RECEIVED BY TIC JAN 22 1973

IS-T-557

SURFACE TENSION OF MOLTEN METALS
USING THE SESSILE DROP METHOD

Ph.D. Thesis Submitted to Iowa State University,
November, 1972

D. R. Sageman

Ames Laboratory, USAEC
Iowa State University
Ames, Iowa 50010

Date of Manuscript: November, 1972

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION
DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

See

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

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

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
Department A
Springfield, VA 22151

Price: Microfiche \$0.95

Surface tension of molten metals
using the sessile drop method

by

David Richard Sageman

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

Approved:

Geo. Burnett
In Charge of Major Work

Geo. Burnett
For the Major Department

Charlotte E. Rodenbeck
For the Graduate College

Iowa State University
Ames, Iowa

1972

TABLE OF CONTENTS

ABSTRACT	Page v
INTRODUCTION	1
LITERATURE SURVEY	7
Preparation of Clean Surfaces	7
Sessile Drop Theory	11
Laplace equation	13
Young equation	18
Related Work	21
EQUIPMENT AND PROCEDURE	32
RESULTS AND DISCUSSION	40
Molten Metal and Substrate Selection	40
Outgassing Phenomena	43
Surface Tension-Temperature Behavior	49
Contamination Effect of Gases	76
Contact Angle Phenomena	90
Surface Tension Correlation for Molten Metals	91
CONCLUSIONS	99
RECOMMENDATIONS	100
BIBLIOGRAPHY	102
ACKNOWLEDGMENTS	106
APPENDIX	107

Surface tension of molten metals
using the sessile drop method

David Richard Sageman

Under the supervision of George Burnet
From the Department of Chemical Engineering
Iowa State University

The surface tension of molten Bi, In, Pb, and Sn was measured near the melting point using the sessile drop method. The tests were performed under ultrahigh vacuum conditions in order to maintain a clean drop surface. The surface tension-temperature behavior of Bi, In, Pb, and Sn is linear near the melting point and in this temperature range, the temperature derivative of surface tension, $\frac{\partial \sigma}{\partial T}$, is negative for all four molten metals.

Gases in solution in the molten metal reduce the surface tension of the metal. These gases can be removed by outgassing at 10^{-9} torr. The surface tension of the molten metal was found to increase with time of outgassing; the increase in surface tension with outgassing was more significant for In and Sn than for Pb and Bi.

Oxygen, nitrogen, and hydrogen reduce the surface tension of molten Bi, In, Pb, and Sn by surface contamination

and dissolution into the molten metal at pressures of 10^{-6} torr and higher. But at 10^{-6} torr the contamination effect is not noticeable until after several hours of contamination.

The surface tension of a molten metal can be related to its heat of vaporization by the equation

$$\frac{5.40}{r_i} \left(\frac{M}{\rho N}\right)^{2/3} \left(\sigma - T \frac{\partial \sigma}{\partial T}\right) = \frac{\Delta H_{\text{vap}} - RT}{N}$$

where r_i is the ionic radius of the highest valence state of the metal. In the melting point region, the error in a value of surface tension calculated by this relationship should be less than ten percent.

The contact angle of a molten metal on a solid surface is very sensitive to the surface preparation of the solid. Oxides on metallic surfaces increase contact angles, but oxygen contamination of alumina reduces contact angles.

INTRODUCTION

One of the results of the growing interest in nuclear power plants has been a growing interest in the properties of molten metals. Molten metals have better heat transfer properties than more common liquids such as water. These better heat transfer properties make molten metals attractive choices as coolants for nuclear reactors, if containment and handling problems for molten metals can be solved. This interest in molten metals has caused research into many of the physical and chemical properties of molten metals; one such property is the surface tension of molten metals.

There have been many problems in obtaining good data on the surface tension of molten metals; most of the data which can be found in the literature will be characterized by a large amount of scatter in the experimental points, and mean values of the experimental points will be inaccurate. The main problems in obtaining good experimental results for the surface tension of molten metals have been the lack of sophistication of experimental techniques, impure metals, and contamination of the liquid surface.

There are two reasons for wanting to measure the surface tension of molten metals accurately. First, as was mentioned above, it has not been done to any great extent before. Second, there is a practical application for such data. Surface tension appears as a parameter in boiling

heat transfer correlations for molten metals. One such correlation by Balzhiser and Caswell (1966) is a correlation for the critical heat flux in boiling liquid metal systems:

$$\left[\frac{(q/A)_c C_p \sigma}{\lambda^2 \rho_v K} \right] \text{Pr}^{-0.71} = 1.02 \times 10^{-6} \left[\frac{\rho_l - \rho_v}{\rho_v} \right]^{0.65} \quad (1)$$

$(q/A)_c$ = critical heat flux

C_p = heat capacity of liquid

σ = surface tension of liquid

λ = heat of vaporization of liquid

ρ_l = density of liquid

ρ_v = density of vapor

K = thermal conductivity of liquid

Pr = Prandtl number of liquid.

Other correlations for which the surface tension is a parameter include: an equation for the heat transfer coefficient for film boiling of potassium on a horizontal plate, by Balzhiser and Padilla (1968), and equations for the superheat needed to initiate boiling, by Fauske (1969) and by Holtz and Singer (1969).

Most of the experimental problems mentioned above have been solved in recent years. Improvements in the sessile drop and maximum bubble pressure methods for measuring surface tension now make it possible to measure the surface

tension of molten metals very accurately; in fact, for molten metals the standard deviation of data points from the mean is usually less than 10 ergs/cm^2 . For sodium, whose surface tension is about 200 ergs/cm^2 , this would be an error of about 5 percent; and, for silver, whose surface tension is about 1000 ergs/cm^2 , this would be an error of about 1 percent. Also, when using the sessile drop method, accurate contact angles are obtained.

The availability of pure materials has been another important factor in improving the accuracy of results. It has been shown by several people that trace amounts of impurities can have a large effect on surface tension values.

The use of ultrahigh vacuum (UHV) equipment has been a big improvement for sessile drop studies. Unwanted contamination of surfaces can be prevented by using UHV equipment. Since a monolayer will adsorb on a surface in about 10^{-6} torr-seconds, pressures on the order of 10^{-9} torr are necessary to maintain clean surfaces for sufficient times to conduct experiments.

The sessile drop method was selected for this study. It is considered one of the two best methods for obtaining molten metal surface tension data, and UHV equipment was available to prevent surface contamination. The sessile drop method also provides contact angle data which are valuable in measuring wetting.

The degree of wetting, which is characterized by the contact angle, has been proposed as a parameter in transport phenomena occurring in molten metal-solid systems. Only recently, however, have actual uses for this parameter been realized. Hlavac et al. (1970) has shown that different conditions of wetting procedure different velocity profiles for fully developed turbulent flow of mercury in an annulus. His study is believed to be the only study of this kind that has been done to date. Fauske (1969) uses dynamic contact angles in his correlation for determining the superheat needed to initiate boiling in molten metal-solid systems. Even though the sessile drop method provides equilibrium contact angles and not dynamic contact angles, knowledge of the equilibrium contact angles could be used to estimate dynamic contact angles.

If meaningful information about interfacial phenomena, such as wetting, is desired, it is very important to be able to prepare a clean surface. There are several ways to clean a solid surface, and the choice depends upon the material to be cleaned and the equipment available. Some of the more common methods used to prepare clean surfaces are high temperature heating under vacuum, evaporation, ion bombardment, and chemical reaction. Then, by having UHV equipment available, a clean surface can be maintained, or a clean surface can be contaminated with a known gaseous substance.

The sessile drop method is particularly suited for vacuum use because measurements can be made from a photograph of the drop; thus, the method can be used with UHV equipment which can produce and maintain clean conditions. Very little data exist for molten metal surface tension and contact angles that have been measured under clean conditions. However, the method cannot determine solid and liquid-solid surface tensions; only the difference can be calculated.

Not only have good surface tension data been lacking, but also, a good correlation for predicting molten metal surface tensions is unavailable. Such a correlation is valuable since metals make up about 80 percent of the elements, and experimental surface tension data, taken under good conditions, can be obtained for only some of the metals. Previous surface tension correlations for molten metals have involved empirical constants which have little or no theoretical basis.

The electron microprobe was used to a limited extent in this study. A focused beam of electrons impinging on a surface will cause X rays to be emitted, and the x rays will be characteristic of the element present. Diameters as small as one micron can be analyzed for content, and by scanning the beam across the interface formed by a drop

of frozen liquid and solid, a map of material distribution can be produced. Thus liquid metal penetration into the solid can be assessed.

LITERATURE SURVEY

A literature survey was conducted in three broad areas. The first area, Clean Surfaces, is devoted to descriptions of various experimental methods that can be used to obtain clean surfaces and to maintain clean surfaces. The second, Sessile Drop Theory, is a summary of basic thermodynamics of plane and curved interfaces, the relation between thermodynamics and the shape of a sessile drop, and a simplified derivation of the Young equation based on surface energy minimization. The third area, Related Work, is a condensation of some recent results in the area of molten metal surface chemistry.

Preparation of Clean Surfaces

Any experiment designed to study the physical or chemical properties of a surface whose composition is to be representative of the bulk material requires the preparation of a surface free of contamination and the maintenance of cleanliness for a time which is sufficient to perform the experiment. If the time of duration of the experiment is on the order of several minutes or several hours, a vacuum of 10^{-9} torr or less is required to maintain the clean surface.

Roberts (1963), in a summary of current methods used to obtain and maintain clean surfaces, has defined an

atomically clean surface as "one free of all but a few percent of a single monolayer of foreign atoms, either absorbed on, or substitutionally replacing, surface atoms of the parent lattice".

There are several techniques for preparing clean surfaces. The proper technique to use depends on the surface to be cleaned and the bulk composition of the material. Surfaces which have physically adsorbed layers are generally easier to clean than surfaces which have chemically adsorbed layers. Four common techniques used to clean surfaces are: evaporation, chemical reaction, ion bombardment, and high temperature heating.

Evaporation is perhaps the simplest method for producing a clean surface. The process involves heating the material and then condensing the vapor on a suitable substrate material. However, Roberts and Vanderslice (1963) have pointed out that films prepared in this manner may have different properties than the bulk material. The film may take on the structure of the substrate, or the film may be discontinuous or rough.

Roberts (1967) has pointed out that ion bombardment is the most energetic cleaning method of the four mentioned. The procedure consists of first degassing the specimen to be cleaned under UHV for several hours. Argon is then admitted to the system up to a pressure of 10^{-3} torr, and

ionized by application of a 200 to 600 volt potential. The resulting ions are accelerated in an electric field and directed toward the specimen surface. The argon ions are at an energy level of about 500 eV; when the argon ions strike the specimen surface, atoms are literally knocked from the lattice. (As a point of reference, atoms at room temperature have a translational energy level of about 0.03 eV.) Ion bombardment of a surface greatly disrupts it and introduces a large number of defects. These defects can greatly affect the activity of the surface. For example, Roberts (1963) found that the activity of bulk nickel for catalyzing the hydrogenation of ethylene is about ten times greater for argon bombarded nickel than for bombarded and annealed nickel.

Perhaps the most convenient method to use to prepare clean surfaces for sessile drop tests of molten metals is heating a material to a high temperature under high vacuum. Holland (1960) has used this method to clean nickel, chromium, and silicon. Tucker (1964, 1966) and Good and Muller (1956) have used this method to clean tantalum, graphite, and tungsten. Ramsey (1956) and D'Amico and Hagstrum (1960) have suggested that pure starting materials should be used to minimize diffusion of impurities from the bulk to the surface during the heat process. In fact, Roberts (1963) found that bulk concentrations of 0.01 percent

carbon in tungsten caused significant surface contamination by diffusion during heating. Oxide films and water are generally chemisorbed and difficult to remove by heating under vacuum. It is not possible to clean all materials by heating as some will decompose or melt before the surface oxide layer can be driven off. Iron is one such substance and its oxide layer is removed better by chemical or more energetic methods. However, Maze (1970) found that prolonged heating under UHV produced a reduction of contact angles in his sessile drop experiments with iron substrates; this suggests either a reduction of the oxide film, a change in the structure of the material, or both.

Cleaning by chemical reaction is commonly done by causing a reaction with the surface in such a way that the products are volatile. These products can then be removed by a vacuum pump. Laukonis and Coleman (1961) used this method to clean iron by heating in an atmosphere of hydrogen. Singleton (1954) removed carbon from a surface by heating in oxygen.

