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REACTIONS OF CERIUM AND LANTHANUM WITH CERAMIC OXIDES

By
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July 1955

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Ames, Iowa

Technical Information Service Extension, Oak Ridge, Tenn.

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F. H. Spedding, Director of Ames Laboratory.

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ABSTRACT

In this study the surface properties of cerium and lanthanum metals were determined for the metals melted on refractory oxide plaques of alumina, beryllia, thoria, and stabilized zirconia. The reactions occurring at the interface between the metals and the refractories were also determined by metallographic and x-ray techniques. The surface tension, contact angle, and work of adhesion were determined at temperatures of 810, 900, and 1000°C for cerium, and at temperatures of 950, 1000, 1100 and 1200°C for lanthanum. The metallographic examination of the reactions was conducted on polished sections of the interfaces. The temperatures to which the specimens were subjected for this phase of the study were 1100°C for cerium and 1200°C for lanthanum. To aid in the microscopic examination of the reactions between cerium and the oxides, mixtures of metal and ceramic powders were heated to temperatures of 500 and 804°C for cerium. Lanthanum and oxide powders were given a similar treatment to temperatures of 600 and 924°C. X-ray diffraction patterns of the mixtures were then obtained for the identification of the phases produced from the reactions.

The surface properties of the metals melted on the ceramic oxides were established by the sessile drop method of determining surface tension. The characteristic dimensions of the drop were obtained from photographs of the profile of the drop. The equilibrium between the known force of gravity acting on the drop and the unknown surface tension could be determined from the shape assumed by the drop. The dimensions obtained from the profile were used also to determine the contact angle displayed between the surface of the drop and the ceramic supporting plaque. The work required to remove the metal from the ceramic was then determined from the contact angle and surface tension from a consideration of the surface forces operative at the point of contact between liquid and solid plaque.

The surface tension determined by the sessile drop method is of reasonable accuracy only when the angle of contact of the surface of the drop with the supporting plane, is greater than 90°. For this reason the surface tension of lanthanum was determined from the run on zirconia. At a temperature of 950°C the surface tension of lanthanum was determined to be 710 dyne/cm ± 5%.

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[1] This report is based on a Ph.D. thesis by George R. Pulliam submitted July, 1955 at Iowa State College, Ames, Iowa. This work was performed under contract with the Atomic Energy Commission.

The surface tension of lanthanum went through values of 693, 648, and 630 dyne/cm as the temperature of measurement became 1000, 1100, 1200°C. The surface tension of cerium was determined from runs of the metal melted on beryllia and zirconia. At temperatures of 810, 900, and 1000°C the surface tension of cerium was determined on zirconia to be 695, 680, and 666 dyne/cm, respectively. At the same temperatures the surface tension of cerium was determined on beryllia to be 740, 697, and 678 dyne/cm, respectively.

The contact angles of both metals was at their highest values when melted on zirconia. The contact angle of lanthanum on the oxides then decreased in the order; alumina, beryllia, and thoria. Cerium metal showed a very high contact angle with beryllia also, but the contact angle of cerium on thoria was assumed to be zero since the metal completely dissolved in the plaque. The rapid attack of alumina by cerium prevented measurement of the contact angle.

The work of adhesion of the metals to the oxides varied considerably between the metals and with the oxide studied. With both metals the work of adhesion was at a minimum for the melts on zirconia. The work of adhesion of the metals to thoria was by far the highest of all the oxides studied.

The work of adhesion of lanthanum to alumina and beryllia was intermediate between the adhesion to zirconia and thoria. The adhesion of cerium to beryllia, though not as low as the adhesion to zirconia, was lower than the adhesion of lanthanum to any of the oxides.

In general the interfacial reactions occurring between the metals and the oxides resulted in simple reduction of the oxides. Alumina was reduced by the metals to form the oxides of the molten metals and alloys of aluminum and the metals. Beryllia was reduced in a similar fashion. However, alloying of the metals with beryllium did not occur. The metals reacted with zirconia to produce both an interfacial layer of the metal oxide and a limited solid solution of metal and zirconia. Both metals produced solid solutions with thoria.

The values determined for the surface tensions of cerium and lanthanum revealed the similarity that was to be expected from the similarity of the other properties of the metals. The value of surface tension decreased linearly with increasing temperature in nearly the same manner for both metals. Generally the work of adhesion of the metals to the oxides increased as the temperature increased. As a result of this the contact angles decreased with increasing temperatures.

Of the materials studied, beryllia was found to be the best refractory for containing the molten metals. The reactions between the metals and beryllia were less extensive than the other refractories, and the metal did not diffuse into the beryllia plaques. Zirconia was found to be a possible container for the molten metals, though the metal did penetrate the refractory by diffusion. Thoria and alumina were found to be poor container materials for the metals.

REACTIONS OF CERIUM AND LANTHANUM

by

George R. Pulliam and Elmer S. Fitzsimmons

INTRODUCTION

The various methods of producing rare earth metals have been reviewed by Spedding, et al (1), Ahmann (2), Daane (3), and Eastman, et al (4). Their summaries attribute the first production of a rare earth metal to Mosander in 1826. He succeeded in obtaining a pyrophoric powder of cerium from the reduction of cerous chloride by potassium. There followed many ingenious schemes for producing the massive metal by reduction with alkali metals. However, in all the methods involving alkali metals a certain amount of alkali chloride was mixed with the rare earth metal and could not be removed. In later methods of producing the rare earth metals, electrolysis of fused chlorides was used. This method had the advantage of producing the massive metal in fair quantities, but the metals contained impurities from the electrode material. Some work was also attempted to produce the metals from their oxides by reduction with alkali and alkaline metals. Due to the refractory nature of the oxides, however, very limited success was realized with this method.

Both cerium and lanthanum metals have been produced in this laboratory following the methods of Ahmann (2) and Daane (3). This method utilized the reductive powers of the alkaline metals magnesium and calcium. Iodine was added as a booster material to provide a side reaction to give additional heat to the reaction which allowed a better aglomeration of the massive metals. The resulting metals produced were alloyed with calcium or magnesium. The final purification, then, involved a vacuum distillation to remove the contaminating metals. The purity of the metals produced by this technique is superior to the previous methods. The usual purity of the metals was greater than 99.5%.

This research project conducted on the two rare earths, cerium and lanthanum, is in line with the overall program at the Ames Laboratory to determine the physical properties of the rare earths. The surface tension of the metals were determined over a 300°C temperature range. Also of particular interest in this study was the wetting characteristics of the metals with respect to the refractory oxides; Al_2O_3, BeO, ThO_2, and stabilized ZrO_2. In conjunction with these determinations metallographic and x-ray analyses of the reaction of metal and ceramic were performed.

The most obvious reason for conducting this research from a ceramic point of view was to determine the likelihood of using these materials in containing the molten metals. The most important reason for the research, however, was to establish the surface tension and wetting characteristics of the metals on the ceramic. The surface tensions of these metals is of particular importance to the theoretical metallurgist as additional data with which to work in establishing an overall theory of metals. The surface tensions of metals is considered to be a significant characteristic for study in eliciting the general behavior of metals. The similarity of the rare earth metals is particularly important in this respect.

The wetting characteristics of the metals on refractories are of more importance to the ceramist. The most favorable condition for good bonding exists when the metal has a contact angle of zero with the refractory and complete wetting occurs. Information concerning the wetting characteristics of metals on ceramics is, therefore, of interest to several fields of ceramics, such as cermets, metal bonded abrasives, and metal-ceramic seals.

The similarity of the rare earths makes them of particular value in establishing general relationships for the characteristics of metals. The melting point of cerium and lanthanum is approximately 75°C apart, their atomic diameters are approximately 0.002 Å different, and, of course, their chemical properties are quite similar. Thus, if the surface tension of metals varies significantly with a particular property this variation may be determined more precisely with these metals since any particular property will be nearly the same with all rare earths.

The refractories were chosen for this work because of their general interest as high temperature refractories, and because the reactivity of the metals to be studied suggested that very stable materials must be used.

This study of the interaction of ceramic and metal was divided into three separate techniques.

1. The study of the wetting effects of the metals on the refractories was conducted in vacuo using the sessile drop method. In this phase of the work the surface tension, contact angle, and the work of adhesion were determined for cerium and lanthanum metals melted on the refractories; Al_2O_3, BeO, ThO_2, and stabilized ZrO_2. The temperatures used for cerium were 810, 900, and 1000°C. The temperatures used for lanthanum were 950, 1000, 1100, and 1200°C. The lower temperature limit in these investigations was set at approximately 20° above the melting point of the metals. The upper temperature limit of 1000° for the cerium study was set by the occurrence of reactions between metal and ceramic sufficient to destroy the accuracy of the measurements. The study of the wetting characteristics of lanthanum on the refractories was terminated at 1200°C because at a higher temperature the vapor pressure of the metal becomes sufficiently high to affect the accuracy of the measurements.

2. The second study of the interactions was a metallographic examination of the metal and ceramic after the heat treatment given in the surface tension determination. A petrographic microscope utilizing reflected light was used to determine the extent of penetration of the metal into the ceramic and to study the method of penetration.

3. The third method of studying the interaction was by x-ray diffraction patterns. Powders of the metals were mixed with powders of each refractory oxide, and heated to 300°C below their melting point and to their melting point. The products of reaction from this treatment were then determined from the x-ray analysis. An attempt was made from this method to determine the range of temperature of reaction of cerium and lanthanum metals with the four oxides. This analysis was also used as an aid in establishing the method of penetration of the metals into the ceramics.

LITERATURE REVIEW

Bashforth and Adams (5) in 1883 were the first to make possible a precise measurement of the surface tension of a liquid using the sessile drop method. The two principal radii of curvature of a liquid surface under the influence of surface tension and gravity are given by the expression,

$$\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz(\rho_1 - \rho_2) + C.$$

Where σ is the surface tension of the liquid, R_1 and R_2 are the principal radii of curvature of a point, g is the gravitational constant, ρ_1 and ρ_2 are the densities of the liquid and surrounding media, respectively, z is the height of the point through which the hydrostatic head of the density difference acts, and C is a constant. Unfortunately the most readily measured radii of curvature occur at a point where z is zero. This prohibits the solution of the equation for surface tension. Bashforth and Adams made a transformation of this equation for the special case of a surface of revolution about a vertical axis. They tabulated parameters of the equation that could be measured directly from the profile of a sessile drop. The parameters could then be used to evaluate the constant, C, and the surface tension of the liquid.

This method of Bashforth and Adams is precise in the range for which they have determined values. Quincke (6) in 1868, however, made use of the surface equation to determine the surface tension of liquids. His method was an approximation which assumed that one radius of curvature could be neglected in the equation. Since the reciprocals of the radii of curvature are added in the equation this approximation may be used if the drops are large. The size of the drop that permits neglecting the one radius depends on the surface tension of the liquids, however, so that no definite size of drop can be specified. Porter (7) discussed many approximation formulae, and gave a criterion for determining the most accurate size of drop. In this discussion, Porter concedes that a drop in the range where Bashforth and Adams tables may be used is the better size, but that there are situations where this is either impossible or impractical.

Dorsey (8) derived a modification of Bashforth and Adams method of determining surface tension. In this method the values prepared by Bashforth and Adams were used in preparing an equation using different characteristic dimensions of the drop. Dorsey felt these dimensions could be measured with greater accuracy. Ferguson (9,10) also, gave various methods of surmounting the difficulty of measuring the principal radii of curvature of bubbles and drops.

Ellefson and Taylor (11,12) were one of the first to use the tables of Bashforth and Adams in the ceramic field. They made use of its unique ability to determine the contact angle of liquid and solid surface as well as the surface tension of the liquid. The surface tensions of fused salts and glasses were determined on graphite, gold, and platinum. They credit the sessile drop method of determining surface tension as being accurate within 5%.

Humenik and Kingery (13) used the method outlined by Ellefson and Taylor in determining the surface tension of silicon, iron, and nickel on several refractory oxides. They state that the plaque material upon which the metals were melted affected the values obtained for the surface tensions of the metals. Factors which influence the contact angle between liquid metal and plaque material were also discussed. The atmosphere present was found to affect both the value of surface tension and contact angle. The values for surface tension were considerably higher in vacuo for the metal nickel. This is to be expected in the case of metals with relatively high vapor pressures. With a liquid in equilibrium with its vapor a certain portion of the attractive bonds at the surface will be directed to the vapor with the result that the surface tension is lowered. In a vacuum this effect is removed and a higher surface tension results.

Several other methods of measuring the surface tensions of liquid metals have been used. Taylor (14) and Adam (15) gave a review of these various methods, and summarized the factors affecting the accuracy of the different methods. The other methods, however, do not give information concerning the contact angle of the liquid in equilibrium with a solid. As a matter of fact, in order to use the capillary height method and the ring detachment method the contact angle must be known.

THEORY AND METHODS

Surface Tension Equation

The static methods of determining the surface tension of liquids are all based on equating the work done in extending a surface under pressure to the work absorbed by the surface under the resistance offered by the surface tension to the formation of a new amount of surface.

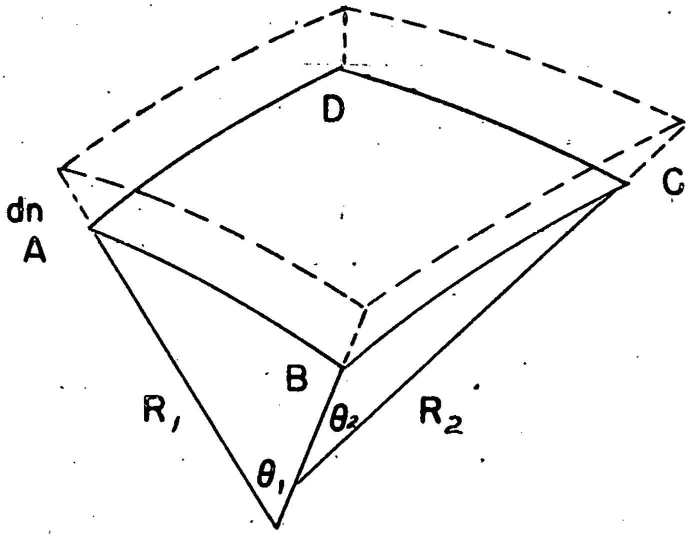


Fig. 1 Curved Surface

In the drawing above the curved surface ABCD is represented as having two principal radii of curvature R_1 and R_2. The angles subtended by AB and BC are, respectively, θ_1 and θ_2. In extending the surface in a parallel manner through the distance dn, the new area becomes $(AB + \theta_1 dn)$ $(BC + \theta_2 dn)$. The angles θ_1 and θ_2 may be replaced by AB/R_1 and BC/R_2. Making this substitution and completing the multiplication show that the area has been increased by ABCD $(dn)\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$. The work done against surface tension in producing this additional surface is, simply, the resistive force of surface tension per unit area, σ, multiplied by the amount of new surface. The expression for the differential amount of work, dw, is thus:

1. $$dw = (\sigma)\ (ABCD)\ (dn)\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

It is now necessary to determine the work required to extend the surface parallel to its original position. If p_1 is considered to be the pressure on the concave side of the surface, and p_2 is considered to be the pressure on the convex side of the surface, the pressure difference across the surface is $(p_1 - p_2)$. This pressure difference acts over an area of ABCD and through a distance of dn. The differential work done in this instance is given by

2. $$dw = (p_1 - p_2)\ \ (ABCD)\ \ (dn).$$

3. $$\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = p_1 - p_2$$

Influence of Gravity and Surface Tension

To apply the above equation to the sessile drop, consider a point P on the surface of the drop as shown in Fig. 2 below. At this point the pressure on the concave and convex sides of the surface will be augmented by the hydrostatic pressure exerted by the mass of the fluid on either side of the surface. With the apex of the drop selected as the reference point the hydrostatic heads of the drop and surrounding fluid will be operative over the height z; the distance from the apex to the point P. The pressure difference across the surface is then $(p_1 - p_2) + gz$ (ρ_1 and ρ_2). Where; ρ_1 and ρ_2 are the densities of the drop and the surrounding fluid, respectively, and g is the gravitational constant. The term $(p_1 - p_2)$ may be considered a constant in any system so that the above equation may be written:

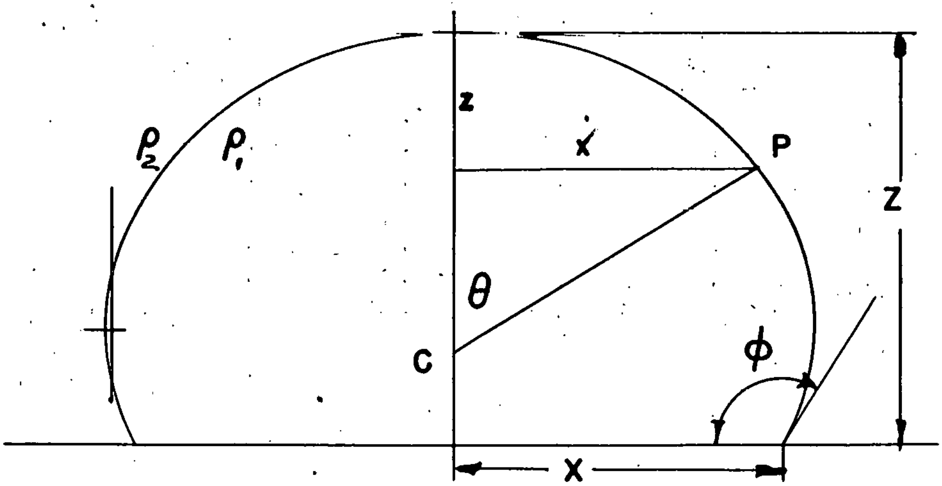


Fig. 2 Sessile drop

4. $$\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = gz\ (\rho_1 - \rho_2) + C.$$

This is the general equation of the surface of a liquid under the influence of gravity and surface tension. Unfortunately the measurement of both radii of curvature at a particular point is virtually impossible. When quantities that can be measured are placed in the equation approximations of the desired accuracy must be made.

