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EFFECT OF NATURE OF SURFACES ON WETTING OF SAPPHIRE BY LIQUID ALUMINUM

John J. Brennan and Joseph A. Pask

April 1968

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ABSTRACT

Contact angles of aluminum drops on sapphire measured under vacuum conditions, from 660 to 1250°C, generally fell into three ranges. Large obtuse contact angles indicating interfacial energies greater than either of the two surface energies were obtained up to about 900°C; van der Waals bonding then existed at a compound interface. In the intermediate range, contact angles were 90° or slightly greater indicating a common interface with an energy ($_s\gamma_\ell$) greater than $_s\gamma_g$ but less than $_\ell\gamma_g$. Acute contact angles indicating a $_s\gamma_\ell$ less than $_s\gamma_g$ and greater

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than ${}_{\ell}\gamma_{g}$ occurred above about 950°C because of the formation of a high temperature complex surface structure with a ${}_{s}\gamma_{g} > {}_{\ell}\gamma_{g}$. A hydroxylated sapphire surface has a lower ${}_{s}\gamma_{g}$ which increases with gradual dehydroxylation and conversion to the high temperature surface structure with a corresponding change in contact angle through the three ranges. Chemical bonding existed in the latter two ranges. Reactions occurred between Al and the sapphire surface to form volatile species at contact angles less than 90°. Molten Al normally has an oxide coating whose effect appears to be removed at about 870°C.

I. INTRODUCTION

Wetting studies of molten aluminum (Al) on sapphire (single crystal Al_2O_3) were made over a range of temperatures by the sessile drop method. In the absence of any surface or interfacial reactions the surface energies and the resulting contact angles, except for a slight temperature effect, should remain essentially constant. Current experiments and reported studies in the literature indicate significant changes in the contact angle under various conditions.

Livey and Murray[1] reported a contact angle of 148° at 970°C which dropped to 47° after 30 minutes at 1255°C; no reactions between Al and Al_2O_3 at the interface were indicated. Carnahan et al.[2] also observed a large contact angle of Al on recrystallized Al_2O_3 at 1240°C in vacuum which decreased to 60° in 20 minutes; on sapphire at 1200°C Al spread and then rapidly contracted to a contact angle of 80°. This behavior continued cyclicly with the volume of the Al drop decreasing at each cycle and "rings" or "steps" being formed on the surface of the sapphire; this was attributed to a reaction at the interface with the formation of Al_2O gas. Wolf et al.[3] observed a continually decreasing contact angle of Al on sapphire from 167° at 700°C to 70° at 1150°C; a reaction was also observed above 935°C resulting in the dissolution of the sapphire and the formation of reaction rings.

The objective of this study was to provide an explanation for the observed variations in contact angles. In the process, changes occurring in the sapphire surface were analyzed. Supporting data was obtained by making measurements on several additional systems: Au-Al_2O_3, Al-MgO, Al-CaO, Al-NiO, and Ni-NiO. Observations on adherence were also made.

II. EXPERIMENTAL PROCEDURE

The single crystal α-Al_2O_3 (sapphire) 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. In some cases an Al_2O_3 plaque was preheated in vacuum at 1300°C just prior to a sessile drop experiment; for some others, soaked in water at room temperature for about a week.

The Al used was obtained from Cominco Products, Inc. in 3/16" diameter rods of 99.999% purity, which were cut and ground into 1/8" by 1/8" cubes just prior to a sessile drop run. In some cases the cut specimens of Al aged for several weeks. The surface of Al oxidizes easily; on exposure to air an oxide coating of about 20 Å thickness forms immediately which increases to about 90 Å after a month.[12] The gold and nickel used were of 99.99% purity and were obtained from the Lawrence Radiation Laboratory.

The MgO and CaO was provided by the Muscle Shoals Electrochemical Corporation in polycrystalline lumps incorporating large crystals one to two inches long which were then cleaved into single crystal plaques. The NiO was obtained from the Marubeni-Ilda Company in Japan in single crystal boules which were cleaved for experimental use. All substrate materials were of approximately 99.7% purity.

Sessile drop observations were made in a graphite tube resistance furnace (shown in Fig. 1) operated at pressures of 2 to 6 x 10^{-5} torr. The graphite tube was connected to water-cooled copper electrodes by graphite holders. Under these conditions, the oxidation of molten Al

during a test did not appear to be a problem. The substrate plaques rested on the flat surface of an alumina "dee" tube which was fitted inside the graphite tube. The Al was placed on the plaque as a chunk; and the Au, as a small coiled spring which formed a drop on melting. 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 a lower oxygen pressure a zirconium getter was placed around the sessile drop specimen.

Representative specimens of sessile drop runs were subjected to a shear test which provided information concerning the strengths of the interfacial bonds. The remaining sessile drop specimens were cut perpendicular to the interface and polished on a diamond wheel using 1/2 to 1 micron diamond grit for observation of the interfacial zone. The zones of the Al-Al_2O_3, Al-MgO, Al-CaO, and Al-NiO systems were scanned with an electron microprobe.

III. RESULTS AND DISCUSSION

A. Contact Angles of Aluminum on Sapphire

The effect of temperature on the contact angle of molten fresh Al on as-received, heat-treated, and water-soaked Al_2O_3, and of oxidized-Al on as-received Al_2O_3, is shown in Fig. 2. The temperature in each case was raised in 50°C increments every 10 minutes from 750 to 1250°C. All specimens were cooled in the furnace, dropping to below red heat in about 3 minutes and to room temperature in 30 to 40 minutes. In no case, even with slower cooling rates, was there a reversal of contact angle

on cooling. The curve for as-received Al_2O_3 with fresh Al is an average of six runs, whose contact angles at a given temperature agreed within ±5 degrees; it includes one run using a disk cut at a 90° orientation from the c-axis. The similarity of values indicated that the contact angles were essentially independent of these orientations of the sapphire; the more easily obtainable disks cut at a 60° orientation from the c-axis were thus used throughout.

