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Wettability and Supercooling Phenomena of Ga

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SYNOPSIS

Surface tension (γ_L) and contact angle (θ) of gallium related to wettability on Teflon and other substrates (Al_2O_3, SiO_2, glass, graphite, BN, Al, Ni, As etc.) were investigated. The values of Teflon were 0.70_6N/m and 158° in pure argon atmosphere, and the ones of other substrates were listed in a table in this text. We were interested especially in the relative values, γ_L's, on the substrates as compared with γ_L on Teflon substrate. Liquid Ga showed spreading wetting on pure Ni metal and adhesional wetting on Al (supposed to be covered by Al_2O_3) and on metallic polycrystal As. Surface tension of Ga was remarkably decreased by a kind of oxide contamination due to oxygen in air. The surface layer coated by the contamination was of amorphous state nearly same as liquid Ga. The amorphous coat caused liquid Ga rather high supercooling of $\Delta T \backsim 35K$. It seems that the contamination layer (oxide film) smeared the crystal nucleation sites on the free surface of liquid Ga

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1. INTRODUCTION

Wetting is closely related with adhesion and is very important for industrial technology, especially for production of metal-matrix composites. Liquid metals at high temperature have been usually used to examine wettability and the wettability has been estimated by work of adhesion, $\gamma_L(1+\cos\theta)$, where γ_L is surface tension and θ is contact angle. In this paper wettability of liquid Ga, of which the melting point is 302.9K, is investigated at room temperature. Wetability is estimated here by the relative values of surface tension (γ_L) of Ga on various substrates to the γ_L on a Teflon substrate. Remarkable supercooling induced by oxidation of Ga surface is also reported.

2. EXPERIMENTAL PROCEDURES

2.1 Measurement of Surface Tension, γ_L

Surface tension of Ga was measured based on the sessile drop method, of which the details was referred to Andreas et al.[1] and the apparatus used is shown in Fig.1. Substrates employed in this

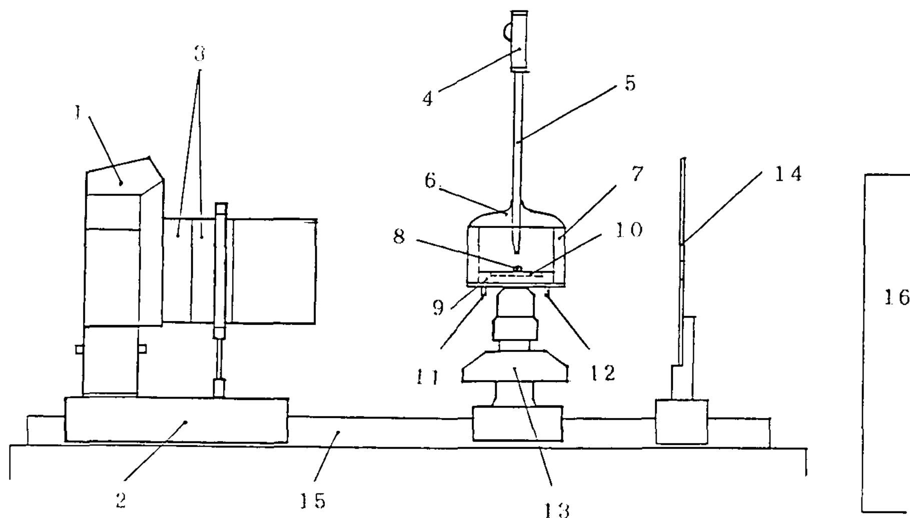

Fig.1 Apparatus used to measure surface tension.
1.Camera 2.Camera table 3.Extension tube 4.Pump
5.Hole pipet 6.Vinyl sheet 7.Acrylate box 8.Ga
9.Substrate support 10.Substrate 11.Gas inlet 12. Gas outlet
13. Goniometer head 14.Iris 15.Rail 16.Light source

Table 1 The substrate materials used and thei surface treatment

Substrate	Surface Treatment
1. Teflon	as producted
2. Al	electro-polished (in 20%$HClO_4$+80%CH_3OH, 10 20V, 273K)
3. Al_2O_3	mirror finished
4. Si	chemically polished (in 50%HF+50%HNO_3)
5. SiO_2	mirror finished
6. graphite	polished with emery abrasive papers up to No.05
7. Ga oxide(a)	formed on evaporated Ga onto slide glass
8. Ga oxide(b)	formed on evaporated Ga onto slide glass, after that heat-treated in furnace at about 500K for 3600s
9. slide glas	convetional micro slide glass
10. Ni	electro-polished (in 20%$HClO_4$+80%CH_3OH, 15V, 278K)
11. boron nitride	as producted (Denki Kagaku Kogyo Co. Ltd., 92%BN), surface roughness slightly coarser than graphite
12. As	polished with emery abrasive papers up to No.05in Ar gas

