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THE WETTING OF ALUMINUM OXIDE
BY LIQUID ALUMINUM

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UNIVERSITY OF CALIFORNIA
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Berkeley, California

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John Joseph Brennan
(M.S. Thesis)

August 18, 1966

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THE WETTING OF ALUMINUM OXIDE BY LIQUID ALUMINUM

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August 18, 1966

ABSTRACT

The wetting of single crystal alumina by liquid aluminum was the primary investigation. During the course of this investigation the wetting of other oxides by aluminum was also studied. Contact angle measurements were made by means of sessile drop experiments. The contact angle between aluminum and alumina was measured over the temperature range 670°C to 1300°C. The initial contact angle upon melting of aluminum was 170°, dropping to 90° by 900°C, the rate of change of the contact angle depending on the surface condition of the aluminum. The contact angle then remained constant at 90° up to 1150°C, at which temperature the angle began dropping, reaching 50° by 1200°C. The angle then began jumping cyclicly from 50° to 70° and back again as the temperature remained constant.

If the aluminum metal had an oxidized surface, a large drop in contact angle was observed at 870°C. This drop in angle was caused by a change in the oxide layer on the aluminum. The drop in angle at 1150°C resulted from a change in the surface structure of the sapphire which led to a dissolution of the sapphire by the aluminum. The contact angle of 90°, maintained from 900°C to 1150°C, was found to be the equilibrium angle between a high surface energy liquid and a lower surface energy solid that are at thermodynamic equilibrium.

I. INTRODUCTION

Ceramic-to-metal seals have been applied to many phases of modern industry such as electronic and electrical components, aerospace structures, machine tooling, and in many other fields. Many different methods of joining ceramics to metals have been used. Clarke¹, et al. lists fifteen ceramic-to-metal joining methods, the most widely used of which are active-metal brazing, glass soldering, refractory-metal powder coating, metal/glass powder coating, metal/metal-oxide powder coating, and refractory-metal salt coating.

A relatively new ceramic-to-metal joining process that is creating widespread interest is the application of a thin metallic coating by volatilization of a metal and its deposition onto the ceramic.² Studies of the mechanisms of adherence which might apply to this type of system have been carried out by Humenik and Kingery,³ Armstrong, et al.,⁴ and Sutton⁵ by the method of contact angle measurements taken on sessile drops of metals on various ceramic substrates. These investigators found that certain elements tend to concentrate at the metal-ceramic interface and aid in the formation of bonds between the two phases. In no case was a microscopic theory of the joining mechanism developed. McDonald, et al.,⁶ did propose a model in terms of the bulk free energies of formation and van der Waals forces, based on the assumption that absorption of metallic atoms on two types of surface sites comprises the major portion of the work of adhesion.

Wetting studies done by Pask and Fulrath⁷ and Borom and Pask⁸ on the nature of glass-to-metal bonding have shown that a balance of bond

energies at the glass-metal interface is necessary for the achievement of chemical bonding which leads to good adherence. This condition corresponds to the existence of thermodynamic equilibrium at the interface. This in turn corresponds to a saturation of each phase with the other. The result is a smooth chemical transition from the elemental metal through an intermediate "equilibrium phase" to the unreacted glass. Theoretically, this equilibrium phase could be as small as a monolayer thick. It is possible that the same type of model can be applied equally well, with some modifications, to a ceramic-metal system.

The purpose of the present investigation is to study the wetting and adherence of a metal to a ceramic in a simplified system that would be expected to attain thermodynamic equilibrium without the complication of a reaction forming an intermediate phase at the interface. The system aluminum metal on single crystal aluminum oxide (sapphire) has been chosen in order to try and establish meaningful relationships between a metal and its oxide without the added complications of interfacially active elements, grain boundaries, or macroscopic chemical reactions. Previous work in this particular system has been very limited.

Livey and Murray⁹ reported that the contact angle between aluminum and alumina is high (148°) at 970°C but at 1255°C drops to a value of 47° after 30 minutes. They found that there was no attack of the Al_2O_3 by the aluminum at the interface whatsoever. Carnahan, et al.¹⁰ found that the contact angle of liquid aluminum on recrystallized alumina at about 1240°C under vacuum decreased within 20 minutes to a steady

value of 60° . On sapphire at 1200°C , the drops spread and then rapidly contracted to a contact angle of 80° . The spreading and contraction were repeated cyclicly, with the volume of the drop decreasing at each cycle and "steps" being formed on the surface of the sapphire. This behavior was attributed to a reaction between the aluminum and the sapphire with the resultant formation of Al_2O gas.

II. EXPERIMENTAL PROCEDURE

A. Sessile Drop Materials

The single crystal alumina plaques used in the sessile drop experiments were obtained from the Linde Company, division of Union Carbide. They were 3/8" diameter by 1/16" thick, were polished to a surface finish of 5-10 micro-inches, and were cut at a 60° orientation from the C axis. Other substrate materials used were single-crystal MgO and CaO, which were obtained from the Muscle Shoals Electrochemical Corporation in polycrystalline lumps incorporating large single crystals one to two inches long which were then cleaved into single crystal plaques 1/2" by 1/2" by 1/16", and single crystal NiO which was obtained from Marubeni-Ilda Company, Japan, in boule form and subsequently cleaved for experimental use. All substrate materials were approximately 99.7% purity.

The aluminum used was obtained from Cominco Products, Inc. in 3/16" diameter rods of 99.999% purity. The rods were cut and ground into 1/8" by 1/8" cubes for sessile drop use. The gold and nickel used were of 99.99% purity and were obtained from the Lawrence Radiation Laboratory.