A run was made in which the sapphire was heated at 1200°C and cooled to about 400°C at $\sim 10^{-5}$ torr; the Al was then dropped onto the sapphire surface and the temperature was raised in increments without any change in pressure. The resulting contact angle-temperature sequence was similar to that obtained for the fresh Al on heat-treated Al_2O_3, which was exposed to air after heat treatment, shown in Fig. 2.

The time-dependence of the contact angles is illustrated by the curves for fresh Al on heat-treated and water-soaked Al_2O_3 at 800 and 900°C in Figs. 3 and 4, respectively.

The data indicates that the contact angles can be generally divided into three ranges: (a) large obtuse angles, (b) small obtuse angles including 90°, and (c) acute contact angles. The first range occurred at temperatures up to about 900°C (using the heating rates of Fig. 2) and the third range, above about 950°C; sharp temperature divisions were not present. The contact angle (obtuse or acute) would be expected to remain essentially constant over a temperature range in the absence of any reactions or significant changes in the structure and composition of the surfaces and interface. Such a contact angle is determined by

B. Sapphire Surfaces

Some significant structural changes of the (001) surface of α-Al_2O_3 have been observed with low-energy electron diffraction (LEED) by Charig.[5] He has shown that a chemically polished surface usually gives rise to a weak diffraction pattern corresponding to the bulk lattice arrangement. This pattern persists for a wide range of vacuum conditions up to 900°C. Heating to 1000°C for as little as 5 minutes results in the formation of a complex two-domain diffraction pattern with many fractional order reflections (observed at room temperature). Again vacuum conditions are not critical, the change occurring equally readily at 5×10^{-10} torr, 10^{-6} torr and in pure oxygen as high as 4×10^{-4}. Once formed the new structure is only influenced at room temperature by exposure to water vapor at $\sim$ 1 mm or air at atmospheric pressure when some loss of intensity and resolution results. Heat treatment up to $\sim$ 1200°C at pressures of 10^{-6} or less causes no further changes. The pattern corresponding to bulk alumina can be recovered by etching away the surface below 900°C. This can be effected by electron bombardment, the rate depending on both electron current and voltage, (e.g. 1 KV 7mA will restore the bulk surface in a few minutes, 100 eV 1mA requires several hours), or by evaporated silicon vapor. The latter will cause epitaxial Si deposition if the rate is too high or the alumina temperature too low. High rates of electron bombardment particularly at the higher temperatures (1 KV 10mA heats the alumina to $\sim$ 1000°C) give such rapid dissociation of the alumina that the system pressure rises significantly.

The occurrence of possible changes in the surface structure of powdered α-Al_2O_3 by heating at higher temperatures in air is also

indicated in streaming potential studies of Robinson et al.[6] Samples heated below 1000°C showed a zero point of charge at pH 9.2 ± 0.2; at 1000°C, a zpc at pH 8.9; and at 1400°C, a zpc at pH 6.7. Exposure of the powder calcined at 1400°C to distilled water at room temperature for a period of a week raised its zpc to a pH of 7.7. The hydroxylation characteristics of the alumina surfaces are thus dependent upon the history of their treatment. Parks has reported studies indicating that temperatures of about 1000°C are needed to completely desorb layers of hydroxyl ions from oxide surfaces.[7]

Of critical importance is the nature of the heat-treated sapphire surfaces. On the basis of the existence of AlO and lesser amounts of Al_2O vapor species above Al_2O_3 at high temperatures,[8,9] it could be postulated that at temperatures above about 900-1000°C and low pressures an oxygen-deficient surface of some unknown thickness exists containing some AlO in a spinel-type structure (which will be referred to subsequently as HTH-surface). It could also be postulated that on cooling dissociation results with the formation of a stoichiometric structure wherein some of the Al^{3+} would have a coordination of four instead of six which would correspond to a structure of a γ-alumina type (which is supported by the work of Frieser[10]). This structure corresponds to the high temperature complex structure observed by Charig and will be referred to subsequently as HTγ-surface. The heat-treated surface experienced by Robinson et al. is probably also of the HTγ-type. In all of these postulates the "two dimensional" structure gains stability from the bulk substrates. The low temperature surface structure contiguous with the bulk structure will be referred to subsequently as α-surface.

In sessile drop experiments these considerations are critical since the sapphire surface energy is dependent upon the nature of its surface. The value of 905 ergs/cm^2 reported by Kingery,[11] which was determined at 1800°C and low pressures, would be expected to correspond to the HTH-surface. The other surface structures should have lower surface energies and on exposure to oxygen or moisture should experience a reduction in surface energy. A value of 560 ergs/cm^2 for γ-Al_2O_3 has been reported.[13]

C. Interpretation of Contact Angles of Al on Sapphire

1. Large Obtuse Contact Angle Region

The initially large angles of about 160°, when ${}_s\gamma_\ell$ is greater than either ${}_\ell\gamma_g$ or ${}_s\gamma_g$, indicate the absence of a common interface. The presence of hydroxylated α-surfaces is associated with this behavior as suggested by the shapes of the curves in Fig. 2 and by the initial angle of 118° for the heat-treated Al_2O_3 which would be expected to have less hydroxylation, if any. Molten Al can react with the hydroxylated surface to form Al_2O_3 and H_2, and thereby a common interface. The kinetic nature of this reaction is indicated by the decrease in contact angles with increase in temperature and time.

The presence of an oxide-like film on Al retards this reaction as shown by the curve for the as-received Al_2O_3 and oxidized Al system. Observations during this experiment also indicated the appearance of "breaks" in the Al surface at 870°C suggesting that "clean" Al comes in contact with the substrate at this point with the formation of a common interface and abrupt large decrease in contact angle. The breaks could be due to a rapid increase of the solubility of the aluminum oxide film in Al because of a possible change in its structure similar to that of

the HTH-surface but occurring at a lower temperature because of a higher energy state due to its thin film configuration. The same difference in behavior between fresh and oxidized Al was also observed on single crystals of MgO oriented <001>. Further support of this significant change in behavior at about 870°C can be gained by comparison of the curves in Figs. 3 and 4 for 800 and 900°C, respectively.

