The Wetting of an Alumina Substrate by Liquid Silver

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The wetting of the Al_2O_3 substrate by liquid silver was investigated by means of the sessile-drop technique in an atmosphere of argon. An empirical relation was established between the contact angle and the temperature or surface tension of the liquid drop by the use of the diameter and the height of the sessile drop. The contact angle was constant as the time increased while it decreased linearly with the increase in the temperature. The variation in the contact angle with the temperature is correlated with the surface tension of the sessile drop. The critical surface tension (γ_c) of Al_2O_3 is 361 dyn cm^{-1}, while the surface tension of liquid silver at 0 K is 790 dyn cm^{-1}.

As for all the properties of the engineering materials, the phenomenon of liquid wetting on a solid surface is an especially important problem, among the many engineering problems on the surface, in the sense that interaction between a solid and a liquid is involved. This phenomenon is also important as a fundamental factor in the related fields of electronics, printing, dyeing and metallurgy, composite materials, adhesion, etc. This wetting phenomenon may be broadly classified into three types of wetting: adhesion, diffusion, and dipping.

Metal-alumina substrates are very attractive as engineering materials. The properties of such substrates are, however, greatly influenced by the nature of the metal-alumina interface. Thus, it is essential to understand metal-alumina interactions in substrate materials.

In the present paper, the wettability of a sintered alumina subetrate, its surface polished and smooth, by liquid silver is investigated by means of the sessile-drop technique in an atmosphere of argon.

Experimental

High-purity silver (99.99%, Ishifuku Co.) was cut into a desk. The disk was 4 mm in diameter and 3 mm thick. The sintered alumina (99.5%, Kyocera Co.) used as the substrate had dimensions of 20×20×3 mm^3, and its surface had been polished to a mirrorlike finish.

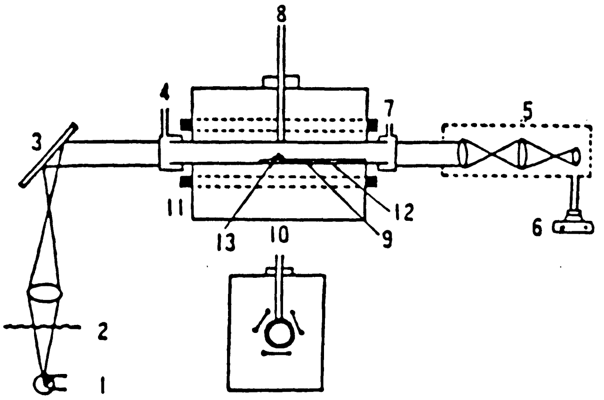

Fig. 1. Experimental apparatus for measuring the wettability. 1: Mercury lamp, 2: Green filter, 3: Reflecting mirror, 4: Argon gas inlet, 5: Microscope, 6: Camera, 7: Argon gas outlet, 8: Pt/Pt13%Rh thermocouple, 9: Porcelain plate, 10: Electric furnace, 11: SiC heater element, 12: Porcelain pipe, 13: Test sample.

An outline of the sessile-drop apparatus used to measure the contact angle is shown in Fig. 1. The temperature of a drop was measured by means of a Pt—Pt. 13% Rh thermocouple, which was located near the drop. The furnace was operated in an atmosphere of argon. The flow rate was about 0.9 L min^{-1}. The silver disk and the substrate were cleaned with acetone and then dried in a vacuum. The silver disk was placed in the furnace on an alumina substrate. The sessile drop was allowed to rest on the substrate at 980 °C for 30 min. The value of the contact angle after 30 min was assumed to be the equilibrium contact angle. The shadow of the sessile drop was then photographed from the back by using light shed by a mercury lamp. The contact angle of the drop was bilaterally measured, and its mean value was taken as the measured value.

In the case of the constant temperature, the contact angle was measured at 5-minute intervals for 60 min. On the other hand, at different temperatures from 960 to 1000 °C the contact angle of a drop was also measured at intervals of 5 °C. From these many photographs taken at 5-minute intervals for 60 min and at intervals of 5 °C, the diameters and the heights of the sessile drops were measured. These dimensions were used to calculate the surface tension of liquid silver and the critical surface tension for spreading (γ_c) for the Ag/Al_2O_3 system.

