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The Wetting of Alumina Substrate by Liquid Gold†

Masumi Ushio* and Yoshihiro Sumiyoshi
Department of Applied Chemistry, Faculty of Engineering, Gunma University,
Tenjin-cho, Kiryu-shi 376
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The wetting of an Al_2O_3 substrate by liquid gold was investigated by means of the sessile-drop method in an atmosphere of argon. An empirical relation was estabilished 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 with time, but decreased linearly with an increase in temperature. The variation in the contact angle with temperature is correlated with the surface tension of the sessile drop. The surface tension of liquid gold was obtained as 933 dyn cm^{-1} at 1080 °C and 917 dyn cm^{-1} at 1100 °C and the temperature coefficient of the surface tension of liquid could be estimated to be −0.80 dyn cm^{-1} °C^{-1}. The critical surface tension (γ_c) and the surface tension of liquid gold at 0 K of Al_2O_3 (γ°_{LV}) were 20 and 2015 dyn cm^{-1}, respectively.

As was reported in the first part,[1] the wetting of an Al_2O_3 substrate by liquid Ag was investigated by the sessile drop technique under an atmosphere of argon. An empirical relation was established between the contact angle and the temperature or surface tension of the liquid drop, by use of Rhee's equation. The contact angle was constant with increasing time and decreased linearly with increasing temperature. The variation of the contact angle with temperature could be correlated with the surface tension of the sessile drop. The critical surface tension (γ_c) of Al_2O_3 is 923 dyn cm^{-1}, and the surface tension of liquid Ag at 0 K was 1130 dyn cm^{-1}.

In the present paper, the wettability of a sintered alumina substrate with a surface that was polished to be flat and smooth by liquid Au was investigated by the sessile drop techniques in an atmosphere of argon in much the same way as was reported in the first part.

This was done in order to obtain values of the surface tension of liquid Au, the temperature coefficient of the surface tension of liquid Au, the critical surface tension (γ_c), and the surface tension of liquid Au at 0 K. Since sufficient results were obtained, details are reported here.

Experimental

The sintered alumina (99.5%, Kyocera Co.) was used as a substrate with dimensions 20×20×3 mm^3, its surface was polished to a mirror-like finish. The high-purity gold (99.99%, Ishifuku Co.) was cut into a disk. The dimensions of the gold disk were 4 mm in diameter and 3 mm in thickness; its purity was 99.99%.

The sessile-drop apparatus used to measure the contact angle was the same as that mensioned in a previous paper.[1] A Pt–Pt13%Rh thermocouple was used for temperature measurements. The furnace was operated in an atmosphere of argon at a rate of about 0.9 L min^{-1}. The gold disk and substrate were cleaned with acetone and then dried in a vaccum. The gold disk after being placed on an alumina substrate was put queitly into the furnace.

After adjusting the horizontal position, argon gas was flowed. The furnace temperature was increased to a specified value and then maintained for 30 min.

The shadow of a sessile drop of gold was then photographed from the back by using light produced 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 a constant temperature of 1080 °C, the contact angle was measured at 5-minute intervals for a period of 60 min. On the other hand, for various temperatures from 1070 to 1100 °C, the contact angle of a gold drop was also measured at intervals of 5 °C. From many photographs, the diameters and heights of the sessile drops of gold were also measured. These diameters were used to calculate the surface tension of liquid gold as well as the critical surface tension for spreading (γ_c) for the Au/Al_2O_3 system.

The human error was found to be about ±1° by measuring the contact angle from ten photographs. The temperature deviation was ±2 °C. The regions of the gold drop/alumina substrate were using an optical microscope and a scanning electron microscope.

Results

In the case of a constant temperature of 1080 °C, the photographs used in measuring the contact angles of the gold drops are shown in Fig. 1, while the measured values of contact angles are shown in Table 1 and Figs. 2 and 3. These experimental results showed that a contact angle of the liquid gold sessile drop resting on an alumina substrate was about 127°. However there were some differences in the wettability, depending on the test pieces of alumina substrates. Each straight line in Figs. 2 and 3 represents the results of two independent runs.

In the case of different temperature between 1070 and 1100 °C, with the contact angle measured at intervals of 5 °C, the photographs used in measuring the contact angle of a liquid gold sessile drop resting on an alumina substrate are shown in Fig. 4. The effect of the temperature on the contact angle is shown

† Study on Preparation and Characteristic of Functional Inorganic Materials. II.