Bashforth and Adams solution

The Bashforth and Adams approach to the solution of the above equation may be visualized by making use of Fig. 2. The figure is assumed to be a profile of a surface of revolution about the vertical axis. The radius of curvature in the plane of the paper at point P may be called p. The other principal radius of curvature at this point is PC or $x/\sin\theta$ since a normal to the surface intersects the axis of revolution at C. These radii may be substituted for R_1 and R_2 in the preceding equation. The value of the constant, C, may be determined by considering P as a point at the apex of the drop. At this point, z is zero, and all radii of curvature are equal. If this radius of curvature is called b, then C is equal to $2\sigma/b$. Substitution of these quantities gives

$$\sigma\left(\frac{1}{p}+\frac{\sin\theta}{x}\right)=gz\,(\rho_1-\rho_2)+\frac{2\sigma}{b}\,.$$

Bashforth and Adams simplified this relationship by introducing the term β that was defined as equal to $g(\rho_1-\rho_2)b^2/\sigma$. The quantity β is, in a certain way, a measure of the shape of the drop. Low values of β indicate a close approximation to a sphere, while high values of β indicate a flattening of the drop. The final relationship used by Bashforth and Adams is obtained by making this substitution, eliminating the σ terms, and multiplying through by b. The final form of the equation is thus:

5. $$\frac{1}{p/b}+\frac{\sin\theta}{x/b}=2+\frac{\beta z}{b}\,.$$

Bashforth and Adams solved this equation in terms of x/b, z/b, and β for various values of θ. The value of x/z was also tabulated versus β for an angle of 90°. Thus the values of x and z are obtained as coordinates of the point on the surface of the drop where the surface is precisely vertical. This point may be established by drawing a line perpendicular to the supporting surface so that it is tangent to the surface of the drop. The quantity x/z may be used to determine the value of β. With β, x, and z known, x/b and z/b are determined from the second table for the value of β and an angle of 90°. Since x and z are known the values of x/b and z/b establish b. The determination of b and β are all that are necessary to evaluate the surface tension of the liquid if the density of the liquid is known. The surface tension is established from the relationship defining β.

6. $$\sigma=\frac{g(\rho_1-\rho_2)\,b^2}{\beta}\,.$$

With the values of β and b determined it is a simple matter to determine the angle of contact between liquid and solid. The quantities X and Z as shown in Fig. 2 are measured as the coordinates of the point of contact of the liquid surface with the solid surface. These quantities are divided by the previously determined b to give x/b and z/b values. The values of x/b and z/b are examined for the particular β and various angles until an angle is found for which the listed values of x/b and z/b agree with the calculated values. This angle is the contact angle between the liquid surface and solid surface, ϕ.

Density Determination

Since the density of most metals is known over only a limited temperature range, a means of determining this value is necessary to permit the surface tension to be evaluated. Bashforth and Adams have also presented an equation for the volume of a surface of revolution in terms of the parameters of their tables.

7. $$V = \frac{\pi b^2 X^2}{\beta} \left(\frac{2}{b} - \frac{2 \sin \theta}{X} + \frac{\beta Z}{b^2} \right) .$$

In this equation; V is the volume of the drop, X and Z are the coordinates of the point of contact of the liquid surface with the solid surface, θ is the contact angle, and the other values are as before.

Work of Adhesion

The work of adhesion between a liquid in contact with a solid is quite simply the work required to remove the liquid from the solid. In making this separation two new surfaces are formed, and energy must be supplied to provide for the surface energies assumed by the exposed surfaces. The work of adhesion is, thus, equal to the sum of the surface tensions of the liquid and solid less the amount of the surface energy of the interface between the liquid and solid that was present before the separation. The Dupré equation for work of adhesion, W_{AD}, is

8. $$W_{AD} = \sigma LA + \sigma SA - \sigma SL.$$

The subscripts refer to the liquid-air, solid-air, and solid-liquid interfaces.

Unfortunately the determination of the surface tension of a solid is very difficult and of limited accuracy. (16) However, the work of adhesion of a liquid to a solid may be determined by making use of the angle of contact and the analagy of surface energies and simple tension forces. In the figure below the surface tension of the solid is opposed by the surface tension of the liquid and the interfacial tension of the surface between the liquid and the solid.

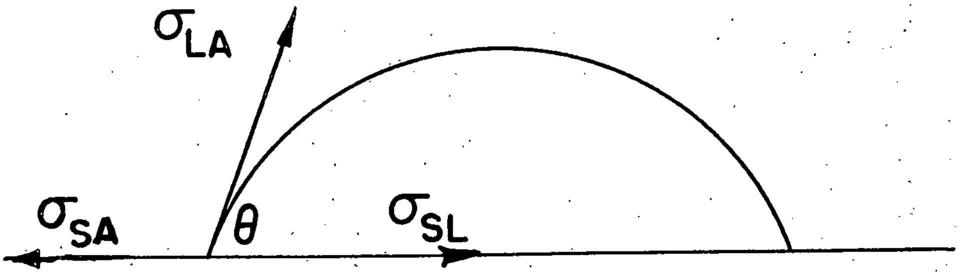


Fig. 3 Surface force diagram

Since the system is at equilibrium, the following equality must hold.

$$\sigma SA = \sigma SL + \sigma LA(\cos \theta).$$

Substitution of this relationship in the Dupré equation above gives

9. $$W_{AD} = \sigma LA(1 + \cos \theta).$$

APPARATUS

Vacuum System

Because of the extreme reactivity of the metals under study all operations were carried out under a vacuum. The low vapor pressures of cerium and lanthanum as reported by Ahman (2) and Daane (3) permit this procedure to be used. The vacuum system is composed of a 100 mm Pyrex glass tube. The schematic diagram of the furnace system in Fig. 4 shows how the tubing was combined. A tube leading to a diffusion vacuum pump is connected at right angles to the horizontal tube which houses the furnace assembly. At one end of the furnace tube a 103/60 glass joint was attached to permit placement of the electrical and thermocouple leads at that end of the assembly. The other end of the furnace housing tube was flanged and ground to a plane surface. In this way the vacuum system could be closed by simply placing a sheet of optically flat glass over the end. The glass sheet was held in place by friction under the force of atmospheric pressure. Three 18 mm tubes and two 10 mm tubes were connected above the right angle

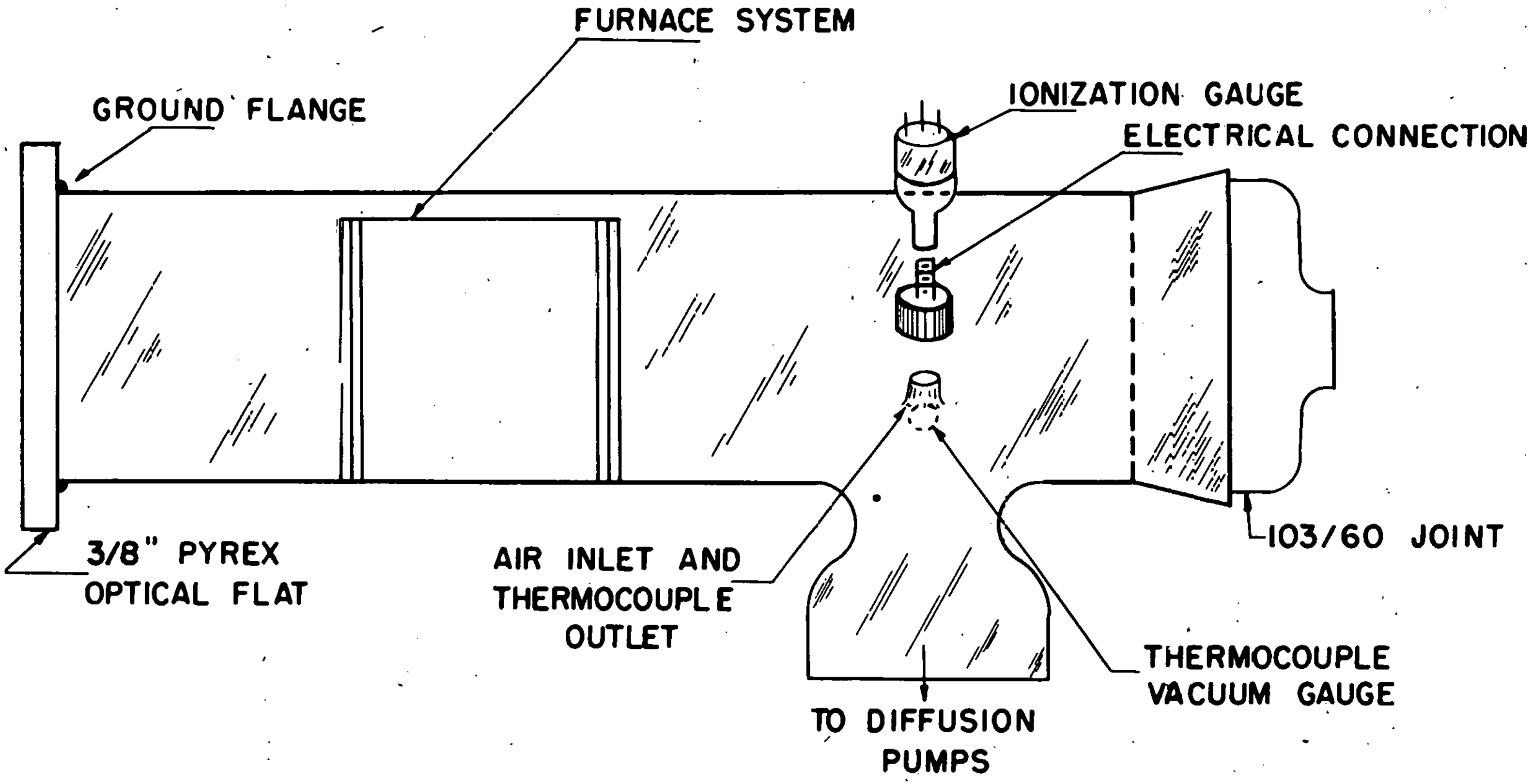


FIG. 4 VACUUM SYSTEM

connection on the horizontal tube for placement of the vacuum gauges, electrical and thermocouple leads, and an air inlet. The detail of the metal-to-glass vacuum seal for the connection of the electrical leads to the 18 mm tubing is shown below.

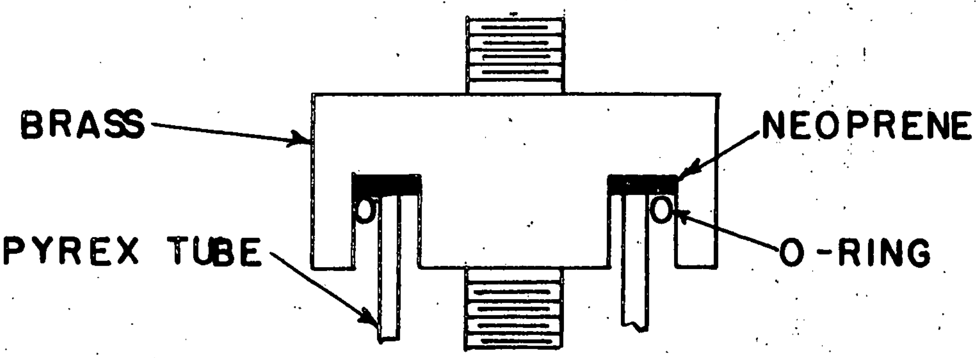


Fig. 5 Glass-metal vacuum seal

Vacuum was obtained using a VMF 260 Distillation Products Inc. diffusion pump in conjunction with a Welch mechanical vacuum pump. The ultimate rated vacuum of the diffusion pump was $1X10^{-6}$ mm Hg. with a pumping speed of 200 liters per second at $1X10^{-3}$ mm Hg. Pressures were determined using a National Research Corp. ionization-thermocouple gauge.

Furnace System

The heating element used in the furnace was 0.020 inch molybdenum wire placed lengthwise to the hot zone. A total of 48 four-inch sections provided sufficient resistance to allow attainment of the maximum operating temperature on a current of eight amperes. As can be seen in Fig. 6a the wire was supported horizontally by threading it through an alumina insulator. The washer shaped insulator had an outside diameter of two inches, and an inside diameter of one inch. The thickness of the alumina insulator was 3/16 inch. The insulators were held apart by a molybdenum cylinder that also acted as a radiation shield. A one inch diameter cylinder of 0.010 inch molybdenum was placed on the inside diameter of the alumina insulator to serve as a support for the specimens.

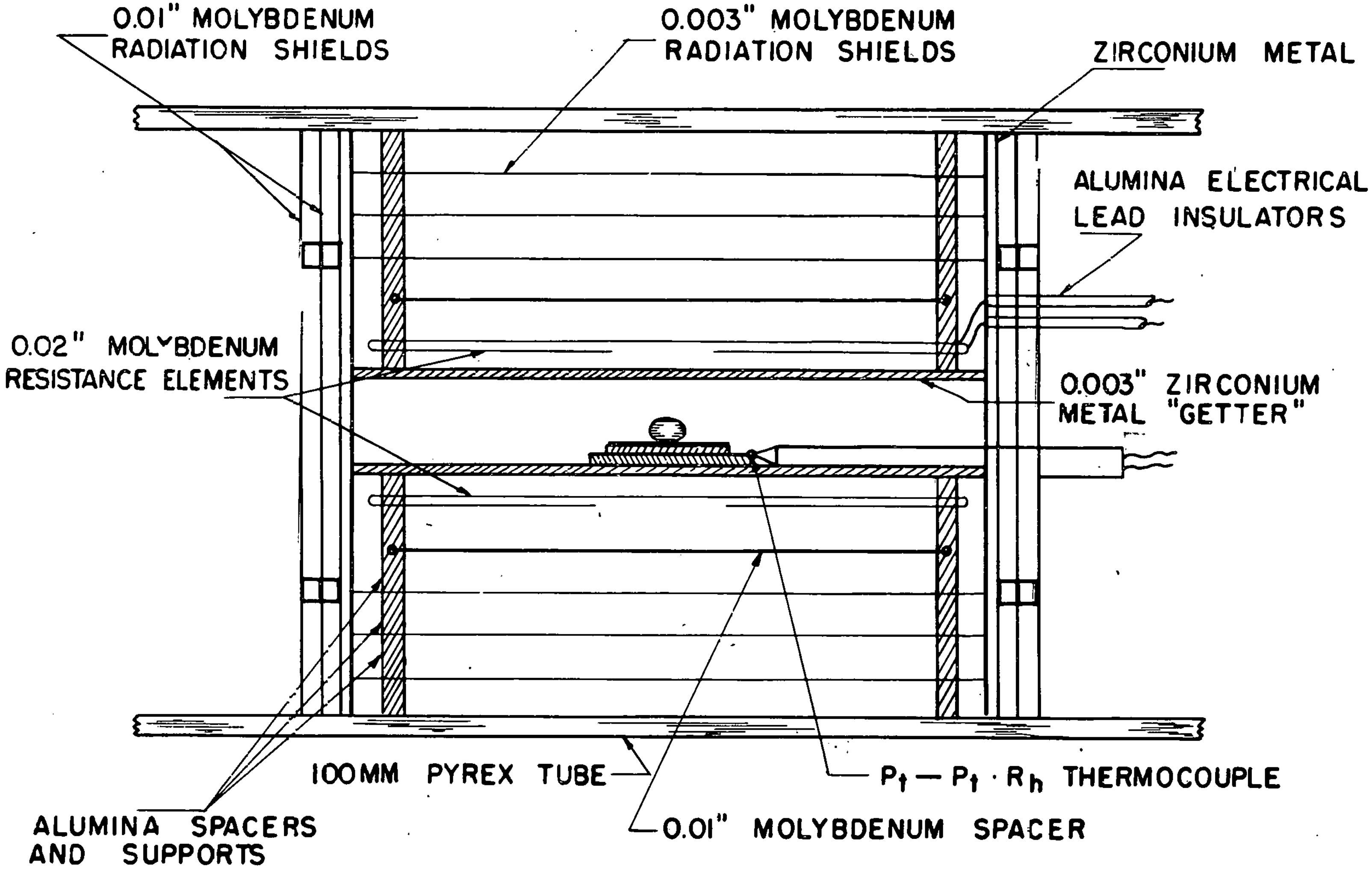


FIG. 6a. FURNACE SYSTEM

The entire assembly described above was placed horizontally inside four concentric cylinders of 0.003 inch molybdenum which were separated by 3/16 inch alumina rings. The four cylinders provided excellent insulation from thermal radiation. To decrease further the heat loss from radiation, 0.010 inch disks of zirconium and molybdenum were placed at the ends of the furnace hot zone.