The human error was found to be about ±1 °C by measuring the contact angle from ten photographs. The temperature deviation was ±2 °C. The silver/alumina interface regions were exemined with an optical microscope and a scanning electron microscope.

Results

In the case of a constant temperature of 980 °C, the photographs used in measuring the contact angles of the drops are shown in Fig 2, while the measured values of the contact angles are shown in Table 1 and Fig. 3. These experimental results shown that a constant angle of a liquid silver sessile drop resting on an alumina substrate was about 90 °C, although there were some differences in the wettability depending on the test pieces of the alumina substances. Each straight line in Fig. 3 represents the results of two independent runs.

In the case of different temperatures from 960 to

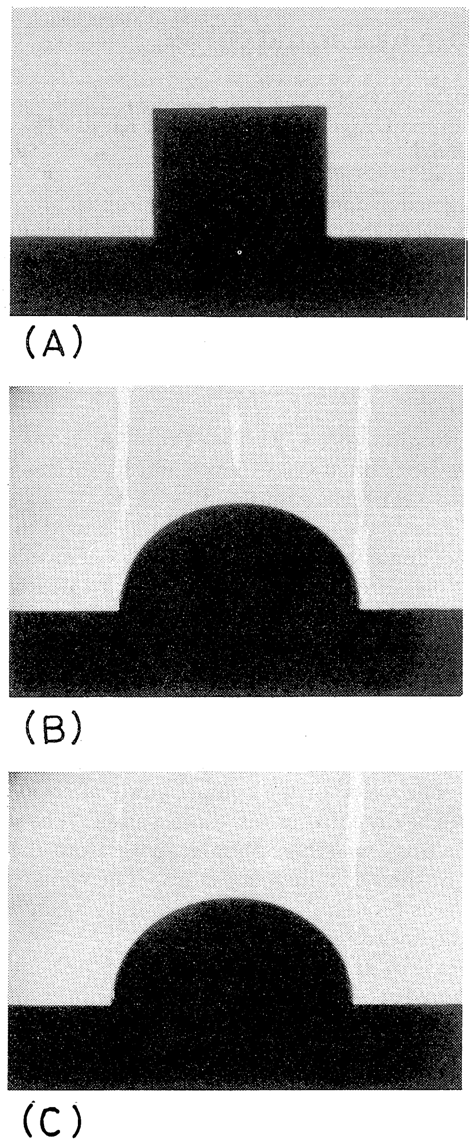

Fig. 2. Sessile drops of liquid silver on alumina at 980 °C for Run No. (S-1). A) T=0 min (Ag metal disk), B) T=30 min, C) T=60 min.

Table 1. Experimental Results of the Contact Angles of Liquid Silver Sessile Drops for Each Substrate at 980 °C

t / min \ Run No.	S-1 θ_1 (°)	S-1 θ_2 (°)	S-2 θ_1 (°)	S-2 θ_2 (°)	$\theta_{ave.}$ (°)
5	90.5	91.8	90.0	89.0	90.3
10	91.0	90.8	89.0	89.0	90.0
15	91.0	90.0	89.0	89.0	89.8
20	90.8	91.3	89.0	89.0	90.0
25	90.8	91.8	89.5	88.0	90.0
30	90.5	90.8	89.5	88.5	89.8
35	90.3	91.8	89.0	89.5	90.2
40	90.0	90.0	89.0	89.0	89.6
45	90.5	90.5	90.0	88.0	89.8
50	90.5	89.8	89.0	88.5	89.5
55	90.5	90.8	89.5	89.0	90.0
60	90.0	90.5	89.5	90.0	90.0
Ave.	90.5	90.8	89.3	88.9	89.9

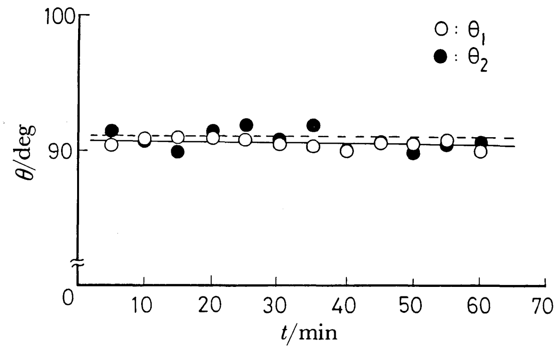

Fig. 3. Change in contact angle with time for a system Ag/Al_2O_3 of Run No. (S-1).