Except 7 and 8, surface of the substrates was washed by aceton.

study are shown in Table 1. The substrate was attached on a goniometer head and the atmosphere was replaced with Ar gas. Liquid Ga, which was washed by HCl-aceton solution to remove oxide on the surface, was dropped on the substrate by a hole pipet. After the equilibrium wetting was established between the Ga droplet and the substrate, a photograph was taken of the silhouette of the droplet, of which an example is shown in Fig.2. The dimension of the sessile drop was measured on the film by NIKON PROFILE PROJECTOR, of which the experimental error was ±0.05mm. Surface tension was calculated from the dimension by Dorsey's method(2). Contact angle was found out from the table of Bashforth and Adams(3).

The above method involves much trouble and is apt to produce errors. In order to lighten the troublesome work and to minimize the errors, computer graphic method is advantageous. In this method, the shades of the droplet silhouette are read as digital values and a contour map of the digital values is drawn, of which an example is shown in Fig.3. Calculation of γ_l and θ by non-linear curve fitting method is in progress.

2.2 Measurement of Supercooling

Supercooling of liquid Ga droplets, one coated with oxide film

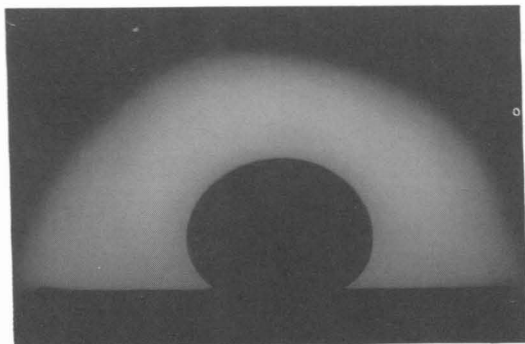

Fig.2 A silhouette of Ga on Teflon

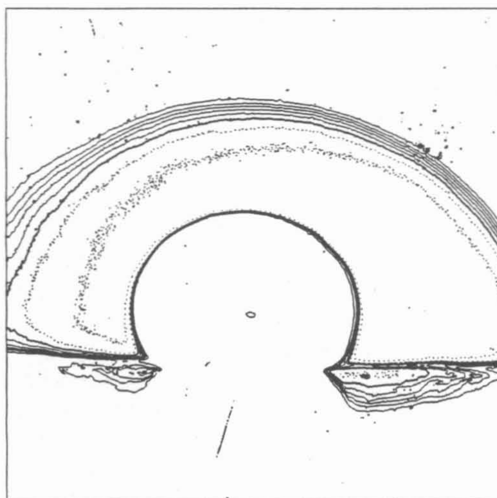

Fig.3 A contour map of droplet silhouette

and the other not coated (clean surface), was measured. Liquid Ga coated with oxide film was cooled by spraying liquid N_2 in air. Clean surface Ga was cooled by Ar gas flow chilled by liquid nitrogen. The droplet was fixed in a dimple on Teflon substrate and the temperature change was measured by a copper-constantan thermocouple inserted into the droplet. The rate of cooling, 0.045K/s and the size of the droplet, ∿10mm, were much the same in the two cases.

2.3 X-ray Diffraction

Ga oxide film was trapped on adhesive tape and the adhesive tape was put on slide glass. X-ray diffraction curve of this sample was obtained with diffractometer at room temperature. This diffraction curve was compared with reference materials (adhesive tape only put on slide glass and liquid Ga evaporated onto slide glass). A chromium target was operated at 45kV/29mA with β-filter.