The hot zone of the furnace was entirely surrounded by zirconium metal. This addition was made after it was shown that the most careful control of the furnace pressure did not eliminate completely the formation of an oxide film on the molten metal. It was decided that the excellent scavenging powers of zirconium metal would be more fruitfully utilized than an attempt to improve the vacuum over that already attainable. According to McPherson and Hansen (17) no liquid is formed between zirconium and molybdenum until a temperature of approximately 1500°C is reached. Since this was well above the maximum temperature to be realized in this study, zirconium metal was placed inside the support cylinder. The zirconium cylinder could not be used as the specimen support because of its low strength at high temperatures. Zirconium disks were also placed at the ends of the furnace, and thus the specimen to be heated was entirely surrounded by zirconium metal.

The complete assembly of the furnace and vacuum system is shown in the photograph of Fig. 6b. The figure shows that the furnace and vacuum system were mounted on an angle iron table equipped with three screw adjusting supports. The adjustable supports permitted easy leveling of the specimens to be fired from the outside of the furnace.

The power to the furnace was supplied from a 110 volt power line to a 216 Powerstat voltage transformer. The transformer allowed the voltage to be varied from zero to 135 volts. With this power control arrangement it was possible to control the temperature of the furnace to within 5°C of the desired temperature.

The temperature of the furnace was measured using a platinum-platinum 10% rhodium thermocouple placed adjacent to the specimens. The temperature measured with the thermocouple was compared with a previously calibrated optical pyrometer and with the melting points of the metals. It was found necessary to apply a plus 20°C correction to the temperature obtained from the thermocouple.

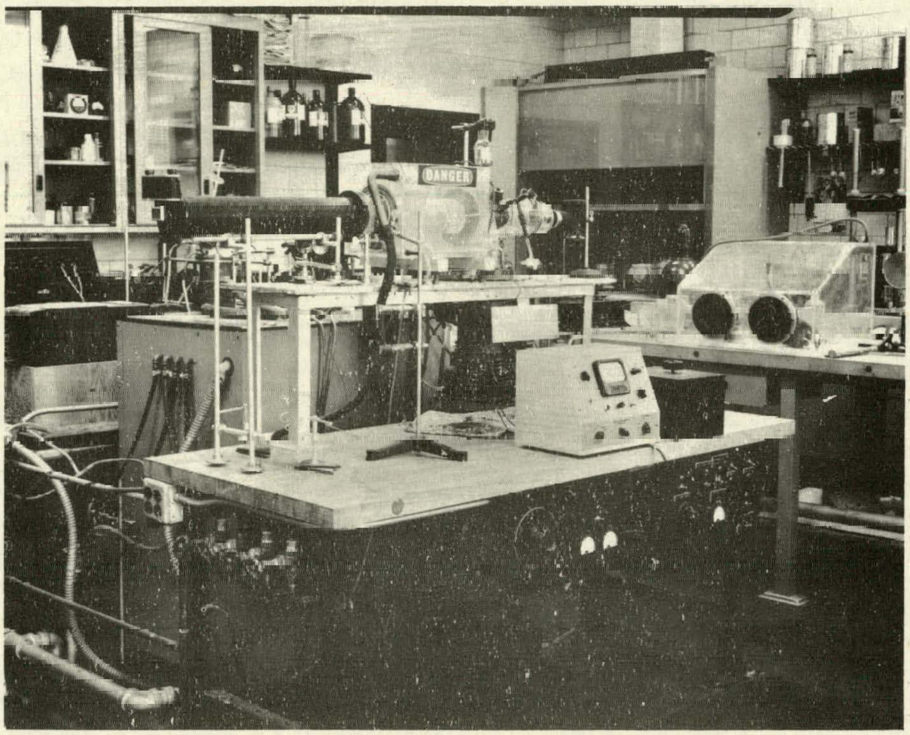


Figure 6b

Optical Equipment

The profiles of the sessile drops used in the determination of the surface tension were recorded at the given temperature with a 35 mm camera. The camera used was built to give a fixed image distance that resulted in a magnification of approximately two diameters. The lens and film adapter systems were mounted on an aluminum cylinder of five inches in diameter and 20 inches in length. The lens and shutter system was a Kodak Ekter Lens with a focal length of 203 mm and a maximum aperture of f/7.7. The fastest opening of the shutter was 1/400 second. The film adapter used was Kodak's 35 mm Film Adapter A equipped with a ground glass focusing screen.

The negatives of the photographs taken with the 35 mm camera were enlarged on 4 x 5 inch sheet film to approximately ten times the original diameter using a Simmon Bros., Inc. enlarger. The lens of the enlarger had a focal length of 135 mm and a maximum aperture of f/4.5. Measurement of the profiles was taken directly from the enlarged negatives using a Gaertner Scientific Corp. traveling microscope accurate to 0.001 mm.

The examination of the penetration of the metals into the ceramic materials was accomplished using a Leitz petrographic microscope with a back reflecting arrangement. A Leitz camera was adapted to the microscope and was used to obtain photomicrographs of the specimens.

Inert Atmosphere Equipment

As a further precaution against the formation of an oxide film on the metal, a helium purification train was built to permit flushing the furnace with helium before and after the metals were heated in a run. The helium was made to flow through 12 inches of glass wool, three tiers of P_2O_5, a dry ice-acetone cold trap, and ten inches of calcium metal turnings heated to 700°C. The purified helium was also used with a dry box in the preparation of the x-ray specimens.

X-ray Equipment

Both North American Phillips and General Electric x-ray machines were used in the x-ray determination of the reaction products. In both cases a copper target was used in conjunction with a nickel filter. Powder diffraction cameras of 57.3 and 114.6 mm diameters were both used in this work.

Firing and Polishing Equipment

The specimens of the refractory oxides to be used in the surface tension measurements were prepared by pressing the powders in a hardened steel mold with a hydraulic press capable of loads of 20,000 pounds. A molybdenum vacuum resistance furnace of the type described by McRitchie and Ault (18) was used to fire the pressed specimens.

Buehler, Ltd. lap wheels were used to polish the surface of the refractory oxide specimens. The oxides were first ground flat using 240 mesh silicon carbide powders, and then further ground with 400 and 600 mesh powders. The final polishing was done on a cloth lap wheel impregnated with six-micron diamond paste.

PROCEDURE

Surface Tension Determination

Preparation of ceramic specimens

The refractory oxides used in the surface tension determination were chemically pure materials with the exception of zirconium oxide. The analysis of the impurities of the four oxides is given in Table 1. The materials as received were approximately 44 microns in particle size. Because of the extememely high fusion point of the materials, however, a very fine particle size was necessary to produce specimens of low porosity. For this reason the materials were given a further treatment to reduce the particle size. The reduction in size was produced by ballmilling the oxides in a steel ball mill for various lengths of time. The procedure used was that outlined by Norton (19). The alumina powder was ballmilled for 24 hours, and the beryllia, thoria, and zirconia powders were ballmilled for periods of 24, 61, and 14 hours respectively.

At the end of these periods the ballmilled powders were washed into beakers with distilled water. Approximately 100 grams of oxide was added to 125 ml of concentrated hydrochloric acid and sufficient water to provide 1000 ml of slip. The reaction of hydrochloric acid with the iron contamination from the ball mill produced iron chloride. The volatile ferrous chloride was removed from the slip by bubbling air through the liquid. After two or three hours of bubbling air through the slip, the suspension was allowed to settle, and the supernatent liquid decanted. More water and hydrochloric acid were added to the slip, and the procedure continued until the supernatent liquid showed no test for iron. The purified material was then dried.

Table 1. Analysis of Minor Constituents

Material	Impurities in Per Cent						
	Al_2O_3	BeO	CaO	Fe_2O_3	MgO	MnO_2	SiO_2
Chemically Pure Alumina*		<0.007	<0.004	0.008-0.30	<0.004		<0.006
Chemically Pure Beryllia*	0.007-0.34		<0.003	<0.003	<0.003		<0.004
Chemically Pure Thoria*	0.025		0.005	0.006	0.004	0.003	0.009
Norton Co. 36 F Stabilized Zirconia	Approximately 95% ZrO_2 and HfO_2.						
Cerium and Lanthanum	Less than 0.50% Ca, Mg, and other rare earth metals.						

*Spectrographic Analysis.

The material in the fine state produced by the ballmilling was then ready for forming by pressing in a hardened steel mold. However, in order to improve the green strength of specimens and to aid in the release from the mold, a binder material was added to the refractory oxides. Carbowax 4000 was added to Al_2O_3 and ZrO_2 in amounts of 1.5% by weight and to BeO and ThO_2 in amounts of 2.5% by weight. The Carbowax was added as a solution in water containing 0.1 gm per cc.

The refractory oxide mixture containing the binder was then granulated through a 20 mesh screen for the final treatment before dry pressing. A sufficient amount of mixture was then weighed out to permit a specimen of 3/16 inch thickness to be formed. This quantity was placed in a hardened steel mold of 3/4 inch diameter and pressed to a pressure of 10,000 psi for Al_2O_3 and a pressure of 5,000 psi for the remaining oxides.

After pressing, the oxide plaques were placed in a globar kiln and heated slowly to 350°C. The furnace was held at this temperature for several hours until the distinctive odor of Carbowax could no longer be detected leaving the furnace. The furnace temperature was then raised to 1000°C.

The specimens were then placed in a molybdenum cylinder resistance furnace and heated in vacuo. The alumina specimens were heated to 1800°C and soaked at that temperature for a period of 30 minutes. The remaining oxides were heated to 1850°C with a 30 minute soaking treatment.

After the firing treatment the refractory oxides were imbedded in wax and ground to a flat surface using a 240 mesh silicon carbide cloth lap wheel. Second and third stage grinding consisted of treatments on 400 and 600 mesh silicon carbide cloth wheels. The oxide plaques were then in the proper condition so that the final polishing on a diamond impregnated lap wheel could be accomplished. The polishing operation was terminated when examination with a microscope indicated that the surface was smooth. The length of time necessary to prepare the final specimen varied considerably with the material polished. Stabilized zirconia and alumina polished quite readily, while beryllia required several hours.

Following the polishing operation the wax was removed from the plaques with acetone. Previous to their use in the surface tension determination, the plaques were placed in a vacuum resistance furnace and outgassed at the maximum temperature of use until a vacuum of 1×10^{-5} mm Hg was attained. The plaques were left under a vacuum until a surface tension run was made.

Firing surface tension samples

Since the metals studied are very reactive the usual chemical cleaning of the surface could not be used. Instead, approximately 5 mm cubes of the metals were cut and the surface made clean by filing with a fine file. The edges and corners of the cubes were rounded to permit the metals to assume more readily a shape approaching the spherical. The cubes were then quickly weighed using a chain type analytical balance. The weight permitted determination of the density at the temperatures of measurement. After weighing, the specimens were placed in an inert atmosphere until they could be placed in the furnace.

A stream of helium was caused to flow through the furnace as the metal cubes were placed on the refractory plaques. The level of the furnace along its horizontal axis remained constant, so it was not necessary to check the furnace before every run. The level of the axis of the furnace was checked periodically, however, and the level position was found to be retained. The screw adjusters on the legs of the table supporting the entire furnace system permitted rapid leveling of the specimens in the plane perpendicular to the axis of the furnace. By casting an image of the specimen on the ground glass screen of the camera, the leveling was accomplished after the vacuum system was closed.

After placement of the specimens in the furnace the vacuum pumps were turned on, and in 45 minutes the pressure in the furnace had reached a value of 5×10^{-6} mm Hg. Helium was then admitted to the system to a pressure of five microns of Hg. and then pumped out. This procedure was repeated three or four times and the surface tension run was then ready to begin.

It was found that to prevent a film of oxide from being formed on the metal the pressure could not be permitted to rise above a value of 1×10^{-4} mm Hg. The temperature of the furnace was, therefore, slowly raised to a temperature of 600°C. After this temperature was reached the specimen was heated more rapidly to the measurement temperature.

When the melting point of the metal had been reached, a photograph was taken of the drop as soon as it had assumed what appeared to be a symmetrical shape. Five minutes later another photograph was taken and this was continued at subsequent five minute intervals until one-half hour had elapsed. Equilibrium was actually established much earlier than this, but a determination of the effect of time on the values measured was also desired. As a further check on equilibrium time, certain runs were held at a constant temperature for two and three hours. A barely discernable change in the value of surface tension occurred in these time periods, but it was not outside the experimental error of the method. The time of one-half hour was, therefore, used in the remainder of the determinations.

At the end of one-half hour at the melting point of the metal the temperature of the furnace was raised to the next temperature. Photographs were thus taken at five minute intervals to one-half hour at temperatures of 810, 900, and 1000°C for cerium metal. The process was repeated for lanthanum at temperatures of 950, 1000, 1100, and 1200°C. At the completion of the one-half hour interval at the final temperature, the furnace was allowed to cool under five microns of helium. When the furnace had cooled to room temperature, the specimens were removed and placed under a vacuum desiccator.

The photographs were taken using background illumination. At temperatures of 1000°C or less an exposure time of 1/200 second could be used with the Kodak Plus-X film used. At 1100°C a photograph could be obtained by using background illumination or by utilizing the light emitted from the drop itself. Exposures utilizing emitted light ranged in time from 1/25 second at 1100°C to 1/50 second at 1200°C.

Enlargement and measurement

The magnification of the camera itself was 1.9 diameters. However, to improve the accuracy of measurement a larger magnification was required. Enlargement of the photographs on print paper was prohibited by the differential shrinkage of print paper. The photographs were, therefore, enlarged on Kodak Process Ortho 4 x 5 inch sheet film. The precise enlargement of the photographs was determined from a photograph of a 0.2538 inch ball bearing. An enlargement of this photograph was made with each series of enlargements of the sessile drops. In this manner the exact magnification of the drops, which varied slightly from run to run, was determined for each run. The measurements were taken directly from the enlarged negative.

The final photographs were prepared for measurement by placing them on a background of graph paper. The graph paper served as a convenient aid for aligning the cross hairs of the traveling microscope since only a portion of the entire drop could be contained in the field of the microscope. The characteristic dimensions measured from the photographs were those shown in Fig. 2. These dimensions were measured to four significant figures with the traveling microscope. Typical calculations of surface tension, density, contact angle, and work of adhesion are given in Appendix A.

The value of x, X and Z could be obtained quite easily from the drop profile. The vertical distance from the apex of the drop to the point on the drop where the surface is precisely vertical is more difficult to measure. Rather than establishing the point of vertical surface by aligning the vertical cross hair of the miscroscope tangent to the surface of the drop, the cross hair was aligned so that it cut a chord into the drop surface one or two tenths of a millimeter in depth. The measurements of z from the apex of the drop to the center of this chord gave consistently better values than those which were measured to the point of tangency of a vertical line.

The values for density and surface tension were obtained using curves of the tabled parameters of Bashforth and Adams as described in Appendix A. Contact angles greater than 90° were also calculated from the curves made from the tables of Bashforth and Adams. Angles less than 90° were measured with a goniometer.