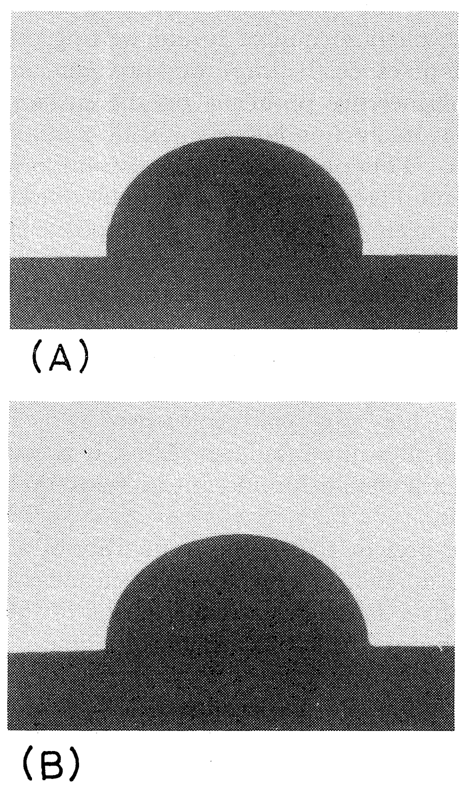

Fig. 4. Sessile drop of liquid silver on alumina for Run No. (S-3). A) At 970 °C, B) at 1000 °C.

1000 °C, with the contact angle measured at intervals of 5 °C, the photographs used in measuring the contact angle of a liquid silver sessile drop resting on an alumina substrate are shown in Fig. 4. The effect of the temperature on the contact angle is shown in Table 2 and Fig. 5. Each straight line in Fig. 5 also represents the results of two independent runs.

Table 2 shows that the degree of the variation in the θ_1 and θ_2 values for runs of (S-3) and (S-4) was different, but the contact angles of a liquid silver on the alumina substrate decrease linearly with an increase in the temperature. That is, a liquid silver is liable to wet an alumina substrate.

The condition of the surface of an alumina substrate was investigated before and after the thermal treatment. Before, it was smooth and flat, but after the thermal treatment, it was revealed that the flatness of

Table 2. Experimental Results of the Effects of Different Temperatures on the Contact Angles of Liquid Silver for Each Substrate at Intervals of 5 °C

Run No. / $\frac{t}{°C}$	S-3 $\frac{\theta_1}{°}$	S-3 $\frac{\theta_2}{°}$	S-4 $\frac{\theta_1}{°}$	S-4 $\frac{\theta_2}{°}$	$\frac{\theta_{ave.}}{°}$
960	97.3	98.9	98.1	97.8	98.0
965	96.8	98.4	96.2	96.8	97.1
970	95.2	96.7	93.8	93.3	94.8
975	93.8	95.9	92.2	93.9	94.0
980	93.1	94.5	90.1	92.8	92.6
985	93.3	94.3	88.7	91.3	91.9
990	91.6	91.8	86.8	89.8	90.0
995	89.9	90.4	85.2	88.5	88.5
1000	89.0	89.7	83.2	87.8	87.4

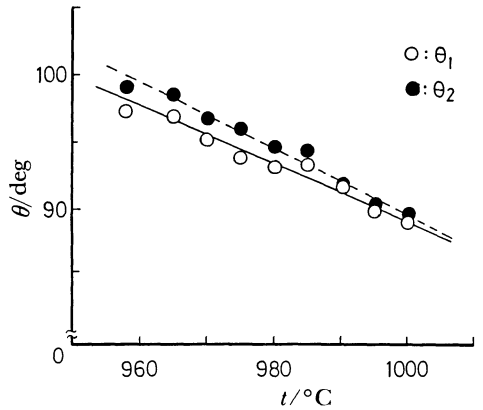

Fig. 5. Change in contact angle with temperature for a system Ag/Al_2O_3 for Run No. (S-3).

the surface had been destroyed. If the surface of an alumina substrate was magnified and then examined, alumina particles were observed on the surface and this surface became rough.