3. RESULTS AND DISCUSSION

3.1 Surface Tension

Values of surface tension and contact angle obtained in this experiment are given in Table 2. Since the droplet of liquid Ga on

Table 2 Measured surface tension (γ_L) and contact angle (θ)

Substrate		Atmosphere	Surface Tension (N/m)	Contact Angle (degree)
#1.	Teflon	Ar gas	0.70_6	158
	Teflon	Air	0.34_9 *1	143
#2.	Al	Ar gas	0.54_8	147
#3.	Al_2O_3(ruby)	Ar gas	0.54_9	148
#4.	Si	Ar gas	0.52_5	152
#5.	SiO_2(quartz)	Ar gas	0.52_7	155
#6.	graphite	Ar gas	0.60_6	150
#7.	Ga oxide(a)	Ar gas	0.48_4	
#8.	Ga oxide(b)	Ar gas	0.52_5	
#9.	slide glass	Ar gas	0.59_8	
	slide glass	Air	0.41_6 *1	143
#10.	Ni	Ar gas	*2	
#11.	boron nitride	Ar gas	0.59_6	150
#12.	Ar	Ar gas	0.59_3	149
#13.	Al_2O_3-Teflon	Ar gas	0.59_8	155
#14.	Teflon-Teflon	Ar gas	0.58_8	150

*1 Surface tension of liquid Ga covered with oxide film formed during retention in air.
*2 Extensive wetting, impossible to calculate surface tension by Dorsey's method.

the substrate was somewhat asymmetric, the values given in Table 2 are average of those obtained from right- and left-hand silhouette. Values of surface tension of Ga reported by the previous authors are 0.735±0.027N/m[4], 0.706N/m[5], and 0.708N/m[6] at the melting point. It is noticed in Table 2 that the change of γ_L reflects the wettability of Ga to the substrate, i.e. the smaller the γ_L, the better the wettability. Possible reason for the change of γ_L with substrate may be contamination of impurities into liquid Ga or deformation of the droplet induced by liquid-substrate interface tension. Main features observed of the wettability of Ga to each individual substrate are as follows.

(1) Ga-Teflon

γ_L of Ga obtained on Teflon was nearly equal to the surface tension of Ga in the reference[5]. True surface tension was obtained on Teflon because Ga hardly wetted Teflon. Compared with the γ_L observed in Ar gas, the γ_L observed in air was smaller by a factor of about 2. It is considered that the shape of Ga droplet

was deformed by the oxide film formed on the surface.

In Table 2 substrate #13 showed interesting change of γ_L. In this case Ga was dropped on Al_2O_3, subsequently rolled onto Teflon, and then γ_L was measured. The γ_L obtained was 0.590N/m, which was lower than the value in the case of substrate #1 (Table 2). It is considered that oxygen adhered on Al_2O_3 was dissolved into Ga during the translation handling and the dissolution of oxygen reduced γ_L of Ga.

(2) Ga-Al and Ga-Al_2O_3, and Ga-Si and Ga-SiO_2

γ_L of Ga on Al and Al_2O_3, 0.548N/m and 0.549N/m respectively, coincide with each other. Ga did not react with Al oxide film on the Al substrate surface and did not contact directly with Al itself. Ga-Si and Ga-SiO_2 was considered to be in the same situation. Ga-Al_2O_3 showed better wettability than Ga-SiO_2.

(3) Ga-Ni

Ga-Ni pair had the best wettability in this text and showed extensive wetting. In the phase diagram Ga-Ni and Ga-Al systems both form solid solution. Different from the case of Al, Ni oxide film was destroyed by Ga in the way similar to the stimulation of flux and Ni-Ga contact was realized.

(4) Ga-graphite

Wettability of Ga-graphite was expected equal to that of Ga-Teflon because graphite is inactive to Ga as well as Teflon. But the γ_L obtained was 0.605N/m, which was smaller than that of Ga-Teflon. This result suggests that Ga atoms (1.39A in radius) entered between the graphite lamellae whose distance was rather large (3.354A). Otherwise, oxygen in the graphite contaminated Ga.

(5) Ga-BN and Ga-As

γ_L of Ga on BN was 0.596N/m. Considering that the BN surface was coarse, Ga-BN showed better wettability than Ga-graphite.

In the case of Ga-As, which has come into prominence as semiconducter, the wettability was nearly equal to that of Ga-graphite. This may be related to the fact that Ga-As system does not form solid solution at room temperature as shown in the phase diagram.

(6) Ga-Ga oxide (a) and (b)

Surface of the evaporated Ga was covered with oxide film formed at room temperature, and thus the γ_L of Ga on Ga-oxide (a)

reflected wettability of Ga to Ga oxide film. Ga oxide (b) was not a film but a kind of oxidized Ga formed at high temperature, and the γ_L on Ga oxide (b) reflected wettability of Ga to this oxidized Ga other than that Ga-oxide film.