2. Small Obtuse Contact Angle Region

With completion of the above reaction and formation of a stable chemically-bonded Al-Al_2O_3 interface, the ${}_s\gamma_\ell$ decreases and approaches ${}_s\gamma_g$; when ${}_s\gamma_\ell = {}_s\gamma_g$, the contact angle is 90°. In this range the ${}_s\gamma_g$ of clean α-surface Al_2O_3 must be less than that for Al. Since the reported values for the surface tension of liquid Al are 712 dynes/cm at 1250°C and 750 dynes/cm at 1100°C,[1] and 900 dynes/cm at 700°C,[13] the ${}_s\gamma_g$ of α-surface Al_2O_3 must be considerably less than the value of 905 dynes/cm for Al_2O_3 with a HTH-surface. The constant angle of 90° indicates that ${}_s\gamma_g$, or solid surface energy, is not lowered by being in contact with the liquid but that ${}_\ell\gamma_g$ is sufficiently lowered by the solid for ${}_s\gamma_\ell$ to become equal to ${}_s\gamma_g$. Contact angle measurements starting with a HTγ-surface are similar to those with an α-surface.

Similar behavior would be expected with any molten metal and its stable lowest valent oxide when the surface energy of the molten metal is greater.[4] Ni on a single crystal of NiO showed a contact angle of 90° after 2 minutes at 1500°C.

The water-soaked Al_2O_3 experiment (Fig. 2) in contrast to the other curves shows a drop in contact angle to about 103° at 850°C followed by a more gradual decrease with no arrest at 90°. This behavior arises

because the energy of the hydroxylated surface is lower than the energy of the α-surface Al_2O_3 and increases with dehydroxylation. The ${}_s\gamma_\ell$ would be expected to be that for an Al_2O_3-Al interface and remain essentially constant after an interface is formed on completion of the reaction of Al with the hydroxylated surface. The gradual drop in contact angle with increasing temperature beyond about 850°C can then be accounted for on the basis of an essentially constant ${}_s\gamma_\ell$ and an increasing ${}_s\gamma_g$ as the sapphire surface gradually dehydroxylates and transforms to a HTH-surface.

3. Acute Contact Angle Region

At higher temperatures the contact angle drops below 90° and decreases with increase in temperature (Fig. 2). This behavior is associated with the transformation of the α-surface to a HTH-surface whose ${}_s\gamma_g$ of 905 dynes/cm is greater than the surface energy of Al of about 750 dynes/cm.

The continuing decrease in contact angle beyond 90° with increasing temperature indicates the occurrence of changes in one or more of the surfaces. There could be a progressive change in the character of the sapphire HTH-surface resulting in a higher ${}_s\gamma_g$, or a lower ${}_\ell\gamma_g$ because of solution of some aluminum oxide in Al, or a decrease of ${}_s\gamma_\ell$ as a result of corresponding changes in the interface or a contribution of the energy of the reactions which are covered in the next section. These reactions are kinetically controlled as shown in Figs. 3 and 4.

D. Reaction Between Al and Al_2O_3

Examination of the interfaces of specimens with an acute angle showed the presence of "rings" on the sapphire surface, which became more noticeable with increase in temperature. Under magnification the rings are shown to be the edges of depressions in the Al_2O_3 which were in contact with Al. The rings become visible due to the reduction in size of the Al drop because of the reaction between Al and the AlO in the HTH-surface to form vapor species, Al_2O, and the appreciable vapor pressure of Al (e.g., approx. 10μ at 1250°C). Each ring represents a cycle consisting of a reduction of the contact angle as the volume of the Al drop decreases without change of interfacial area until a large enough unbalance of surface tension forces causes the drop to jump to its equilibrium angle where the process for the formation of a new ring starts again (e.g., a change between 70 and 50° about every six minutes at 1200°C). Carnahan et al.[2] and Wolf et al.[3] observed similar phenomena.

This behavior supports the hypothesis of the presence of a HTH-surface and the formation of vapor species by reaction. This reaction would presumably continue since the Al_2O_3 at the interface would continue to form a HTH-surface. If the process was only one of solution of Al_2O_3 by Al, then it would be expected that the solution would cease when the Al became saturated with Al_2O_3, especially since the volume of Al is decreasing by vaporization. It is possible that the energy of this reaction could contribute to a lowering of the interfacial energy with a corresponding contribution to the decrease in contact angle. On the basis of the sessile drop data, however, this contribution does not appear to be large.

Some solution of an oxide species does occur since crystallization of Al_2O_3 at the interface was observed on cooling from the higher temperatures when the contact angle was less than 90°. Figure 6, taken through the sapphire, shows small angular needlelike crystals at the interface of a specimen that had been heated to 1300°C. Specimens with an α-surface Al_2O_3 and contact angles of 90° or greater showed no reaction, i.e., the polishing scratches on the sapphire surface were still visible at the interface.

E. Gold on Sapphire

In order to illustrate further the dependence of the nature of the sapphire surface on the history of its treatment, contact angle versus time data of molten gold on heat-treated and water-soaked Al_2O_3 at 1100°C was obtained (Fig. 7) after reaching the temperature in 4 or 5 minutes. The former specimen showed a constant angle of 140° after about 3 hours; on cooling the Au adhered weakly. The watersoaked Al_2O_3 specimen showed an angle of 125° after 6 hours; the Au adhered strongly. In the latter case it is postulated that the Au reacted with an hydroxylated layer, which was not completely dehydroxylated in the time that it took to reach the melting point of Au (1063°C) when the interface was formed, to form a gold oxide layer at the interface contiguous with both bulk phases. Although bulk gold oxide is unstable at these temperatures, the oxide could persist as a "layer" at the interfacial zone, essentially in equilibrium with both phases, to provide a bonding mechanism. The formation of such a layer is not possible on heat-treated Al_2O_3 because of the absence of a hydroxylated layer.