A combination of heating under high vacuum and chemical cleaning using gases appear to be the best methods available for sessile drop tests.

Sessile Drop Theory

Thermodynamics of interfaces serves as the basis for determining equilibrium surface tension and contact angles from sessile drop shapes (Figure 1).

Two important equations can be derived from thermodynamic considerations for the purpose of calculating surface tension and contact angles. The Laplace equation describes the relationship between curvature, surface tension, and pressure drop across the interface. Secondly, the Young equation is a force balance relating equilibrium forces acting at the three-phase junction (solid-liquid-vapor).

McLaughlin and de Bruyn (1969) have listed three conditions that must be fulfilled for equilibrium to exist at the three-phase junction:

- a. Equality of temperature and chemical potential throughout the system;
- b. Satisfaction of the Laplace equation at all points of the liquid-vapor interface;
- c. Satisfaction of the Young equation at all points of the three-phase junction line.

Also, the solid surface is assumed to be regular and completely rigid. The assumption of rigidity is essential since the solid surface energy is in part determined by its condition of mechanical strain. This should be constant

x, z, ϕ = COORDINATES
 R_1, R_2 = PRINCIPLE RADII OF CURVATURE
 Θ = CONTACT ANGLE
 h = DROP HEIGHT

Figure 1. Sessile drop coordinate system and important parameters

throughout the solid phase so that no orientation dependence will be present.

Laplace equation

The total differential in internal energy for a reversible change is given by

$$dE = TdS - PdV + \sum \mu_i d\eta_i \quad (2)$$

which can be integrated at constant T , P , and μ_i to give

$$E = TS - PV + \sum \mu_i \eta_i \quad (3)$$

For convenience a new state function is defined

$$\Omega \equiv E - TS - \sum \mu_i \eta_i = -PV \quad (4)$$

Differentiating Equation 4 and substitution Equation 1 for dE one obtains

$$d\Omega = -SdT - PdV - \sum \eta_i d\mu_i \quad (5)$$

for the total system.

Gibbs (1948) and de Bruyn (1966) have shown that for a two phase multi-component system in equilibrium, the total differential free energy, including interfaces and curvature, can be written in place of Equation 5 as

$$d\Omega = -SdT - \sum \eta_i d\mu_i - P^\alpha dv^\alpha - P^\beta dv^\beta + \sigma dA + C_1 dR_1 + C_2 dR_2 \quad (6)$$

R_1, R_2 = principle radii of curvature

C_1, C_2 = constants

A = area

α, β = reference to phases α and β .

Surface tension is defined from Equation 6 as

$$\sigma \equiv \left. \frac{\partial \Omega}{\partial A} \right|_{T, \mu, R, V} \quad (7)$$

Since $d\Omega$ is an exact differential, Equation 6 can be integrated maintaining all intensive properties constant, including curvature, to yield

$$\Omega = \sigma A - p^\alpha V^\alpha - p^\beta V^\beta \quad (8)$$

Rearranging Equation 8

$$\sigma A = \Omega + p^\alpha V^\alpha + p^\beta V^\beta \quad (9)$$

Examination of Equation 9 reveals that it gives the total surface free energy since this is the difference between the total PV and that for each phase.

Placement of the dividing surface (Figure 2) between bulk phases α and β fixes the values of $p^\alpha V^\alpha$ and $p^\beta V^\beta$. As can be seen, the exact location of the dividing surface is arbitrary, and its placement is a matter of convention. For a fixed total Ω , the difference between the total and that for both bulk phases, Equation 9, must be associated

Figure 2. Dividing surface location in interfacial region

with the interface.

Defining

$$\Omega^A = \sigma A \quad . \quad (10)$$

And differentiating

$$d\Omega^A = \sigma dA + A d\sigma \quad . \quad (11)$$

Then from Equation 6 at constant temperature and chemical potential

$$d\Omega^A = \sigma dA + C_1 dR_1 + C_2 dR_2 \quad . \quad (12)$$

Subtracting Equation 11 from Equation 12 gives

$$A d\sigma = C_1 dR_1 + C_2 dR_2 \quad . \quad (13)$$

At this point the restriction of a spherical interface is imposed for simplification. For the spherical interface imagine a small isothermal displacement normal to the surface with the physical content of the system constant, then

$$\delta\Omega = 0, \quad \delta A = 2A\delta R/R; \quad \delta V^\alpha = A\delta R = -\delta V^\beta \quad (14)$$

$$R_1 = R_2 = R = \text{constant curvature.}$$

From Equation 8

$$\delta(\sigma A) = (p^\alpha - p^\beta)\delta V^\alpha \quad . \quad (15)$$

Substituting for δV^α and δA in Equation 15 gives

$$A(\delta\sigma) + \frac{\partial\sigma}{\partial R} A\delta R = (P^\alpha - P^\beta)A\delta R \quad (16)$$

and upon rearranging Equation 16 the Laplace equation for a spherical interface is obtained.

$$P^\alpha - P^\beta = \frac{\partial\sigma}{\partial R} + \left. \frac{\partial\sigma}{\partial R} \right|_{T,\mu} \quad (17)$$

By proper location of the dividing surface in the interfacial zone, $(\partial\sigma/\partial R)$ can be made to vanish and the surface tension is at a minimum. This surface is commonly called the surface of tension.

In general, the Laplace equation for any curved surface is

$$P^\alpha - P^\beta = \sigma J + \frac{\partial\sigma}{\partial J} (2K - J^2) \quad (18)$$

$P^\alpha - P^\beta$ = pressure difference between the two contiguous phases

J = mean curvature = $1/R_1 + 1/R_2$

K = Gaussian curvature = $1/R_1 R_2$

and $(\partial\sigma/\partial J)$ can be made to vanish as before. Rigorous derivation of Equation 18 has been done by McLaughlin and de Bruyn (1969). The influence of curvature on surface tension dies out a few molecular diameters from the surface tension, and is only important when curvature and molecular dimensions are of the same order.

Young equation

The Young equation can be derived by minimizing the total surface free energy for a spherical cap of fluid of constant volume resting on a flat surface. The expression for total free energy is

$$F = A_l \sigma_l + A_s \sigma_s + A_{sl} \sigma_{sl} \quad (19)$$

l, s, sl refer to liquid, solid, and solid-liquid interfaces

A = area.

Starting with a unit solid area Equation 19 becomes, for a spherical cap of radius R and height h

$$F = \sigma_s [1 - \pi(2Rh - h^2)] + 2\pi Rh \sigma_l + \pi(2Rh - h^2) \sigma_{sl} \quad (20)$$

$$A_l = 2\pi Rh$$

$$A_s = 1 - \pi(2Rh - h^2)$$

$$A_{sl} = \pi(2Rh - h^2) \quad .$$

The cap volume is

$$V = \frac{\pi h^2}{3} (3R - h) \quad . \quad (21)$$

Since the cap volume is constant, solving Equation 21 for R

$$R = \frac{3V + \pi h^3}{3\pi h^2} \quad . \quad (22)$$

Substituting Equation 22 into Equation 20 for R and setting

$$\left. \frac{\partial F}{\partial h} \right|_V = 0$$

for minimum free energy results in the Young equation

$$\sigma_{sl} - \sigma_s + \left(\frac{3V - 2\pi h^3}{3V - \pi h^3} \right) \sigma_l = 0 \quad (23)$$

The cosine of the contact angle is found to be

$$\cos \theta = \frac{3V - 2\pi h^3}{3V - \pi h^3} \quad (24)$$

θ = contact angle.

A more familiar form of the Young equation is

$$\sigma_l \cos \theta = \sigma_s - \sigma_{sl} \quad (25)$$

Since independent determination of σ_s and σ_{sl} have never been made, Young's equation has never been experimentally verified.

The sessile drop, Figure 1, can be described using the Laplace Equation 18:

$$p^\alpha - p^\beta = \text{static pressure} + \text{constant contribution} \\ \text{from surface tension}$$

$$\Delta P = p^\alpha - p^\beta = gz(\rho^\alpha - \rho^\beta) + c \quad (26)$$

g = gravitational constant

ρ = density

$C = \text{constant}$

$z = z \text{ coordinate.}$

From Equation 18 and 26

$$\Delta P = \sigma_1 J = g(\rho^\alpha - \rho^\beta) + C \quad (27)$$

At the drop apex

$$z = 0, \quad 1/b \equiv 1/R_1 = 1/R_2$$

$$J = 2/b$$

$b = \text{radius of curvature.}$

The constant C appearing in Equation 27 is evaluated by substituting the parameters determined at the drop apex into Equation 27 giving

$$C = \frac{\partial \sigma_1}{b} \quad (28)$$

The coordinates of a sessile drop are usually expressed as:

$$dx = \cos \phi \, ds \quad (29a)$$

$$dz = \sin \phi \, ds \quad (29b)$$

$$d\phi = 1/R_1 \, ds \quad (29c)$$

where

$x, z = \text{coordinates}$

$\phi = \text{angle between } R_1 \text{ and the } z\text{-axis}$

$s = \text{arc length.}$

From the geometry of the drop, Figure 1, $1/R_2 = \sin \phi/x$. Substituting this into Equation 27, then solving for $1/R_1$ gives

$$1/R_1 = \frac{g(\rho^\alpha - \rho^\beta)z}{\sigma_1} - \frac{\sin \phi}{x} + \frac{2}{b} \quad . \quad (30)$$

Equation 30 is the form used in Equation 29c. Knowing σ_1 and b , a given drop shape can be calculated by numerical integration of Equation 29. Conversely if the shape is known or can be measured, the parameters σ_1 and b can be determined using a nonlinear regression computer program by Maze and Burnet (1969). The contact angle is found as the upper limit of the normal angle ϕ , and can be calculated numerically once σ_1 and b have been established.

Related Work

Until recently it was very difficult to measure the surface tension of liquid metals, mercury being the only exception. This may be one reason that there are not much published data on the surface tension of molten metals and only data published in the past few years have much reliability. Flint (1965) and White (1968) have written review articles on the surface tension of molten metals and alloys. These articles cover the various techniques used to measure the surface tension of molten metals and

the important sources of error in these techniques. There are at least six different methods available for measuring the surface tension of molten metals; however, the maximum bubble pressure method and the sessile drop method are the most useful since they give the most accurate results.

The important sources of error in these methods are: the purity of the molten metal, the inability to establish thermodynamic equilibrium, and inaccurate values for the density of the molten metal.

White (1966, 1971, 1972) measured the surface tension of Cd, In, Pb, Sn, and Zn using the sessile drop method. During his experiments his test chamber was filled with either H_2 or He at a pressure of 760 torr. By using H_2 or He, he chose to neglect surface contamination of the molten metal by the gas. His decision was based on some earlier work by Nicholas et al. (1961) who measured the surface tension of Hg at $25^\circ C$ in the presence of several different gases. They found that He, H_2 , N_2 , O_2 , CO_2 , and CH_4 had no affect on the surface tension of Hg. However, it must be pointed out that there was no step in their procedure for outgassing the Hg prior to the surface tension experiments. White found that the surface tension-temperature behavior of In, Pb, and Sn was that which has been commonly assumed for molten metals, namely, the temperature derivative of surface tension is negative. His results are

summarized by the following relationships:

$$\sigma_{\text{In}} = 568.0 - 0.04t(^{\circ}\text{C}) - 7.08 \times 10^{-5}t^2(^{\circ}\text{C}) \quad (31)$$

$$\sigma_{\text{Pb}} = 472.7 - 0.085t(^{\circ}\text{C}) \quad (32)$$

$$\sigma_{\text{Sn}} = 569.0 - 0.080t(^{\circ}\text{C}) \quad (33)$$

White's results for Cd and Zn showed that both had a positive temperature derivative of surface tension near their melting points, up to 100°C above their melting points. He was the first person to publish results showing a positive temperature derivative. As was mentioned above, it had always been assumed that molten metals had negative temperature derivatives of surface tension over the entire liquid region. In another result obtained with Zn, White showed that high vaporization rates of the molten metal, a nonequilibrium condition, changed the surface tension. To cause high vaporization rates, White designed a sessile drop furnace which had "cold spots" near the drop; these "cold spots" condensed Zn vapor. He ran these experiments at 80 torr instead of 760 torr. For the temperature range just above the melting point, $420\text{--}460^{\circ}\text{C}$, the large vaporization rates caused a five percent increase in the surface tension of Zn. He has neglected the fact that a reduction in pressure reduced the surface contamination which may have accounted for part of the increase in the surface

tension.