X-ray Determination of Reaction

In this part of the study the metal powders of cerium and lanthanum were mixed with powders of the oxides and heated to 300°C below their melting point and to their melting point. Because of their rapid attack by oxygen even at room temperatures, the metal powders were obtained by filing the massive metal with a fine file in a dry box under an inert atmosphere. Any iron contamination that may have been introduced in this operation was removed with a strong magnet. The powder mixtures were then weighed out on the basis of equal volume of metal and oxide. The mixed powders of oxide and metal were placed in crucibles in the form of loose compacts, since it was felt that to press the materials might introduce some oxide reaction from handling in air. The crucibles in which the powders were placed were composed of the same oxide as that being reacted with the metal.

The powders were slowly heated in the furnace until a temperature 300°C below the melting point was reached. The furnace was then held at this temperature for a period of one-half hour. As in the case of the surface tension determination, the pressure of the furnace was maintained at less than 1×10^{-4} mm Hg at all times. The furnace was also flushed in the manner described in the surface tension determination.

Upon completion of the run, a helium atmosphere was admitted to the furnace and the specimens removed. The mixtures were then kept under a vacuum in a desiccator until an x-ray analysis was run. The x-ray method used was a powder diffraction analysis using a cylindrical camera and the Straumanis technique. The compact from the furnace was ground under a helium atmosphere in an alumina mortar until all passed a 200 mesh screen. The powder was then tamped into a fine glass capillary and loaded into the center of the x-ray camera. Both ends of the glass capillary were well sealed with wax to prevent oxidation during the exposure to the x-rays. The x-ray beam used in the analysis was the K peak from a copper target filtered through a nickel filter. The compounds formed in the reaction were identified using the d spacings and intensity patterns given by the ASTM Index of Diffraction Data (20).

Microscopic Examination of Reaction

The specimens used in this phase of the work were those obtained from the surface tension determination. A cross section of the metal resting on the ceramic was prepared by cutting through the specimen with a silicon carbide cut-off wheel. This cut was imbedded in Bakelite and the surface ground using 400 and 600 mesh silicon carbide powders. The final polish was achieved on a cloth lap wheel impregnated with 6 micron size diamond paste. When the microscope revealed a smooth surface the penetration of the metal into the ceramic was studied using back reflected light. Photomicrographs were taken of the interface between the metal and ceramic. These photographs are shown in Fig. 12, 13, 14, and 15.

RESULTS

Surface Tension and Wetting Characteristics

Lanthanum

The results of the surface tension, contact angle, and work of adhesion determinations are shown in Fig. 7 to 11 and in Tables 2 to 8. The surface tension of lanthanum could only be determined in contact with zirconium oxide. The Bashforth and Adams technique for determining surface tension can be applied with reasonable accuracy only when the angle of contact between metal and solid is greater than 90°. Since the oxides of aluminum, beryllium, and thorium exhibited angles of contact less than 90°, these materials could not be used to obtain a value of surface tension.

The value of surface tension determined for lanthanum metal at 950°C was 710 dyne/cm. This value was determined using a density value of 5.88 g/cc. The determination of the density of the metal is subject to the same errors as the quantity b^2/β. Since both factors are necessary to establish the surface tension of the liquid, the values of density and b^2/β are both listed in the tables along with the surface tension. When the high temperature densities of the metals are established more reliably, the value of b^2/β may be used to give a more accurate value of surface tension.

In all, four runs were made on zirconium oxide, but only two were used in fixing the value of surface tension. One run was discarded because a portion of the surface of the drop had become contaminated with an oxide film. The second discarded run had assumed a non-symmetrical shape. However, within a given run at a particular temperature, the values obtained were generally within 3% of the average value when a confidence limit based on a 90% significance level was applied. Since the values of the two runs were within this range no further runs were made. Using the deviations from the averages of density and b^2/β for the case of lanthanum on zirconia at 950°C the precision of the experiment was determined to be ± 16 dyne/cm. On a statistical basis, however, this value would have to be multiplied by approximately 6.0, the value of Student's t for one degree of freedom. The results of the runs, however, indicate the reported accuracy of $\pm 5\%$ is probably correct.

As the temperature of measurement was increased from 950 to 1200°C, the value of surface tension falls off in a straight line from 710 to 630 dyne/cm. This change of surface tension with temperature is shown in Fig. 7 and Table 2. The rate of change of surface tension with temperature was calculated to be -0.27 dyne/cm/°C over the temperature range studied. For most metals the general order of magnitude for this rate of change is -0.1 dyne/cm/°C. The value obtained for lanthanum is, therefore, high. As will be seen from the results on cerium, however, the rate of change with temperature is dependent to a certain extent on the plaque material upon which the determination is being made.

The change of contact angle with temperature is shown in Fig. 8 and Table 3. At 950°C zirconia was least wetted by lanthanum. At this temperature the contact angle of lanthanum on zirconia was 144°. Alumina had a contact angle of 133° at 950°C, and beryllia showed values ranging from 100 to 120° at this temperature. The angle displayed by thoria at 950°C was 66°. The existence of interfacial reactions prohibits determination of the actual value of the interfacial energies between the metal and oxide, but these values do give a measure of the work of adhesion for the particular system.

As the temperature of the furnace was raised to 1000°C, the contact angle of lanthanum on alumina changed abruptly to a value of 81°. This was attributed to the formation of an alloy between aluminum and lanthanum. This alloy was formed from the reduction of alumina to aluminum metal by lanthanum. Further raising the temperature caused the formation of a more aluminum rich alloy that increased the contact angle slightly. It was found by Kingery (16) that adding small amounts of silicon to iron changed the contact angle by approximately 20%, although the surface tension of the iron changed only slightly.

The contact angle of lanthanum on beryllia was 90° at 1000°C. At 1200°C the contact angle had decreased in a linear fashion to 71°. This reduction in contact angle was not due to alloy formation or solid solution formation between lanthanum and beryllia. Since the surface tension of the metal and the solid changes slightly with temperature, the decrease in contact angle could be attributed to either the decrease in the surface energy of the liquid, or to a decrease in the interfacial energy of the surface between metal and solid.

Table 2. Surface Tension of Lanthanum on Zirconium Oxide

Temperature	Density		b^2/β		Surface Tension	
Degree Centigrade	gm/cc		cm^2		Dyne/cm	
	Run		Run		Run	
	I	II	I	II	I	II
950	5.818	5.924	0.1342	0.1263	773	728
			0.1174	0.1255	676	723
			0.1273	0.1252	734	722
			0.1221	0.1240	704	714
			0.1154	0.1226	665	706
			0.1128	0.1263	650	728
					700	720
Average	5.876				710	
1000	5.724	5.812	0.1253	0.1210	709	685
			0.1205	0.1231	662	697
			0.1144	0.1270	643	720
			0.1221	0.1262	692	715
				0.1218		690
				0.1254		710
					683	703
Average	5.776				693	
1100	5.630		0.1150	0.1183	635	652
			0.1202	0.1198	663	661
			0.1162	0.1196	641	660
				0.1159		640
				0.1144		631
					646	649
Average	5.630				648	
1200	5.486		0.1124		615	
			0.1117		612	
			0.1151		630	
			0.1178		646	
			0.1180		646	
Average	5.486				630	

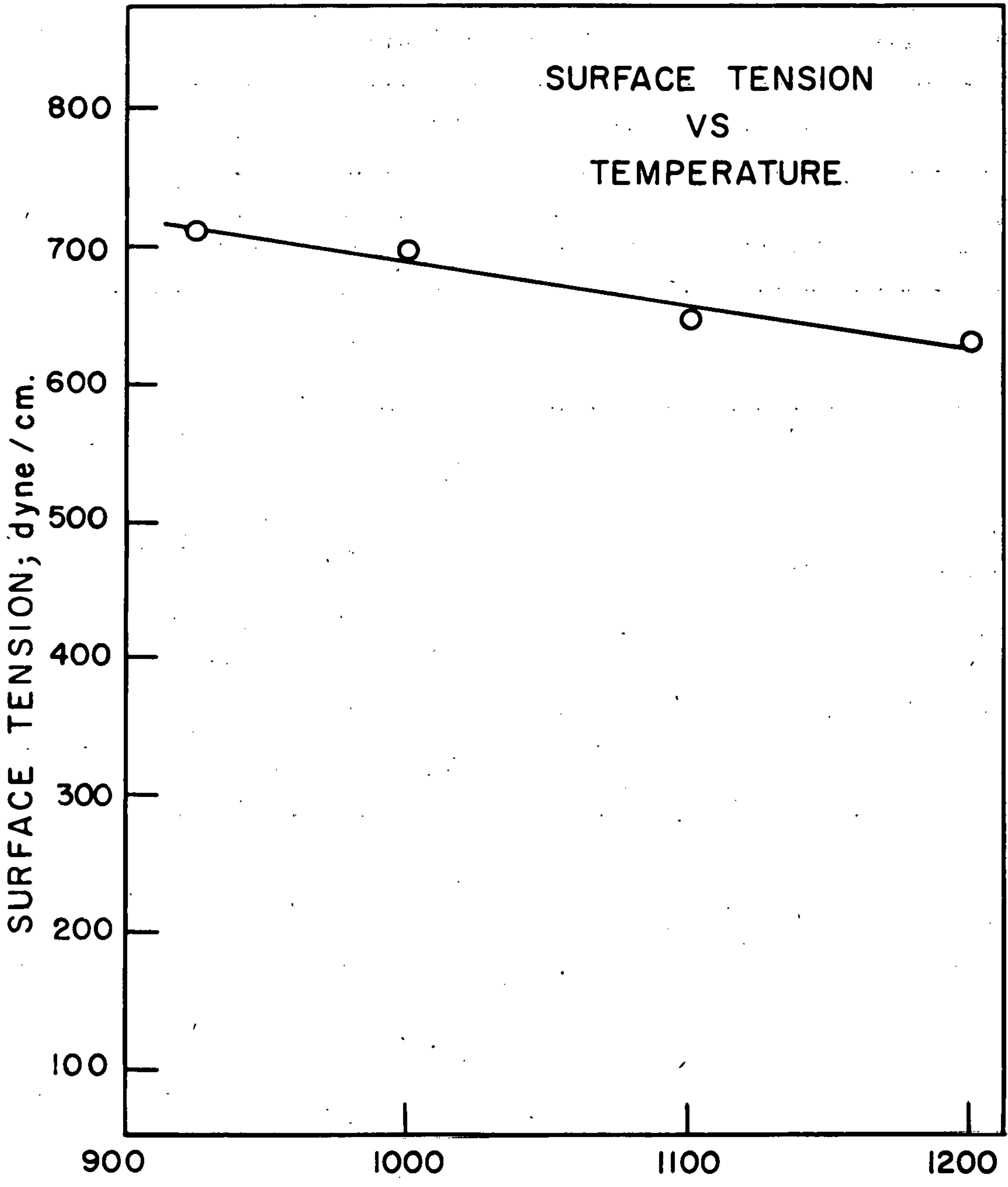


FIG. 7 LANTHANUM ON ZIRCONIUM OXIDE

Table 3. Contact Angle of Lanthanum with the Oxides

Temperature	Refractory Guide							
	Alumina		Beryllia		Thoria		Zirconia	
Degree Centigrade	Angle in degrees		Angle in degrees		Anglo in degrees		Angle in degrees	
	Run I	Run II	Run I	Run II	Run I	Run II	Run I	Run II
950	133				69	63	141	147
Average	133				66		144	
1000	80	81	90	90	64	55	130	146
Average	81		90		59		138	
1100	82	82	85	76	52	52	129	141
Average	82		80		52		135	
1200	84	82	71	70	46	40	128	
Average	83		71		43		128	

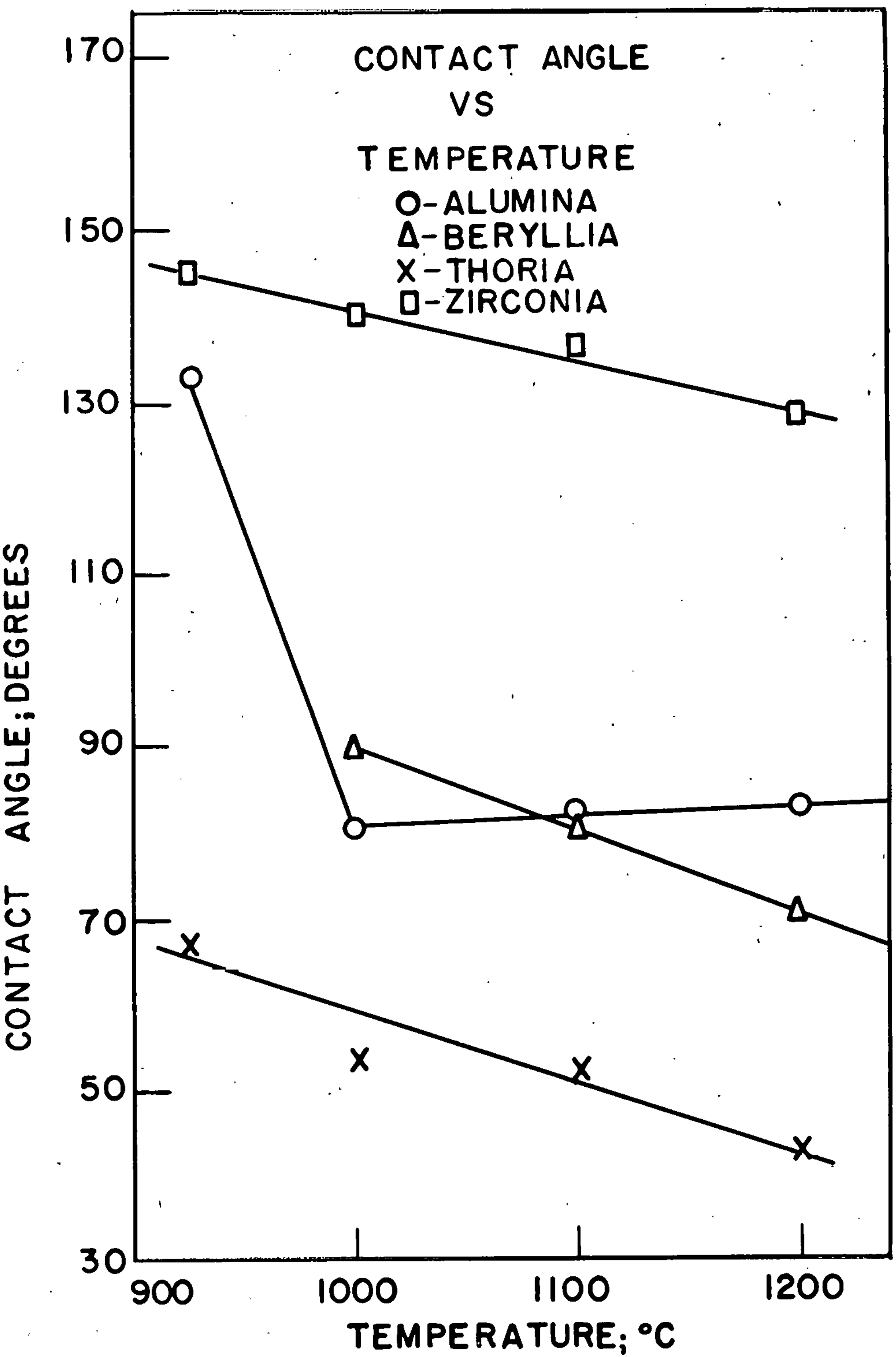


FIG. 8 LANTHANUM CONTACT ANGLES

The contact angle of lanthanum on thoria was the lowest of all the oxides. The angle of contact ranged from the value at 950°C of 66° to a value of 43° at 1200°C. In this oxide the wetting was aided by the diffusion of the metal into the plaque. The contact angle was, thus, not strictly that of the metal against the pure oxide, but, rather, that of the metal against a limited solid solution of metal and oxide. The low contact angle was that which would be expected from such a system.

The contact angle of lanthanum on zirconia decreased from a value of 144° at 950°C to a value of 128° at a temperature of 1200°C. In this case as with thoria there occurred a slight diffusion of the metal into the ceramic. In this particular case, however, a low angle did not result.

The work of adhesion of lanthanum on the oxides at the various temperatures is shown in Table 4. The work of adhesion of lanthanum on thoria was the highest of all the oxides. The values of the work of adhesion on this oxide ranged from 997 to 1090 dyne/cm. The values found for the adhesion to beryllia ranged from 695 dyne/cm at 1000°C to 840 dyne/cm at 1200°C. As was indicated by the high contact angle, the work of adhesion of lanthanum on zirconia was the lowest of all the oxides. At 950°C the work of adhesion to zirconia was 133 dyne/cm. At 1200°C, however, the value had increased to 242 dyne/cm. Only the work of adhesion on alumina approached that of zirconia, and this was found only at a temperature of 950°C. The value of 233 dyne/cm found at this temperature had increased by more than threefold as the temperature was raised to 1000°C. This abrupt change was attributed earlier to the formation of an alloy of aluminum and lanthanum.