F. Aluminum on Other Oxides

Sessile drop experiments were also made with Al on MgO, CaO and NiO. Extensive reactions were observed at the interfaces as soon as a common interface was formed at about 900°C. The reaction with NiO was most intense, as would be expected on the basis of the relative oxidation potentials. In such cases the contact angle measurements are meaningless because of the appearance of a complex interface as well as a lack of a steady state condition.

G. Shear Strength

The shear strength for all the Al-Al_2O_3 interfaces, except those of the specimens with the large obtuse contact angles, was high with failure occurring by yielding in the Al; in these cases chemical bonding was present at the interfaces since thermodynamic equilibrium exists between the bulk phases. The Al drop sheared off at the interface for the specimens with van der Waals bonding at the interfaces (large obtuse angles).

In the Ni-NiO specimen fracture occurred along cleavage planes in NiO since the system was highly stressed because of thermal strains which developed on cooling. The interface did not fail because of the presence of chemical bonding.

IV. CONCLUSIONS

Al and Al_2O_3 are the only bulk phases in the Al-O system that are thermodynamically stable at normal pressures.[14] They thus formed a stable interface that exhibited chemical bonding. The analysis of these experimental contact angle changes, with pertinent information from the literature, has led to the following conclusions and deductions concerning the nature of the surfaces and interfaces in this system:

(1) The structure of a sapphire (001) surface is contiguous with that of its bulk structure (referred to in this paper as α-surface) at temperatures up to about 900-1000°C (Charig[5]). Its ${}_s\gamma_g$ is less than ${}_\ell\gamma_g$ of molten Al, reported[1,12] as about 750-800 dynes/cm.

(2) At temperatures above about 900-1000°C at low pressures the sapphire surface structure is postulated to be oxygen-deficient and to contain some AlO in a spinel-type structure (referred to in this paper as HTH-surface). Its ${}_s\gamma_g$ is greater than ${}_\ell\gamma_g$ of molten Al and probably corresponds to the value of 905 ergs/cm^2 reported by Kingery.[11]

(3) On cooling the HTH-surface below 900-1000°C at low pressures the surface structure is unstable and changes to one related to the γ-Al_2O_3 structure, a defect spinel in which some of the Al^{3+} ions occupy tetrahedral sites (referred to in this paper as HTγ-surface and observed by Charig[5]). Its ${}_s\gamma_g$ is less than ${}_\ell\gamma_g$ of molten Al. On exposure to air or moisture the LEED patterns (Charig) show a loss in intensity and resolution, probably with a corresponding decrease in the HTγ-surface energy. The α-surface is regained by etching below 900°C.

(4) At temperatures above 1000°C in air surface structural changes must also occur as indicated by reported surface charge measurements.[6,7] Its structure and energy are probably similar to those for the HTγ-surface.

(5) Both the α-surface and HTγ-surface become hydroxylated on exposure to moisture in the air or on water-soaking; the resulting hydrated layers on the two surfaces, however, are not the same. Dehydroxylation in each case is a kinetic process, but it is generally completed by about 900-1000°C. The surface energies change correspondingly, being lower for the hydroxylated surfaces.

(6) The AlO in the HTH-surface reacts with Al above about 900°C to form a volatile species, Al_2O. It appears that the HTH-surface keeps reforming at the interface allowing the reaction to continue. Neither the α-surface nor the HTγ-surface react with molten Al.

(7) Molten Al appears to have an oxide-type coating whose thickness is dependent on the amount of aging in air. At low pressures it disappears at about 870°C. This may correspond to the formation of a suboxide structure and subsequent reaction with Al as described in (2) and (6), occurring at a lower temperature and more abruptly because of its presence as a thin film.

(8) At temperatures up to about 870°C a common interface does not form easily in the presence of hydroxylated surfaces on Al_2O_3 and oxide-type coatings on Al; van der Waals bonding and poor adherence then exist.

(9) At higher temperatures a common interface of Al-Al_2O_3 forms and is retained on cooling; strong chemical bonding and good adherence then exist. At temperatures above about 900°C with the formation of a HTH-surface, reaction maintains an Al-Al_2O_3 interface.

(10) No specific temperatures can be quoted for the transformations and reactions because they are kinetic processes.

This paper is a contribution toward the phenomenological understanding of the nature of surfaces of Al_2O_3 and interfaces between Al_2O_3 and Al. A more definitive explanation and quantitative analysis of the contact angle changes in this system would require a fundamental study of the mechanisms and kinetics of the indicated reactions, and of the character of the surfaces and interfaces. Just as important is

the need for the information that would be provided by a complete Pressure-Temperature-Composition diagram of the Aluminum-Oxygen system.

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REFERENCES

1. D. T. Livey and P. Murray, The Wetting Properties of Solid Oxides and Carbides by Liquid Metals, Plansee Proceedings, 387, 1955.
2. R. D. Carnahan, T. L. Johnston, and C. H. Li, Some Observations on the Wetting of Al_2O_3 by Aluminum, J. Am. Ceram. Soc., 41, 9, 343-347, 1958.
3. S. M. Wolf, A. P. Levitt, and J. Brown, Whisker-Metal Matrix Bonding, Chem. Eng. Prog., 62, 3, 74-78, 1966.
4. Joseph A. Pask and M. P. Borom, Physical Chemistry of Glass-Metal Interfaces, Proceedings VII Int. Glass Congress (Brussels), Sect. 11.3, No. 81, 11 p., 1965.
5. J. M. Charig, Low-Energy Electron Diffraction Observations of α-Alumina, Applied Physics Letters, 10, 5, 139-140, 1967; and private communication.
6. M. Robinson, J. A. Pask, and D. W. Fuerstenau, Surface Charge of Alumina and Magnesia in Aqueous Media, J. Am. Ceram. Soc. 47, 10, 516-520, 1964.
7. G. A. Parks, The Composition and Reaction Capability of Oxide Surfaces, Research in Mineral Proc., Prog. Rept. 65-1, Stanford Univ. June 1965.
8. Leo Brewer and A. W. Searcy, Gaseous Species of the $Al-Al_2O_3$ System, J. Am. Chem. Soc., 73, 11, 5308-14, 1951.
9. R. F. Porter, P. Schissel, and M. G. Ingram, A Mass Spectrometric Study of Gaseous Species in the $Al-Al_2O_3$ System, J. Chem. Phys., 23, 2, 339-342, 1955.