Kingery and Allen (1959) measured the surface tension of Sn between 800° and 1000°C. They used the sessile drop method, and their experiments were run at a pressure of 10^{-5} torr. When their results are extrapolated to the melting point, their values are 60 ergs/cm² or 10 percent larger than the results of White (1971).

Aldrich and Keller (1968) measured the surface tension of In under UHV conditions. The sessile drop method was used, and the experiments were run at a pressure of 10^{-10} torr. Also, they ran experiments in the presence of H₂, N₂ and O₂. They found that N₂ and H₂ did not change the surface tension of In for the pressure range: 10^{-10} torr to 1 torr; however, O₂ reduced the surface tension of In if the O₂ pressure was greater than 10^{-6} torr.

Bernard and Lupis (1971b) measured the surface tension of Ag in vacuum and in the presence of O₂ up to a pressure of 15 torr. The sessile drop method was used. They found that at 980°C in vacuum the surface tension was 910 ergs/cm² and when the pressure was raised to 15 torr, the surface tension was reduced to 700 ergs/cm².

Besides Aldrich and Keller (1968), Maze (1970) is the only author that has published data taken under UHV conditions. Maze (1970) measured the surface tension of Pb, Bi, and the Pb-Bi eutectic, using the sessile drop method.

He reported that the surface tension-temperature behavior of Ph and Bi is described by a curve which passes through a maximum; he attributed this behavior to vapor transport. He found that ppm additions of zirconium to the Pb-Bi eutectic increased the surface tension when the pressure was 10^{-9} torr; however, when the pressure was 10^{-6} torr the surface tension decreased upon zirconium additions. In some earlier work, Maze and Burnet (1969) wrote a computer program which calculates the surface tension of a molten metal from the sessile drop profile, which can be measured from a photograph of the drop.

Schwaneke (1971) measured the surface tension of Sn using the maximum bubble pressure method. His result is:

$$\sigma_{\text{Sn}} = 566.84 - 0.0476t(^{\circ}\text{C}) \quad . \quad (34)$$

Bohdansky and Schins (1967, 1968a, 1968b) measured the surface tension of several molten metals at temperatures for which their vapor pressures are 20 to 400 torr. The maximum bubble pressure method was used. They reported a linear surface tension-temperature behavior with a negative slope for each metal tested. Their results for Pb and Bi are

$$\sigma_{\text{Pb}} = 507 - 0.114t(^{\circ}\text{C}) \quad (35)$$

$$\sigma_{\text{Bi}} = 398 - 0.088t(^{\circ}\text{C}) \quad . \quad (36)$$

For most metals tested, the temperature range of the experiments was 1000-2000°C.

Bohdansky (1968) developed an expression to calculate the temperature dependence of the surface tension of molten metals by treating the metal ions as harmonic oscillators; however, his final result has three uncertain constants. One of the constants can be determined from the extrapolated liquid density at absolute zero and a surface packing factor. The other two constants can be determined only if surface tension data is available for the metal in question.

Very little work has been done in the area of a general surface tension correlation which could be used to predict the surface tension of a molten metal. Grosse (1962, 1964, 1968) has published three papers in this area. However, when using any of his correlations, an error of 10-15 percent should be expected. In his first paper, Grosse (1962) showed that the Law of Eötvös

$$\sigma = V^{-2/3} K_{E\ddot{o}} (T_c - T) \quad (37)$$

V = atomic volume

$K_{E\ddot{o}}$ = Eötvös constant

did apply to some metals. He found that the Eötvös constant for metals (except Hg, Cd, and Zn) was

$$K_{E\ddot{o}} = 0.64 \text{ ergs}/(\text{gm-atom})^{2/3} \text{ } ^\circ\text{K} \quad (38)$$

whereas for homopolar liquids

$$K_{E\sigma} = 2.12 \text{ ergs}/(\text{mole})^{2/3} \text{ } ^\circ\text{K} \quad . \quad (39)$$

In addition to the lack of good surface tension data upon which to base $K_{E\sigma}$, values of T_c have not been measures for many metals. For his relationship, Grosse estimated T_c by extrapolating surface tension data to the temperature at which $\sigma = 0$.

In a later paper, Grosse (1964) developed an empirical relationship between the surface tension at the melting point and the heat of vaporization at the melting point. For metals with cubic or tetragonal lattices

$$\sigma_{m.p.} = 0.274 \left(\frac{\Delta H_{vap}}{V} \right)^{0.934} \quad (40)$$

$\sigma_{m.p.}$ = surface tension at the melting point

ΔH_{vap} = heat of vaporization

V = atomic volume.

For metals with hexagonal or rhombohedral lattices (Zn, Cd, Hg, and Bi)

$$\sigma_{m.p.} = 5.740 \left(\frac{\Delta H_{vap}}{V} \right)^{0.62} \quad . \quad (41)$$

In a third paper, Grosse (1968) showed that a plot of reduced surfact tension vs. reduced temperature for molten metals, closely coincided to a similar plot for argon; the

plot for argon had been determined experimentally. Where

$$\sigma_{\text{red}} = \frac{\sigma}{\sigma_{\text{m.p.}}} \quad (42)$$

and

$$T_{\text{red}} = \frac{T - T_{\text{m.p.}}}{T_c - T_{\text{m.p.}}} \quad (43)$$

He compared some experimental data of Bohdanský and Schins (1967) with the argon plot; there was a 10 percent error between the two. This correlation is not of much use unless accurate data are available on the surface tension at the melting point and the critical temperature of the metal; such data are generally not available. Also, this reduced plot would not be useful for metals such as Zn and Cd which have a positive temperature derivative of surface tension near the melting point.

To date, attempts to formulate a general correlation for molten metal surface tension have not been very accurate; errors of 10-15 percent are common. It is not surprising that there has been a lack of success in this area for molten metals since surface tension correlations for ordinary liquids have been just slightly more successful. Two common relationships which are found in surface chemistry texts, like those of Adam (1941) and of Bikerman (1970), are the Law of Eötvös

$$\sigma \left(\frac{M}{\rho} \right)^{2/3} = k(T_c - T) \quad (44)$$

and the Ramsay and Shields variation

$$\sigma \left(\frac{M}{\rho} \right)^{2/3} = k(T_c - T - 6) \quad (45)$$

M = molecular weight

ρ = density

k = a constant.

Both are empirical relationships which were derived in 1886 and 1893 respectively. The relationships are useful for describing the temperature behavior of surface tension for liquids for which k is known. The constant k was thought to be a universal constant; and indeed many hydrocarbons have $k \approx 2.1$, but it is not a universal constant. It was also thought that k, "the constant of Eötvös", was a measure of the degree of association of liquids; however, Adam (1941) has pointed out that not only is k frequently not constant, but its actual numerical value is without significance with regard to determining the molecular complexity of liquids. But, several handbooks do list experimentally determined values of k for many liquids.

One could list a number of other empirical relationships which fit classes of liquids. In a text by Bikerman (1970) there is a relationship which has a thermodynamic basis; the relationship relates the surface tension of a

liquid to its heat of vaporization. The free surface energy (σ , ergs/cm²) is the work required to move so many molecules from the bulk into the surface as to cover one square centimeter with them. The total energy, including heat effects is

$$U_s = \sigma - T \frac{\partial \sigma}{\partial T} \quad (46)$$

If a molecule in the surface is considered as one half free, and a molecule in the vapor phase is considered wholly free, then it has been suggested that the latent heat of vaporization of a substance would be twice as great as its total surface energy. But, since only the internal heat, which does not include the external work, should be compared with U_s , the value of ΔH_{vap} should be diminished by RT . So, if A_m is the area occupied by molecule in the surface

$$2 U_s A_m = \frac{\Delta H_{\text{vap}} - RT}{N} \quad (47)$$

For molecules which are isometric A_m should be proportional to $(\frac{M}{\rho N})^{2/3}$, and the final equation is

$$(\text{constant}) \left(\frac{M}{\rho N}\right)^{2/3} \left(\sigma - T \frac{\partial \sigma}{\partial T}\right) = \frac{\Delta H_{\text{vap}} - RT}{N} \quad (48)$$

The "constant" in Equation 48 has been found to vary between 2.6 and 2.9 for some ordinary liquids.

For liquid metals, Zadumkin (1961) has postulated that

the surface area occupied by an atom depended on the crystal structure of the metal in the solid state and that this structure also determined the number of neighbors lost by atoms when moving from the bulk into the surface.

So instead of ΔH_{vap} , he has suggested that $L_0 - \Delta H_{\text{fus}}$ be used; where L_0 is the heat of sublimation at 0°K and ΔH_{fus} is the heat of fusion. So for liquid metals Equation 49 becomes

$$(\text{constant}) \left(\frac{M}{\rho N} \right)^{2/3} \left(\sigma - T \frac{\partial \sigma}{\partial T} \right) = \frac{L_0 - \Delta H_{\text{fus}} - RT}{N} \quad (49)$$

EQUIPMENT AND PROCEDURE

High energy surfaces of molten metals are easily contaminated, so care must be taken to maintain clean surfaces while measuring surface tension. At a pressure of 10^{-9} torr or less, it takes at least one hour before a monolayer could form on the surface. At 10^{-9} torr it is unlikely that any measurable contamination effects could be detected for a period of three or four days.

In this work, surface tension and contact angles were determined from photographs taken of liquid metal drops resting on a flat surface. These drops were formed under UHV conditions and deposited on a heated surface.

The UHV system used in this study consists of a 350 liter per second ionization pump with titanium sublimation filaments, two molecular sieve sorption pumps, and a liquid nitrogen cold trap located in the basewell assembly. The entire system is bakable to 250°C and constructed from stainless steel, and oxygen free copper gaskets are used throughout. Since no oil pumps are in the system, contaminant free operation is assured. Figure 3 is a photograph of the system with the bakeout equipment removed.

The bakeout oven, shown in the background of Figure 3, is a split aluminum cylinder containing radiant heaters. When installed, the bakeout oven completely encloses the

Figure 3. Ultrahigh vacuum system with bakeout shroud removed

vacuum system. Baking the system at 250°C for 24 hours will permit testing in the 10^{-11} torr range. Baking cleans the system and should be done occasionally to prevent contaminant build-up.

Accurate pressure measurements from 10^{-5} to 10^{-11} torr were made using a nude ionization gauge mounted on a 1 1/2-inch port located just below the baseplate flange.

The sessile drop furnace, with its heat shield in place, is shown in Figure 4 and Figure 5. The sessile drop furnace is rectangular in shape and of stainless steel construction; and it is heated by tantalum wire threaded through the furnace walls. A tantalum crucible is placed in a hole in the top of the furnace. The crucible holds the molten metal until it is time to form a drop. A drop is formed by raising a tantalum rod that plugs a hole in the base of the crucible. The molten metal drops onto the test substrate which is placed directly below the crucible. The substrate rests on a heated stainless steel plate which contains a thermocouple attached to a temperature controller. The heated plate can be leveled by means of screws located in the heater stand, and the furnace is surrounded by a tantalum radiation shield.

Drops were photographed with a 4 x 5 Calumet view camera equipped with an f/4.5, 150 mm lens. Polaroid P/N 55 film was used for the drop photographs. Backlighting for the

Figure 4. Sessile drop furnace surrounded by heat shield, front view

Figure 5. Sessile drop furnace surrounded by heat shield, rear view

photographs was accomplished using a General Electric, Gouldcrest Model 910, 650 watt lamp. The most common exposure for a drop photograph was f/6 at 1/50 second.

Drop dimensions were read from the photograph negative using a modified Gaertner M 1225-37 coordinate comparator with graduations of 0.001 cm in the horizontal direction, 0.0005 cm in the vertical direction, and one minute in the angular direction. The most critical step in making drop measurements is the proper alignment of the drop base under the horizontal cross hair, as an error of one minute will produce a 0.8 percent error in surface tension.

If reliable contact angle data are desired from a study, the preparation of the substrate surface is an important step since the preparation can affect the contact angle. As was mentioned earlier, no single method is best to clean all solid surfaces.

For this study a nonmetallic substrate specimen was taken as being clean after it had been heated at least as high as the maximum test temperature and evacuated to a pressure of 10^{-9} torr at that temperature. This procedure should have removed everything from the surface except chemisorbed oxygen, and even oxygen could have been removed in some cases.