B. Sessile Drop Preparation

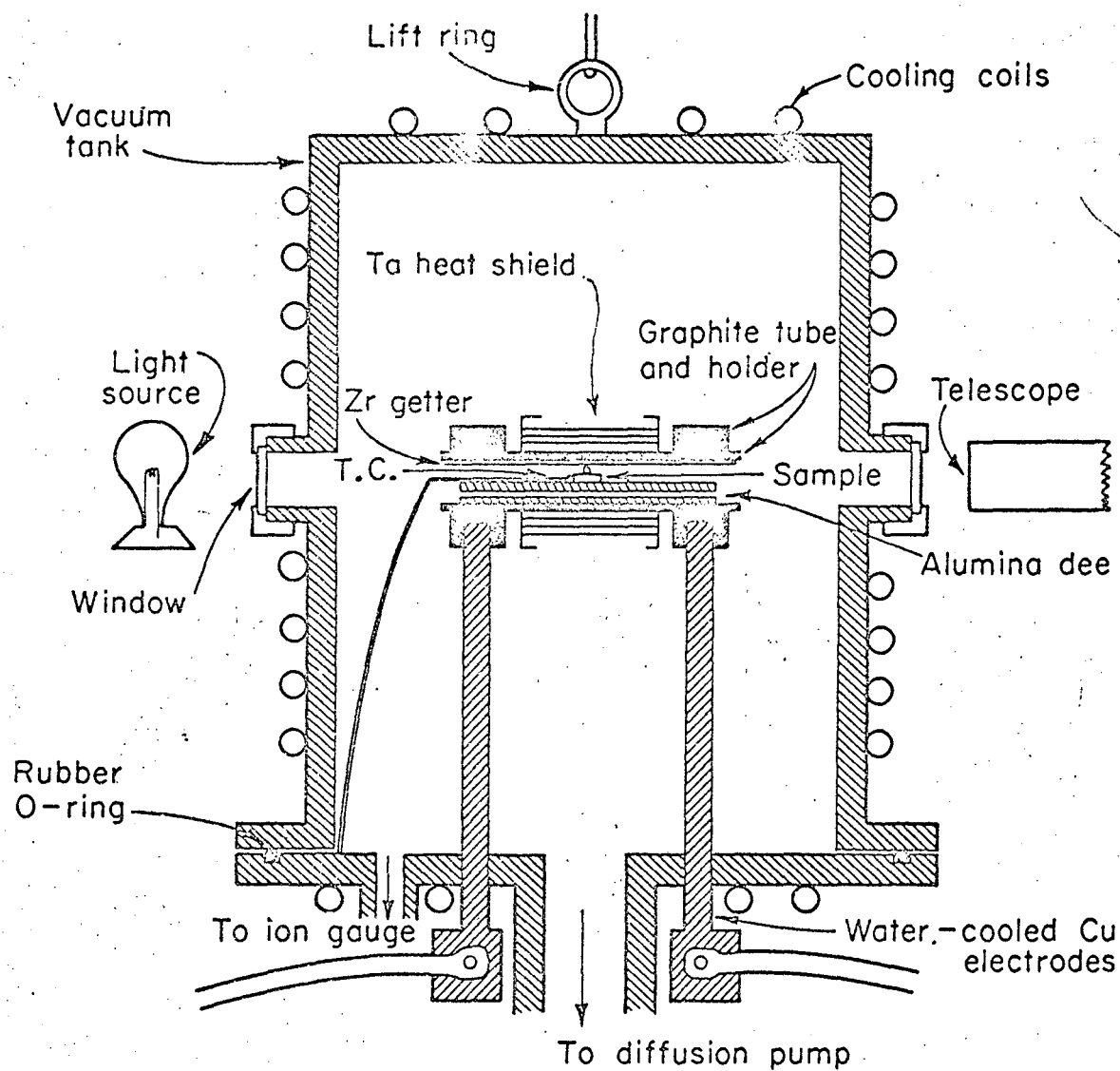
Early sessile drop experiments were conducted in a tantalum-tube resistance furnace under vacuum conditions of from 2 to 6×10^{-5} mm Hg pressure. The tantalum tube was connected to water-cooled copper electrodes by copper holders. Due to temperature limitations of these copper holders, the tantalum tube and the holders were replaced by a graphite tube and graphite holders. Previous experimental runs were

found to be reproducible with this setup. The graphite resistance furnace is shown in Figure 1.

The sessile drop samples rested on the flat surface of an alumina "dee" tube which was fitted inside the graphite tube. Careful adjustments were made before each run to make sure that the surface of the "dee" was perfectly horizontal. Temperature measurement and control were by means of a platinum-platinum/rhodium thermocouple which rested on the alumina "dee" with the thermocouple tip just touching the sessile drop substrate. Contact angle measurements were made by sighting along the alumina "dee" through fused silica windows incorporated in the vacuum chamber with a telescope which was capable of measuring contact angles within plus or minus one degree. For lower oxygen pressure a zirconium getter was placed around the sessile drop specimen.

All samples were thoroughly cleaned in an ultrasonic cleaner and then rinsed with ethyl alcohol and then with distilled water, and dried in a warm air stream. Samples not used immediately were stored in a vacuum dessicator. Before each run the interior of the vacuum chamber was given a thorough cleaning to remove any deposited impurities.

Sessile drop experiments of Al on Al_2O_3 and Al on MgO were run over the temperature range of 660°C , the melting point of aluminum, to 1300°C . Some of the experiments consisted of bringing the sample to the desired temperature and then holding at this temperature for a specific length of time. The contact angle was measured every two minutes to determine if there was any change with time. Other experiments consisted of raising the temperature in 10°C increments every 10 minutes between 700°C and 900°C and in 50°C increments every 10 minutes from



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Fig. I. Schematic of contact angle furnace.

900°C to 1300°C. Ten minutes at each temperature was considered sufficient time for steady state conditions to be established.

Contact angle measurements were made with Al on CaO and NiO over the temperature range of 660°C to 900°C. Examination of the two systems indicated severe reactions occurring. Sessile drop runs of Au on Al₂O₃ and on MgO were run from 1063°C, the melting point of Au, up to 1300°C, with contact angle measurements being taken every 50°C. Sufficient time was allowed for the drop to come to steady state. Ni on NiO was run at a constant temperature of 1500°C for two minutes. All runs were done under a vacuum of approximately 4×10^{-5} mm Hg. All samples were furnace cooled, reaching room temperature in 40 to 60 minutes.

C. Sessile Drop Tests and Analysis

Representative samples of sessile drop runs at different temperatures were further analyzed. A shear test was devised from which was obtained semi-quantitative data concerning the strengths of the interfacial bonds.

Photomicrographs were taken of representative samples showing both interfacial zones and any reaction zones present. All samples were cut perpendicular to the interface and polished on a diamond wheel using 1/2 to 1 micron diamond grit.

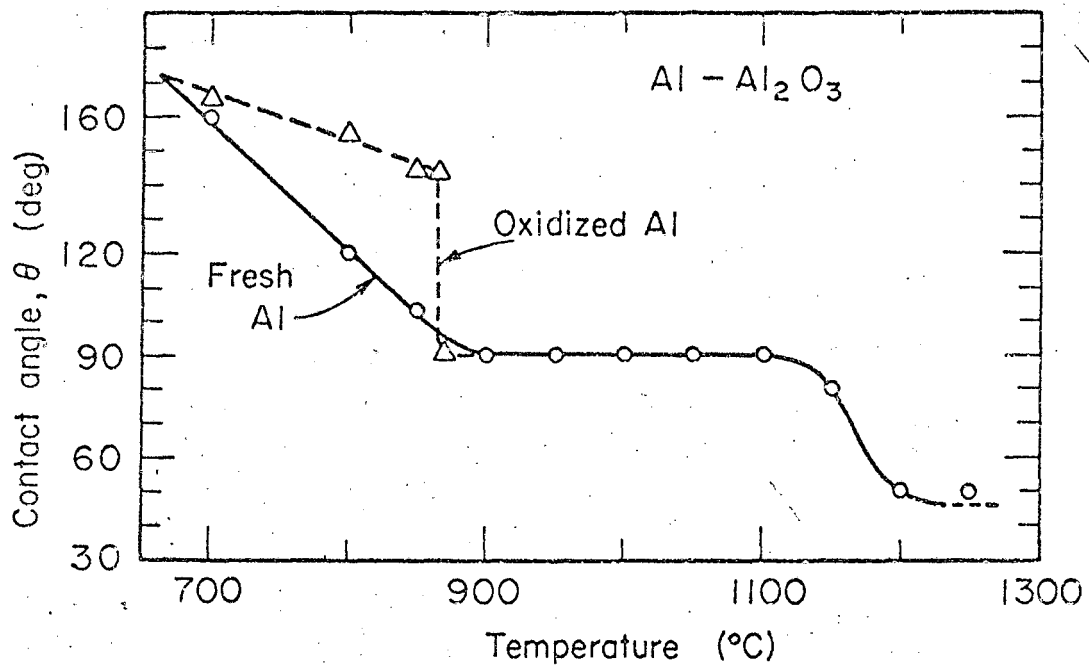
The Al-Al₂O₃, Al-MgO, Al-CaO, and Al-NiO systems were subjected to electron microprobe analysis. All interfacial zones were probed in order to determine if any reaction product was present and to try to identify its composition.