10. R. G. Frieser, Phase Changes in Thin Reactivity Sputtered Alumina Films, J. Electrochem. Soc. 113, 4, 357-360, 1966.

11. W. D. Kingery, Introduction to Ceramics, John Wiley and Sons, Inc. New York, 1960, p. 194.

12. G. Hass, Concerning the Growth and Structure of Thin Oxide Films on Aluminum (in German), Optik 1, 134-43, 1946.

13. A. Bondi, The Spreading of Liquid Metals on Solid Surfaces, Chemical Reviews, 52, 2, 417-458, 1953.

14. Hiroaki Yanagida and F. A. Kroger, Condensed Phases in the System Al_2O_3-Al, presented at 70th Annual Meeting, Am. Ceram. Soc., Chicago, Ill., paper 69-B-68, 1968.

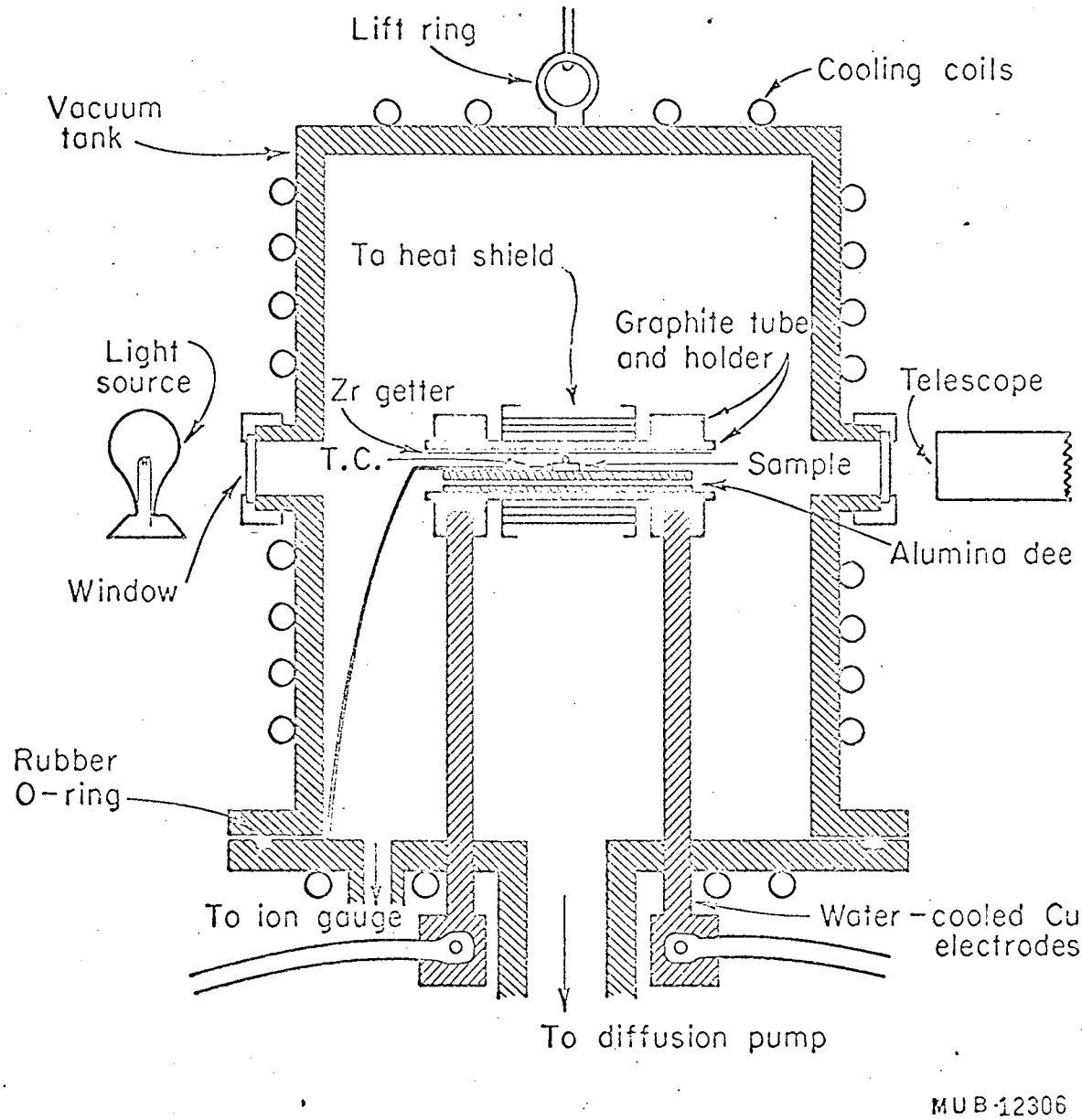
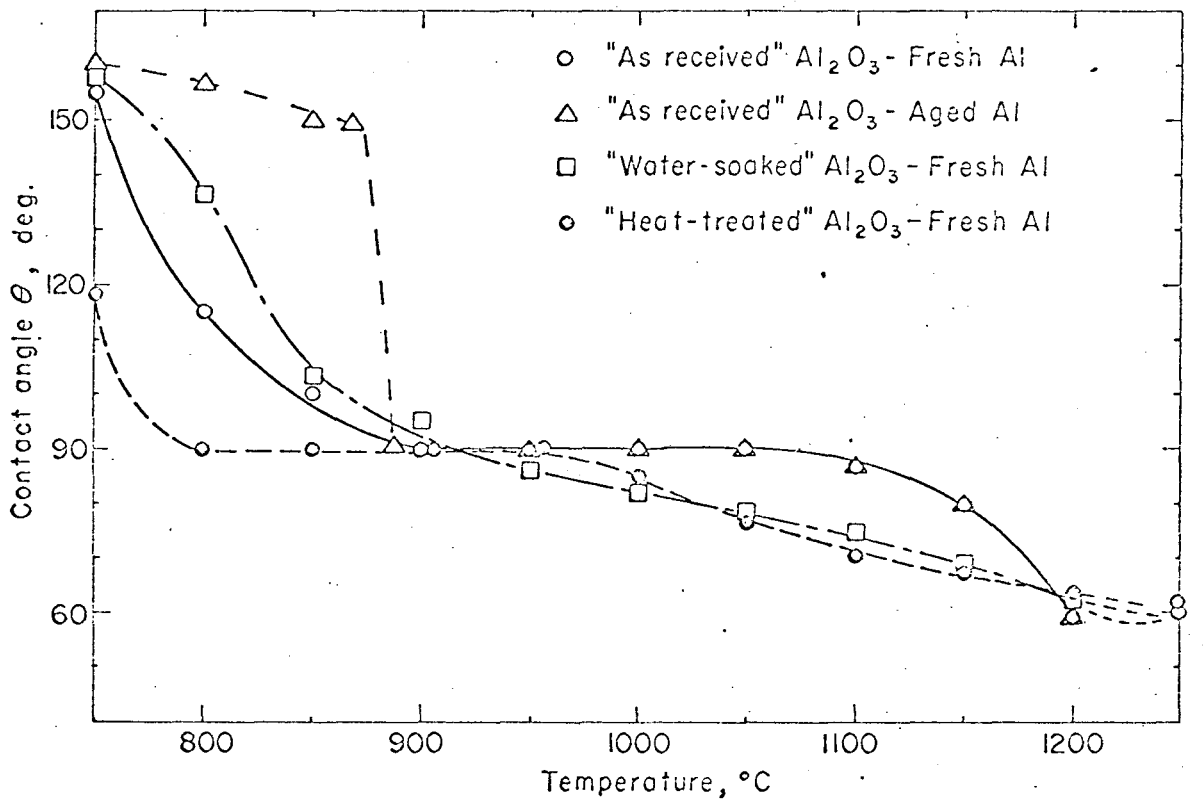