Maze (1970) found that mechanical polishing was the best method for polishing metal substrate specimens for

sessile drop tests. Electropolishing resulted in specimens upon which the drops would spread unevenly in different directions. Metallic substrate specimens were mechanically polished, and a specimen was considered clean after it had been heated to the maximum test temperature and evacuated to a pressure of 10^{-9} torr at that temperature. In the case of iron and steel specimens, an additional cleaning step consisted of heating the specimen in a reducing atmosphere of hydrogen and then evacuating to a pressure of 10^{-9} torr.

After the substrate surface was cleaned, a drop was formed and photographed at different temperatures above its melting point. In some cases a cleaned substrate surface was contaminated with a known substance prior to the formation of a drop. Drop dimensions were measured on the comparator mentioned above. The dimensions were fed into a computer program which calculated the surface tension and contact angle; the program was written by Maze and Burnet (1969) and further documentation of the program can be found in a thesis by Maze (1970). The program was modified slightly for this study when a computational problem arose. The program was designed to calculate surface tension and contact angle from drop dimensions taken anywhere on the drop profile; however, results could not be obtained from the program unless the drop dimensions came from a small

portion of the profile, about 25 percent of the profile, just above the maximum drop width. The problem was traced to an interpolation step which called for the number 1.0 to be placed in the first column of a matrix; in the original program this was done by raising the difference between a measured and a calculated drop dimension to the zero power. However, if the difference was ever zero, the computer would stop the calculation since it cannot handle zero to the zero power. The program was changed by having the number 1.0 read into the first column of that matrix. With this change, drop dimensions could be taken anywhere on the drop profile. When drop dimensions were taken over the entire drop profile, the scatter in calculated values of surface tension and contact angle was reduced.

After a sessile drop test is completed, the solidified drop-solid specimen can be cut in half and examined by microprobe to determine the distribution of elements across the interface. However, a sessile drop test usually lasts only a few hours and thus the microprobe examination would not show much; so, a different procedure was used to prepare specimens for a microprobe study. A small piece of the solid specimen was placed in a small tantalum crucible which was $3/8$ inch in diameter and 1 inch long. The prospective molten metal (in solid form) was added to the crucible. The crucible and contents were outgassed to a

pressure of 10^{-9} torr at a temperature just below the melting point of the molten metal. After outgassing the crucible was heated to the desired test temperature; and that temperature was maintained for the length of the test, usually 48 hours. After the test the crucible was cut in half and the solidified drop-solid specimen interface was examined by the microprobe.

High purity materials were used, and in the Appendix is a list of these materials and their nominal purities.

RESULTS AND DISCUSSION

Surface tension and contact angle data were collected for bismuth, indium, lead, and tin on substrates of alumina, graphite, iron, and tantalum. The data were collected in the temperature range from near the melting point of the liquid metals to several hundred degrees above the melting point. Data were collected at pressures of 10^{-9} , 10^{-6} , and 760 torr.

This portion of the study has been divided into six subsections: (1) Molten metal and substrate selection; (2) Outgassing phenomena; (3) Surface tension-temperature behavior; (4) Contamination effect of gases; (5) Contact angle phenomena; (6) Surface tension correlation for molten metals.

Molten Metal and Substrate Selection

The four molten metals chosen for this study meet two main conditions. They have low melting points, and they have low vapor pressures. The four metals melt between 150 and 330°C , and at their respective melting points, their vapor pressures are 10^{-9} torr or lower. The condition of low melting point is for equipment convenience; that is, being able to construct an adequate sessile drop furnace and being able to maintain UHV conditions. By using metals with low vapor pressure, it is easier to establish thermodynamic

equilibrium during the sessile drop tests. However, at least three of the metals used in this study have already received consideration for practical applications. Shimotake and Hesson (1967) have pointed out that bismuth and lead are being considered as heat transfer media for nuclear reactors; also, bismuth, lead, and tin are being considered for use in regenerative emf cells.

If reliable surface tension data are to be obtained, great care must be taken in the selection of a substrate material. Unless the substrate is resistant to dissolution by the molten metal, the drop will become contaminated which will produce error in the results.

Shimotake and Hesson (1967) have summarized the static corrosion tests done with bismuth and lead. And, in conjunction with this sessile drop study, Donakowski (1971) made some static corrosion tests using tin. He used the microprobe to examine the interface; his results are summarized in Table 1. Several materials were resistant to corrosion by bismuth, lead, and tin, and presumably resistant to corrosion by indium although corrosion data for indium has not been taken. Alumina, graphite and tantalum are resistant to corrosion by these molten metals, so they were selected for this study. They were also selected because they are significantly different solid materials, and it was thought that they would produce significantly

Table 1. Results of static corrosion tests for tin

Element	Nominal Purity	Comments
Fe	99.99 + %	wetted by tin, dissolved throughout the melt at a concentration of 25%, inter-metallic compounds likely.
Ni	99.99 + %	wetted by tin, dissolved throughout the melt at a concentration of 21%, inter-metallics very likely.
Co	99.99%	dissolved throughout the melt at a concentration of 17%, intermetallics very likely.
Zr	99.99%	dissolved to a distance of 48 microns at a concentration of 24% not wetted by tin, no dissolution, inward diffusion by tin to a depth of 65 microns.
Ta	99.98%	not wetted by tin, no dissolution, inward diffusion by tin to a depth of 65 microns.
Ti	99.97%	dissolved to a distance of 200 microns, two distinct concentration levels of 22% and 24%.
321 stainless steel		wetted by tin.
Si	99.95%	slight dissolution into tin.
Cr	99.98%	not wetted by tin, hint of some dissolution.
Nb	99.95%	not wetted by tin, no dissolution.
W	99.95%	not wetted by tin, no dissolution.
Al ₂ O ₃	99.7%	not wetted by tin, some tin diffusion into porous alumina to a depth of 15 microns.
Mo	99.95%	not wetted by tin, no dissolution.

Note: all concentrations in weight percent.

different contact angles. Iron was chosen as a substrate so that contact angle data could be obtained for this widely used construction material.

Outgassing Phenomena

At the beginning of this study it was thought that the UHV equipment would serve two important functions, namely, the preparation of a clean substrate surface and the prevention of gaseous contamination of the sessile drop. However, a third important function has been found for the UHV equipment, namely, the outgassing of the molten metal.

Gases in solution in the drop and contamination of the drop surface by gases are two areas of sessile drop work that have been ignored by most authors. Not only have they neglected to outgas the molten metal, but also, they have made sessile drop tests at gas pressures for which surface contamination was a certainty. The experimental technique used by White (1966, 1971, 1972) is common; namely, the sessile drop tests are run in an inert gas atmosphere at a pressure of 760 torr. Although the inert gases used do not oxidize the metal surface, they are soluble in the molten metal. By using vacuum equipment, dissolved gases and gases entrapped in the metal during the melting process can be removed; surface contamination is also minimized by using vacuum equipment. Winkler and Bakish (1971) have summarized

data on the solubility of gases in molten metals; as the pressure decreases the solubility of the gas decreases. And at a pressure of 10^{-9} torr, the solubility of gases in molten metals is about 10^{-3} weight percent.

The effect of complete outgassing is illustrated in Figure 6 by the curve for Sn-Ta-5. The curve shows that the surface tension of tin increased at constant temperature as time increased, and after a long time the surface tension began to level off at one value. It is felt that continued outgassing was the only phenomena occurring during that period. For the run, Sn-Ta-5, the system was evacuated to 10^{-9} torr at the test temperature prior to the drop formation. However, it is not illogical that further outgassing of the metal took place after the formation of the drop since the exposed surface area to volume ratio for the sessile drop is greater than the exposed surface area to volume ratio for the molten metal in the crucible. The increase in the surface tension of tin due to outgassing was significant in this case, nearly 60 ergs/cm^2 or 10 percent.

As was mentioned earlier, White (1966) has demonstrated that high vapor transport can cause an increase in the surface tension of a molten metal. And low pressures like 10^{-9} torr mean that molecules in the vapor phase have a large mean free path and this would be conducive to vapor transport.

Figure 6. The effect of outgassing on the surface tension of molten indium and tin

Thus, it is possible that the increase in the surface tension of tin illustrated in Figure 6 might be partially due to vaporization of tin. However, the system pressure is not the only factor which determines whether or not high vapor transport can occur; perhaps the most important factor is the vapor pressure of the metal. Figure 7 illustrates the vapor pressures of the metals used in this study, the data were taken from Hultgren et al. (1963). At 486°C , the vapor pressure of tin is about 10^{-12} torr; this is a very low vapor pressure. When White (1966) demonstrated the vapor transport effect, he was using zinc which has a vapor pressure of 0.15 torr at the melting point, he had constructed a sessile drop furnace with a "cold spot" near the drop, and he reduced the system pressure to 80 torr from 760 torr. So, he had a metal with a high vapor pressure, he had a cold spot near the drop which could condense zinc vapors, and he reduced the system pressure. Under these conditions, the vapor transport effect was about 50 ergs/cm^2 or 7 percent. If a metal with a vapor pressure of 0.15 torr causes an increase in surface tension of 50 ergs/cm^2 , it seems very unlikely that a metal with a vapor pressure of 10^{-12} torr could produce a vapor transport effect that could be noticed by present experimental techniques. In fact, it seems unlikely that any of the metals used in this study have a vapor pressure high enough, in the region of their melting points, to produce a

Figure 7. The vapor pressure of bismuth, indium, lead, and tin

significant vapor transport effect. Lead has the highest vapor pressure of the metals tested; at its melting point, lead has a vapor pressure of 4×10^{-9} torr while zinc has a vapor pressure of 0.15 torr. Thus, the increase in the surface tension of tin in Figure 6 can be attributed largely to outgassing only.

The outgassing phenomena was demonstrated for indium also; this is illustrated by the curve for In-Ta-5 in Figure 6. For this experiment, the drop was formed at a pressure of 10^{-9} torr and then the pressure was raised to 760 torr with dry nitrogen (99.7% pure). The pressure increase produced a lowering of the surface tension and the surface of the drop became oxidized. After 30 minutes the pressure was reduced, eventually to 10^{-9} torr. At 10^{-9} torr the oxidation on the drop surface disappeared and the surface tension increased as is shown in Figure 6. Thus it is possible to contaminate a drop surface with a gas and then clean the surface by heating under UHV conditions.

An experiment similar to Sn-Ta-5 was attempted using alumina, Al_2O_3 , as the substrate. The results are illustrated by the curve for Sn- Al_2O_3 -7 in Figure 6. In this case, the surface tension of tin decreased with time rather than increased as was the case with Sn-Ta-6. The decrease in surface tension is attributed to surface contamination of the drop. The contamination might have been caused by a

substance which had been adsorbed on the alumina, or it is possible that the alumina dissociated and contaminated the surface. Drowart et al. (1960) found that, at high temperatures and UHV conditions, Al_2O_3 dissociated to Al, O, AlO, Al_2O , and Al_2O_2 . And it would take only trace amounts of contamination to cause the decrease illustrated in Figure 6. Therefore, alumina is not a good substrate to use under conditions of high temperature, very low pressure (10^{-9} torr), and long times (more than several hours). However, under other conditions alumina should be a good substrate; oxides such as alumina have one advantage over metals such as tantalum. When an oxide is used as a substrate, the contact angle is usually very large; and it is much easier to form a symmetric sessile drop if the contact angle is large.

Surface Tension-Temperature Behavior

The surface tension and contact angle data collected in this study are shown in Table 2. The surface tension-temperature relationships of the metals tested were all linear near their respective melting points. The relationships have negative slopes; a least squares analysis was used to determine the best linear relationship for the data.

Some of the data shown in Table 2 were collected before the full importance of outgassing was realized. In order to

Table 2. Surface tension and contact angle data

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
Ta-5	20	1.8×10^{-9}	485	545	94
"	1100	1.4×10^{-9}	486	555	94
"	1440	1.1×10^{-9}	487	561	88
"	2600	1.1×10^{-9}	486	586	87
"	2795	1.1×10^{-9}	486	590	86
"	2920;120 ^a	2×10^{-6} H ₂	486	588	87
"	3040;240	2×10^{-6} H ₂	486	585	96
"	5465	1.1×10^{-9}	486	590	88
"	5625;150	2×10^{-6} O ₂	486	583	87
"	5715;240	2×10^{-6} O ₂	486	576	87
"	8660	1.1×10^{-9}	486	593	88
"	8790;120	2×10^{-6} N ₂	486	585	87
"	8880;210	2×10^{-6} N ₂	486	574	87
"	10320	1.1×10^{-9}	488	600	86
"	10365	1×10^{-9}	407	602	87
"	10410	1×10^{-9}	355	605	86
"	10455	1×10^{-9}	301	616	86
"	10500	1×10^{-9}	260	606	86

^aSecond time indicates length of time of contamination.