III. RESULTS AND DISCUSSION

The change in contact angle with temperature of molten aluminum on sapphire is shown in Figure II. Figure II is the average of six runs, all of which agreed within plus or minus five degrees. It can be seen that freshly cleaned aluminum on sapphire has an initial contact angle on melting (660°C) of 170° or essentially a case of non-wetting. With an increase in temperature, however, the contact angle decreases gradually, reaching a value of 90° by 900°C . The contact angle of 90° is maintained upon increase in temperature until a temperature of around 1150°C is reached, at which temperature the angle drops below 90° . By 1250°C the contact angle has reached approximately 50° . If the temperature is held constant at 1250°C , the contact angle will change with time, increasing abruptly from 50° to 70° and then dropping slowly back to 50° . This abrupt change in angle is repeated about every six minutes, with the size of the drop decreasing gradually with time.

A. Low Temperature Contact Angle Change (660°C - 900°C)

On exposure to air aluminum immediately forms an oxide coating of about $20 \text{ \AA}$ thickness which on further exposure will increase to $90 \text{ \AA}$ after about a month.¹¹ It was found that if oxidized pieces of aluminum were used in the sessile drop runs of aluminum on sapphire, a different contact angle vs temperature curve was obtained. This is also plotted in Figure II. On melting of the aluminum, the contact angle is the same as before (170°) but on increasing the temperature the contact angle remains high up to 870°C , where a sudden drop in angle occurs. At 860°C the contact angle is 145° . On increasing the temperature 10° to 870°C , the contact angle falls quite rapidly over a period of about



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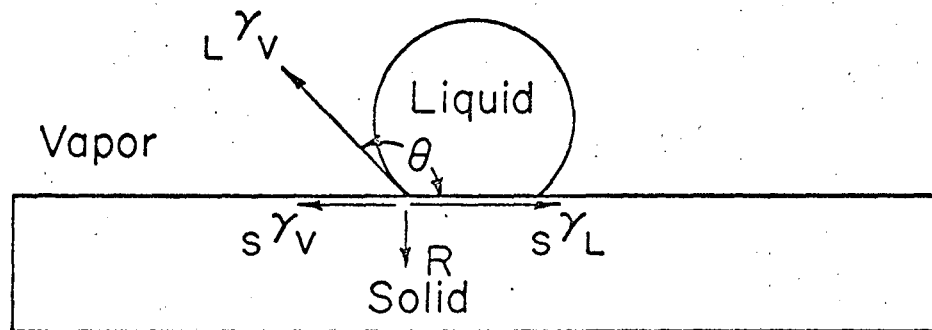
Fig. II. Change in contact angle with temperature for the system Al-Al₂O₃.

10 minutes to 90° . Above this temperature an oxide covered drop of aluminum behaves the same as a freshly cleaned drop, maintaining the angle of 90° up to 1150°C and then decreasing to 50° by 1250°C .

From Young's Equation it can be seen that for the contact angle to decrease, one or more of the three surface energy components has to change. (See Figure III.) Either the surface energy between the solid and vapor has to increase or the interfacial energy between the solid and the liquid has to decrease or, in the case of an obtuse angle, the surface energy of the liquid must increase.

From Figure III it can be seen that if the liquid-vapor surface tension (energy) was solely responsible for the drop in contact angle, it would have to increase to infinity for the contact angle to drop to 90° . Therefore, although the liquid-vapor surface tension might be changing, either the solid-vapor or solid-liquid tension must also change. To determine whether or not the surface tension of the sapphire was changing, a test was run with oxidized aluminum on MgO . From Figure IV it can be seen that again there is a large drop in the contact angle at 870°C , although only down to 110° . Therefore, the surface tension of the alumina is not the component that is changing at 870°C . On that basis, the interfacial energy between the liquid and the solid must be decreasing.

It is obvious that the oxide layer on the aluminum is the cause of the drop in contact angle. It appears that below 870°C this layer is inhibiting the establishment of equilibrium at the interface but that above this temperature changes so as to allow equilibrium to establish.



$$s\gamma_V = s\gamma_L + L\gamma_V \cos \theta \quad \text{Young's equation}$$

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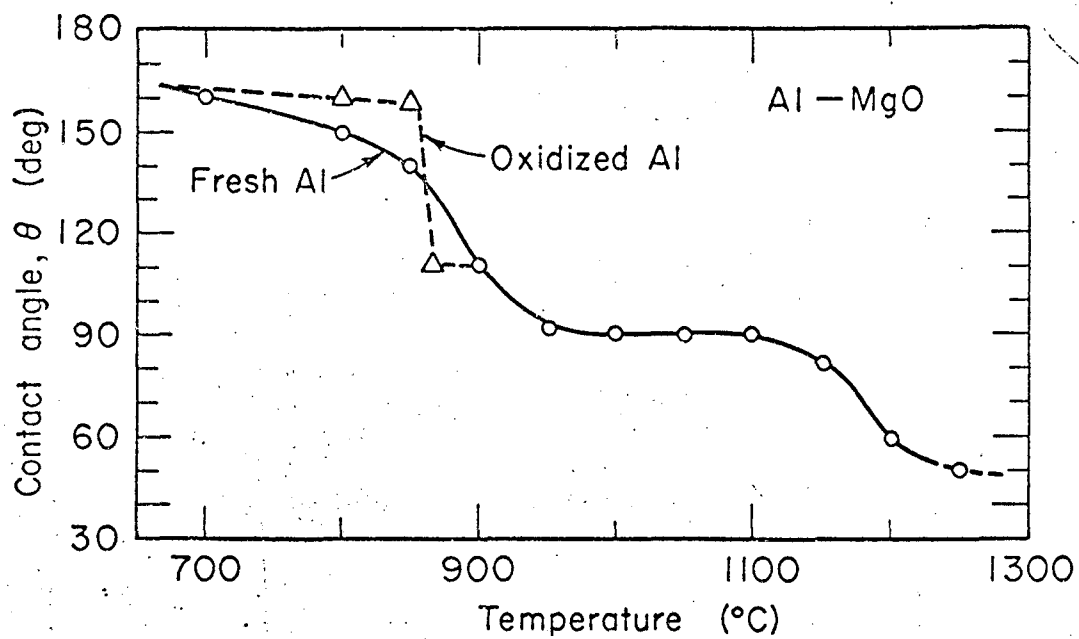
$L\gamma_V$ = liquid-vapor interfacial tension

$s\gamma_V$ = solid-liquid interfacial tension

$s\gamma_V$ = solid-vapor interfacial tension

R = reaction force

Fig. III. Forces acting on obtuse angle sessile drop.



