Bubble-Growth for Wetting and Nonwetting System in the Maximum Bubble Pressure Method

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This paper describes a new measuring apparatus for the maximum bubble pressure method to confirm the pressure change pattern during bubble formation for wetting and nonwetting systems. Generally speaking, a sawtooth pressure pattern has been widely accepted by many researchers in the maximum bubble pressure method. Nevertheless, when the accumulated gas volume is very small, the pressure change pattern shows a chopping wave pattern as theoretically estimated for both systems. These phenomena were confirmed by the observation of the bubbles during the measurement in an aqueous system, and also confirmed by the identical pressure pattern in a mercury system.

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1. Introduction

The surface tension of liquid metals and alloys have frequently been measured by the maximum bubble pressure method (abbreviated as MBPM).1-4) The popularity stems from the reason that each successive measurement is made on a freshly formed surface.5) As a result, surface contamination effects are reduced to a minimum. The maximum pressure value during the measurement is used for the calculation of surface tension. As is well-known, the pressure during the measurement is mainly determined by the curvature of a bubble. The bubble pressure passes through a maximum pressure when forming a gas bubble. This maximum pressure generally corresponds to the minimum bubble curvature. In the case of wetting and nonwetting systems, the maximum curvature equals the reverse capillary tube radius, 1/r, in which r is the inner or outer radius of the tube in the absence of gravity. Therefore, the correction for gravity in the calculation has been carried out by many researchers such as Schrödinger6) and Sugden.7,8) Also, the pressure drop across the length of tubing between the pressure transducer and the tip of the capillary has been discussed for the measurement.9)

Furthermore, the discussion and observation of bubble formation has been done by a small number of researchers such as Hallowell and Hirn9) and Sano and Mori.10) Hallowell9) showed the relation between bubble formation and the pressure change using an aqueous solution with and without a surfactant and showed that the pressure curves have a sawtooth pattern without a surfactant. Sano10) reported a model of the pressure change during the formation of one bubble at the tip of a thick-walled nozzle with sharp edges. If we consider the bubble formation for MBPM, the pressure curve of a wetting system does not have a sawtooth pattern.11) Therefore, we investigated the bubble formation using a transparent aqueous solution and mercury by MBPM for wetting and nonwetting systems.

2. Model of Pressure Curve for Wetting and Nonwetting Systems

If we consider the models of bubble formation and the pressure change during the measurement using wetting and nonwetting systems, they can be schematically shown as in Figs. 1(a) and (b). As the bubble continues to grow, the radius of curvature decreases to r3 in both systems. In these systems, the pressure change pattern should be identical to that shown in Fig. 1(c). The increase in the curvature leads to mechanical instability due to the compressibility of the gas and the buoyancy that causes bubble detachment from the capillary and an immediate decrease in pressure. The pressure curve then has a sawtooth pattern. Is this true? If we consider the change in the bubble curvature, the radius (r3) of the bubble is the smallest at t1 and the maximum pressure, Pmax should be at t1 as shown in Fig. 1(c) in which P0 is the equilibrated pressure in the capillary. Nevertheless, no one has experimentally shown this chopping pattern. Therefore, we suspected the influence of accumulated gas volume on the pressure curve in the measuring system. We then developed our new measuring method.11) In this paper, we would like to discuss the influence of wettability and surfactant on the bubble formation and the pressure change. This means that the change in the bubble formation and the pressure curve due to the accumulated gas volume is studied in this paper.

3. Experimental Procedure

We developed a new pressure measuring apparatus11) as shown in Fig. 2, using a micro-syringe, in which a semiconductor pressure transducer was installed at the tip of a piston. Using this piston-type system, we can easily change the accumulated gas volume, the maximum volume being 1.0 x 10⁴ mm³, in this research. A flat capillary consisted of transparent quartz-glass (abbreviated QG) and polytetrafluoroethylene (abbreviated PTFE). The inside and outside diameters of the QG were 0.83 and 2.01 mm, and those of the PTFE were 1.05 and 2.00 mm, respectively. The smooth tip surface of the QG capillary was polished with a #4000 SiC pa-
per and the PTFE was cut with a surgical knife. These rough surfaces were produced by uni-directional scratching with a #1500 SiC paper.

The measurement was carried out at room temperature in the atmosphere in a rectangular quart glass photo cell to avoid the distortion of the image. The liquids are water, passed through an ion-exchange filter and single-distilled, and twice-distilled mercury. As for the surfactant for the water, we selected sodium dodecyl sulfate (abbreviated SDS). The aqueous solutions of SDS were prepared in a concentration range from submicellar (2 mM) to the nearly critical concentration (8 mM). The critical micelle concentration is 8.3 mM.

The piston was pushed very slowly by a pulse-gear motor to form a bubble at more than every 6 s. The formation of the bubble was observed and recorded at 30 frames/s with an S-VHS video recorder using a CCD camera. The pressure change was recorded by digital data recorder every 0.1 ms.