Table 4

Work of Adhesion of Lanthanum on the Oxides

Temperature	Refractory Oxide			
	Alumina	Beryllia	Thoria	Zirconia
Degree Centigrade	Dyne/cm	Dyne/cm	Dyne/cm	Dyne/cm
950	233		997	133
1000	808	695	1050	167
1100	734	753	1040	182
1200	707	840	1090	242

The value found for the work of adhesion of lanthanum on the various oxides were obtained by using Equation 8. In using this equation the surface tension calculated for lanthanum melted on zirconia was used for all oxides. The work of adhesion of all the oxides except alumina went through a slight linear increase with temperature. This would indicate that the interfacial energies were decreasing at a rate faster than the decrease in the energies of the solid and liquid. The rate of increase in the work of adhesion of lanthanum on zirconia and thoria was approximately 0.4 dyne/cm/°C. The rate of increase of the work of adhesion of lanthanum on beryllia was 0.72 dyne/cm/°C. The rate of decrease of the interfacial energies may be obtained from differentiation of the Dupre equation.

$$W_{AD} = \sigma_{LA} + \sigma_{Sa} - \sigma_{SL},$$

or

$$\frac{dW_{AD}}{dT} = \frac{d\sigma_{LA}}{dT} + \frac{d\sigma_{SA}}{dT} - \frac{d\sigma_{SL}}{dT}.$$

The rate of change of the liquid-air surface energy with temperature was -0.27 dyne/cm/°C. The change of work of adhesion with temperature was + 0.4 dyne/cm/°C. A value of -0.1 dyne/cm/°C may be assumed for the rate of change of the solid surface energy. From this, the rate of change of the interfacial energy of the surface between lanthanum and zirconia is equal to - (0.4 + 0.27 + 0.1) dyne/cm/°C, or - 0.77 dyne/cm/°C. Though, of course, the above value is only of the correct order of magnitude, the calculation serves to show that the interfacial energy is decreasing at a rate of 0.4 dyne/cm faster than the algebraic sum of the decrease of the liquid-air and solid-air surfaces.

Cerium

The surface tension of cerium was determined on beryllia and zirconia. The reaction of cerium with alumina was so pronounced that no reasonable value of contact angle could be established, nor could a determination of the surface tension be completed. Thoria could not be used to establish the value of the surface tension of cerium due to a zero contact angle. Upon melting on thoria the metal completely diffused into the plaque forming an oxygen deficient solid solution.

The density used in determining the surface tension at 900 and 1000°C was that value obtained from the metal melted on beryllia. At 810° the density values from the runs on zirconia were 6.66 and 6.71 gm/cc. Two beryllia runs at this temperature gave density values of 6.74 and 6.66 gm/cc. The combined average of the four runs at 810°C was 6.70 gm/cc. As the temperature was raised above the melting point, however, the density obtained from the zirconia determinations was in error due to the diffusion of the metal into the plaque. This caused the measured volume of the drop to be reduced. Since the density was determined using the weight of the metal before firing, this decrease in measured volume gave a high value to the calculated density. The metal did not diffuse into the beryllia, and, therefore, the density obtained in the beryllia determination was considered to be a more accurate value.

The surface tension of cerium melted on zirconia was 695 dyne/cm at 810°C. The surface tension decreased in a linear manner as the temperature was raised. The surface tension took on a value of 680 dyne/cm at 900°C and a value of 666 dyne/cm at 1000°C. The surface tension of the metal melted on beryllia plaques decreased in a similar manner. In going through the same temperature range as the runs on zirconia the surface tension of the samples melted on beryllia assumed values of 740, 697, and 678 dyne/cm.

The rate of change with temperature of the surface tension of cerium melted on zirconia and beryllia is shown in Fig. 9 and 10 and in Tables 5 and 6. The slope of the surface tension-temperature curve for the runs on beryllia was -0.25 dyne/cm/°C. The rate of change with temperature for the determinations obtained in the zirconia runs was -0.14 dyne/cm/°C. As with lanthanum these values are higher than the more usual value of approximately -0.1 dyne/cm/°C found with most metals. It is difficult to conceive a theoretical basis for the difference in this property between the two plaque materials. The difference found between the surface tension measured on the two materials is also without fundamental basis. One can only assume the difference to be due to slight impurities introduced from the plaque material, or that the difference is experimental error. In this latter respect, it is interesting to note that the surface tension determined at 810°C varied by an amount equal to 45 dyne/cm between the two supporting plaque materials. As the temperature reached 1000°C, however, the difference between the surface tensions of the two determinations had become well within the experimental error. The surface tension of cerium obtained by melting on the two plaques was 678 and 666 dyne/cm at this temperature.

The contact angle between cerium metal and the oxides is shown with its variation with temperature in Fig. 11 and Table 7. Cerium exhibited a very high contact angle with both beryllia and zirconia. The contact angle on beryllia was 152° at 810°C and it decreased only slightly at 900°C to 149°C. At 1000°C the contact angle on beryllia decreased more abruptly to 129°. The contact angle of cerium on zirconia went through a slight maximum as the temperature was raised to 1000°. As the temperature was raised from 810 to 900 and 1000°C, the contact angle took on values of 162°, 166°, and 165°, respectively. It should be pointed out that this

Table 5. Surface Tension of Cerium on Zirconium Oxide

Temperature	Density		b^2/β		Surface tension	
Degrees Contigrade	gm/cc		cm^2		Dyne/cm	
	Run		Run		Run	
	I	II	I	II	I	II
810	6.657	6.708	0.1146	0.1119	752	735
	6.740	6.665	0.1071	0.1075	703	706
			0.1053	0.1095	691	719
			0.1052	0.1018	691	668
			0.1037	0.1094	681	718
			0.1062	0.1022	697	671
					693	696
Average	6.696				695	
900	6.611	6.613	0.0982	0.1021	636	662
			0.1028	0.1005	666	652
			0.1029	0.1008	667	654
			0.1065	0.1041	690	675
			0.1129	0.1131	732	733
			0.1075	0.1088	697	705
					681	680
Average	6.612				680	
1000	6.250		0.1136	0.1049	699	643
			0.1088	0.1063	667	652
			0.1163	0.1030	712	631
			0.1025	0.1146	628	702
			0.1098	0.1063	673	652
				0.1097		672
				0.1098		673
					672	661
Average	6.250				666	

Table 6. Surface Tension of Cerium on Beryllium Oxide

Temperature	Density		b^2/β		Surface Tension	
Degree Centigrade	gm/cc		cm^2		Dyne/cm	
	Run		Run		Run	
	I	II	I	II	I	II
810	6.657	6.708	0.1212	0.1121	795	736
	6.750	6.665	0.1127	0.1098	740	721
			0.1142	0.1127	750	740
			0.1126	0.1161	739	762
			0.1115	0.1177	732	773
			0.1099	0.1128	722	740
			0.1099	0.1167	722	766
			0.1086		713	
					731	748
Average	6.696				740	
900	6.611	6.613	0.1065	0.1091	690	707
			0.1055	0.1082	684	701
			0.1065	0.1118	690	725
			0.1090	0.1085	707	703
			0.1055	0.1062	684	689
			0.1054	0.1092	683	708
			0.1042	0.1098	675	712
					688	706
Average	6.612				697	
1000		6.250		0.1133		694
				0.1093		670
				0.1094		670
				0.1108		679
				0.1095		671
				0.1126		690
				0.1095		671
						678
Average	6.250				678	

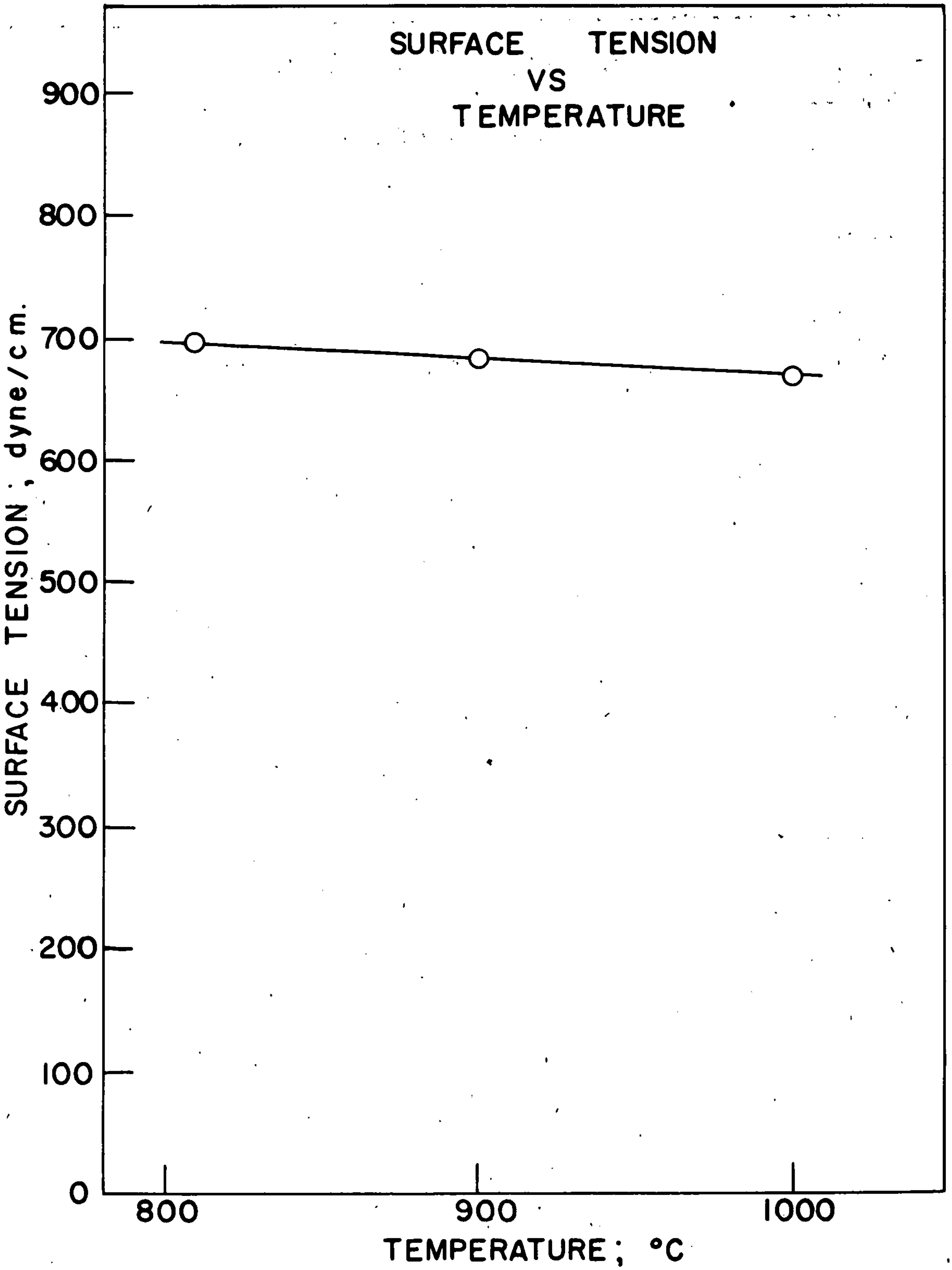


FIG. 9 CERIUM ON ZIRCONIUM OXIDE

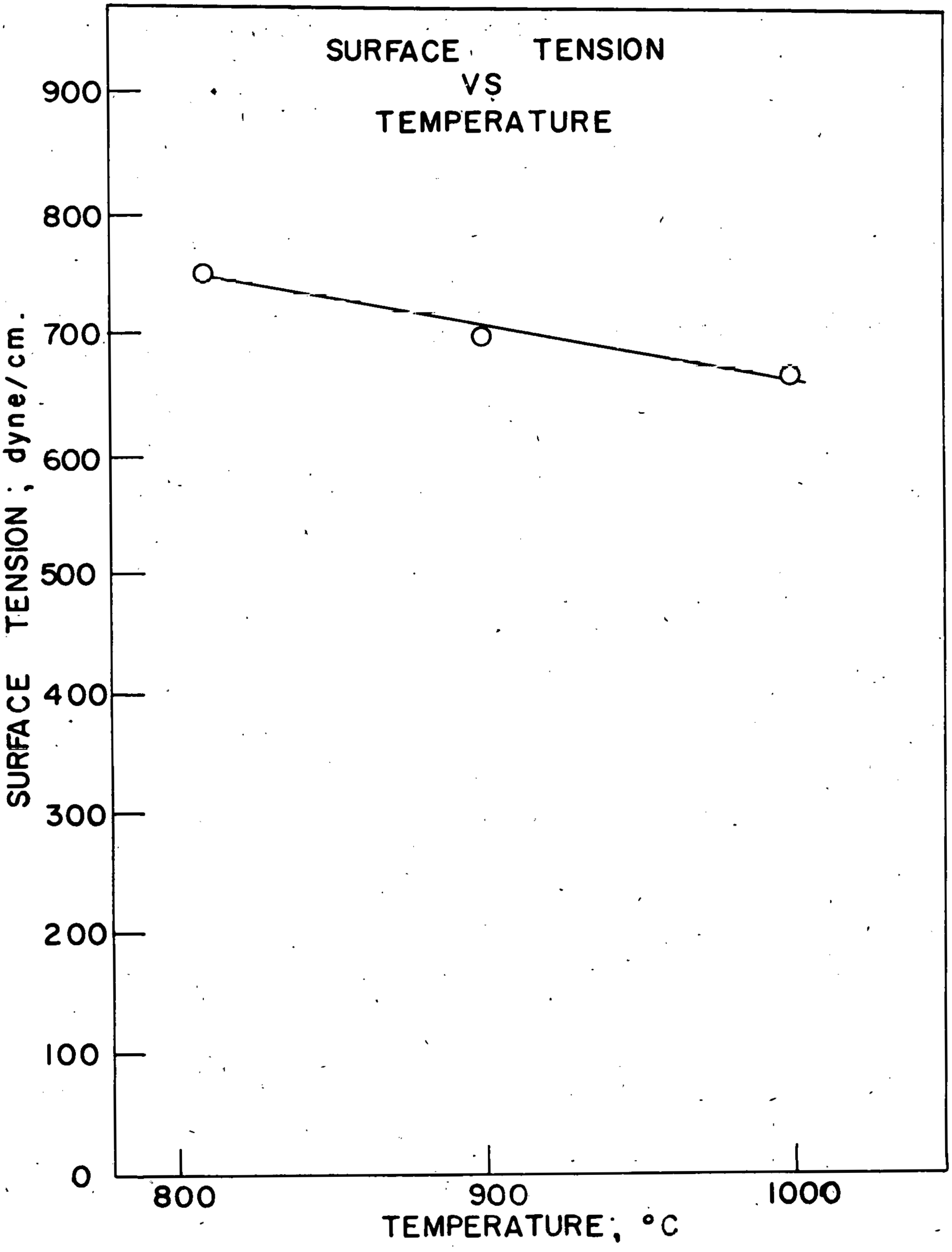


FIG 10 CERIUM ON BERYLLIUM OXIDE

variation is within the error of the experiment. The values definitely indicate, however, that the contact angle of cerium on zirconia is little affected by a change in temperature. As was pointed out earlier no values for the contact angle of cerium on alumina could be established due to the rapid reaction of the metal with the oxide. The zero contact angle of cerium on thoria was evidenced by the fact that the metal completely disappeared in the plaque.

The work of adhesion of cerium on the oxides is shown with its variation with temperature in Table 8. The work of adhesion of cerium to zirconia was nearly constant at a value of between 20 and 34 dyne/cm. The work of adhesion of cerium to beryllia increased slightly from 86 to 93 dyne/cm in going from a temperature of 810 to 900°C, but at 1000°C the adhesion increased more than twice these values to 251 dyne/cm. The work of adhesion of cerium to alumina could not be determined. The adherence of cerium to thoria was twice the value of the metal's surface tension at all temperatures. This is due to the zero contact angle exhibited by the metal on thoria.