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
Ta-1	200	2.1×10^{-9}	270	584	109
"	210	2.1×10^{-9}	267	595	109
"	255	2.1×10^{-9}	339	580	110
"	270	2.1×10^{-9}	338	588	109
"	315	2.1×10^{-9}	406	573	111
"	330	2.1×10^{-9}	408	566	111
"	375	2.3×10^{-9}	502	562	112
"	390	2.3×10^{-9}	503	570	111
"	1385	2.1×10^{-9}	506	573	111
"	1400	2.1×10^{-9}	506	584	110
"	1645	1×10^{-9}	258	581	110
"	1655;10	$2 \times 10^{-6} \text{O}_2$	258	562	111
"	1717;72	$2 \times 10^{-6} \text{O}_2$	401	547	113
"	1729;84	$2 \times 10^{-6} \text{O}_2$	401	552	112
"	1775;130	$2 \times 10^{-6} \text{O}_2$	547	543	114
"	1818;173	$2 \times 10^{-6} \text{O}_2$	644	546	113
Ta-2					
Ta-2	25	3.4×10^{-9}	499	544	123
"	65	3.1×10^{-9}	439	539	124
"	105	2.9×10^{-9}	374	539	124
"	145	2.6×10^{-9}	297	550	123

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
Ta-2	265;120	$2 \times 10^{-6} \text{N}_2$	296	545	123
"	310;165	$2 \times 10^{-6} \text{N}_2$	369	539	123
"	360;215	$2 \times 10^{-6} \text{N}_2$	448	543	123
"	405;260	$2 \times 10^{-6} \text{N}_2$	515	532	124
"	445;300	$2 \times 10^{-6} \text{N}_2$	593	521	125
Ta-3	15	6×10^{-9}	492	543	122
"	20	6×10^{-9}	492	536	123
"	85,60	$2 \times 10^{-6} \text{H}_2$	489	541	122
"	145,120	$2 \times 10^{-6} \text{H}_2$	489	535	124
"	205,180	$2 \times 10^{-6} \text{H}_2$	489	539	122
Fe-1	20	2.5×10^{-9}	507	497	111
"	55	2.5×10^{-9}	449	535	105
"	95	2.5×10^{-9}	373	527	105
"	135	2.5×10^{-9}	308	513	106
"	175	2.5×10^{-9}	244	508	107
"	1570	2.5×10^{-9}	400	578	94
C-4	35	5×10^{-9}	492	527	137
"	85	5×10^{-9}	415	521	138

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
C-4	125	4.1×10^{-9}	346	535	137
"	170	3.4×10^{-9}	268	541	138
Al ₂ O ₃ -6	15	3×10^{-9}	492	542	150
"	55	3×10^{-9}	448	539	151
"	95	1.8×10^{-9}	406	545	149
"	135	1.7×10^{-9}	353	546	150
"	175	1.6×10^{-9}	304	551	149
"	215	1.3×10^{-9}	262	552	149
Al ₂ O ₃ -2 ^b	85	1.4×10^{-9}	264	570	150
"	116	1.4×10^{-9}	295	552	158
"	135	1.3×10^{-9}	318	557	156
"	173	1.2×10^{-9}	352	553	157
"	195	1.1×10^{-9}	385	560	153
"	220	1.1×10^{-9}	414	566	152
"	247	1.1×10^{-9}	463	542	161
"	281	1.1×10^{-9}	504	558	153
"	573	2×10^{-9}	538	545	156

^bFor Al₂O₃-2, Al₂O₃-3, Al₂O₃-4, Al₂O₃-5 the Al₂O₃ is only 85% pure.

2

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
Al ₂ O ₃ -2 ^b	613	3 x 10 ⁻⁹	580	541	157
"	640	8 x 10 ⁻⁹	634	538	157
Al ₂ O ₃ -3 ^b	50	2 x 10 ⁻⁶ O ₂	246	545	141
"	65	2 x 10 ⁻⁶ O ₂	246	544	141
"	110	2 x 10 ⁻⁶ O ₂	307	547	141
"	125	2 x 10 ⁻⁶ O ₂	306	539	141
"	175	2 x 10 ⁻⁶ O ₂	390	541	137
"	190	2 x 10 ⁻⁶ O ₂	390	522	145
"	240	2 x 10 ⁻⁶ O ₂	463	527	142
"	255	2 x 10 ⁻⁶ O ₂	463	521	143
"	300	2 x 10 ⁻⁶ O ₂	543	530	141
"	315	2 x 10 ⁻⁶ O ₂	543	534	140
Al ₂ O ₃ -4 ^b	20	2 x 10 ⁻⁶ O ₂	253	545	141
"	35	2 x 10 ⁻⁶ O ₂	253	550	140
"	75	2 x 10 ⁻⁶ O ₂	341	550	139
"	90	2 x 10 ⁻⁶ O ₂	344	552	139
"	135	2 x 10 ⁻⁶ O ₂	426	531	142
"	150	2 x 10 ⁻⁶ O ₂	426	541	138
"	195	2 x 10 ⁻⁶ O ₂	506	537	140
"	205	2 x 10 ⁻⁶ O ₂	506	538	144

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Tin					
Al ₂ O ₃ -5 ^{bc}	88	2 x 10 ⁻⁶ O ₂	252	473	140
"	100	2 x 10 ⁻⁶ O ₂	252	474	138
"	140	2 x 10 ⁻⁶ O ₂	346	500	136
"	155	2 x 10 ⁻⁶ O ₂	346	510	135
"	195	2 x 10 ⁻⁶ O ₂	445	517	132
"	205	2 x 10 ⁻⁶ O ₂	446	517	133
"	245	2 x 10 ⁻⁶ O ₂	532	535	131
"	255	2 x 10 ⁻⁶ O ₂	532	540	129
Indium					
Al ₂ O ₃ -7	32	4.7 x 10 ⁻⁹	483	555	140
"	1277	3 x 10 ⁻⁹	483	546	141
"	2757	2.1 x 10 ⁻⁹	483	539	141
"	4762	1.8 x 10 ⁻⁹	483	540	141
"	5647	1.7 x 10 ⁻⁹	485	539	144
Indium					
Ta-6	7500	1 x 10 ⁻⁹	190	589	96
"	7550	1 x 10 ⁻⁹	269	600	96
"	7665	1 x 10 ⁻⁹	330	593	95

^cAl₂O₃-5 contaminated with O₂ at 2 x 10⁻⁶ torr prior to drop formation.

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Indium					
Ta-6	7710	1×10^{-9}	403	585	95
"	7845	1×10^{-9}	454	590	96
"	8040;195	$2 \times 10^{-6} \text{N}_2$	455	580	94
"	8050;205	$2 \times 10^{-6} \text{N}_2$	455	577	94
"	8705	1×10^{-9}	454	593	95
"	8825;120	$2 \times 10^{-6} \text{H}_2$	454	576	96
"	8925;220	$2 \times 10^{-6} \text{H}_2$	454	574	95
"	10025;	1×10^{-9}	452	577	95
"	10145;120	$2 \times 10^{-6} \text{O}_2$	452	553	96
"	10280;255	$2 \times 10^{-6} \text{O}_2$	452	566	95
Ta-2	20	4×10^{-9}	447	561	105
"	60	3.5×10^{-9}	352	573	103
"	100	3×10^{-9}	261	578	103
"	140	2.5×10^{-9}	212	577	103
"	205;60	$2 \times 10^{-6} \text{N}_2$	213	582	102
"	245;100	$2 \times 10^{-6} \text{N}_2$	257	575	102
"	285;140	$2 \times 10^{-6} \text{N}_2$	350	556	104
"	330;185	$2 \times 10^{-6} \text{N}_2$	449	556	104
"	370;225	$2 \times 10^{-6} \text{N}_2$	538	555	103

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Indium					
Ta-5	30	3.3×10^{-9}	456	559	99
"	150	3.0×10^{-9}	456	572	99
-d					
Ta-5	2695	1.7×10^{-9}	449	514	101
"	4020	1.4×10^{-9}	449	553	98
"	5605	1.1×10^{-9}	449	567	97
"	6825	1.1×10^{-9}	449	580	95
C-1	35	5×10^{-9}	449	548	130
"	80	4×10^{-9}	357	555	129
"	90	3.7×10^{-9}	357	561	127
"	130	2.5×10^{-9}	279	556	128
"	175	1.7×10^{-9}	222	567	126
Al ₂ O ₃ -1	60	3.5×10^{-9}	396	544	149
"	100	3.3×10^{-9}	352	539	149
"	140	2.8×10^{-9}	297	540	150
"	190	2.5×10^{-9}	242	549	144
"	270	2.1×10^{-9}	192	555	148

^dRaised pressure to 760 torr atm with dry N₂ and then started outgassing again.

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Indium					
Al ₂ O ₃ -1	310;30	$2 \times 10^{-6} \text{O}_2$	192	545	149
"	350;70	$2 \times 10^{-6} \text{O}_2$	240	552	149
"	385;105	$2 \times 10^{-6} \text{O}_2$	289	540	150
"	420;140	$2 \times 10^{-6} \text{O}_2$	344	536	149
"	460;180	$2 \times 10^{-6} \text{O}_2$	398	537	148
Ta-7	2360	1.6×10^{-9}	476	587	95
"	2790	1×10^{-9}	188	594	95
"	2895;85	760H ₂	243	561	100
"	2930;120	760H ₂	293	562	100
"	2970;160	760H ₂	350	557	100
"	3010;200	760H ₂	400	554	101
"	3050;240	760H ₂	442	559	101
Bismuth					
Ta-4	4245	1.7×10^{-9}	279	398	89
"	4320	1.7×10^{-9}	296	386	90
"	4350	1.8×10^{-9}	312	382	90
"	4385	1.9×10^{-9}	345	383	91
"	4435;40	$2 \times 10^{-6} \text{H}_2$	386	374	92
"	4470;75	$2 \times 10^{-6} \text{H}_2$	407	376	91

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Bismuth					
Ta-4	4500;105	$2 \times 10^{-6} \text{H}_2$	440	381	90
"	4590;195	$2 \times 10^{-6} \text{H}_2$	349	377	90
"	4620;255	$2 \times 10^{-6} \text{H}_2$	349	377	90
"	5610	1.5×10^{-9}	345	382	90
"	5730;120	$2 \times 10^{-6} \text{N}_2$	345	379	92
"	5850;240	$2 \times 10^{-6} \text{N}_2$	345	375	91
"	9920	1.4×10^{-9}	345	384	92
"	10070;150	$2 \times 10^{-6} \text{O}_2$	345	379	90
"	10160;240	$2 \times 10^{-6} \text{O}_2$	345	378	93
"	10170;250	$2 \times 10^{-6} \text{O}_2$	345	376	92
Ta-2	30	4.3×10^{-9}	346	385	110
"	60	4.0×10^{-9}	323	379	111
"	90	3.6×10^{-9}	305	385	110
"	120	3.3×10^{-9}	292	390	109
"	150;30	$2 \times 10^{-6} \text{N}_2$	291	381	110
"	180;60	$2 \times 10^{-6} \text{N}_2$	319	380	109
"	210;90	$2 \times 10^{-6} \text{N}_2$	357	376	110
"	240;120	$2 \times 10^{-6} \text{N}_2$	393	372	110

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Bismuth					
Ta-3	25	2.8×10^{-9}	348	365	117
"	30	2.8×10^{-9}	348	365	116
"	90;60	$2 \times 10^{-6} \text{H}_2$	348	365	116
"	150;120	$2 \times 10^{-6} \text{H}_2$	348	364	116
"	210;180	$2 \times 10^{-6} \text{H}_2$	348	360	118
Fe-1 ^e	20	1.7×10^{-9}	394	376	118
"	50	1.7×10^{-9}	351	374	114
"	80	1.4×10^{-9}	323	384	117
"	110	1.3×10^{-9}	305	381	118
"	140	1.2×10^{-9}	284	382	115
Fe-2	20	2.8×10^{-9}	395	382	102
"	60	2.8×10^{-9}	358	386	97
"	100	2.4×10^{-9}	318	398	98
"	140	2.2×10^{-9}	284	392	99
"	380	2.4×10^{-9}	347	388	99
C-1	20	4.4×10^{-0}	351	378	134
"	50	5.5×10^{-9}	388	371	137

^eFe-1 not cleaned with hydrogen prior to drop formation.