Discussion

As for runs of (S-1) and (S-2), the effect of the time on the contact angle of a liquid silver sessile drop resting on the alumina substrates was investigated at a constant temperature of 980 °C. Each straight line in Fig. 3 can be fitted by means of this equation:

Run (S-1)

$$\theta_1 = -0.0121\,x + 91.0$$

$$\theta_2 = -0.0030\,x + 91.4$$

Run (S-2)

$$\theta_1 = 0.0014\,x + 91.4$$

$$\theta_2 = 0.0045\,x + 88.7$$

where x is the time in minutes and where θ is the contact angle.

The slopes of these equations were within the range of the absolute value: $|0.0014\text{—}0.00121|$. These values were very small. Therefore, it can be assumed, considering the accuracy of the temperature control, the human errors of the measurements, etc., that the contact angle of a liquid silver on an alumina substrate was scarcely changed at a constant temperature of 980 °C. That is, it is not too much to say that the contact angle does not change within the present experimental range if the temperature is kept constant.

The effect of the temperature on the constant angle of a liquid silver on an alumina substrate was also investigated for the runs of (S-3) and (S-4). The values of the slopes of all the straight lines are negative, as is obvious from Fig. 5. The figure indicates that the contact angle decreases linearly with an increase in the temperature and that a liquid silver is apt to wet an alumina substrate better. The reason for this may be considered to be that the contact angle becomes small as the forces between molecules of silver decrease with an increase in the temperature and that the surface tension of silver therefore decreases.

The amount of scattering in the measured values of the contact angle (θ_1 and θ_2) is shown in Tables 1 and 2. It may be assummed, considering the human errors of measurement of ±2 °C, etc., that its scattering is due to other causes. That is, if the sintered alumina is used as a substrate, the effect of the binder agents, the difficulty of producing homogeneous finished goods, the effect of the atmosphere, etc. must be considered.

The alumina substrate was chemically inert to liquid silver in the temperature range investigated, judging from the optical-microscopy and scanning-electron-microscope studies. However, from the surface observation after the thermal treatment shown in Fig. 6, the surface of an alumina substrate became fairly rough. If the surface was worn by the thermal treatment and the atmosphere, the rough surface may be fairly much influenced by the contact angle of the liquid silver. It is necessary to increase the reproducibility in order to produce homogeneous finished goods, to clean the surface of the alumina substrate, to standarize the roughness of the work surface, to decrease the temperature fluctuation, etc.

The values of the surface tension of liquid silver have been variously reported.

The values of the surface tension were 800 dyn cm^{-1} (1 dyn=10^{-5} N) at 970 °C in air,[1)] 893 dyn cm^{-1} at

Table 3. Critical Surface Tension (γ_c) and Surface Tension at 0 K (γ°_{LV}) for the Ag/Al_2O_3, AlN, and TiC Systems

Liquid metal		γ_c ($dyn\,cm^{-1}$) for ceramic	γ°_{LV} ($dyn\,cm^{-1}$) for liquid silver
Ag	Al_2O_3	361	790
	AlN	873[4)]	1474[4)]
	TiC	783[4)]	1474[4)]