Fig. 1 Schematic of sessile drop furnace



XBL 678-1648

Fig. 2 Change in contact angle with temperature for the system $Al-Al_2O_3$

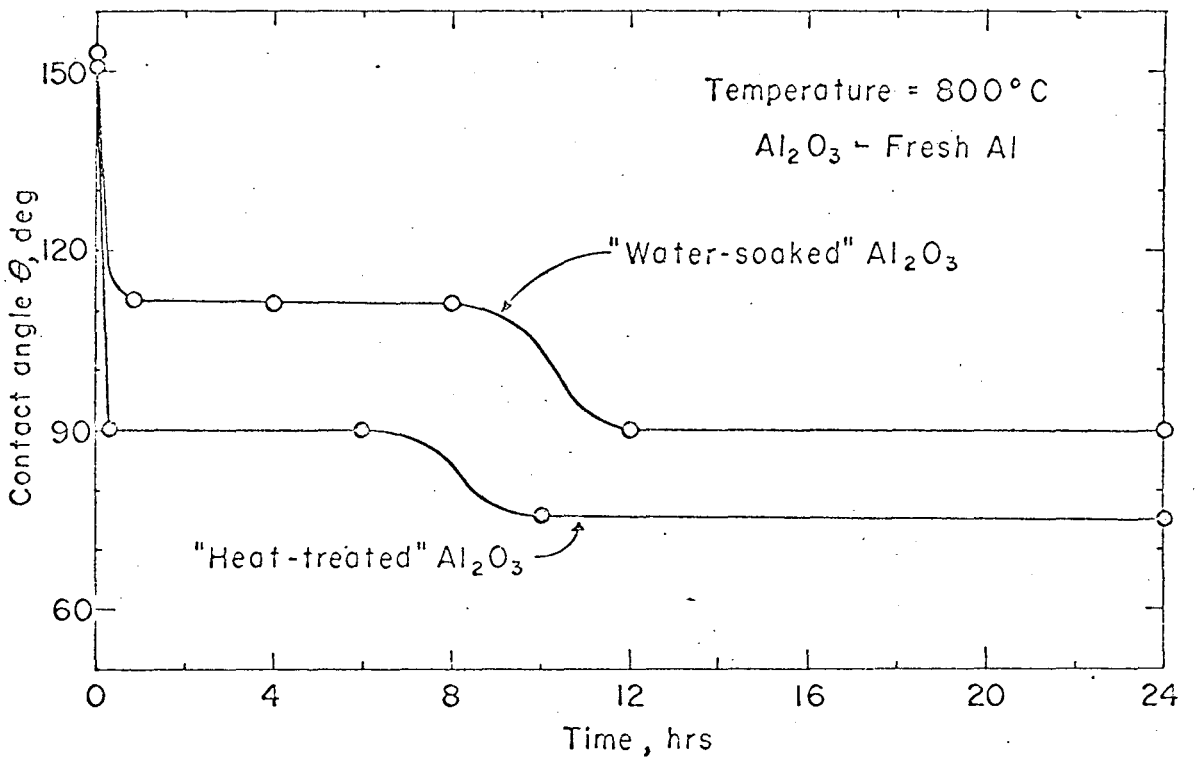


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Fig. 3 Change in contact angle with time for the system Al-Al_2O_3 at 800°C