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Bismuth					
C-1	85	3.7×10^{-9}	330	376	134
"	115	3.5×10^{-9}	310	379	134
"	145	3.2×10^{-9}	288	382	132
ASTM-387 Steel-1	40	4×10^{-9}	296	389	122
"	85	4×10^{-9}	296	390	121
"	130	2.5×10^{-9}	315	383	123
"	140	2.5×10^{-9}	315	383	123
"	175	2×10^{-9}	338	388	122
"	210	2×10^{-9}	359	380	124
Al ₂ O ₃ -1	20	4×10^{-9}	402	369	123
"	40	3.5×10^{-9}	383	365	123
"	115	3×10^{-9}	334	361	123
"	160	2.5×10^{-9}	309	363	123
"	180	2.5×10^{-9}	290	360	123
"	220;30	$2 \times 10^{-6} \text{O}_2$	291	364	123
"	266;76	$2 \times 10^{-6} \text{O}_2$	330	359	123
"	306;116	$2 \times 10^{-6} \text{O}_2$	381	360	124
"	340;150	$2 \times 10^{-6} \text{O}_2$	424	344	127
"	370;180	$2 \times 10^{-6} \text{O}_2$	472	342	128

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Lead					
Ta-3	1525	1×10^{-9}	350	448	95
"	1565	1×10^{-9}	382	441	95
"	1605	1×10^{-9}	413	447	96
"	1645	1.2×10^{-9}	450	449	96
"	1770;125	$2 \times 10^{-6} \text{H}_2$	450	446	98
"	1860;215	$2 \times 10^{-6} \text{H}_2$	450	447	98
"	4830	1.4×10^{-9}	447	460	98
"	4950;120	$2 \times 10^{-6} \text{O}_2$	447	458	97
"	5070;240	$2 \times 10^{-6} \text{O}_2$	447	454	97
"	6540	1.5×10^{-9}	445	452	100
"	6700;160	$2 \times 10^{-6} \text{N}_2$	445	444	101
"	6840;300	$2 \times 10^{-6} \text{N}_2$	445	441	101
Ta-2					
Ta-2	30	2.6×10^{-9}	438	453	111
"	60	2.4×10^{-9}	406	455	112
"	90	2.1×10^{-9}	375	458	110
"	120	2.1×10^{-9}	344	462	110
"	180;60	$2 \times 10^{-6} \text{N}_2$	344	460	108

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension (ergs/cm ²)	Contact Angle (degree)
Lead					
Ta-2	220;100	$2 \times 10^{-6} \text{N}_2$	395	455	109
"	250;130	$2 \times 10^{-6} \text{N}_2$	442	453	108
"	280;160	$2 \times 10^{-6} \text{N}_2$	494	440	111
Ta-1	28	1×10^{-8}	435	419	114
"	58	1×10^{-8}	354	430	112
"	88	1×10^{-8}	539	419	114
"	93	1×10^{-8}	539	417	115
"	153;60	$2 \times 10^{-6} \text{N}_2$	540	414	114
"	183;90	$2 \times 10^{-6} \text{N}_2$	540	419	111
Fe-2	20	2.1×10^{-9}	442	446	107
"	70	1.8×10^{-9}	400	453	105
"	110	1.6×10^{-9}	338	451	104
Al ₂ O ₃ -1	15	5×10^{-9}	491	419	154
"	60	5×10^{-9}	446	423	152
"	70	5×10^{-9}	448	421	154
"	120	4×10^{-9}	401	423	154

Table 2 (Continued)

Substrate and Number	Age of Drop (min)	Press (torr)	Temp (°C)	Surface Tension ₂ (ergs/cm ²)	Contact Angle (degree)
		Lead			
Al ₂ O ₃ -1	130	4 x 10 ⁻⁹	401	419	154
"	180	4 x 10 ⁻⁹	361	420	155
"	230;40	2 x 10 ⁻⁶ O ₂	360	415	156
"	270;80	2 x 10 ⁻⁶ O ₂	403	414	152
"	310;120	2 x 10 ⁻⁶ O ₂	452	390	163
"	350;160	2 x 10 ⁻⁶ O ₂	498	387	161
C-1	30	3.5 x 10 ⁻⁹	496	444	135
"	60	3.2 x 10 ⁻⁹	460	434	139
"	90	2.8 x 10 ⁻⁹	419	436	137
"	120	2.5 x 10 ⁻⁹	387	443	138
"	150	2.2 x 10 ⁻⁹	348	443	137

determine the best value of surface tension at a metal's melting point, only data which were collected under conditions of complete outgassing were used. But data from most of the sessile drop tests were used in determining the temperature derivative of the surface tension of the molten metal.

The age of each drop is also shown in Table 2; the age tells the length of time of outgassing or the length of time of contamination of the sessile drops. The age of the drop is important due to the phenomena of outgassing. The length of time needed to outgas indium and tin drops was longer than was needed for bismuth and lead drops. This may be largely due to the fact that the surface tensions of indium and tin are larger than the surface tensions of bismuth and lead; and thus the same percentage increase in surface tension is a larger absolute increase in surface tension for either indium or tin.

In Figure 8, the best data collected for tin (Sn-Ta-5) are shown along with surface tension temperature relationships recently published by White (1971) and Schwaneke (1971). White used the sessile drop method in hydrogen at a pressure of 760 torr; his substrate material was graphite. Schwaneke used the maximum bubble pressure method. The melting point values of surface tension are: 612 ergs/cm^2 , in this study; 550 ergs/cm^2 , by White (1971); and 556 ergs/cm^2 , by Schwaneke

Figure 8. The surface tension of tin, Sn-Ta-5 outgassed at 500°C for 10,000-10,500 minutes

(1971). The larger value obtained in the present work, about an 11 percent increase, is attributed to the fact that the molten metal was completely outgassed and surface contamination was prevented.

The importance of outgassing tin is illustrated again in Figure 9 which shows three sets of data which were collected at different lengths of time of outgassing. At longer times of outgassing, the surface tension of tin increased.

In Figure 10, the best data obtained in this study for indium (In-Ta-6) are shown along with the results recently published by White (1972). White used the sessile drop method in hydrogen at 760 torr. White obtained 560 ergs/cm^2 for the surface tension of indium at the melting point; in this study the result is 595 ergs/cm^2 . The larger value obtained in the present work is attributed to outgassing the indium and the prevention of surface contamination by gases.

Figure 10 also shows data taken for indium in hydrogen at 760 torr after the indium had been outgassed. The surface tension of indium was reduced due to the presence of hydrogen; in fact, the results previously obtained by White (1972) were nearly duplicated.

For tin and indium it was found that significant outgassing took place after the sessile drop was formed; this

Figure 9. The effect of outgassing on the surface tension of tin

Figure 10. The surface tension of indium, In-Ta-6 outgassed at 500°C for 7500-7800 minutes, In-Ta-7 outgassed at 500°C for 2800 minutes and contaminated for 85-240 minutes

phenomena was not observed for lead and bismuth. Figure 11 shows several sets of data collected for lead along with the results published by Bohdanský and Schins (1968b) and White (1971). For Pb-Ta-3 the drop was outgassed for 1500 minutes before data were taken; whereas for Pb-Ta-2 and Pb-Fe-2 the data were obtained immediately after the drops were formed. As is shown in Figure 11 the data nearly coincide. White's result is lower than the present work; at the melting point, White obtained 445 ergs/cm^2 for the surface tension of lead, and in this study the result was 454 ergs/cm^2 . The lower value obtained by White can be attributed to the fact that his data were obtained in hydrogen at a pressure of 760 torr.

Bohdanský and Schins (1968b) obtained their data between 1200 and 1700°C using the maximum bubble pressure method. The result shown in Figure 11 is an extrapolation of their data to the melting point region. It is very likely that the temperature derivative of the surface tension is not constant between 330°C and 1200°C , and that might explain why their results differ from the present work.

Maze (1970) reported nonlinear surface tension temperature behavior for both lead and bismuth; similar results were not obtained in the present work. Maze reported that for the first 50 to 75°C above the melting point, the surface tensions of lead and bismuth increased with temperature; then at higher temperatures, the surface tensions of lead

Figure 11. The surface tension of lead, Pb-Ta-2 outgassed at 450°C for 1500-1650 minutes, other drops outgassed for 30-180 minutes

and bismuth decreased as temperature increased. He attributed the nonlinear behavior to vapor transport; however, as was mentioned earlier, the vapor pressures of lead and bismuth are very low near their melting point, so it is unlikely that vapor transport effects could be observed using the sessile drop technique. What Maze may have observed were two opposing phenomena occurring at the same time. The first phenomena, namely outgassing, would tend to increase the surface tension, and the second phenomena, namely increasing the temperature, would tend to cause a decrease in the surface tension. Since Maze (1970) began his experiments at the lower temperatures and proceeded to take data at higher and higher temperatures, it seems possible that the outgassing phenomena predominated at the beginning of the experiment and then later, as outgassing became complete, the surface tension decreased as the temperature was increased. This would explain the nonlinear behavior that he observed.

The data obtained for bismuth are shown in Figure 12 along with the result of Bohdansky and Schins (1968b). In the present study, the value obtained for the surface tension of bismuth at its melting point is 390 ergs/cm^2 . This value is larger than the value of Bohdansky and Schins; however their data were taken between 1100 and 1300°C using the maximum bubble pressure method. And the line in Figure 12 indicating their result is an extrapolation to the melting

Figure 12. The surface tension of bismuth, Bi-Ta-4 outgassed at 450°C for 4200-4400 minutes, other drops outgassed for 20-380 minutes

point region.

Listed in Table 3 are the values obtained for the surface tension of bismuth, indium, lead, and tin at their respective melting points.

Table 3. Surface tensions of bismuth, indium, lead, and tin at their melting points after complete outgassing

Molten Metal	Melting Point Temperature (°C)	Surface Tension at Melting Point (ergs/cm ²)
Bi	271.3	390
In	156.4	595
Pb	327.4	454
Sn	231.9	612

Listed in Table 4 are the values obtained for the temperature derivative of surface tension of molten bismuth, indium, lead, and tin. Values are listed for many experimental runs. Values for $\partial\sigma/\partial t$ were obtained by using a least squares analysis to find the best straight line to fit the data.

Table 4. Temperature derivative of surface tension of bismuth, lead, indium, and tin

Metal and Substrate	$\frac{\partial \sigma}{\partial t}$ (ergs/cm ² °C)	Std. dev. of expt'l. pts. from straight line (ergs/cm ²)	Average value of $\frac{\partial \sigma}{\partial t}$ (ergs/cm ² °C)
Bi-Ta-4			
Bi-Ta-2			
Bi-Fe-1	-0.095	4.7	-0.095
Bi-Fe-2			
Bi-C-1			
Bi-Steel-1			
Pb-Ta-3			
Pb-Ta-2	-00.45	5.4	
Pb-Fe-2			-0.076
Pb-Ta-1	-0.057	2.5	
Pb-Ta-2(N ₂)	-0.125	2.5	
In-Ta-6	-0.024	6.7	
In-Ta-2	-0.070	2.7	
In-Ta-2(N ₂)	-0.072	6.4	-0.060
In-C-1	-0.069	3.9	
In-Al ₂ O ₃ -1	-0.063	3.8	
Sn-Ta-5	-0.048	4.0	
Sn-Ta-1	-0.113	7.6	
Sn-Ta-2(N ₂)	-0.073	4.1	-0.071
Sn-Al ₂ O ₃ -2	-0.063	6.8	
Sn-Al ₂ O ₃ -6	-0.053	1.9	
Sn-C-1	-0.074	4.6	

The surface tension-temperature behavior for bismuth, indium, lead, and tin are represented by the following relationships:

$$\sigma_{\text{Bi}} = 390 - 0.095 (t - t_{\text{m.p.}}) \quad (50)$$

$$\sigma_{\text{In}} = 595 - 0.060 (t - t_{\text{m.p.}}) \quad (51)$$

$$\sigma_{\text{Pb}} = 454 - 0.076 (t - t_{\text{m.p.}}) \quad (52)$$

$$\sigma_{\text{Sn}} = 612 - 0.071 (t - t_{\text{m.p.}}) \quad (53)$$

Contamination Effect of Gases

The effect of gas contamination on a molten metal sessile drop or the effect of gas dissolution in a molten metal sessile drop has caused some controversy. Several authors have reported that gas contamination reduces the surface tension of molten metals, and others have reported that gases do not affect the surface tension of molten metals. Consequently, a number of experiments were performed to determine the effect of hydrogen, nitrogen, and oxygen on the surface tension of bismuth, indium, lead and tin.