3.2 Supercooling Phenomena of Ga and Structure of Ga Oxide Film

Surface tension and supercooling of Ga was drastically affected in the oxide film. Further to clarify the cause of the supercooling, structure of the oxide film was examined.

(1) Supercooing phenomena of Ga

Temperature change of Ga with cooling was shown in Fig.4. Temperature increased rapidly owing to the release of the latent heat of solidification. In the case of Ga with clean surface, the starting temperature of solidification was 298.7K and thus the amount of supercooling was 4.2K. On the other hand, in the case of Ga with oxide film on the surface, the starting point of solidification was 267.8K and the amount 35.1K.

(2) X-ray diffraction of Ga and Ga oxide film

X-ray diffraction patterns of three samples, (a) liquid Ga evaporated onto slide glass, (b) Ga oxide film collected onto adhesive tape and (c) adhesive tape alone are shown in Fig.5. Though the surface of the evaporated liquid Ga was covered by thin

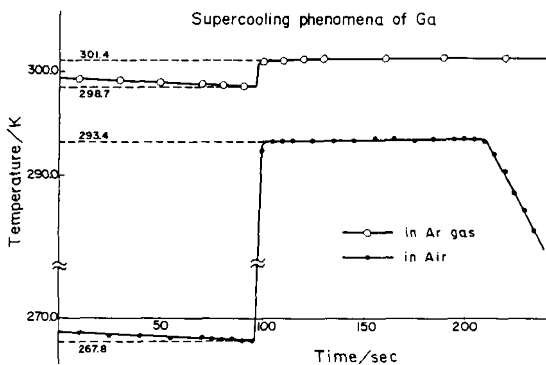

Fig.4 Cooling curves of liquid Ga in Ar and in air. Remarkable supercooling was observed in air.

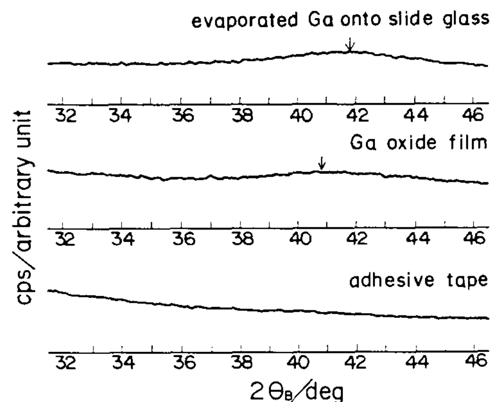

Fig.5 X-ray diffraction patterns of (a) evaporated liquid Ga onto glass, (b) a kind of Ga oxide collected onto adhesive tape, (c) adhesive tape only.

oxide film, diffraction pattern in Fig.5(a) was almost that of pure liquid Ga because the amount of evaporated Ga was enough in thickness. Intensity peak was observed (indicated by arrows in Fig.5) only in the diffraction patterns of both samples (a) and (b). The halo peak of the sample (a) shifted the position from that of (b) by $2\theta\sim1.0°$. Taking account of the tape thickness, true shift was estimated to be $2\theta\sim0.5°$. These results suggest that the sample (b) was amorphous with almost the same structure as the sample (a) and that Ga oxide film had a structure similar to that of liquid Ga which absorbed plenty of oxygen atoms. This is also suggested by the fact that Ga-Ga bond distance was increased by supercooling(7). The cause of supercooling over 35K is therefore considered to be that the nucleation site for solidification may be smeared by the amorphous layer which has almost the same structure as liquid Ga.

REFERENCES

(1) J. M. Andreas, E. A. Hauser and W. B. Tucker: J. Phys. Chem., 42(1938), 1001.

(2) W. D. Kingery and M. Humenik Jr.: J. Phys. Chem., 57(1953), 359.

(3) F. Bashforth and J. C. Adams: An Attempt to Test the Theoretical and Measured Forms of Drops of Fluid, University Press, Cambridge (1883).

(4) G. L. Mack, J. K. Davis and F. E. Bartell: J. Phys. Chem., 45(1941), 846.

(5) J. J. Bikerman: Physical Surface, Academic Press, New York and London (1970).

(6) W. D. Wilkinson: McGraw-Hill Encyclopedia of Science & Technology, McGraw-Hill, New York (1982), p21.

(7) M. Hida, H. Maeda, Y. Tsu, S. Iida, H. Terauchi, N. Kamijo, T. Murata and I. Watanabe: Photon Factory Activity Report, 1983/1984, VI-48.