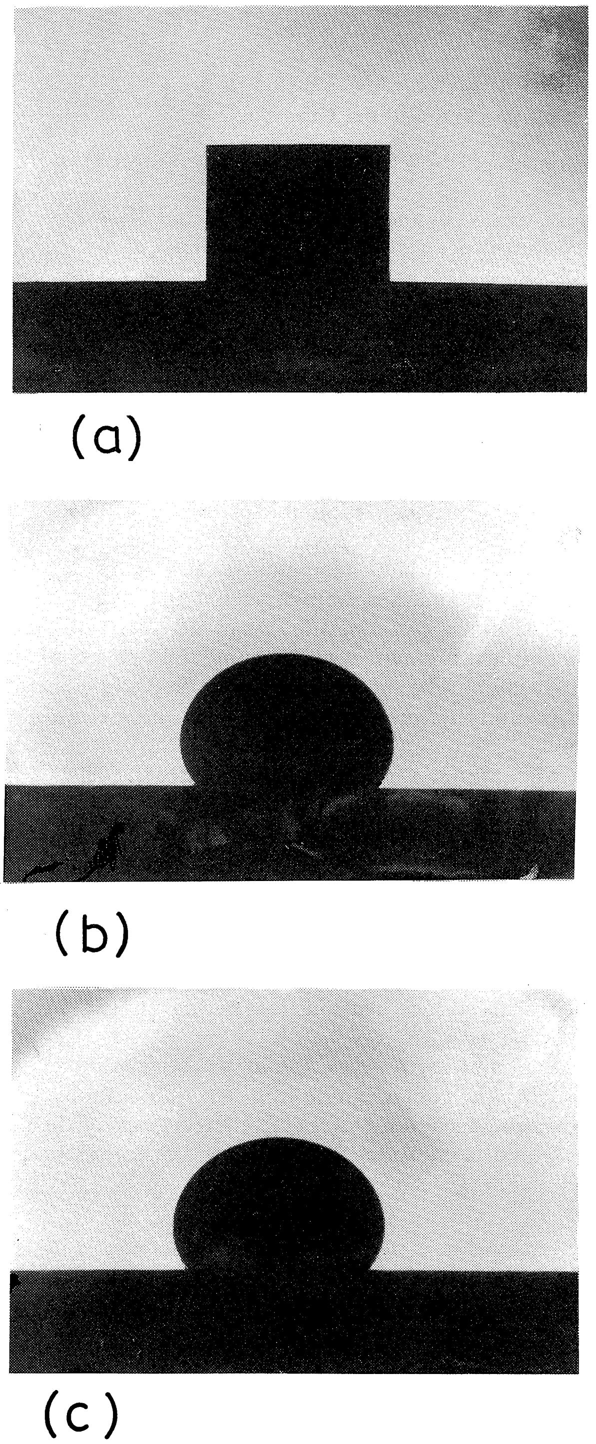


Fig. 1. Sessile drops of liquid gold on alumina at 1080 °C for Run No. (T-1).
(a) T=0 min (Au metal disk), (b) T=30 min, (c) T=60 min.

in Table 2 and Figs. 5 and 6. Each straight line in Figs. 5 and 6 also represents the results of two independent runs.

Table 2 shows that the contact angles of liquid gold on the alumina substrate decrease linearly with an increase in the temperature. That is, liquid gold is

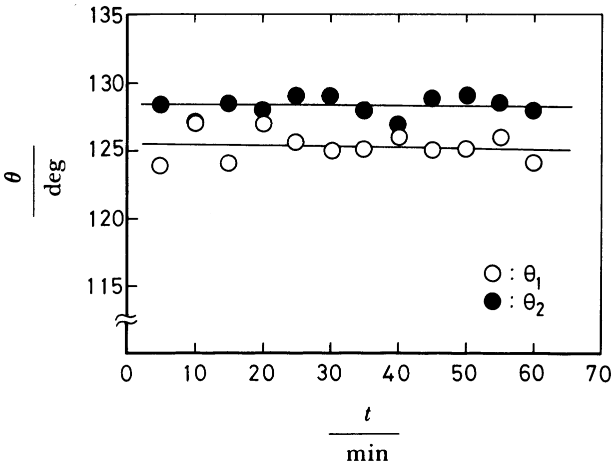


Fig. 2. Change in contact angle with time for a system Au/Al_2O_3 of Run No. (T-1).