In Figure 10 it has already been shown that hydrogen at 760 torr reduced the surface tension of indium. Additional data have been obtained for each of the four metals in high purity hydrogen, nitrogen, and oxygen (see the Appendix for purities) at 10^{-6} torr. For each case the drop was outgassed

at 10^{-9} torr and then high purity gas was introduced. The exact length of time of outgassing and contamination for each data point can be found in Table 2. The results of these experiments are shown in Figures 13 through 23. Even though the gas pressure was only 10^{-6} torr, each gas caused a slight lowering of the surface tension of each metal; in some cases, the reduction in surface tension was barely noticeable after four hours. And for $\text{Pb-Al}_2\text{O}_3$ and $\text{In-Al}_2\text{O}_3$, oxygen produced visible oxidation on the surface of the drop.

It was expected that the gases would change the surface tension of the molten metals since gases are soluble in molten metals and the Gibbs adsorption equation is very well known in surface chemistry. The Gibbs adsorption equation is:

$$\Gamma_2 = - \frac{C_2}{RT} \frac{\partial \sigma}{\partial C_2} \quad (54)$$

Γ_2 = surface concentration of solute

C_2 = bulk concentration of solute

σ = surface tension of solution .

The Gibbs equation has been experimentally verified for many ordinary liquids (see Adam (1941)).

It was also expected that gas contamination would reduce the surface tension of the molten metal. After the

Figure 13. The effect of hydrogen at 10^{-6} torr on the surface tension of bismuth, indium, lead, and tin; outgassing times at 10^{-9} torr were: Bi - 4300 minutes, In - 8700 minutes, Pb - 1600 minutes, and Sn - 2800 minutes

Figure 14. The effect of nitrogen at 10^{-6} torr on the surface tension of bismuth, indium, lead, and tin; outgassing times at 10^{-9} torr were: Bi - 5600 minutes, In - 7800 minutes, Pb - 6500 minutes, and Sn - 8600 minutes

Figure 15. The effect of oxygen at 10^{-6} torr on the surface tension of bismuth, indium, lead, and tin; outgassing times at 10^{-9} torr were: Bi - 10,000 minutes, In - 10,000 minutes, Pb - 4800 minutes, and Sn - 5400 minutes

Figure 16. The effect of nitrogen at 10^{-6} torr on the surface tension of bismuth, drop outgassed at 10^{-9} torr for 30-120 minutes and contaminated for 30-120 minutes

Figure 17. The effect of nitrogen at 10^{-6} torr on the surface tension of indium, drop outgassed at 10^{-9} torr for 20-140 minutes and contaminated for 60-225 minutes

Figure 18. The effect of nitrogen at 10^{-6} torr on the surface tension of lead, drop outgassed at 10^{-9} torr for 30-120 minutes and contaminated for 60-160 minutes

Figure 19. The effect of nitrogen at 10^{-6} torr on the surface tension of tin, drop outgassed at 10^{-9} torr for 24-145 minutes and contaminated for 120-300 minutes

Figure 20. The effect of oxygen at 10⁻⁶ torr on the surface tension of bismuth, drop outgassed at 10⁻⁹ torr for 20-180 minutes and contaminated for 30-180 minutes

Figure 21. The effect of oxygen at 10^{-6} torr on the surface tension of indium, drop outgassed at 10^{-9} torr for 60-270 minutes and contaminated for 30-180 minutes

Figure 22. The effect of oxygen at 10⁻⁶ torr on the surface tension of lead, drop outgassed at 10⁻⁹ torr for 15-180 minutes and contaminated for 40-160 minutes

Figure 23. The effect of oxygen at 10⁻⁶ torr on the surface tension of tin, Sn-Al₂O₃ outgassed at 10⁻⁹ torr for 20-640 minutes; other drops outgassed at 10⁻⁹ torr for 20 minutes and contaminated for 20-315 minutes

drop of metal is contaminated by a gas, a solution remains, although it is a very dilute solution of gas in a molten metal. And it is likely that the surface tension of the solution would lie somewhere between the surface tension of the pure solvent and the surface tension of the pure solute. Now, the surface tension of hydrogen, nitrogen, and oxygen in the liquid state are about 10 ergs/cm^2 (see Weast (1970)); thus, it should be expected that these gases in solution in a molten metal would reduce the surface tension of the molten metal.

The fact that the gas contamination effect is very small at low pressures for periods of several hours means that it may be possible to obtain acceptable surface tension data for metals whose vapor pressures are larger than the metals used in this study. By making tests at pressures of 10^{-6} torr or somewhat higher net vaporization of the metal can be reduced and contamination of the drop surface can be held at a minimum. By operating at 10^{-6} torr instead of 10^{-9} torr, the mean free path of molecules in the vapor is reduced. By reducing the mean free path of molecules, the likelihood of a metal molecule in the vapor phase, a molecule which had just entered the vapor phase from the drop, striking the drop again is increased; thus the net rate of vaporization is reduced. But, the higher pressures also mean more surface contamination; so the lowest pressure possible should

be used. Also, the molten metal should be completely outgassed first if possible.

Contact Angle Phenomena

The contact angle data collected in this study are listed in Table 2. The contact angle is very sensitive to preparation of the substrate surface and to the surface tension of the molten metal. Therefore, when examining the contact angle data in Table 2, one must keep in mind three other items:

- (a) the surface tension of the molten metal
- (b) the temperature at which the substrate was outgassed--the maximum test temperature in this study
- (c) the final pressure obtained during outgassing--about 10^{-9} torr in this work; for tests run at 10^{-9} torr, the final pressure is also shown in Table 2.

In the cases of tantalum and iron contact angles were lower when the substrates had been outgassed at lower pressures; this would indicate that the reduction of oxides on the metal substrate surface resulted in a reduction in the contact angle.

Contact angles on alumina substrates were larger than contact angles on tantalum and iron substrates. And contact angles on graphite substrates were usually greater than the

contact angles on metals but less than the contact angles on alumina substrates. The contact angle of tin on alumina was reduced when the alumina was contaminated with oxygen prior to the formation of a sessile drop.

The contact angle data obtained in this study were nonsensitive to temperature changes after a sessile drop had been formed.

Surface Tension Correlation for Molten Metals

Equation 55 has been suggested as a relationship which relates the surface tension of a molten metal to its heat of vaporization.

$$B\left(\frac{M}{\rho N}\right)^{2/3} \left(\sigma - T \frac{\partial \sigma}{\partial T}\right) = \frac{\Delta H_{\text{vap.}} - RT}{N} \quad (55)$$

$B = \text{constant}$.

Using the surface tension data obtained for bismuth, indium, lead, and tin, the constant "B" has been calculated. The data used for the calculation are shown in Table 5; the thermodynamic data were taken from Hultgren et al. (1963). Equation 55 should apply at any temperature; in this study calculations were made at the melting point for each metal. Most surface tension data that are available for molten metals were collected for the melting point region.

The values obtained for the constant "B" are shown in Table 6.

Table 5. Data needed for Equation 55 for bismuth, lead, indium, and tin

Metal	M	ρ (gm/cm ³)	T _{m.p.} (°K)	$\sigma_{m.p.}$ (ergs/cm ²)	$\frac{\partial \sigma}{\partial T}$ (ergs/cm ² °K)	$\Delta H_{vap.} - RT$ (ergs)
Bi	209.00	10.0561	544.4	390	-0.095	1.905×10^{12}
Pb	207.21	10.5857	600.6	454	-0.076	1.835×10^{12}
In	114.76	7.0314	429.4	595	-0.060	2.310×10^{12}
Sn	118.70	6.9937	505.1	612	-0.071	2.905×10^{12}

Table 6. Calculated value of the constant in Equation 55

Metal	Constant
Bi	6.75
Pb	6.02
In	6.68
Sn	8.03

The constant in Equation 55 is not universal for the metals tested; however, the magnitude of the constant is very interesting. For ordinary liquids the constant had been found to vary between 2.6 and 2.9; and in the derivation of Equation 55, molecules on the surface were assumed to be half free which led to a constant of approximately 2. However, the assumption that a surface molecule is half free neglects any interaction between neighboring molecules on the surface. The larger value of B obtained for metals suggests that metallic surface atoms are less than half free. Because of the electron cloud nature of metallic bands, one might expect metallic surface atoms to be attracted to each other and to atoms in the bulk more than surface molecules for ordinary liquids. Thus, the larger value of B obtained for metals should not be surprising.

Equation 55 would be useful in predicting the surface tension of molten metals if

$$B = Cf \quad (56)$$

where C is a universal constant for all metals and f is a correction factor that is some tabulated property of metals and that accounts for different degrees of attraction for metallic surface atoms.

Since for electrostatic forces, the potential energy is proportional to $1/r$, where r is the distance of separation of the ions, $1/r_i$, where r_i is the ionic radius of a metallic ion, is proposed for the correction factor f in Equation 56. Values for the ionic radius of the metals were taken from Lange (1967) and Weast (1970); for consistency, the value of the ionic radius of the largest valence state was used for metals with more than one valence state.

Table 7 lists the value of r_i used for bismuth, indium, lead, and tin and value calculated for C , the universal constant. The average value obtained for C is 5.40.

Table 8 shows a comparison of the experimental value of surface tension and the value calculated by Equation 55 using $5.40/r_i$ as the constant. The calculated values of Equation 55 are very good when compared to the results of empirical relationships of other authors, as those empirical relationships were often in error between 10 and 15 percent. Equation 55 was tested on some data recently reported by

Table 7. Ionic radii of bismuth, indium, lead, and tin and the universal constant for Equation 55

Metal	Ionic Radius (Angstroms)	Universal Constant for Equation
Bi	.74	4.99
Pb	.92	5.50
In	.81	5.41
Sn	.71	5.69

Table 8. Surface tension of bismuth, lead, indium, and tin at the melting point, experimental and calculated by Equation 55

Metal	Experimental surface tension (ergs/cm ²)	Calculated surface tension (ergs/cm ²)	Percent difference
Bi	390	359	-7.9
Pb	454	468	+3.1
In	595	596	+0.2
Sn	612	645	+5.4

Table 9. Surface tension at melting point, experimental and calculated by Equation 55

Metal	$\frac{\partial \sigma}{\partial T}$ (ergs/cm ² °K)	Experimental surface tension (ergs/cm ²)	Calculated surface tension (ergs/cm ²)	Percent difference
Ag	-0.117	910	862	- 5.3
Au	-0.120	1140	1180	+ 3.5
Ba	-0.075	276	286	+ 3.6
Cd	+0.460	590	649	+10.0
Na	-0.080	220	225	+ 2.3
Zn	+0.450	760	745	- 1.9
Hg ^a	-0.220	484	194	-59.8

^aAt 25°C.

others, and the results are shown in Table 9. Surface tension data were taken from Bernard and Lupis (1971a), Bohdansky and Schins (1967, 1968a), and White (1966, 1972). Thermodynamic data were taken from Hultgren *et al.* (1963). And ionic radii data were taken from Lange (1967) and Weast (1970).

With the exception of mercury, Equation 55 does a reasonably good job of predicting the surface tension of molten metals. The large difference between experimental and calculated values for mercury is very interesting since the surface tension of mercury at 25°C is about the only

value of surface tension for a liquid metal that is widely accepted. The large difference in these values may be the result of the value used for $\frac{\partial \sigma}{\partial T}$. When Grosse (1962, 1964) presented his empirical correlations, he found that mercury, cadmium, and zinc did not fit the same correlation as other liquid metals. And White (1966, 1972) has recently shown that zinc and cadmium have a positive value of $\frac{\partial \sigma}{\partial T}$ near the melting point. Prior to White's work it had always been supposed that $\frac{\partial \sigma}{\partial T}$ was negative for all molten metals. If mercury has a positive value of $\frac{\partial \sigma}{\partial T}$ between its melting point and 25°C, the result calculated by Equation 55 would be in better agreement with the experimental value. At present, surface tension data are not available for mercury between its melting point and 25°C, nor have surface tension data for mercury been obtained under UHV conditions.