4. Experimental Results and Discussion

4.1 Wetting smooth quartz/water system

The change in the pressure and shape of a bubble in a wetting system consisting of the smooth QG/water, is shown in Fig. 3. In this case, the accumulated gas volume, $V_a$, was $8 \times 10^3$ mm$^3$. As can be clearly seen, the pressure curve does not have a sawtooth pattern. The maximum pressure, $P_{\text{max}}$, corresponds to the point in bubble growth when the bubble radius is equal to the inner radius of the tube. After this point, the bubble pressure rapidly decreases due to the compressibility of the gas. The sudden drop $\Delta P$ in the pressure is due to the compressibility of the gas. After the sudden drop in pressure, the bubble grows in place until it detaches from the tip. The small pressure drop just after the bubble detachment $\Delta p$ is caused by the $\Delta h$ due to the pressure drop in the accumulation chamber originating with the bubble detachment, namely, overblowing. The volume of the detached bubble, $V_b$, is about $1 \times 10^2$ mm$^3$ because the diameter is larger than the diameter of the capillary tube.

If we summarize these experimental results for the influence of the accumulated gas volume on the pressure curves, we obtain the result schematically shown in Fig. 4. From this figure, it is very clear that the accumulated gas volume $V_a$ affects the pressure curves. When the volume is nearly the volume of one bubble shown as 0 mm$^3$ in the figure, the $\Delta P$ should be null, and the curve then shows the chopping wave pattern as already mentioned. This model can be written by the following equations in which $\Delta V$ is the gas volume change in the accumulation chamber due to the bubble detachment.

\[
\Delta V = V_a \times \Delta P / P_0 \gg V_b
\]

$\rightarrow$ sawtooth pattern

\[
\Delta V = V_a \times \Delta P / P_0 \geq V_b
\]

$\rightarrow$ intermediate pattern as shown in Fig. 3

\[
\Delta V = V_a \times \Delta P / P_0 < V_b
\]

$\rightarrow$ chopping pattern

Also, these results show that there is no influence of the volume of $V_a$ on the $P_{\text{max}}$ value.

4.2 Nonwetting PTFE/water system

The change in the pressure and shape of a bubble in the nonwetting system consisting of the smooth PTFE/water is shown in Fig. 5 in which the accumulated gas volume is $2.0 \times 10^3$ mm$^3$. As can be clearly seen, the pressure curve is nearly identical with that in Fig. 3 except for the shape of the bubble. The shape of the bubble shows that the bubble grows on the inner diameter in the beginning and transfers to the outer diameter. The pressure suddenly decreased due to the bubble transfer from the inner to the outer diameter. This pattern is completely identical with Levin's model.\(^{12}\) If
we adopted the maximum pressure for the calculation of the surface tension by the Schrödinger equation\(^6\) based on the outer diameter,\(^1-3\) it becomes 124 mN/m. This is very high compared with the reference value of 72.6 mN/m because the maximum pressure occurs due to the bubble being generated on the inner diameter. The details will be described later.

For generating a bubble at the outer diameter from the beginning, we adopted a rough surface. The result is shown in Fig. 6. As can be clearly seen, the bubble is generated and grows on the outer diameter, and the pressure curve then becomes smooth because the bubble transfer does not occur. The calculated surface tension using the \(P_{\text{max}}\) was 70.2 mN/m.

Why is a bubble generated at the outer diameter from the beginning? One of the reason may be based on the effect of surface roughness on the contact angle\(^13\) or the contact line.\(^14\) The height roughness\(^15\) should be changed by the polishing materials, as already mentioned. Nevertheless, the true surface area does not change very much because the pattern should be identical without the size.\(^15\)

On the other hand, if a rough interface consists of a solid and a vapor, the contact angle is determined by the ratio of the solid area and the vapor area at the contact line.\(^15\) Therefore, the contact angle increases more than that of the above men-
tioned calculations. These theoretical results show that the rough surface increases the contact angle in a nonwetting system. Also, in the case of a non-wettable rough surface, the gas phase can exist in the grooves of the scratched surface, so-called “channel effect”.[10] Therefore, a bubble can be easily propagated from the inner to the outer diameter. This model is identical with the model of Fig. 1(b). Nevertheless, there is a sudden pressure drop $\Delta P$ due to the accumulated gas volume. If the $\Delta P$ becomes null, the pressure curve should show the chopping pattern. In this case, the shape of the pressure peak is not as sharp compared with Fig. 3, because the volume of a bubble is much bigger than that in a wetting wetting system.