Table 7

Contact Angle of Cerium with the Oxides

Temperature	Refractory Oxide							
	Al_2O_3		BeO		ThO_2		ZrO_2	
Degree Centigrade	Angle in degrees		Angle in degrees		Angle in degrees		Angle in degrees	
	Run I	Run II	Run I	Run II	Run I	Run II	Run I	Run II
810			150	155			162	162
Average			152				162	
900			149	149			169	163
Average			149				166	
1000			128	130			167	163
Average			129				165	

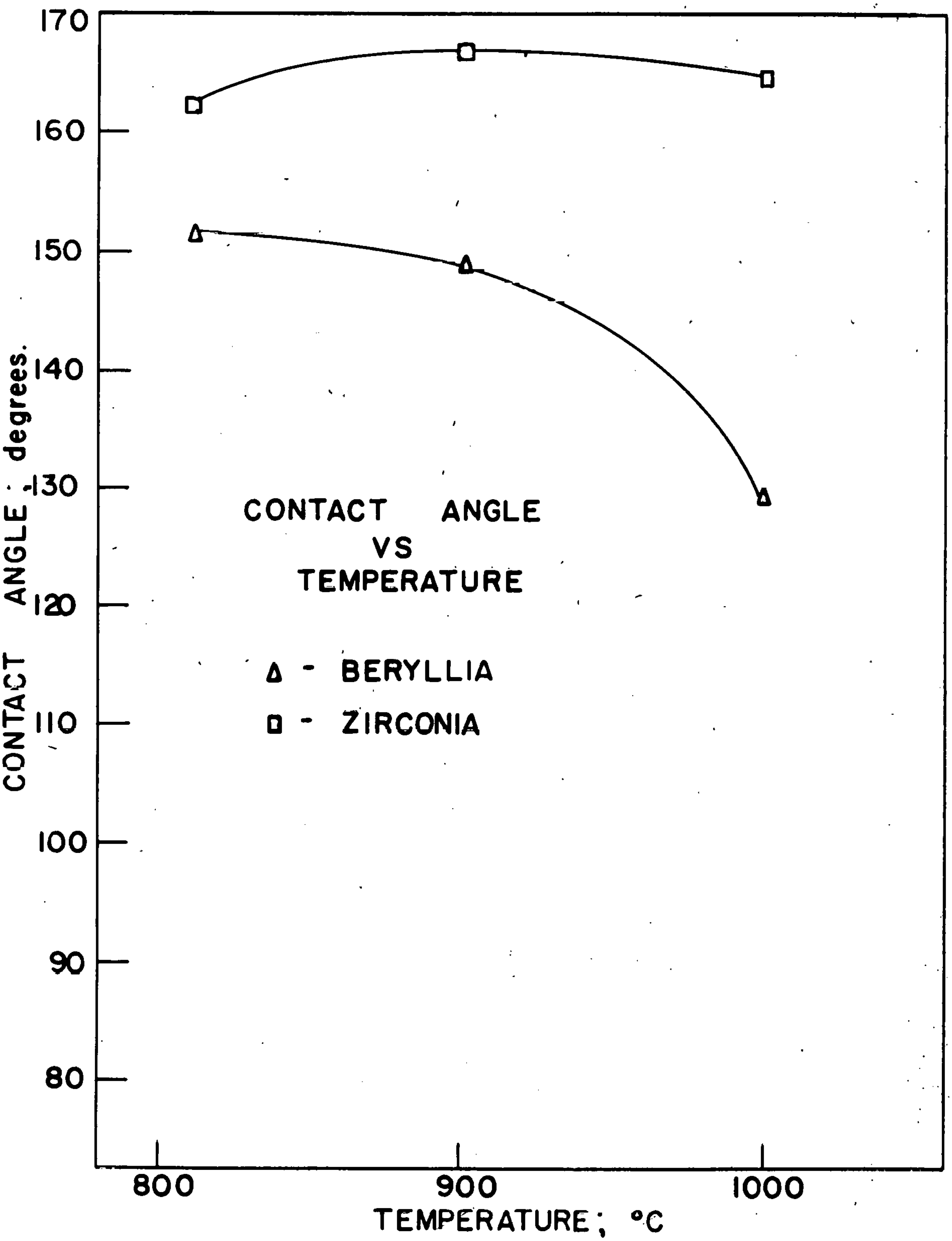


FIG 11 CERIUM CONTACT ANGLES

Table 8

Work of Adhesion of Cerium on the Oxides

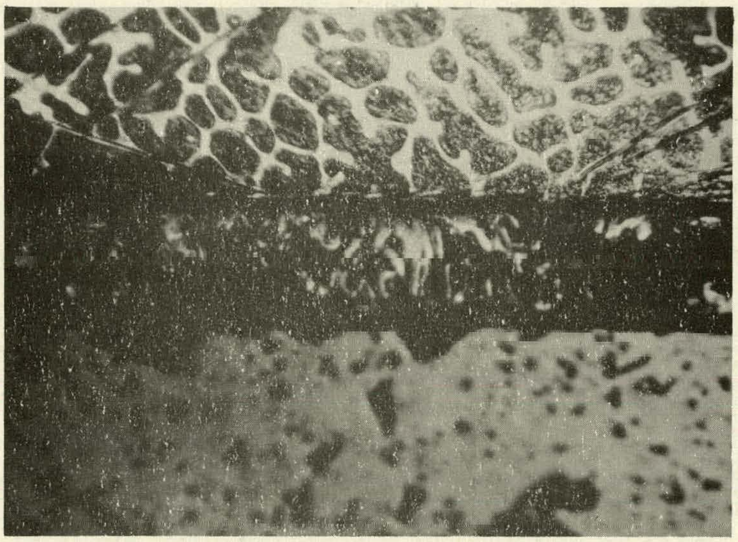
Temperature	Refractory Oxide			
	Al_2O_3	BeO	ThO_2	ZrO_2
Degree Centigrade	Dyne/cm	Dyne/cm	Dyne/cm	Dyne/cm
810		86	1440	34
900		93	1377	20
1000		251	1344	23

Microscopic Examination of Reactions

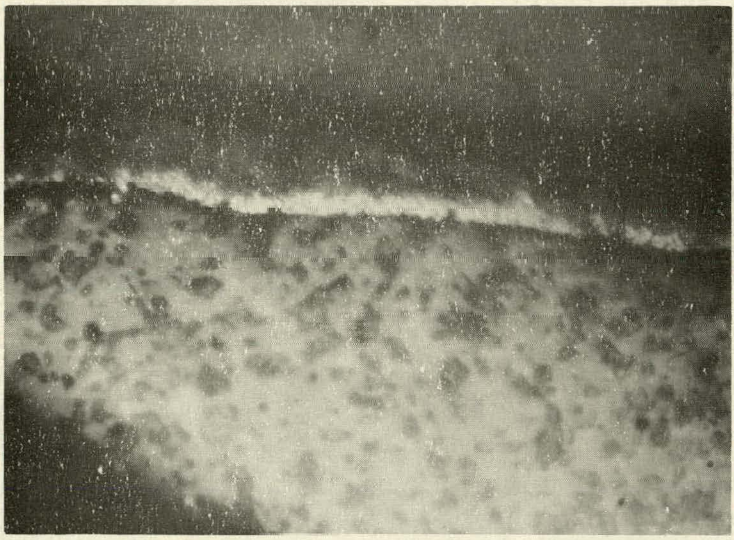
Lanthanum

Figs. 12 and 13 show that lanthanum has reacted to a certain extent with all the oxides at 1200°C. The reaction of lanthanum and alumina is seen to give an alloy of lanthanum and aluminum. This can be seen in the upper part of the photomicrograph where the eutectic alloy of aluminum and lanthanum surrounds the islands of lanthanum that had separated out on cooling. The interface shows the needle-like structure of lanthanum oxide that was the remaining product of reaction. Beneath the interface the unchanged appearance of the alumina indicates the reaction proceeded by the diffusion of lanthanum through the interfacial layer. This type of penetration, of course, is limited by the rate of diffusion of lanthanum through the layer of lanthanum oxide. The dark areas in the alumina portion of the photomicrograph are pores and were not produced by the reaction.

The reaction of lanthanum with beryllia produced a two layer interface. The upper part of the interfacial layer is again the needle-like lanthanum oxide. The bright strip along the bottom of the interface is beryllium metal, or, perhaps, a high beryllium content alloy. This reaction is like that of lanthanum and alumina in that the reaction is limited by the speed with which the lanthanum can diffuse through the interface of lanthanum oxide. In this particular case the lanthanum must also travel through the beryllium metal. Beryllium is not removed by back diffusion through the lanthanum oxide layer to form an alloy as in the case of aluminum; or, if it does, the rate of diffusion is slow enough to permit the beryllium to be removed from the alloy by distillation faster than the alloy can be formed.

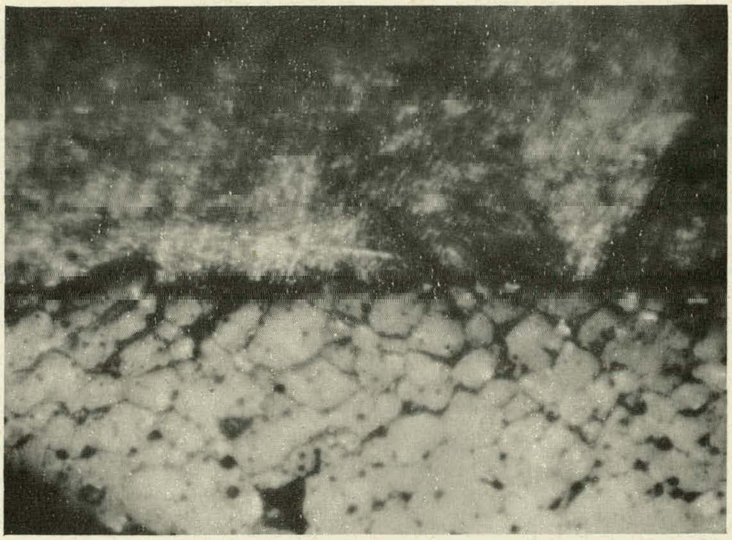


Lanthanum on Alumina X125

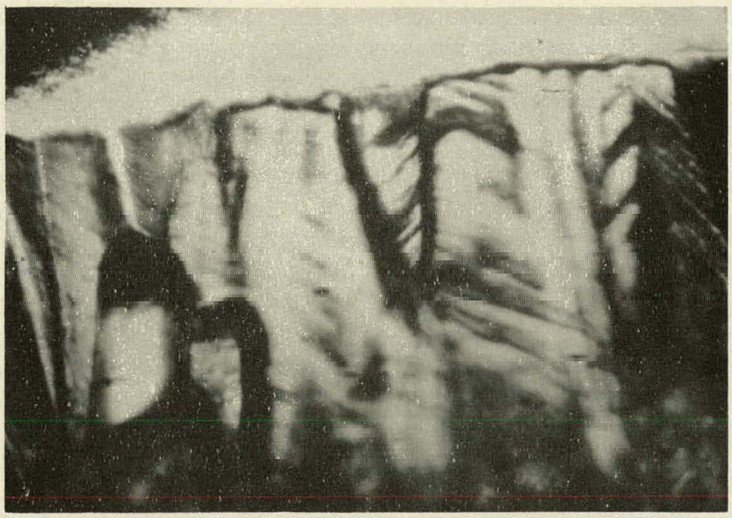


Lanthanum on Beryllia X562

Fig. 12 Lanthanum-Ceramic Interface



Lanthanum on Thoria X562



Lanthanum on Zirconia x562

Fig. 13 Lanthanum-Ceramic Interface

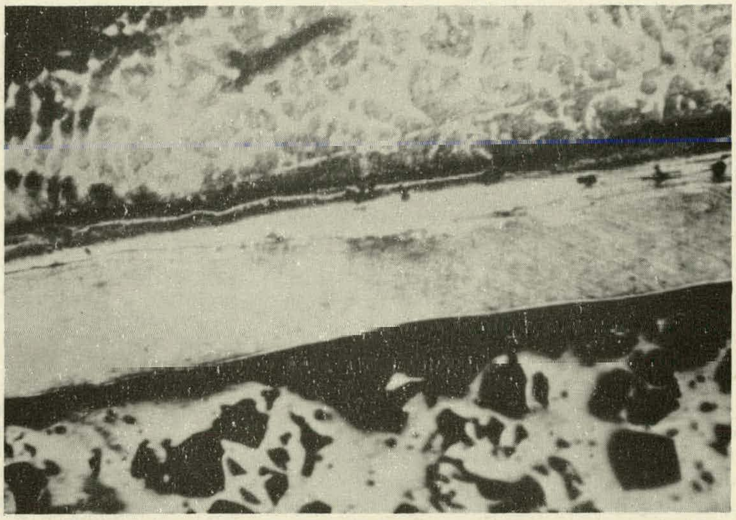
Molten lanthanum does not produce an interfacial reaction layer with thoria. Rather, the metal penetrates the oxide by entering the high energy zone between the grain boundaries. The lanthanum can be seen to be loosening some grains near the surface between metal and oxide so that the grains of thoria seem to be floating in lanthanum metal. The surrounding of the grains is followed by the diffusion of the metal into the grains themselves to form a limited solid solution of metal and oxide. This type of penetration is not hampered by the formation of interfacial layers that slow up the progress of the reaction. The metal was seen to penetrate entirely through the plaque in some areas with the subsequent discoloration of the thoria.

The reaction of lanthanum with zirconia proceeded in two stages. The metal diffused into the plaque with the usual discoloration of the oxide, but an interfacial layer of lanthanum oxide was also formed. A complete study of the interface could not be made since the metal broke loose from the oxide on cooling. It was obvious from a study of the plaque and the metal, however, that the metal diffused through the interfacial layer of lanthanum oxide faster than its reaction with zirconia.

Cerium

The reaction of cerium metal with the oxides was very similar to the methods of penetration of lanthanum metal. These results are shown in the photomicrographs of Figs. 14 and 15. Molten cerium on alumina produced the same type of alloy with aluminum as did lanthanum. The characteristic islanding effect is shown for the cerium metal within the eutectic mixture of cerium and aluminum. A certain amount of cerium oxide is present at the interface, but not as a definite interfacial layer. It would seem from the rapid attack of the metal on the plaque that the cerium oxide was dissolved to a certain extent in the resulting alloy. The interface between the alloy and the plaque was an unidentifiable phase that was thought to be a solid solution of the alloy eutectic solution and cerium oxide. This phase at one point on the surface of the plaque was seen to give way gradually to the alloy of cerium and aluminum. The solution of the cerium oxide would explain the rapid attack by the removal of a hampering interface that restrains the contact of the reacting materials.

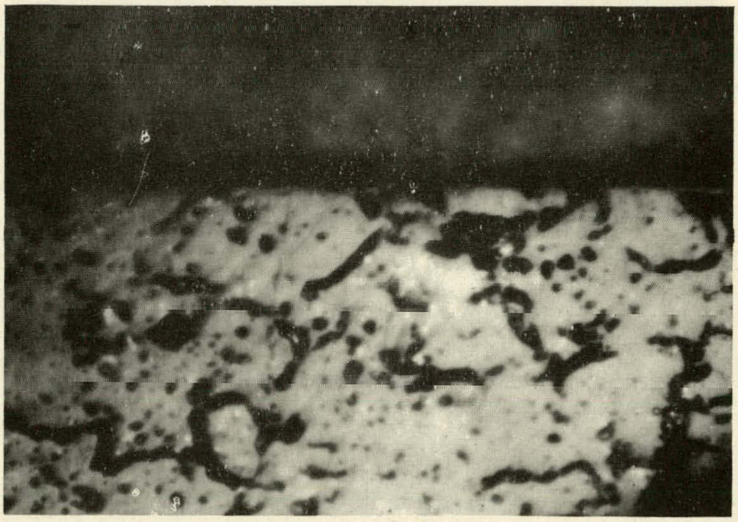
The reaction of cerium with beryllia occurred in the same manner as the reaction of lanthanum with beryllia. The interface between the metal and the plaque was again composed of two phases. The upper phase was cerium oxide with a lower phase of beryllium metal. As before the diffusion of the metal through the interfacial oxide phase resulted in reaction with beryllia. The metal did not diffuse into the beryllium oxide plaque.



Cerium on Alumina X125

Cerium on Beryllia X562

Fig. 14 Cerium-Ceramic Interface



Cerium on Thoria X562

Cerium on Zirconia X562

Fig. 15 Cerium-Ceramic Interface

The reaction of cerium with thoria was also similar to the reaction with lanthanum. The metal penetrated into the high energy grain boundaries as before, but in this system a more complete solid solution was formed so that the grains were not isolated so much as with lanthanum. The solid solution of the metal into the thoria was more rapid, and the metal was not made to collect in the areas surrounding the grains as lanthanum did.

The interface between cerium and zirconia contained the interfacial layer of oxide similar to that present in the lanthanum reaction. In this particular system, however, a definite solid solution occurs so that the cerium oxide formed at the interface blends smoothly into the zirconia-ceria solid solution.