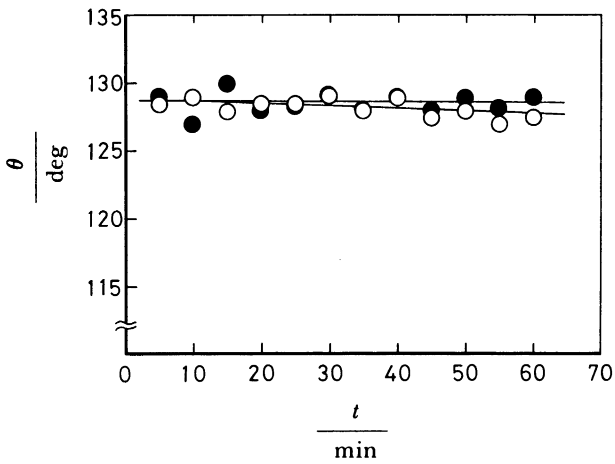
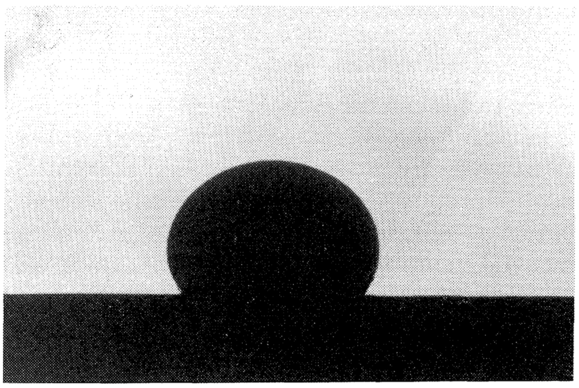


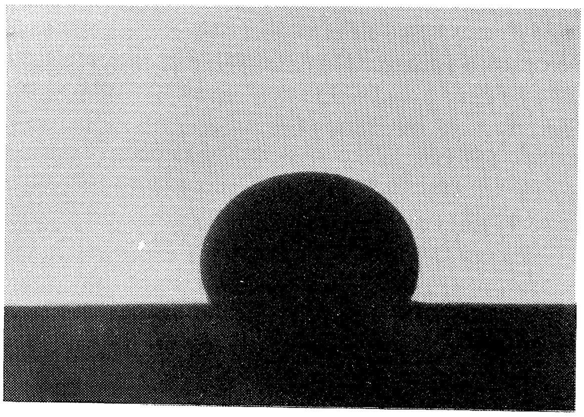
Fig. 3. Change in contact angle with time for a system Au/Al_2O_5 of Run No. (T-2).

Table 1. Experimental Results of the Contact Angles of Liquid Gold Sessile Drops for Each Substrate at 1080 °C

Run No. / t/min	T-1		T-2		$\theta_{ave.}$ / °
	θ_1 / °	θ_2 / °	θ_1 / °	θ_2 / °	
5	124.0	128.0	128.5	129.0	127.0
10	127.0	127.0	129.0	127.0	127.5
15	124.0	128.5	128.0	130.0	127.6
20	127.0	128.0	128.5	128.0	127.9
25	125.5	129.0	128.5	128.5	127.9
30	125.0	129.0	129.0	129.0	128.0
35	125.0	128.0	128.0	128.0	127.3
40	126.0	127.0	129.0	129.0	127.8
45	125.0	129.0	127.5	128.0	127.4
50	125.0	129.0	128.0	129.0	127.8
55	126.0	129.5	127.0	128.0	127.4
60	124.0	128.0	127.5	129.0	127.1
Ave.	125.3	128.3	128.2	128.5	127.6



(a)



(b)

Fig. 4. Sessile drops of liquid gold on alumina for Run No. (T-3).
(a) At 1070 °C, (b) at 1100 °C.