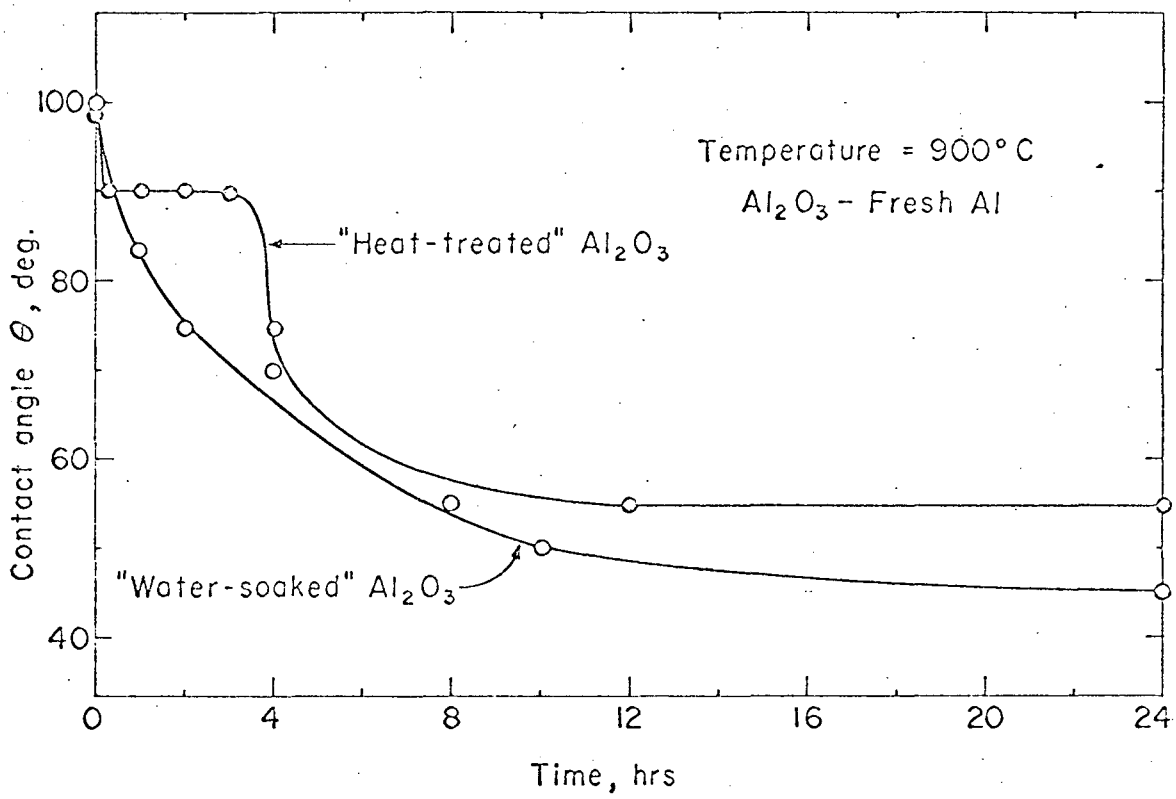

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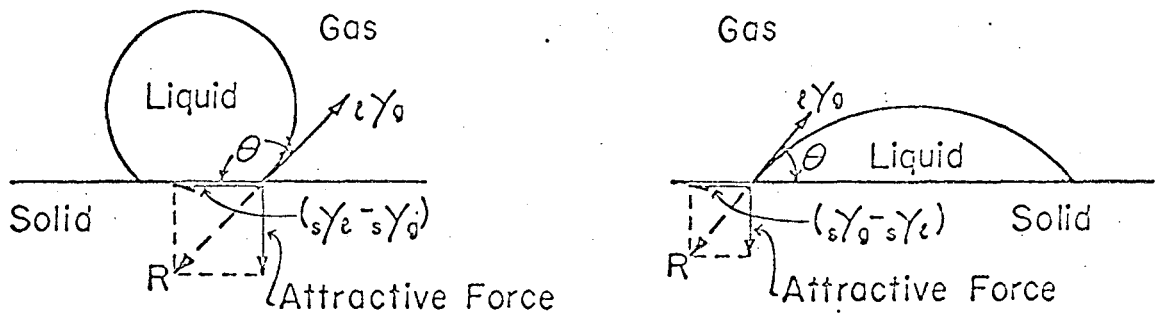
Fig. 4 Change in contact angle with time for the system $Al-Al_2O_3$ at 900°C



$(_s\gamma_g - {}_s\gamma_\ell) = {}_{\ell}\gamma_g \cos\theta$ Young's Equation

$_{\ell}\gamma_g$ = liquid - gas interfacial tension

$_s\gamma_g$ = solid - gas interfacial tension

$_s\gamma_\ell$ = solid - liquid interfacial tension

R = reaction force

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Fig. 5 Forces acting on obtuse and acute angle sessile drops.