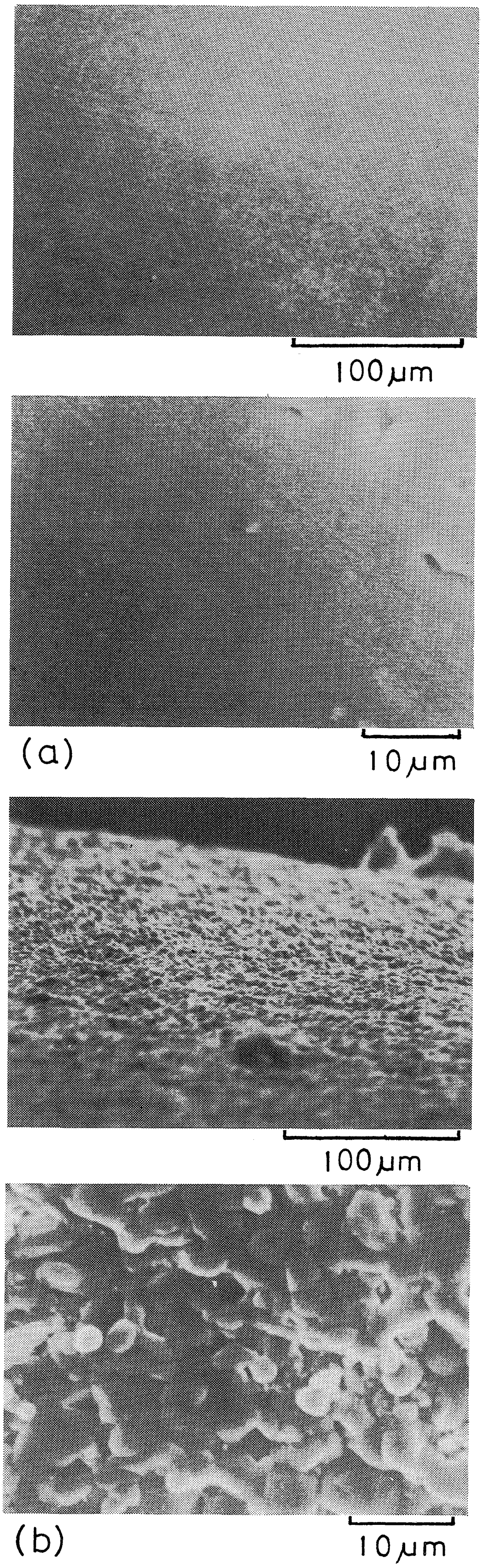

Fig. 6. Photographs of the surfaces of alumina before and after treatment for Run No. (S-3). (a) Before heat treatment, (b) after heat treatment.

1000 °C, and 849 dyn cm^{-1} at 1250 °C.[2] According to Semenchenko's publication,[3] the values of the surface tension of liquid silver are 940 dyn cm^{-1} as calculated by the Zadumkin formula, 991 dyn cm^{-1} as calculated by the Samoilovich formula, and 904 dyn cm^{-1} as calculated by the Kunin formula. On the other hand, Rhee reported that the surface tension of liquid silver followed the following equation: γ_{LV}(Ag)(dyn cm^{-1})=1092−0.14 T (°C).[4] Therefore, the surface tension at 961 °C (melting point) could be estimated to be 957 dyn cm^{-1} by the use of this equation. The values reported by Flint[5] vary from about 785 to 980 dyn cm^{-1}. Krause et al.[6] obtained the values of 930 dyn cm^{-1} at 980.8 °C and 923 dyn cm^{-1} at 1000 °C. According to Kingery,[7] the surface tension of liquid silver is 920 dyn cm^{-1} at 1000 °C in vacuo or in an atmosphere of inert gas. The surface tension of 1140 dyn cm^{-1} at 1180 K (907 °C) has also been reported.[8]

The liquid-solid interface energy, γ_{LS}, is 126 dyn cm^{-1} for silver.[9] It has also been reported that, for metal, $\gamma_{LS}=(0.12\pm0.03)\ T_m$, where T_m is the melting point (K).[10] From this equation, we can now estimate it to be from 111 to 185 dyn cm^{-1}, while Southin et al. and Zellenmoyer reported that γ_{LS}=130 dyn cm^{-1} on the average.[11]

The temperature coefficient of the surface tension of liquid silver was reported by Rhee[4] to be −0.14 dyn cm^{-1} °C, while Krause et al.[6] reported the very near value of −0.15 dyn cm^{-1} °C. On the other hand, Pawlek et al. reported a somewhat smaller value of −0.11 dyn cm^{-1} °C.[12] We should, therefore, pay special attention to controlling the temperature when high accuracy is required.