X-ray Examination

The results of the x-ray analysis of the reaction products of heated mixtures of the metal and oxide are shown in Tables 9 and 10. The ideal conditions for the reaction provided by the powders resulted in a slight reaction of the metals at temperatures 300°C below the melting point of the metals. The solid solutions evidenced by the diffusion of the metals into the refractories thoria and zirconia occurred even at this low temperature. Lanthanum showed a slight amount of metal in the mixture with zirconia at 600°C, but at 924°C only lanthanum oxide and zirconia phases were present. Thoria was the only phase detected for the lanthanum-thoria mixtures heated to temperatures of 600 and 924°C. Solid solutions occurred with cerium and the thoria and zirconia refractories at a temperature of 500°C.

A slight amount of reaction of cerium with alumina occurred at 500°C. At the melting point of cerium no cerium oxide was found, but, rather, patterns for impure cerium and alumina were all that were detected. The reaction of lanthanum with alumina had begun by 600°C. The products of the reaction were: alumina, lanthanum oxide, and a fourth phase that was not identified. At the melting point of lanthanum the metal was still present, but the intensity of the lanthanum oxide lines had increased. The unknown phase was not in evidence at this temperature.

The reaction of cerium with beryllia was clearly in evidence at 500°C, and at the melting point the predominant phases were beryllia and ceria. Very little reaction occurred between lanthanum and beryllia at 600°C, but at the melting point of lanthanum only a faint trace of lanthanum metal could be detected. The predominant phases at the metal's melting point were beryllia and lanthana.

Table 9

X-ray Analysis of the Lanthanum Reactions

Refractory	Reaction Products
Alumina	
600°C	The strongest phases present were alumina and lanthanum. A readily detectable reaction had occurred, however, with the formation of lanthanum oxide and an unidentifiable phase.
924°C	The lanthanum oxide phase had increased in intensity. Lanthanum metal, probably in the form of an alloy, was present along with alumina, but the unidentified phase was no longer present.
Beryllia	
600°C	The predominant phases were lanthanum and beryllia. A slight amount of lanthanum oxide was in evidence.
924°C	The predominant phases were beryllia and lanthanum oxide. A very faint trace of lanthanum was still detectable.
Thoria	
600°C	The only detectable phase present was thoria. The lanthanum had apparently gone into solid solution without changing the lattice constant of thoria.
924°C	The only detectable phase present was thoria.
Zirconia	
600°C	The predominant phase was zirconia. Slight amounts of lanthanum and lanthanum oxide were present.
924°C	The only phases present were zirconia and lanthanum oxide. It is probably in this case also that some lanthanum entered into solid solution with zirconia.

Table 10

X-ray Analysis of the Cerium Reactions

Refractory	Reaction Products
Alumina	
500°C	The only phases present were alumina and cerium.
810°C	The only phases present were alumina and an impure form of cerium.
Beryllia	
500°C	The predominant phase was beryllia. A readily detectable pattern for cerium and cerium oxide were also present.
810°C	The predominant phases were beryllia and cerium oxide. Only a slight pattern for cerium was obtained.
Thoria	
500°C	The patterns showed the lattice of thoria to be shifted somewhat. A slight amount of cerium was detectable.
810°C	The most predominant phases were a solid solution of thoria and cerium oxide in a three to one ratio.
Zirconia	
500°C	The pattern for cerium, zirconia, and ceria-zirconia solid solution is so similar that the pattern produced could not definitely be said to be any of the phases. The absence of cerium oxide favored the acceptance of the solid solution as the phase present, however.
810°C	The solid solution of ceria and zirconia was the predominant phase.

DISCUSSION OF RESULTS

Metal Ceramic Interactions

Wetting characteristics

The close agreement found for the surface tension of cerium and lanthanum is what would be expected from their close chemical relation. Several attempts have been made to relate the surface tension of a metal to other properties of the metal. Attempts have been made also to establish a theoretical basis for surface tension based on the electron theory of metals and on physico-chemical grounds. In this regard certain assumptions are necessary that restrict the agreement of the calculated values with the experimental values to being in the correct order of magnitude. As an example of the electron theories of the surface tension of metals Hume-Rothery (21) describes the approach of Brager and Schuschowitzky (22). Taylor (14) reduced their expression for surface tension to an equation involving the atomic volume to a negative 4/3 power times a constant 56,400. Using this expression in the case of lanthanum results in a value of 830 dyne/cm for the surface tension. A value of 980 dyne/cm is calculated for cerium by this relationship.

A more empirical relationship for the surface tension of metals was developed by Schytil (23). The proposed relationship states that the surface tension of a metal is proportional to the melting temperature of the metal divided by the atomic volume to the 2/3 power. A curve of the experimental values of the surface tension of metals versus the ratio $T_m/M_v^{2/3}$ is shown in Fig. 16. The curve was constructed from the values of surface tension compiled by Taylor (14). The values determined here for cerium and lanthanum are also included. From this curve a value of 525 and 570 dyne/cm would be predicted for cerium and lanthanum, respectively.

Kingery (16) has reported values of surface energies for alumina and zirconia at 1850°C to be 905 and 590 dyne/cm, respectively. Assuming both materials decrease in surface energy by 0.1 dyne/cm/°C, the values at 950°C would become 995 and 680 dyne/cm. The high contact angle of the metals on zirconia relative to the other oxides can be explained to a certain extent by these values. The work of adhesion of a metal on an oxide may be completely defined from the contact angle and the surface tension of the metal. The work of adhesion is also equal to the sum of the surface energies of the metal and oxide less the interfacial energy. Thus, for lanthanum to assume the same contact angle on alumina as with zirconia the interfacial energy of lanthanum and alumina must be 315 dyne/cm greater than the interfacial energy of lanthanum and zirconia. The figure for the work of adhesion of lanthanum on alumina at 950°C

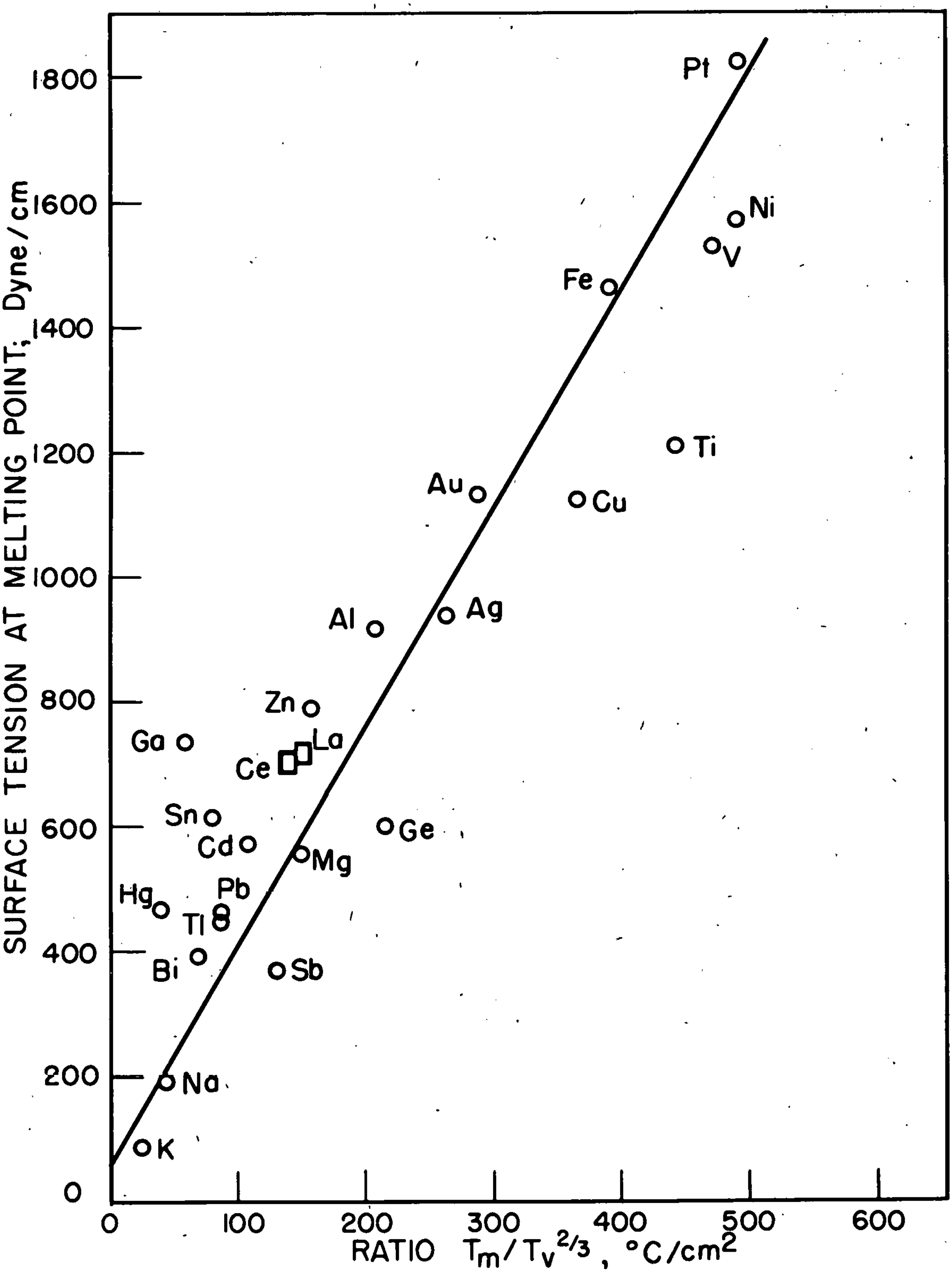


FIG. 16 SCHYTIL'S SURFACE TENSION RELATIONSHIP

of 233 dyne/cm compared to 133 dyne/cm for zirconia shows that the interfacial energy falls short by 100 dyne/cm for identical contact angles. Using the figures of Kingery the interfacial energy of lanthanum on alumina would be 1462 dyne/cm opposed to 1257 dyne/cm for lanthanum on zirconia.

The work of adhesion values of Tables 4 and 8 indicate that lanthanum has an adhesion to zirconia of 167 dyne/cm compared to 23 dyne/cm for the adhesion of cerium to zirconia. The work of adhesion is a measure of the bond between metal and ceramic, so that one would expect the metal with the strongest oxygen bond to be the metal that would wet the refractory most readily. This in fact was the case for lanthanum and cerium metals. Brewer (24) estimated the free energies of formation for cerium and lanthanum oxides at 25°C to be -116 and -145 Kcal/mole oxygen, respectively.

Metal penetration

Cerium and lanthanum metals attacked the refractory oxides in all the common methods of penetration of metals into refractories. These methods of penetration may be listed as those below.

1. The metal may penetrate into a refractory by simple reaction with the refractory. In this case an interfacial layer of reaction product between metal and refractory is formed, and the rate with which the reaction will proceed depends on the diffusion of the metal through the interfacial layer.

2. The more rapid method of penetration of a metal into a refractory occurs where the reaction produces a product that is soluble in either reacting phase. This method is aided by the removal of the reaction products so that the reaction may continue without the reacting materials becoming separated by the products of the reaction.

3. Solid solution formation is also a common method of penetration of refractories by metals. In this method the metal enters into solid solution in the high energy grain boundaries, and continues the penetration by diffusion into the grains. A formation of a hampering layer of reaction product may or may not occur.

The first method of penetration was in evidence for the reaction of cerium and lanthanum with beryllia. In this system a two layer interface of reaction products resulted. A combination of the first and second methods of penetration was found for the reaction of lanthanum with alumina. Aluminum was one product of the reaction and this metal went into solution with the lanthanum. Lanthanum oxide, the other product of the reaction, was insoluble in both reactants and became an interfacial layer between the reactants. The very rapid method of penetration by solution was found for cerium and alumina. In this system both products of the reaction were soluble in the reactants. As a consequence the metal attacked the refractory with little difficulty. The third method of penetration was found in the reactions of the metals with thoria and zirconia. Both lanthanum and cerium penetrated thoria plaques by diffusion through grain boundaries into the grains. No hampering interfacial layer was formed in these reactions. The metals penetrated zirconia by diffusion and solid solution also. In both of the zirconia systems an interfacial layer was formed.

Powder mixture reactions

As would be expected from the reactive nature of the metals their combination with the refractories in a finely divided form resulted in reactions at low temperature. Most refractories were attacked to a slight extent at temperatures where the reacting components were in the solid state. At the melting point of the metals the reactions had proceeded to virtual completion with most of the oxides. Alumina was the only oxide that did not produce the oxides of the metals, refractory oxides and solid solutions as the predominant phases at the melting point of the metals. In the alumina system the unreacted metals remaining were in the form of an alloy.

Errors

The most sensitive area for error in the Bashforth and Adams treatment of the sessile drop method of determining surface tension was mentioned in the section on theory. This source of error was the measurement of the dimension z; the distance from the apex of the drop to the point of tangency of a 90° line to the surface of the drop. The accuracy with which this dimension could be reproduced was considered to be 0.005 mm. The x dimension was reproducible to within 0.002 mm. The maximum error in the β value from this variation in z and x was 0.06 from a nominal value of 1.90. The maximum error in determining the radius of curvature at the apex, b, was 0.004 mm with a nominal value of 4.5 mm. Carrying the calculations through to give the maximum error resulted in a maximum range of less than 3% for the surface tension.

The determination of the density of the metal at a given temperature is more subject to error in that any inherent errors in measurement will be compounded. However, the b^2/β term that contributes to the error in surface tension enters into the density equation in the numerator in one factor, and in the denominator in another factor. In this way the effect of the error in b^2/β is reduced. Other dimensions contribute to the error in density so that a range of approximately 3% is obtained. Combining the errors from the density and from the b^2/β factor gives a maximum range of error of slightly less than 10%.

A very large source of error in the sessile drop method of surface tension determination results from the fact that the surface is static. Contrary to the maximum bubble pressure method of determining surface tension the surface is not replaced as the measurements proceed. This permits the formation of an oxide film on the surface of the drop if the oxygen content of the system is sufficiently high. The film on the drop results in a certain "bag effect". This phenomenon was observed on certain runs in this work when the pressure of the furnace was allowed to rise to a few tenths of a micron. These runs were discarded, however, and only runs which produced a bright shiny surface were used in the calculation of surface tension.

A minor source of error in the surface tension value of these metals resulted from their measurement in a vacuum. As was pointed out previously, the bonds of attraction that would normally be directed toward the vapor at atmospheric pressure are no longer satisfied due to the removal of the vapor phase. This error constitutes an inherent error in the system and can not be determined definitely. Metals of low vapor pressures, such as lanthanum and cerium, however, are only slightly affected by this error.

The measurement of the contact angle of the metals on the various plaque materials is affected by an error due to the metals themselves more than to the method of measurement. Most liquids suffer a hysteresis loss in going from an advancing state to the receding state. The difference observed between the advancing angle of a liquid and a receding angle may be as much as 20 degrees according to Adams (15). An angle between that of the receding angle and the advancing angle is under no strong influence to assume either angle. At higher temperatures, however, one would expect equilibrium to be reached more rapidly than at room temperatures. The low energy differences that cause an angle to remain between the advancing and receding angles should be altered at the higher temperatures.

The chief source of error in this determination of the contact angle and work of adhesion of lanthanum and cerium on the oxides was the presence of interfacial reactions. The value of the work of adhesion was not precisely that of the metals and the oxides, but rather the adhesion of the metals to their interfacial layer. The contact angle and adhesion of lanthanum to thoria was more nearly the correct value, although even in this case the thoria was contaminated by the influence of the limited solid solution with the metal from the diffusion of the metal into the thoria. The values reported for contact angle and work of adhesion are correct only in the particular system for which they were measured. The contact angle and work of adhesion may be of value in application of a general order of magnitude, however.

CONCLUSIONS

From this study of the interaction of cerium and lanthanum metals with the refractory oxides of aluminum, beryllium, thorium and zirconium the following conclusions may be drawn.

1. The sessile drop method of determining surface tension outlined by Ellefson and Taylor for glasses and Kingery and Humenik for metals has been successfully applied to the reactive metals lanthanum and cerium.

2. The surface tensions of the metals lanthanum and cerium are very similar as are other characteristics of the metals.

3. The surface tensions of the metals decreases linearly with temperature over the temperature range studied.

4. The degree with which lanthanum wets the refractory oxides increases in the order; zirconia, alumina, beryllia, and thoria. The same order of wetting is retained by cerium for the refractories zirconia, beryllia, and thoria. In most cases wetting was promoted by increasing temperature. The wetting of zirconia by cerium was virtually unaffected by temperature, however.