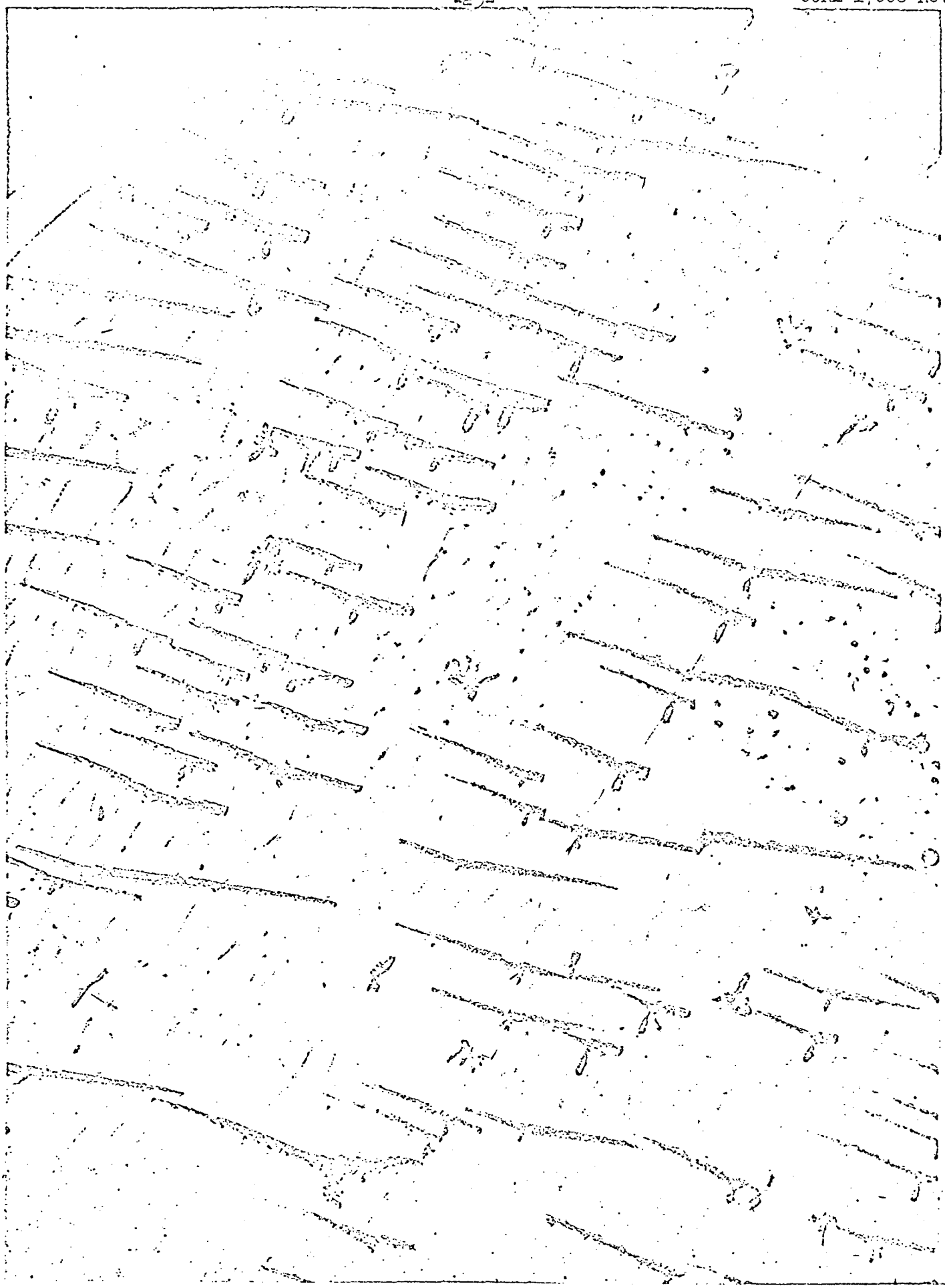

Fig. 6 Interface of $Al-Al_2O_3$ system as seen through sapphire 1300°C

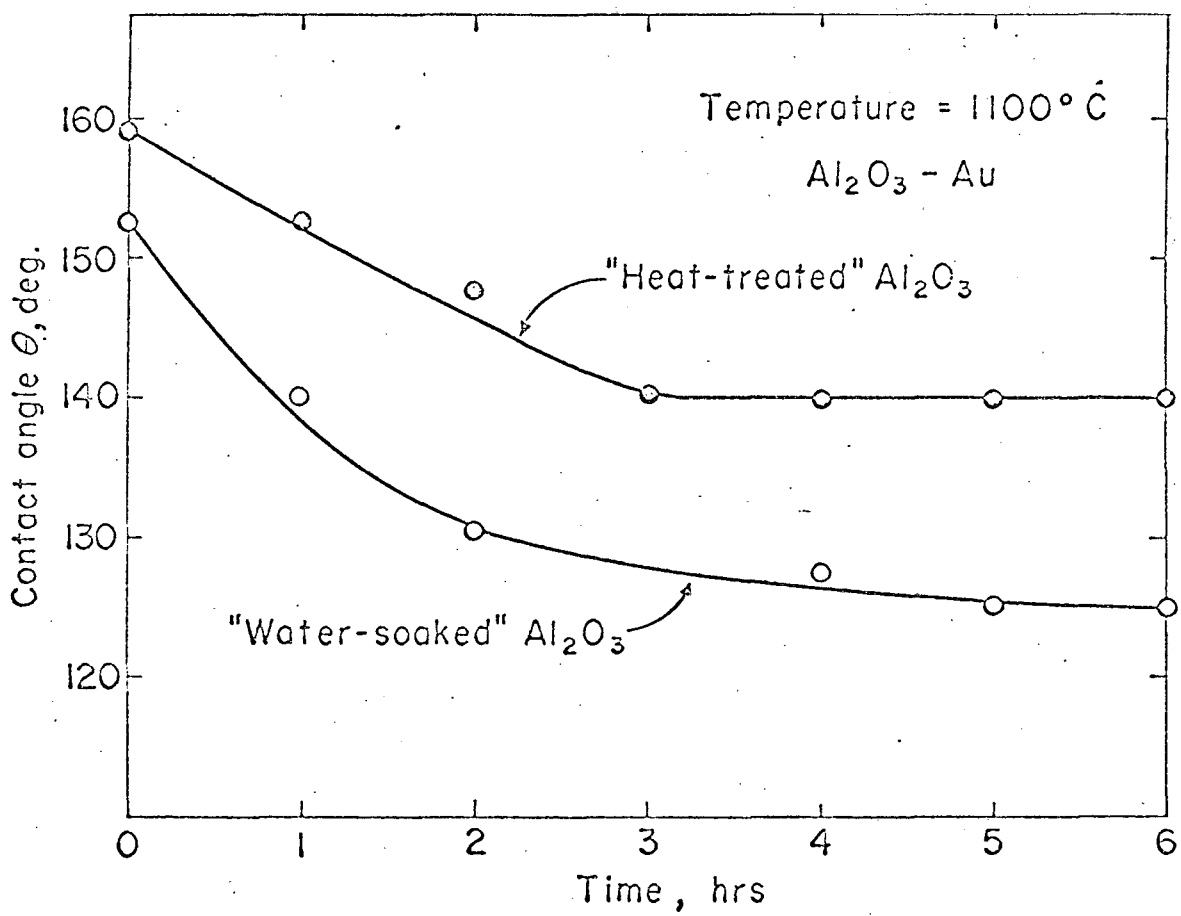

Fig. 7 Change in contact angle with time for the system $AuAl_2O_3$ at 1100°C