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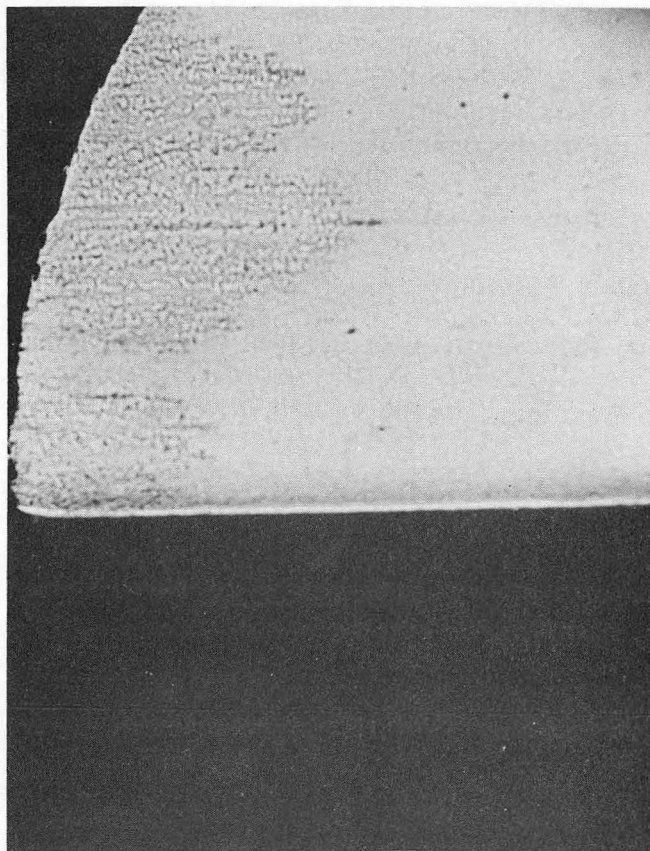
Fig. IV. Change in contact angle with temperature for the system Al-MgO.

What these changes in the surface of the aluminum and at the interface are has not been determined.

It has been reported by Hass¹¹ that the oxide formed on aluminum in vacuum at low temperatures is amorphous and becomes crystalline at 500°C. This is supported by the work of Estill¹² who found that diffuse gamma alumina x-ray diffraction lines showed up when the oxide on aluminum was heated above 550°C while no lines showed up below this temperature. Konig¹³ found that all alumina films that were in contact with aluminum at 800°C gave a cubic lattice constant of 7.89 angstroms, regardless of their previous history. This lattice constant is typical of either eta or gamma alumina, both of which could be slightly hydroxylated forms of Al_2O_3 . The observed change in contact angle at 870°C could be due to another change in this oxide layer.

Photomicrographs of the interfacial region between an oxidized aluminum drop and sapphire which had been heated to 900°C do not show any reaction product at the interface. However, an even polish was not obtainable due to the large difference in hardness between the aluminum and the sapphire. Attempts to polish these specimens resulted in a "step" being formed at the interface. Good, clear photomicrographs were not obtainable. Figure V shows this interface. Electron probe analysis showed that no interdiffusion whatsoever took place.

Photomicrographs of an oxidized Al-Mgo interface heated to 900°C do show an interfacial phase. (Figures VI and VII.) From electron microprobe analysis this phase was found to contain a weight percentage of aluminum indicative of Al_2O_3 . This can qualitatively be seen in Figures VIII and IX which are oscilloscope traces of the interface.



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Fig. V.

Fig. V. Sessile Drop of Aluminum on Sapphire at 900°C. (63X)

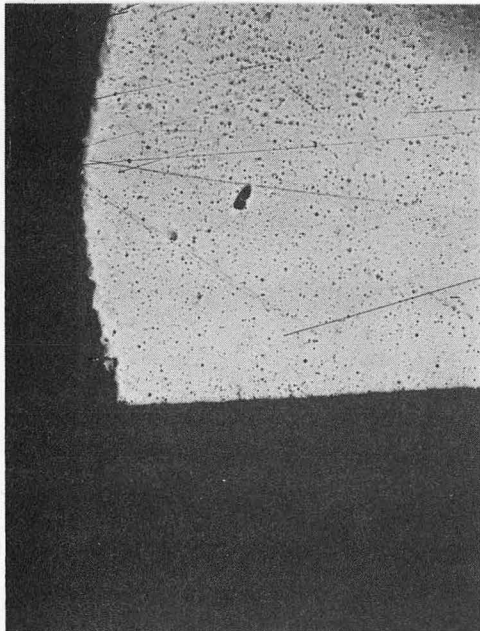


Fig. VI.

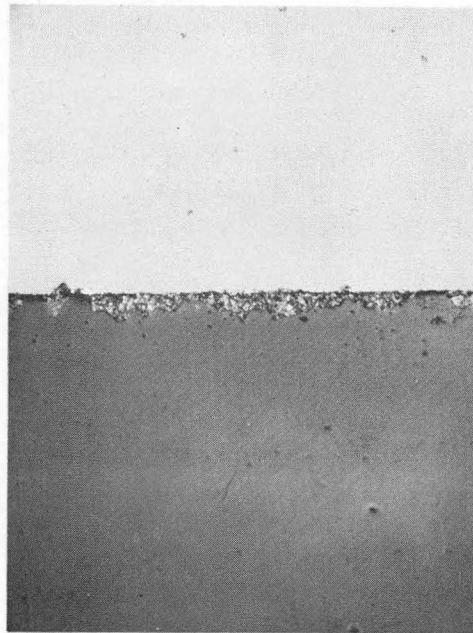


Fig. VII.

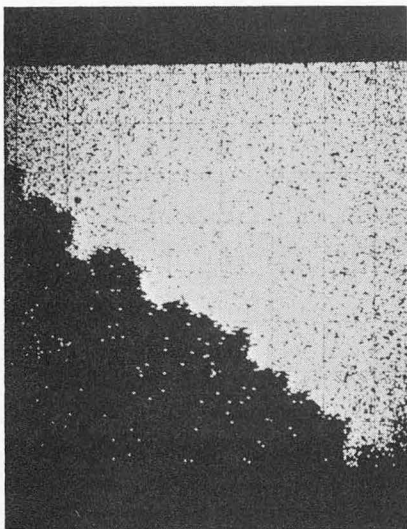


Fig. VIII.