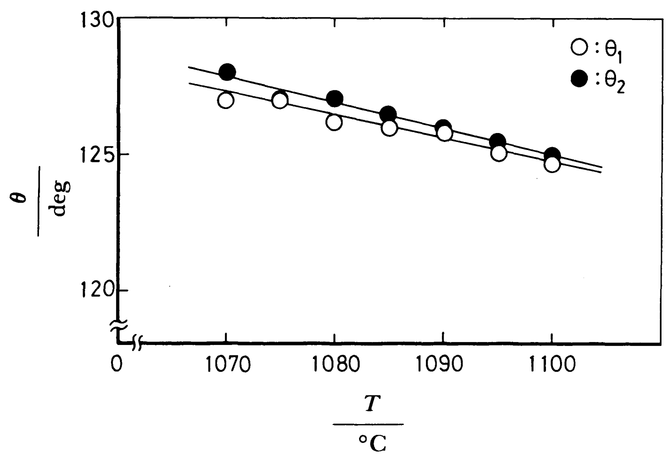


Fig. 5. Change in contact angle with temperature for a system Au/Al_2O_5 for Run No. (T-3).

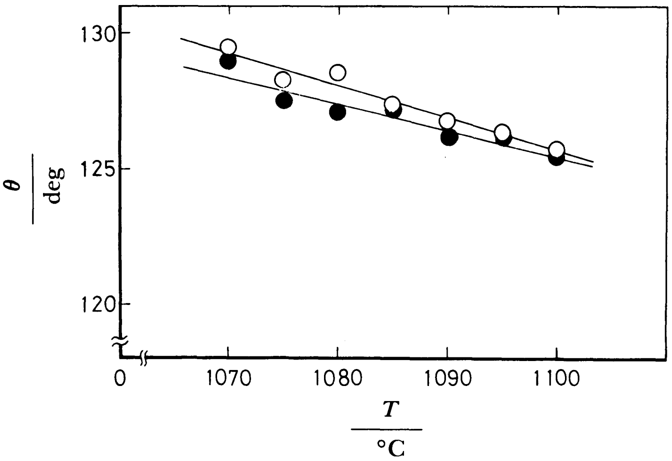


Fig. 6. Change in contact angle with temperature for a system Au/Al_2O_3 for Run No. (T-4).

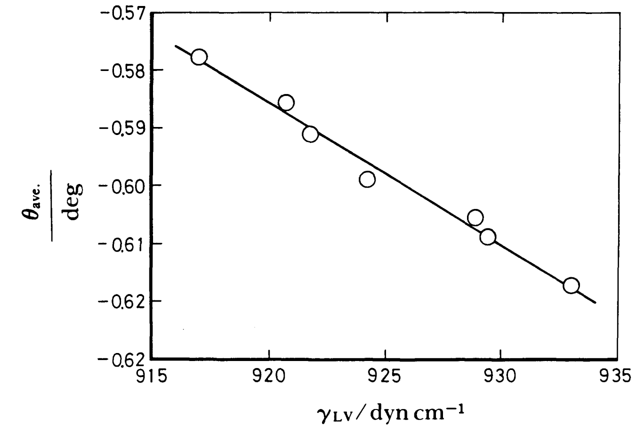


Fig. 7. Cosine of contact angle vs. surface tension of liquid gold for Au/Al_2O_3.

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

Run No.	T-3		T-4		
t / °C	θ_1 / °	θ_2 / °	θ_1 / °	θ_2 / °	$\theta_{ave.}$ / °
1070	127.0	128.0	129.5	128.0	128.1
1075	127.0	127.0	128.3	127.5	127.5
1080	126.2	127.1	128.6	127.1	127.3
1085	126.0	126.5	127.4	127.2	126.8
1090	125.8	126.0	126.8	126.2	126.2
1095	125.1	125.5	126.4	126.3	125.8
1100	124.7	125.0	125.8	125.5	125.3

liable to wet an alumina substrate.

The state of the surface of an alumina substrate directly under liquid gold was investigated before and after thermal treatment. Before the thermal treatment, it was smooth and flat; however, it was revealed that the flatness of the surface had been destroyed after the treatment. It seems that a reaction between an alumina substrate and liquid gold took place. A comparison with the case of liquid silver, showed that it had been destroyed less than for liquid gold.[1)]

Discussion

The effect of time on the contact angle of a liquid gold sessile drop resting on an alumima substrate was examined at a contact temperature of 1080 °C for runs of (T-1) and (T-2). Each straight line in Fig. 2 can be fitted by means of the following equations:

Run (T-1)

$$\theta_1 = -0.0073x + 125.5$$

$$\theta_2 = 0.0105x + 127.9$$

Run (T-2)

$$\theta_1 = -0.023x + 129.0$$

$$\theta_2 = 0.017x + 128.5$$

In the above x is the time in minutes and θ is the contact angle.