5. The interfacial energy of the metal-oxide surface is greater for cerium on beryllia and zirconia than for lanthanum on the same oxides. The work of adhesion is, therefore, greater for lanthanum than for cerium on the refractories beryllia and zirconia. In all but the case of cerium on zirconia the adhesion of the metals to the oxides was greatly promoted by an increase in temperature in the temperature range studied.

6. Of the materials studied, the best refractory for containing the molten metals is beryllia. Using the criteria of low wetting (high contact angle) and low work of adhesion, the best refractory for melting these metals would appear to be zirconia. However, these criteria ignore interfacial reactions. Thus, in the final analysis, the small reaction interface of beryllia with the metals makes it the better container. Although the reactions of the metals with zirconia are severe, the high contact angle exhibited by the metals toward this refractory make it worthy of consideration as a possible container material. The rapid attack of alumina by the metals makes it a poor refractory for melting the metals. The diffusion and solution of the metals into thoria make this material unsuitable for containing the molten metals. The unsuitability of thoria as a container is also indicated by the low contact angle and the high work of adhesion displayed by the metals toward this oxide.

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APPENDIX A

Sample Calculations

Contact angle and surface tension

The contact angle and surface tension of the metals melted on the oxides are obtained from four measurements of the sessile drop profile. These dimensions are x, z, X and Z where:

x = the maximum diameter of the drop measured in a horizontal plane from the axis of revolution to the surface of the drop;

z = the vertical distance of the apex of the drop to the point of tangency of a 90° line to the surface of the drop;

X = the horizontal distance of the axis of revolution to the point of contact of the liquid surface with the supporting plaque;

Z = the overall height of the drop measured from the apex of the drop to the supporting plaque.

The dimensions may be readily visualized by making use of Fig. 2. The calculations may be illustrated by using the measurements for the run of cerium on beryllia at 810°C. For this run the values of the above dimensions were those given below:

$$x = 0.37275 \text{ cm},$$

$$z = 0.30211 \text{ cm},$$

$$X = 0.28548 \text{ cm},$$

$$Z = 0.46512 \text{ cm}.$$

With these measurements the value of the ratio x/z becomes 1.2338. From the curve of x/z versus β, such as shown in reduced scale in Fig. 17, the value of β is determined to be 1.853. Fig. 18 is next used to give values of x/b and z/b. The values of these quantities appropriate to a β value of

1.853 are found from the figure to be 0.8264 and 0.6698 cm, respectively. Since Fig. 18 was drawn holding the angle of the surface constant at 90°, x/b and z/b are related to the quantities x and z, that are coordinates of a point on the 90° surface. Thus, b may be determined by dividing the values of x and z by x/b and z/b. Thus, b is found to be

$$\frac{0.37275}{0.8264} = 0.4510 \text{ cm, and}$$

$$\frac{0.30211}{0.6698} = 0.4510 \text{ cm.}$$

With the values of β and b established the contact angle may then be determined. Fig. 19 contains three variables; β, Z/b, and contact angle. In order to determine the contact angle, the ratio Z/b must, therefore, be determined. The value of Z is 0.46512 cm, and dividing this quantity by 0.4510 cm gives 1.031. Substituting this value and the value for β into the curve that is shown in reduced form in Fig. 19 results in a value of 152° for the contact angle, θ.

All the quantities for determining the density of the drop are now available. The density is determined from the volume equation

$$V = \frac{\pi b^2 X^2}{\beta}\left(\frac{2}{b} - \frac{2 \sin \theta}{X} + \frac{Z}{b^2}\right) .$$

Substitution of the values results in

$$= \left(\frac{3.142(0.4510)^2 \quad (0.28548)^2}{1.853}\right)\left(\frac{2}{0.4510} - \frac{2(0.4802)}{0.28548} + \frac{1.853(0.46512)}{(0.4510)^2}\right) .$$

Partial completion of the calculation gives

$$V = 0.02811 \quad (4.424 - 3.364 + 4.236)$$

The final volume is seen to be 0.1492 cc. The weight of the drop before firing was 1.0077 gm. The density, therefore, was 6.741 gm/cc.

With the determination of the density all the quantities necessary to establish the surface tension have been evaluated. The surface tension is finally determined from the equation defining β. Rearrangement of the defining equation gives

$$\sigma = \frac{g b^2 \rho}{\beta} .$$

Substitution of the previously determined values gives

$$= \frac{980.6(0.4510)^2 \quad (6.741)}{1.853}$$

or 725 dyne/cm.

Work of adhesion

The determination of the surface tension of the metal and the contact angle are all that are necessary to determine the work required to remove the metal from the oxide plaque. The work of adhesion is determined from the simple relationship

$$W_{AD} = \sigma(1 + \cos \theta).$$

Using the value from the example above, this equation would become

$$W_{AD} = 725(1 + \cos 152^{\circ}), \text{ or}$$

$$W_{AD} = 725(1.000 - 0.883).$$

The value determined for the work of adhesion of cerium to beryllia at 810°C is, thus, 85 dyne/cm.

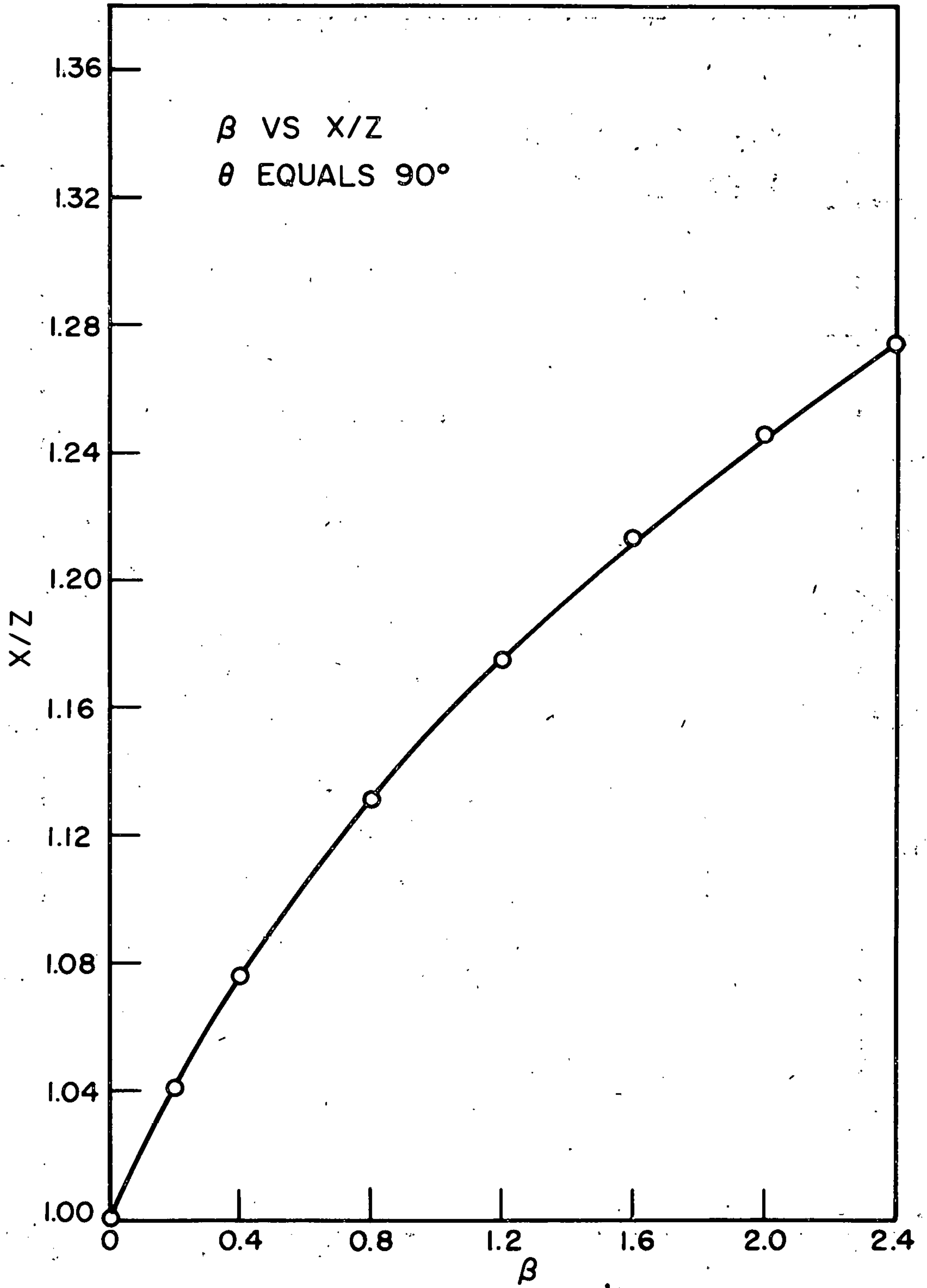

FIG. 17 BASHFORTH AND ADAMS' β RELATIONSHIP

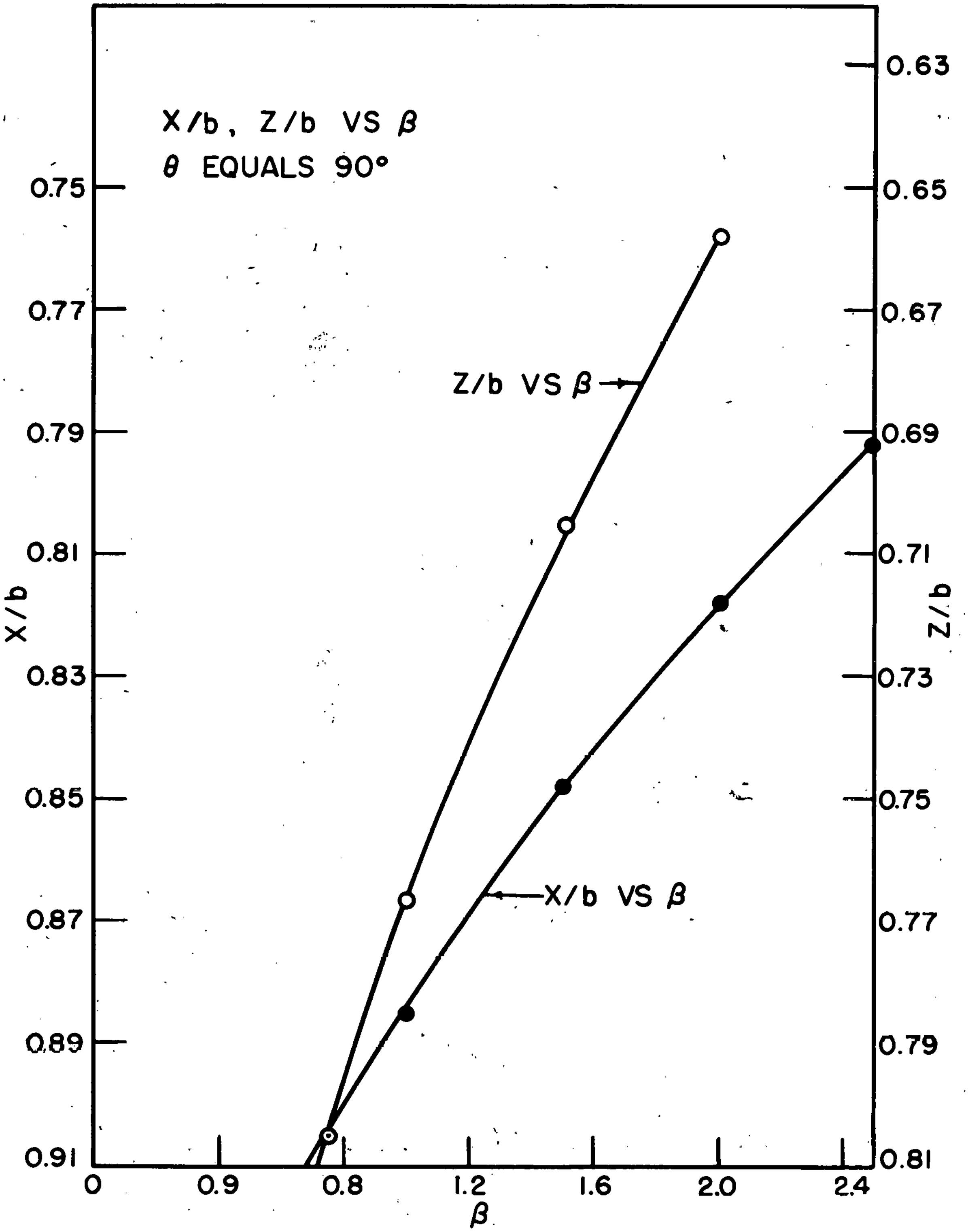

FIG.18 X/b, Z/b, AND β RELATIONSHIP AT AN ANGLE OF 90°

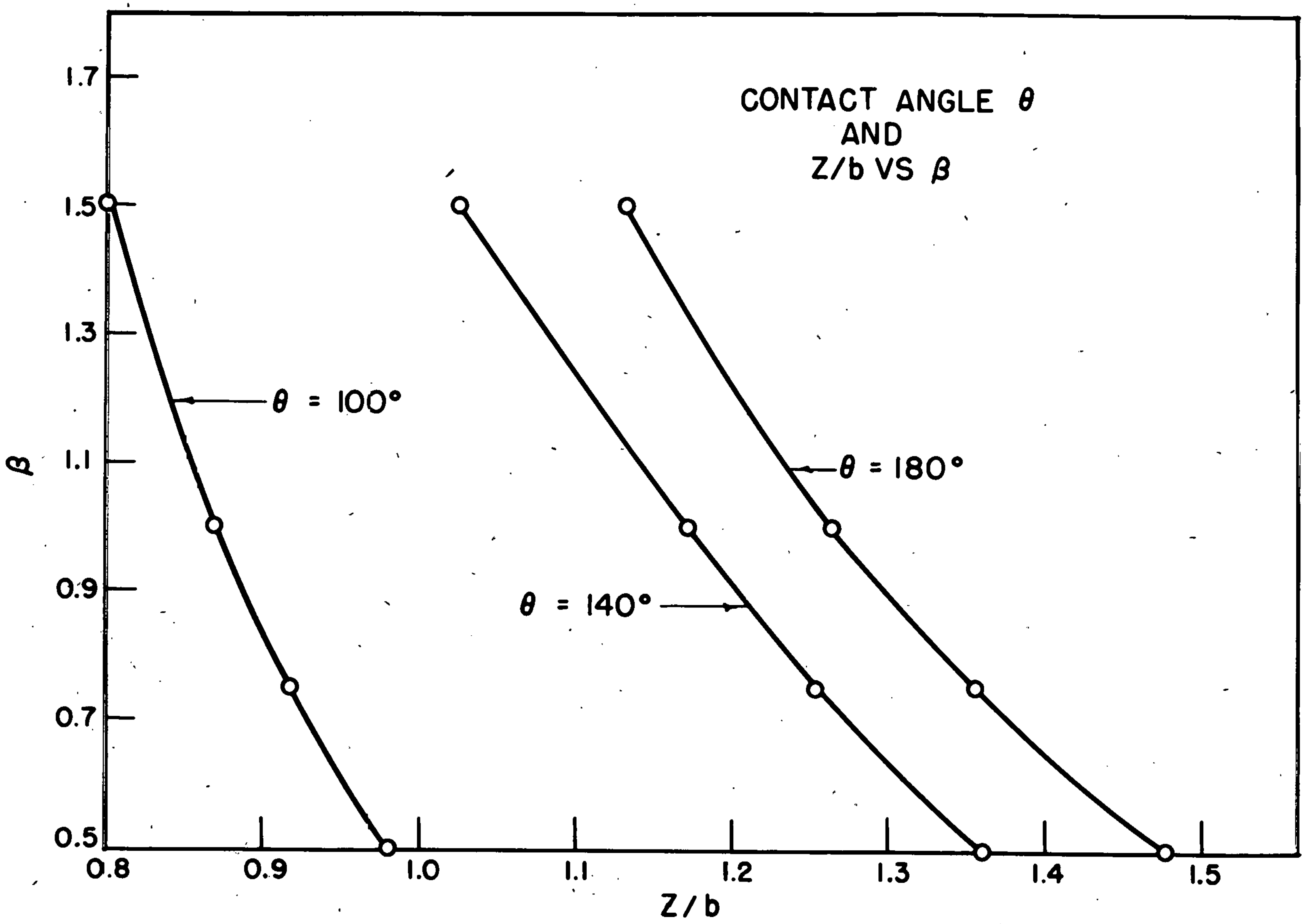

FIG. 19 BASHFORTH AND ADAMS' RELATIONSHIP FOR β AND θ

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