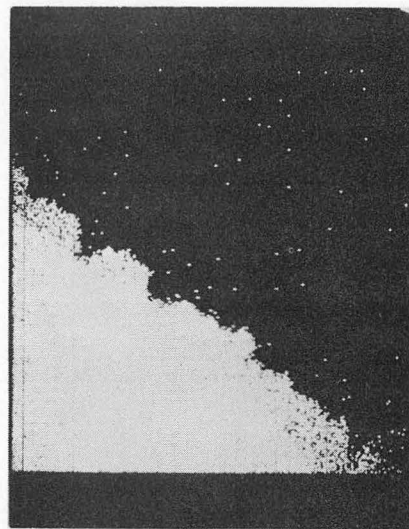
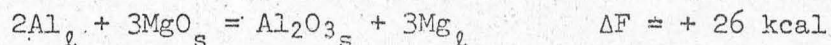


Fig. IX.

- Fig. VI. Sessile Drop of Al on MgO at 900°C. (63X)
- Fig. VII. Interface between Al and MgO, 900°C. (250X)
- Fig. VIII. Oscilloscope trace of Al-MgO interface, 900°C, using Mg radiation. (200X)
- Fig. IX. Oscilloscope trace of Al-MgO interface, 900°C, using Al radiation. (200X)

These pictures show that the interfacial phase does not contain magnesium and appears to have a lower aluminum concentration than pure aluminum metal.

Unoxidized Al-MgO sessile drops also seem to have very small amounts of Al_2O_3 at the interface at 900°C . This observation along with the observation that with oxidized or unoxidized Al-MgO samples a large reaction zone of Al_2O_3 is present at higher temperatures leads to the conclusion that a reaction takes place between Al and MgO. (See Figures X, XI, XII, and XIII.) This reaction seems to be enhanced by the presence of small amounts of Al_2O_3 from the aluminum surface. The probable reaction is:



Due to the rapid evaporation of the magnesium under vacuum, this reaction is driven towards the right making it thermodynamically feasible. That the magnesium goes off in vapor form is evidenced by the pinhole effect noticeable in the aluminum next to the interface as shown in Figure XIII.

Essentially then the Al-MgO system is the same as the Al- Al_2O_3 system after about 950°C , in that the surface that the aluminum is in contact with is alumina and not MgO. In fact, from Figures II and IV it can be seen that above 950°C the Al-MgO system has the same contact angle vs temperature curve as the Al- Al_2O_3 system.

To determine if the large drop in contact angle at 870°C occurred with aluminum resting on other substrates, sessile drop tests of Al on CaO and Al on NiO were performed. The results of these tests were inconclusive, however, since a large amount of reaction product was formed at the interface. For Al on CaO, the reaction product was found

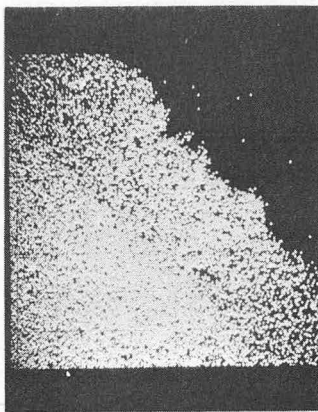


Fig. X.

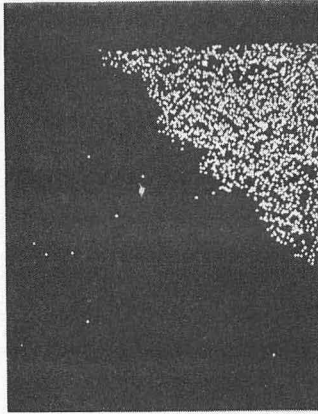


Fig. XI.

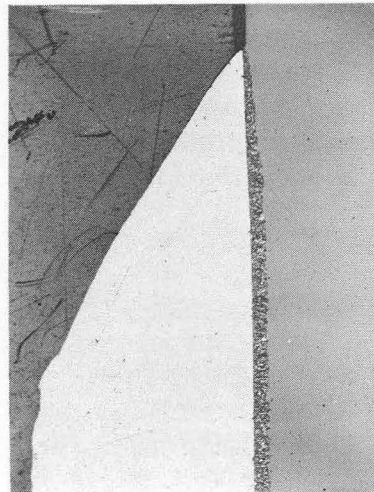


Fig. XII.

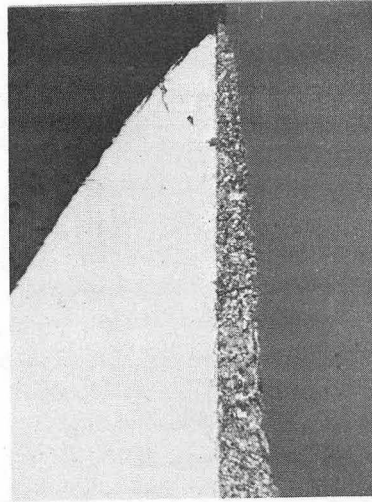


Fig. XIII.

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- Fig. X. Oscilloscope trace of Al-MgO interface, 1250°C, using Al radiation. (200X)
- Fig. XI. Oscilloscope trace of Al-MgO interface, 1250°C, using Mg radiation. (200X)
- Fig. XII. Sessile drop of Al-MgO with Al_2O_3 reaction product, 1250°C. (63X)
- Fig. XIII. Sessile drop of Al-MgO with Al_2O_3 reaction product, 1250°C. (250X)

by electron microprobe analysis to contain a ratio of two Al atoms to three Ca atoms. Figure XIV is a photomicrograph of the interface. The reaction started soon after the aluminum melted, causing the contact angle to drop rapidly down to 85° by 850°C .

An even greater reaction took place with Al on NiO. The reaction zone extended about 150 microns into the NiO and completely throughout the aluminum drop as shown in Figures XV and XVI. The white platelets are aluminum metal while the surrounding grey matrix was found by microprobe analysis to contain a ratio of two Al atoms to one Ni atom. In this system a high contact angle was maintained, due to much of the drop being solidified due to the reaction product. The reaction began immediately upon melting of the aluminum and progressed to the stage shown by 900°C in 40 minutes.

B. High Temperature Contact Angle Change (1150°C - 1250°C)

Returning to the Al- Al_2O_3 system, it was found that the contact angle of 90° , first established at about 900°C , was maintained up to a temperature of about 1150°C . At this temperature the angle began dropping rapidly below 90° , reaching 50° by 1200°C . For the contact angle to drop below 90° , the surface tension of the solid must be greater than that of the interface. This can occur by either the interfacial tension between the solid and the liquid being reduced or the surface tension of the solid being increased. Either one or both may be changing.