The slopes of these equations were within the absolute value of $|0.0105—0.023|$; they were very small and near zero. Therefore, it can be assumed that the contact angle of liquid gold on an alumina substrate is scarcely changed at a constant temperature of 1080 °C. This result is the same as that observed for a system Ag/Al_2O_3.[1)]

The effect of the temperature on the contact angle of liquid gold on an alumina substrate was also investigated for runs of (T-3) and (T-4). The values of the slopes of all the straight lines are negative, as is obvious from Fig. 5. This figure indicates that the contact angle decreases linearly with an increase in temperature and that liquid gold 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 gold decreases with an increase in temperature causing a decrease in the surface tension of gold. However, the contact angle of liquid gold on an alumina substrate was larger than that of liquid silver. That is, using liquid gold it was rather more difficult to wet an alumina substrate than using liquid silver.

The amounts of scatter in the measured values of the contact angle (θ_1 and θ_2) are shown in Tables 1 and 2. It may be assumed that this scatter was due to human measurements errors of ±2°, etc. That is, since sintered alumina was used as a substrate, the effect of binder agents, the difficulty in producing homogeneous finished goods, atmospheric effects, etc. must be considerd.

The alumina substrate was chemically inert to liquid gold in the temperature range investigated, judging from the optical-microscopy and scanning-electron microscope studies. However, the surface of an alumina substrate became fairly rough, judged from surface observations after thermal treatments.

If the surface of an alumina substrate was worn by a thermal treatment, the contact angle of the liquid gold was fairly influenced.

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, and to decrease the temperature fluctuation, etc.

Various values of the surface tension of liquid gold have been reported. Values of the surface tension ranged between 580 and 1000 dyn cm^{-1} at 1070 °C in air[2)] and 1410 dyn cm^{-1} at 1027 °C.[3)] On the other hand, the values of the surface tension of liquid gold by the creep method were 1100 dyn cm^{-1} at 1130 °C in air and 1400 dyn cm^{-1} at 1030 °C in helium.[4)]

The surface tension at 1200 °C in hydrogen gas was 1120 dyn cm^{-1}. Another report concerning the surface tension of liquid gold at 1120 °C in hydrogen gas was 1128 dyn cm^{-1} and 1120 dyn cm^{-1} at 1200 °C and 1110 dyn cm^{-1} at 1300 °C.[6)] In turn, the surface tension of the solid, that is, gold foil, was 1205 dyn cm^{-1} at 700 °C.[7)]

The liquid–solid interface energy, γ_{LS}, is 133 dyn cm^{-1} for gold.[8)] It has also been reported that for metal, $\gamma_{LS}=(0.12\pm0.03)\ T_m$, where T_m is the melting point (K).[9)] From this equation, we can now estimate it to be between 121 and 201 dyn cm^{-1}, while Southin et al. and Zettlemoyer reported that $\gamma_{LS}=130$ dyn cm^{-1} of the mean value.[10)]

Another emprical relation is

$$\gamma_{LS} = \frac{K\Delta H_m}{N_o^{1/3} V_m^{2/3}}$$

where ΔH_m is the latent heat of fusion per mole, V_m the molar volume, N_o Avogadro's number and $K=0.45$ for metals.[9)] From this empirical equation, we estimate γ_{LS} to be 126 and 123 dyn cm^{-1}, using $K=0.45$, $N_o=6.02\times10^{23}$ mol^{-1}, $V_m=10.2_2$ cm^3, $\Delta H_m=12.7$ kJ mol^{-1},[11)] and 2.955 kcal mol^{-1} (about 12.4 kJ mol^{-1})[12)] respectively.

The temperature coefficient of the surface tension of liquid gold has not yet been reported.

From Dorsey's empirical formula,[13)] based on Bashforth and Adams table, we can estimate the surface tension of liquid gold to be 933 dyn cm^{-1} at 1080 °C and 917 dyn cm^{-1} at 1100 °C, by using the present experimental results of the maximum diameter, the θ-value of the sessile drop and the distance from the sessile drop and the distance from the apex of the drop to be a 45° tangent: 0.468 cm, 127.6° (at 1080 °C), and 0.109 cm, respectively, and 0.478 cm, 125.5° (at 1100 °C), and 0.112 cm, respectively.