The two-transfer model for a nonwetting system, as shown in Fig. 7(a), is Levin’s model[17] and (b) is identical with that of Fig. 1(b). In the case of (a), a bubble transfers from the inner to the outer radius of the capillary. The inner and outer radius are described as $r_\text{in}$ and $r_\text{out}$ respectively, and the radius of the bubble is $R$. At the beginning, the gas pressure is negative, at $R_1$ and $R_2$. When the pressure increases, the gas pressure becomes zero when $R$ is $R_3 = \infty$, and the $P$ increases with time up to $R_4$ and then decreases to $R_5$. Afterwards, the pressure again increases to $R_6$ when the radius is $r_\text{out}$ and decreases once more due to the bubble detachment.[10] Therefore, in this model, the pressure curve should have two maximum peaks.[12]

Levin[12] also showed that $P_4$, the critical contact angle that occurs in the bubble transfer from the inner to the outer radius, can be calculated by the following relation, where $\sigma$ is the surface tension of the liquid and $\theta$ is the contact angle.

$$ P_4 = 2\sigma/R_4 = 2\sigma \sin(180 - \theta)/r_\text{in} = 2\sigma \sin \theta/r_\text{in} $$

If we calculate the critical $\theta_c$ using $P_4$, $r_\text{in}$ and $\sigma$, then $\sin \theta_c$ is 0.735; therefore, the critical $\theta_c$ is 132°. The contact angle between PTFE/water/gas is 108.5° as reported.[17] Therefore, 132° should be reasonable.

In the case where $\theta$ is less than $\theta_c$, $P_4$ is then greater than $P_6$, and the pressure curve should show two maximum peaks as mentioned before. Therefore, we can not calculate the facetension value using the maximum pressure. The details will be discussed later. Nevertheless, if $\theta$ is more than $\theta_c$, then $P_6$ is greater than $P_4$, and the pressure curve then has only one peak as shown in Figs. 1(b) and 6.

4.3 Nonwetting quartz/mercury system

The pressure curve with a smooth surface is shown in Fig. 8 and for the rough surface in Fig. 9. In these cases, the accumulated gas volume was $2.0 \times 10^3$ mm$^3$ and the depth was 30 mm. If we calculate the surface tension with this 1st peak using the inner and outer radius, the values are 351 mN/m and 824 N/m respectively. These values do not agree with the reference value of 482 mN/m for the above mentioned reason.

In the case of a smooth surface, Fig. 8, the pressure curve appears as a sawtooth pattern. Is this true? The sharp drop is not at a right angle and is slightly declined. Moreover, during the sharp drop, we can recognize a small overlapped peak, denoted by the arrows as the 2nd peak in the figure. Therefore, we expand the time axis in this range as shown in Fig. 10. As can be clearly seen, there are two peaks after the sharp drop, namely the 2nd and 3rd peaks. The pressure of the 2nd peak is nearly identical with the peak value of Fig. 9. The 2nd and 3rd peaks should be a dynamic phenomenon. What does this mean? The maximum value in Fig. 8 is the pressure of a bubble on the inner diameter as already mentioned in Fig. 5. The second one is identical with the maximum pressure of the outer bubble, denoted by the arrow, in Figs. 5, 6 and 9. This means that the bubble is generated initially on the inner diameter and grows up to the first peak and then propagates to the outer diameter within 0.02 or 0.04 s as shown in Fig. 10 and detaches from the capillary just after the 3rd peak. Therefore, if we use a conventional analog measuring system for this case, the curve must be observed as a sawtooth pattern.

This is completely identical with Fig. 10, regarding the meaning of the two peaks, except for the 3rd peak. The
3rd peak must be due to the dynamic instability of the bubble. These phenomena must be the reason why the silica tube yielded erroneous values for mercury as reported by Lang.10

In the case of mercury, the surface tension and the density are much higher than those of an aqueous solution; therefore, the sudden drop $\Delta P$ is much larger than that in an aqueous solution system. The pressure curve then looks like a sawtooth pattern, but it is simply an intermediate pattern as shown in Fig. 3.

4.4 Influence of surfactant in a wetting smooth quartz/water system

The influence of the surfactant on the pressure curves is shown as a function of the concentration of SDS in Fig. 11. These curves are slightly different from the pattern reported by Hallowell et al.,9 because their data was strongly affected by the accumulated gas volume, as already mentioned.

Not only there is a decrease in the peak value with the increase in the surfactant content but also the pattern is changed. There are two main changes due to the addition of SDS. One is the sudden drop in the value of $\Delta P$; it becomes much smaller with the increase in surfactant content due to the decrease in the surface tension. The second is the increasing rate of the pressure. The increasing rate is changed during the measurement at the points denoted by the arrows in the Fig. 8. In the beginning stage of the measurement, the increasing rate of the surface area of a bubble is much higher than that at a later time. Therefore, the diffusion of the surfactant is not sufficient to become saturated. This change most probably originates from the diffusion of the surfactant. Therefore, using this measuring method, the diffusion rate of the surfactant can be studied.

5. Conclusions

We have developed a new measuring apparatus for the maximum bubble pressure method to confirm the pressure change pattern during bubble formation for wetting and nonwetting systems. A piston-type micro-syringe was used, whose maximum accumulated gas volume was $8 \times 10^{-3}$ mm$^3$. The sawtooth pressure pattern has been widely accepted by many researchers in the maximum bubble pressure method. Nevertheless, when the accumulated gas volume is very small, the pressure pattern has a chopping wave pattern as theoretically estimated for both systems. These phenomena were confirmed by the observation of the bubbles during the measurement for an aqueous solution and a mercury system.

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