It has been reported by Parks¹⁴ that the surface of alumina and other oxides consists of absorbed layers of hydroxyl ions, the last of which does not appear to dehydroxylate until about 1000°C . This change in surface for Al_2O_3 above 1000°C is supported by the ZPC work of

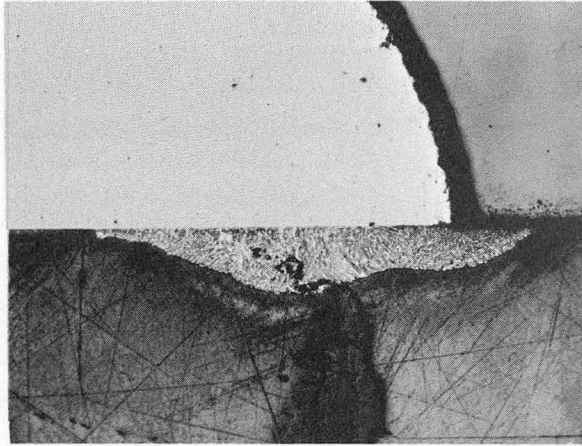


Fig. XIV.



Fig. XV.



Fig. XVI.

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Fig. XIV. Sessile drop of Al on CaO with interfacial reaction product, 900°C. (63X)

Fig. XV. Sessile drop of Al on NiO, 900°C. (63X)

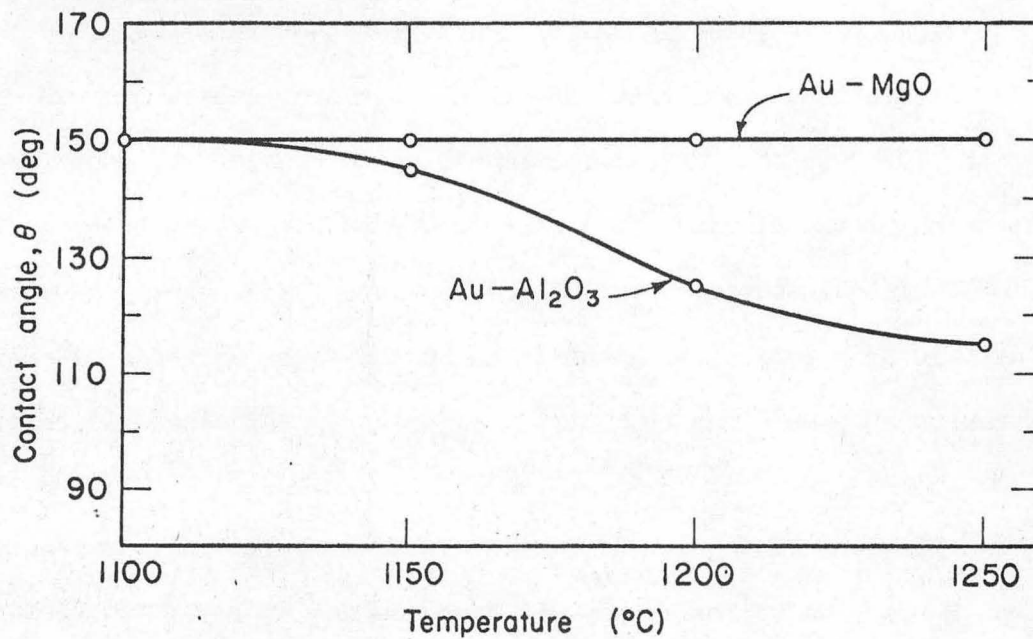
Fig. XVI. Interfacial region of Al-NiO system, 900°C. (250X)

Robinson, et al.¹⁵ The removal of this last monolayer of hydroxyl ions would tend to increase the surface tension of the alumina, due to the resulting poorer screening of the surface atoms without the presence of the hydroxyls. This, therefore, could account for the drop in contact angle at about 1150°C.

To determine whether or not the surface tension of the alumina is changing at 1150°C, a sessile drop test of Al on MgO was performed in this temperature range. It would be expected that no drop in contact angle would be observed if it was the alumina that was responsible for the change in angle in the Al-Al₂O₃ system. However, as discussed previously, a reaction took place between Al-MgO to form Al₂O₃ at the interface, thus explaining the observed drop in contact angle at 1150°C as shown in Figure IV. Therefore, the Al-MgO system does not provide a check on a possible change in the alumina surface tension.

To provide this check, a non-reactive metal was used as a sessile drop on both Al₂O₃ and MgO. This metal was gold and contact angle runs between it and the two substrates were conducted in the temperature range 1100°C-1250°C. Figure XVII shows the results of these experiments. Gold on MgO shows no change in contact angle from 1100°C to 1250°C while gold on sapphire shows a marked drop in contact angle from 150° to 115° over this temperature range. Since both of these systems are quite non-reactive it seems likely that the surface tension of the sapphire is increased at about 1200°C leading to a drop in contact angle.

The surface tension of Al₂O₃ as usually given is that calculated by Kingery¹⁶ as 905 dynes/cm at 1800°C. Correcting for temperature



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Fig. XVII. Change in contact angle with temperature of Au-MgO and Au-Al₂O₃ systems.

change, this value would be 960 dynes/cm at 1250°C. Using the value given by Semenchenko¹⁷ of 1125 dynes/cm for the surface tension of liquid gold and knowing the contact angle to be 115° at 1250°C, the value of the solid-liquid interfacial energy can be calculated using Young's Equation. This value is calculated to be 1440 dynes/cm.

If it is assumed that the change in contact angle of gold on alumina from 1100°C to 1250°C is due primarily to a change in the surface tension of the alumina, as it appears to be, and using the same values for the liquid surface tension and the interfacial energy as were used at 1250°C, a rough approximation as to the value of the solid surface tension at 1100°C can be made. This value is calculated to be about 500 to 600 dynes/cm.

The surface tension of liquid aluminum at 1100°C is given by Livey and Murray⁹ as approximately 750 dynes/cm and at 1250°C as 712 dynes/cm. It appears then that below about 1150°C the surface tension of the aluminum is higher than that of the alumina while above this temperature the opposite is true.

Another possible explanation for this observed drop in contact angle could be that above 1150°C Al and Al₂O₃ are not in equilibrium but become reactive, influenced by the change in surface structure of the Al₂O₃. This idea is supported by the microscopic observation of steps or "rings" formed on the surface of the sapphire if heated above 1250°C. The rings become visible due to the reduction in size of the aluminum drop at this temperature due to its appreciable vapor pressure ($\sim 10\mu$ at 1250°C). Under the microscope these "rings" are shown to be the edges of depressions in the sapphire where it has been covered by

the aluminum. Above 1150°C the aluminum begins to appreciably dissolve the sapphire. On cooling, the dissolved alumina then would recrystallize out again because of the decrease in solubility. Figure XVIII, taken looking through the sapphire, shows the interface between a drop of aluminum and sapphire which has been heated to 1300°C and then cooled. Small, angular crystals can be seen at the interface. Under the microscope these appear to be crystalline needles of alumina. Figure XIX shows a comparable interface heated to only 1000°C. Notice the polishing scratches on the surface of the sapphire at the interface which are gone at 1300°C, indicating dissolution of the sapphire.