The temperature coefficient of the surface tension of liquid gold could be estimated to be −0.80 dyn cm^{-1} °C^{-1} from the present experiment results shown in Table 2.

It is found that the calculated values of the surface tension of liquid gold by using other formulas[14] were about 15 to 25% smaller than the values predicted by the Dorsey formula.

We also attempted to calculate the critical surface tension and the surface tension at 0 K for the Au/Al_2O_3 system and, therefore, adopted the values obtained by using the Dorsey formula. The critical surface tension and the surface tension at 0 K were discussed by Rhee.[1,15]

As described above, the cosine of the contact angle increases linearly with an increase in temperature in the Au/Al_2O_3 system. The variation of the cosine of the contact angle with a decrease in the surface tension of liquid gold is shown in Fig. 7 for the Au/Al_2O_3 system. The extrapolation of the straight line to cos $\theta=+1$ produces the critical surface tension for spreading (γ_c=20 dyn cm^{-1}) for the Au/Al_2O_3 system, with the surface tension (γ_{LV}°=2015 dyn cm^{-1}) of liquid gold at 0 K.

For liquid gold, γ_c for Al_2O_3 system, with the surface tension (γ_c=361 dyn cm^{-1}),[1] but γ_{LV}°= for Al_2O_3 is larger that for liquid silver (γ_{LV}°=790 dyn cm^{-1}).

The melting point and the boiling point for Au are 1063 °C and 2707 °C, respectively. For gold, the values of the vapor pressures follow the Antoine equation:

$$\log_{10} P = -\frac{52.23\,B}{T} + C,$$

where P is the vapor pressure of gold in mm of mercury and T is the absolute temperature. Values for constants B and C are 385 and 9.853, respectively.[16] For the temperature range 2315 to 2500 °C, vapor pressures of 121 values to 399 mmHg (1 mmHg= 133.322 Pa) can be obtained. Other vapor-pressure values are 20 mmHg at 2256 °C and 100 mmHg at 2521 °C, obtained from the Harlacher-Braun equation.[17]

When measuring values of the critical surface tension, etc, the gold vapor near the melting point may be ignored and assumed not being absorbed on the Al_2O_3 substrate.

Conclusion

1) The surface tension of liquid gold in argon was obtained as 933 dyn cm^{-1} at 1080 °C and 917 dyn cm^{-1} at 1100 °C, and expressed in the temperature range 1070 to 1100 °C by γ_{LV} (dyn cm^{-1})=1797−0.80 T(°C). On the other hand, for liquid silver, the surface tension was 650 dyn cm^{-1} (960 °C) and 610 dyn cm^{-1} (1000 °C), the surface tension was 650 dyn cm^{-1} (960 °C) and 610 dyn cm^{-1} (1000 °C), expressed in the temperature range 960 to 1000 °C by γ_{LV} (dyn cm^{-1})= 1610−1.0 T (°C).[1]

2) In a liquid gold/alumina system, a linear relation exists between the cosine of the contact angle and the surface tension of a gold sessile drop when the temperature of the system is varied. This result with a system Au/Al_2O_3 is the same as that with a system Ag/Al_2O_3.[1]

The temperature coefficient of the surface tension of liquid gold in argon was obtained to be −0.80 dyn cm^{-1} °C^{-1}, compared with −1.00 dyn cm^{-1} °C^{-1} of a liquid silver.[1]

3) The liquid–solid interface energy, γ_{LS} was obtained to be 123—126 dyn cm^{-1} in comparison with 115 dyn cm^{-1} of a liquid silver.

4) The critical surface tension, γ_c of a liquid gold was obtained 20 dyn cm^{-1}, against 361 dyn cm^{-1} of a liquid silver.[1]

5) The obtained surface tension at 0 K (γ_{LV}°) for the Au/Al_2O_3 system was to be 2015 dyn cm^{-1} compared with 790 dyn cm^{-1} for liquid silver.[1]

6) According to the Antoine equation, the gold vapor near the melting point can be ignored and thought of as not being absorbed on the Al_2O_3 substrate same as for silver vapor.[1]

The difference between liquid gold and liquid silver of these measured values were attributed to the difference in the electronegativities or electric charges of the atomic nucleus for each metal, although a d-orbital (4s or 5d-orbital) and an s-orbital (5s or 6s-orbital) were similarly used to form the bond.

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