Although most of the calculations presented in this study were done at the melting point, Equation 55 should apply in its present form for the melting point region. However, it is likely that the universal constant is temperature dependent, and at higher temperatures, 500 to 1000°C above the melting point or higher, larger errors may result when using the present form of Equation 55. Also, if Equation 55 is to be used to predict surface tension, a

value for $\frac{\partial \sigma}{\partial T}$ must be estimated. Most metals have a value between -0.06 and -0.12 for $\frac{\partial \sigma}{\partial T}$; therefore, as an approximation, -0.1 could be used for $\frac{\partial \sigma}{\partial T}$.

CONCLUSIONS

1. The surface tension temperature behavior of Bi, Pb, In, and Sn is linear near the melting point; $\frac{\partial \sigma}{\partial T}$ is negative for all four.

2. The surface tension of a molten metal can be related to its heat of vaporization by the equation

$$\frac{5.40}{r_1} \left(\frac{M}{\rho N} \right)^{2/3} \left(\sigma - T \frac{\partial \sigma}{\partial T} \right) = \frac{\Delta H_{\text{vap}} - RT}{N} .$$

In the melting point region, the error in the calculated value of surface tension should be less than ten percent.

3. Gases dissolved in a molten metal and gas contamination of the liquid-vapor surface reduce the surface tension of liquid metals.

4. For sessile drop tests, molten metals can be out-gassed and surface contamination can be minimized by using UHV equipment.

5. Contact angles are very sensitive to the surface preparation of the substrate.

6. Oxides on metallic surfaces increase contact angles.

7. Contamination by oxygen enhances the wetting of alumina by molten metals.

8. Alumina is not a good substrate material for use at high temperature and UHV conditions since it will dissociate and contaminate the sessile drop.

RECOMMENDATIONS

1. Accurate data on the surface tension should be collected for more metals, so that the surface tension correlation presented in this study can be improved. Although some surface tension data are available for many molten metals, only the data for a few metals have been collected under clean conditions. And while the results of an UHV study of additional metals may not be greatly different from previous data, it is likely that the differences will be measurable by present techniques.

2. Surface tension data for liquid metals should be collected over a large temperature range, such as 1000°C , in order to determine the temperature dependence of $\frac{\partial\sigma}{\partial T}$ and the constant appearing in the surface tension correlation presented in this study.

3. The surface tension of Hg should be measured between its melting point and room temperature. Since Zn, Cd, and Hg are in the same group in the Periodic Table of the Elements, it is likely that Hg has a positive value of $\frac{\partial\sigma}{\partial T}$ near its melting point. A refrigeration unit will have to be constructed for such an experiment.

4. Surface tension data should be collected for binary mixtures of Bi, In, Pb, and Sn in order to determine the relationship between the surface tension of an alloy and

the surface tension of its pure components. Although some surface tension data are already available for mixtures, little work has been done relating the surface tension of a molten alloy to the surface tension of its pure components.

5. Sessile drop and microprobe studies of molten metals with and without corrosion inhibitors should be conducted in order to determine the manner in which inhibitors reduce corrosion and the relationship between wetting and corrosion.

6. Advancing and receding contact angles for molten metals on construction materials, namely steels, should be measured. These data are needed for the superheat correlation by Fauske (1969); at the present, such data are not available.

BIBLIOGRAPHY

- Adam, N. K. 1941. The physics and chemistry of surfaces. 3rd ed. Oxford University Press, London, Eng.
- Aldrich, R. G. and Keller, D. V., Jr. 1968. A sessile drop study of liquid-solid adhesion for the system indium (R)--aluminum using ultrahigh vacuum technique. J. Phys. Chem. 72: 1092-1099.
- Balzhiser, R. E. and Caswell, B. F. 1966. The critical heat flux for boiling liquid metal systems. Heat Transfer-Los Angeles, Chem. Eng. Prog. Symposium Series No. 64, 62:41-46.
- Balzhiser, R. E. and Padilla, A. 1968. Film boiling of potassium on a horizontal plate. Heat Transfer-Seattle, Chem. Eng. Prog. Symposium Series No. 82, 64:81-87.
- Bernard, G. and Lupis, C. H. P. 1971a. The surface tension of liquid silver alloys: part I. Silver-gold alloys. Met. Trans. 2: 555-559.
- Bernard, G. and Lupis, C. H. P. 1971b. The surface tension of liquid silver alloys: part II. Ag-O-alloys. Met. Trans. 2: 2991-2998.
- Bikerman, J. J. 1970. Physical surfaces. Academic Press, New York, N.Y.
- Bohdansky, J. 1968. Temperature dependence of surface tension for liquid metals. J. Chem. Phys. 49: 2982-2983.
- Bohdansky, J. and Schins, H. E. J. 1967. The surface tension of the alkali metals. J. Inorg. Nucl. Chem. 29: 2173-2179.
- Bohdansky, J. and Schins, H. E. J. 1968a. Surface tension and density of the alkaline metals Mg, Ca, Sr, and Ba. J. Inorg. Nucl. Chem. 30: 2331-2337.
- Bohdansky, J. and Schins, H. E. J. 1968b. The surface tension of Ag, Tl, Pb, and Bi at high temperatures. J. Inorg. Nucl. Chem. 30: 3362-3365.
- D'Amico, C. and Hagstrum, H. D. 1960. Production and demonstration of atomically clean metal surfaces. J. Appl. Phys. 31: 715-723.

- de Bruyn, P. L. 1966. Some aspects of classical surface thermodynamics. In Bonis, L. J., de Bruyn, P. L. and Duga, J. J., eds. Fundamental phenomena in material sciences. Vol. 3. Pp. 1-36. Plenum Press, New York, N.Y.
- Donakowski, T. D. 1971. A report of summer research in chemical engineering division of the Ames Laboratory USAEC.
- Drowart, J., De Maria, G., Burns, R. P., and Inghram, M. G. 1960. Thermodynamic study of Al_2O_3 using a mass spectrometer. J. Chem. Phys. 32: 1366-1372.
- Fauske, H. K. 1969. Liquid metal boiling in relation to liquid metal fast breeder reactor safety design. Heat Transfer-Philadelphia, Chem. Eng. Prog. Symposium Series No. 92, 65: 138-149.
- Flint, O. 1965. Surface tension of liquid metals. I. Nucl. Mat. 16: 233-248.
- Gibbs, J. W. 1948. Collected works. Vol. I. Yale University Press, New Haven, Conn.
- Good, R. H., Jr. and Muller, E. W. 1956. Field emission. Handbuck der physik. Vol. 21. Springer-Verlag, Berlin, Germany.
- Grosse, A. V. 1962. The relationship between the surface tension and energies of liquid metals and their critical temperatures. J. Inorg. Nucl. Chem. 24: 149-156.
- Grosse, A. V. 1964. The relationship between surface tension and energy of liquid metals and their heat of vaporization at the melting point. J. Inorg. Nucl. Chem. 26: 1349-1361.
- Grosse, A. V. 1968. Surface tension of the alkali metals from the melting point to the critical region. J. Inorg. Nucl. Chem. 30: 1169-1174.
- Hlavac, P. J., Nimmo, B. G., and Dwyer, O. E. 1970. Fluid-dynamic study of fully developed turbulent flow of Hg in annuli. In Liquid metal heat transfer and fluid dynamics. Am. Soc. Mech. Eng., New York, N.Y.
- Holland, L. 1960. Vacuum deposition of thin films. John Wiley and Sons, Inc., New York, N.Y.

- Holtz, R. E. and Singer, R. M. 1969. On the initiation of pool boiling in sodium. Heat Transfer-Philadelphia, Chem. Eng. Prog. Symposium Series No. 92, 65: 121-128.
- Hultgren, R., Orr, R. L., Anderson, P. D., and Kelley, K. K. 1963. Thermodynamic properties of metals and alloys. John Wiley and Sons, Inc., New York, N.Y.
- Kingery, W. D. and Allen, B. C. 1959. Surface tension and contact angles in some liquid metal-solid ceramic systems at elevated temperatures. Trans. Met. Soc., AIME 215: 30-37.
- Lange, N. E., Ed. 1967. Handbook of Chemistry. Revised 10th ed. McGraw-Hill Book Company, New York, N.Y.
- Laukonis, U. J. and Coleman, R. B. 1961. Iron whisker surface rearrangements resulting from hydrogen reduction of oxides and from thermal etching. J. Appl. Phys. 32: 242-247.
- Maze, R. C. 1970. An ultrahigh vacuum study of wetting in liquid metal-solid metal systems. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University.
- Maze, C. and Burnet, G. 1969. A nonlinear regression method for calculating surface tension and contact angle from the shape of a sessile drop. Surface Science 13: 451-470.
- McLaughlin, B. D. and de Bruyn, P. L. 1969. The dynamics and thermodynamics of solid-fluid-fluid three-phase contact. J. Colloid and Interface Science, 30 (1): 21-33.
- Nicholas, M. E., Joynes, P. A., Tessem, B. J., and Olson, M. D. 1961. The effect of various gases and vapors on the surface tension of mercury. J. Phys. Chem. 65: 1373-1375.
- Ramsey, N. F. Molecular beams. 1956. Oxford University Press, London, Eng.
- Roberts, R. W. 1963. Generation of clean surfaces in high vacuum. J. Appl. Phys. 14: 537-543.
- Roberts, R. W. 1967. Clean surfaces: their preparation and characterization. General Electric Report No. 67-C-087 [Schenectady, N.Y.]. March.

- Roberts, R. W. and Vanderslice, T. A. 1963. Ultrahigh vacuum and its applications. Prentice Hall, Inc., Englewood Cliffs, N.J.
- Schwaneke, A. 1971. U.S. Bureau of Mines Report No. 7372.
- Shimotake, H. and Hesson, J. C. 1967. Corrosion by fused salts and heavy liquid metals--a survey. In Gould, R. F., ed. Regenerative EMF cells. Pp. 149-185. Am. Chem. Soc., Washington, D.C.
- Singleton, J. H. 1954. Interaction of oxygen with incandescent filaments. J. Appl. Phys. 30: 1671-1673.
- Tucker, C. W., Jr. 1964. Low-energy electron diffraction studies of gas adsorption on platinum (100), (110), and (111) surfaces. J. Appl. Phys. 35: 1897-1905.
- Tucker, C. W., Jr. 1966. Chemisorbed coincidence lattices on rhodium. J. Appl. Phys. 37: 3013-3019.
- Weast, R. C., Ed. 1970. Handbook of Chemistry and Physics. 51st ed. The Chemical Rubber Company, Cleveland, Ohio.
- White, D. W. G. 1966. The surface tension of zinc. Trans. Met. Soc. AIME 236: 796-803. May.
- White, D. W. G. 1968. The surface tension of liquid metals and alloys. Metals and Materials Review 134: 73-96. July.
- White, D. W. G. 1971. The surface tensions of Pb, Sn, and Pb-Sn alloys. Met. Trans. 2: 3067-3071.
- White, D. W. G. 1972. The surface tension of indium and cadmium. Met. Trans. 3: 1933-1936.
- Winkler, O. and Bakish, R., Eds. 1971. Vacuum metallurgy. Elsevier Publishing Company, New York, N.Y.
- Zadumkin, S. N. 1961. A variation on the statistical electron theory of surface tensions of metals. Physics of Metals and Metallography 11 (3): 11-26.

ACKNOWLEDGMENTS

I would like to thank Dr. George Burnet for helping me determine the direction that this study has taken; and I appreciate his help organizing this dissertation. Also, I would like to thank Harvey Jensen for his help with the experimental equipment. This work was supported in part by grants from the National Aeronautics and Space Administration (NASA) and the Iowa State Research Foundation.

APPENDIX

The following is a list of the materials used in this study and their nominal purities.

Bismuth	99.9999%
Lead	99.9999%
Indium	99.999%
Tin	99.999%
Tantalum	99.98%
Alumina	85%
Alumina	99.8%
Graphite	Spectrographic grade, < 5 ppm ash
Iron	99.99+%
Steel	ASTM A-387 Grade B