The reduction in size of the aluminum drop and the dissolution of the sapphire cause the drop to jump from a low contact angle of 50° up to an angle of about 70° every six minutes or so at 1250°C. Carnahan, et al.,¹⁰ observed similar phenomena during the course of their investigation concerning the wetting of alumina by aluminum. They explained it on the basis of the drop, which is decreasing in volume due to evaporation, being held up by the step in the surface of the sapphire. As the surface tension forces acting on the edge of the drop build up to overcome this step, the drop suddenly contracts to assume its equilibrium position, leaving the dissolution step behind.

Since the aluminum drop is continuously dissolving the sapphire, it appears that a gaseous reaction product such as Al_2O is also being formed. If this was not the case the aluminum, since it is continually decreasing in volume, would soon become saturated with alumina and the dissolution of the alumina would cease. This is not observed. Observations by Carnahan, et al.,¹⁰ and Brewer and Searcy¹⁸ indicate that Al_2O

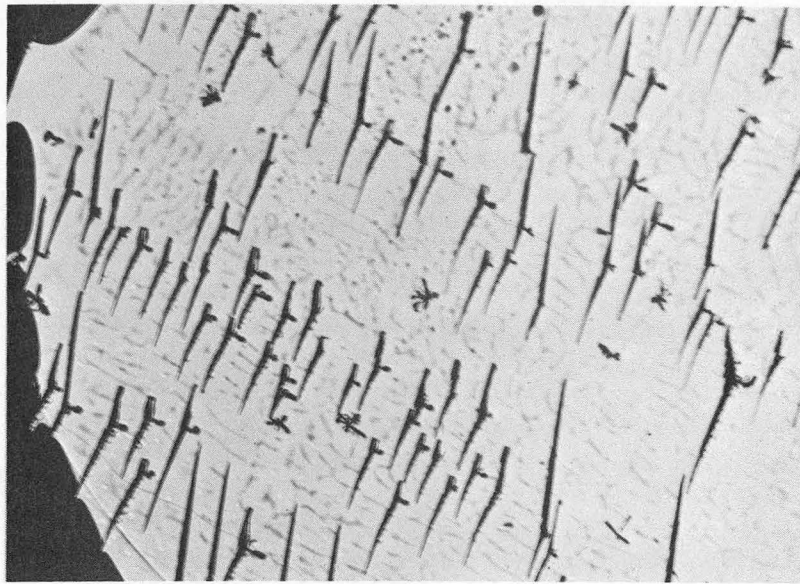


Fig. XVIII.

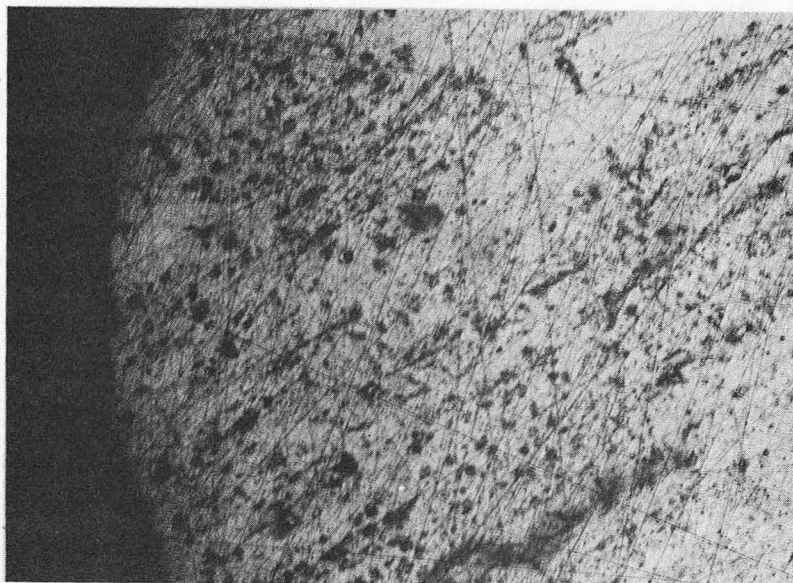


Fig. XIX.

ZN-5806

Fig. XVIII. Interface of Al-Al₂O₃ system as seen looking through the sapphire, 1300°C. (63X)

Fig. XIX. Interface of Al-Al₂O₃ system as seen looking through the sapphire, 1000°C. (63X)

gas is indeed forming.

No mention was made by either Livey and Murray⁹ or Carnahan, et al.,¹⁰ concerning the presence of crystals at the Al-Al₂O₃ interface which formed on cooling. These crystals, while not positively identified, indicate that the sapphire actually goes into solution in the molten aluminum while also reacting with the aluminum to form a gaseous product such as Al₂O.

It is also a possibility that aluminum and alumina react at about 1150°C to form another solid oxide of aluminum. By high-temperature x-ray techniques, Hoch and Johnston¹⁹ found that Al and Al₂O₃ were the stable phases below 1100°C, Al₂O between 1100°C and 1400°C and AlO above 1400°C. On cooling, these phases were found to be unstable and decomposed to Al and Al₂O₃. So it is possible that the low contact angle at 1150°C results from a reaction between the Al and Al₂O₃ to form Al₂O which, upon cooling, changes back into Al and Al₂O₃. The crystalline dendrites at the interface could be recrystallized Al₂O₃. These observations are subject to doubt, however. Brewer²⁰ observes that the phases seen by Hoch and Johnston¹⁹ are actually aluminum oxy-carbides or aluminum carbides formed by reaction of the binding glue used with the Al-Al₂O₃ compact.

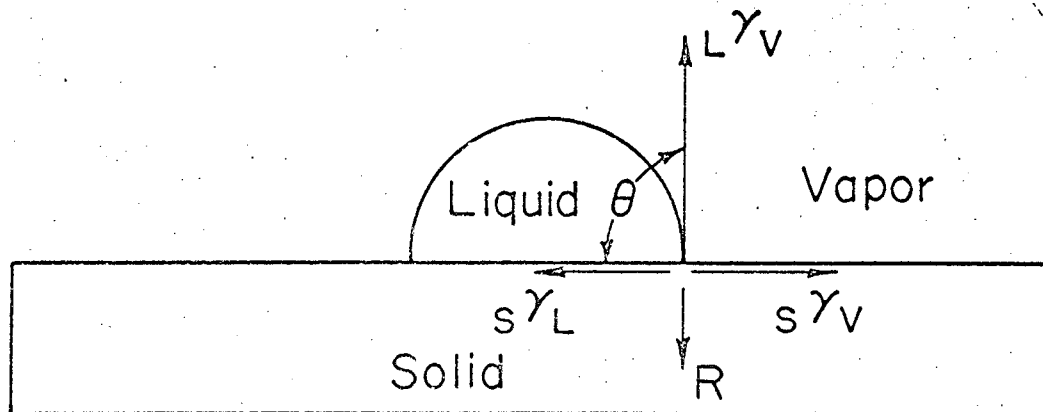
C. Intermediate Temperature Contact Angle Stability (900°C-1150°C)

As stated previously, the contact angle of Al on Al₂O₃ remained constant at 90° from 900°C to 1150°C with the aluminum being in equilibrium with the sapphire in this temperature range. No reactions or phase changes took place. Each phase should then be saturated with the other,

and it appears that this is true. Ninety degrees appears then to be the equilibrium angle between a metal and its stable oxide or in fact between any high surface energy liquid on a lower surface energy solid. To test this idea a sessile drop run was performed using nickel on NiO. The contact angle was measured after two minutes at 1500°C and was observed to be 90°.