By using the present experimental results of the total height, the drop height above the maximum diameter, the maximum diameter, and the θ-value of the sessile drop that is, 0.322, 0.295, 0.499 cm and 98° (at 980 °C) respectively, and 0.311, 0.254, 0.523 cm and 89° (at 1000 °C) respectively, the surface tension of liquid silver was calculated. The calculated values of the surface tension of liquid silver were from 390 to 420 dyn cm^{-1}, as predicted by Tartar et al.'s formula,[13] 380 to 550 dyn cm^{-1} as predicted by the Porter formula,[14] and 610 dyn cm^{-1} as predicted by the Dorsey formula[15] and other formulas.[3] It was found that the values calculated by using their formulas were about 15 to 25% smaller than the values in the literature cited above.

We also attempted to calculate the critical surface tension and the surface tension at 0 K for the Ag/Al_2O_3 system and therefore adopted the values obtained by using the Dorsey formula.[15] The critical surface tension and the surface tension at 0 K were discussed by Rhee.[4]

The work of the adhesion of a liquid-solid interface can be generally defined by this equation:

$$S_{LS}=(\gamma_{LV}+\gamma_{SV})-\gamma_{LS}$$

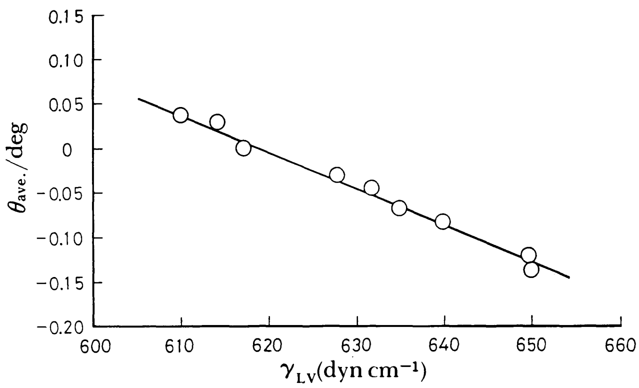

Fig. 7. Cosine of contact angle vs. surface tension of liquid silver for system Ag/Al_2O_3.

where γ_{LV}, γ_{SV}, and γ_{LS} represent the interfacial energies between the phases actually present in the Ag/Al_2O_3 system at the time of measurement. Substituting Young's equation, $\gamma_{SV}-\gamma_{LS}=\gamma_{LV}\cos\theta$, where θ is the contact angle, into the above equation gives:

$$S_{LS}=\gamma_{LV}(1+\cos\theta).$$

Since S_{LS} and $\cos\theta$ are linear functions of the temperature in the Ag/Al_2O_3 system, S_{LS} and $(\gamma_{SV}-\gamma_{LS})$ in Young's equation will vary parabolically with the temperature. If complete wetting occurs, that is, if $\cos\theta=+1$, and $\gamma_{LV}=\gamma_c$, then:

$$S_{LS}=2\gamma_{LV}=2\gamma_c=S_{LL}$$

where γ_c is the critical surface tension. The work of the adhesion of the liquid become equal to the work of cohesion. That is, the layer of vapor adsorbed on the solid surface behaves as does the liquid itself. Therefore, the critical surface tension for spreading is the surface tension of the solid with adsorbed vapor which has attained a liquidlike behavior.

As has been described above, the cosine of the contact angle increases linearly with an incresse in the temperature in the Ag/Al_2O_3 system. The variation in the cosine of the contact angle with a decrease in the surface tension of liquid silver is shown in Fig. 7 for the Ag/Al_2O_3 system. The extrapolation of the straight line to $\cos\theta=+1$ produces the critical surface tension for spreading (γ_c) for the Ag/Al_2O_3 system, with the surface tension of liquid silver at 0 K. For a liquid silver, γ_c for Al_2O_3 is always smaller than that for aluminium nitride (783 dyn cm^{-1}) and for TiC (873 dyn cm^{-1} [4]). When we obtain the values of the critical surface tension, etc., the silver vapor near the melting point may be nearly ignored and thought not to absorb on the Al_2O_3 substrate.

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