma M p_0 / d \rho R T \quad (b)$$

$$\dot{m} = \Delta p (M/2RT)^{0.5} \quad (c)$$

hence substituting the values given above into Eq.s' (a), (b), and (c) :

$$\rho = \frac{0.75 \times 0.75 \times 10^{-1}}{2} = 0.028125 \text{ cms.}$$

$$\Delta p = \frac{761.0 \times 65.37 \times 2 \times 1.33 \times 10^2}{773 \times 6.47 \times 0.028125 \times 8.314 \times 10^7}$$

$$= 1.1315 \times 10^{-3} \text{ N/m}^2$$

$$m = \frac{1.131 \times 10^{-3} \times 10^3 \times 65.37^{0.5}}{10^2 \times 10^2 \times (2 \times \pi \times 8.314 \times 773 \times 10^3)^{0.5}}$$

$$= 1.4396 \times 10^{-7} \text{ gms/cm}^2\text{-sec.}$$

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