At 90° the surface tension of the solid-vapor interface is equal to the surface tension of the solid-liquid interface as is shown in Figure XX. The surface tension of the solid has not been reduced by the presence of the liquid. The surface tension of the liquid has been reduced by the solid, forming the interface in the first place. If the liquid was not reduced by the solid the contact angle would be 180°. Reduction of the surface tension of the liquid by the solid leads to the formation of the liquid-solid interface and the lowering of the contact angle from 180° down to a minimum of 90° at equilibrium. Only if the surface energy of the solid is reduced by the liquid through chemical reaction at the interface or possibly a change in the surface structure of the solid, resulting in a surface energy higher than the interfacial energy, will the contact angle drop below 90°.

It appears then that for a high surface energy liquid on a low surface energy solid the minimum contact angle without a reaction taking place is 90° and can be considered as the angle of complete "wetting" under these conditions. In the case of a metal on its stable oxide, 90° can also be considered as the equilibrium angle between the two phases, each being saturated at the interface with the other.



$$s\gamma_V = s\gamma_L + L\gamma_V \cos \theta \quad \theta = 90^\circ$$

$$\underline{\underline{s\gamma_V = s\gamma_L}}$$

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$L\gamma_V$ = liquid-vapor interfacial tension

$s\gamma_L$ = solid-liquid interfacial tension

$s\gamma_V$ = solid-vapor interfacial tension

R = reaction force

Fig. XX. Forces acting on sessile drop of 90° contact angle.

D. Shear Test Results

From Table I it can be seen that all samples of aluminum on sapphire had very strong interfacial bonding except those samples which had been heated to just above the melting point of aluminum. Any yielding that took place during the test occurred in the aluminum and not at the interface. Even the samples that did yield before the limit of the testing apparatus was reached, yielded in the aluminum and not at the interface. It appears that almost as soon as the aluminum melts, strong bonds are being formed at the interface between the aluminum and the sapphire. Due to the softness of the aluminum, it is impossible to determine whether these bonds are chemical or merely strong Van der Waals' bonds. Van der Waals' bonds may be the source of strength up to 900° or so (contact angle down to 90°) and then chemical bonds above that temperature.

Sessile drop samples of Al on MgO exhibited good strength, but not as good as the Al_2O_3 system. The failure in the Al-MgO system seemed to occur partly in the aluminum and partly at the interface, with the aluminum shearing up to a certain stress and then a quick break at the interface. This leads one to believe that while chemical bonds are probably the main source of adherence at the interface, the overall strength is weaker than that in the Al- Al_2O_3 system, due to the intermediate polycrystalline Al_2O_3 reaction zone.

The sessile drop samples of Al on CaO and NiO broke at quite low stresses. Fracture occurred at the interface, between the reaction zone and the pure substrate. This observation substantiates Sutton's⁵ view that if the reaction zone is more than a few microns thick, it

Table I. Results of Shear Tests

System	Contact Angle - θ	Maximum Temp.	Shear Strength	Remarks
Al-Al ₂ O ₃ (clean Al)	170°	670°C	1800 psi	Broke at interface
"	120°	800°C	over 8000 psi	Exceeded limit of testing machine. Only yield was in Al metal
"	90°	900°C	" " "	"
"	50°	1250°C	" " "	"
Al-Al ₂ O ₃ (oxidized Al)	155°	800°C	7500 psi	Yield was in Al metal
"	90°	900°C	over 8000 psi	"
"	50°	1250°C	" " "	"
Al-MgO	90°	950°C	6500 psi	Yield partly in metal, partly at interface
Al-CaO	85°	950°C	3500 psi	Broke in interfacial reaction zone
Al-NiO	120°	950°C	3000 psi	"
Ni-NiO	90°	1500°C	2000 psi	Fractured in NiO
Au-Al ₂ O ₃	115°	1250°C	1800 psi	Broke clean at interface
Au-MgO	150°	1250°C	1500 psi	"

weakens the interface and leads to fracture at low stresses.

The sample of Ni on NiO exhibited poor strength; however the NiO was highly stressed and fracture occurred along cleavage planes in the NiO and not at the interface. The bonds formed at the interface seemed to be quite strong, as expected.

The sessile drop specimens of gold on MgO and Al₂O₃ exhibited quite weak shear strengths. Fracture occurred at the interface with the gold breaking cleanly from the substrates. It is evident here that adherence at the interface was due to Van der Waals' bonds between the two phases.

IV. SUMMARY AND CONCLUSIONS

The contact angle vs temperature curve for the system Al-Al₂O₃ shows major changes in angle for certain samples at 870°C and 1150°C. The lowering of the contact angle at 870°C can be attributed to the presence of an oxide layer on the aluminum metal. It seems that at this temperature a change takes place in this oxide layer which leads to a lowering of the liquid-solid interfacial energy, thus lowering the contact angle to 90°.

The drop in contact angle at 1150°C below 90° could be a combination of surface energy changes. It appears that at this temperature the surface of the Al₂O₃ changes in structure, resulting in an increase in the solid-vapor surface energy, causing a reduction of the solid surface energy by the liquid. It also has been shown that at this temperature the aluminum and sapphire react, with the aluminum appearing to dissolve the sapphire and also producing gaseous Al₂O. This could lead to a reduction in the liquid-solid interfacial tension and a corresponding reduction in the contact angle.

From 900°C to 1150°C the contact angle of aluminum on sapphire remains constant at 90°. This angle of 90° appears to be the equilibrium angle between a high surface energy liquid and a lower surface energy solid that are at thermodynamic equilibrium. The contact angle will fall below 90° only when the surface tension of the solid is reduced by the liquid.

During the course of the investigation it was found that aluminum on other substrates such as MgO, CaO, and NiO will react to form a third phase. Considerable reaction product was observed in the Al-Cao

and Al-NiO systems and greatly affected the adherence. A relatively small amount of reaction product was observed in the Al-Mgo system and was not detrimental to the adherence.

Future work in the fundamental systems such as Al-Al₂O₃ needs to be done and will be undertaken by the author in the near future, with emphasis on high-temperature x-ray diffraction studies and on the solubility of alumina in aluminum at high temperatures. Other metal-metal oxide systems will also be investigated.

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