Original Paper

Surface tension measurement of glass melts by the maximum bubble pressure method

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The maximum bubble pressure method was used to obtain accurate surface tension measurements. The dependence of apparent surface tension value on bubble growth time was measured for times from several to longer than a thousand seconds. The static surface tension value was obtained by extrapolating bubble growth time to infinity. The dynamic surface tension, which is familiar in colloids, could not be directly obtained because of the high viscosity of glass melt. The effects of capillary tip material and shape were also examined. This method is applicable to melts with viscosity less than $10^{3.5}$ dPa s. The reproducibility in the measurement was within a few percent.

Oberflächenspannungsmessung von Glasschmelzen durch Bestimmung des maximalen Blasendrucks

Die Methode zur Bestimmung des maximalen Blasendrucks wurde angewendet, um genaue Oberflächenspannungswerte zu erhalten. Es wurde die scheinbare Oberflächenspannung in Abhängigkeit von der Dauer des Blasenwachstum für Zeiten von wenigen bis zu über tausend Sekunden gemessen. Der Wert der statischen Oberflächenspannung wurde durch Extrapolation der Blasenwachstumszeit gegen unendlich erhalten. Die in Kolloiden üblicherweise vorkommende dynamische Oberflächenspannung konnte wegen der hohen Viskosität der Glasschmelze nicht direkt ermittelt werden. Der Einfluß des Materials und der Form der Kapillarenden wurde ebenfalls untersucht. Die Methode, die Oberflächenspannung an Hand der Messung des maximalen Blasendrucks zu bestimmen, eignet sich für Schmelzen mit einer Viskosität von weniger als $10^{3.5}$ dPa s. Die Reproduzierbarkeit der Meßwerte lag innerhalb weniger Prozent.

1. Introduction

Computer simulation is one of the best ways to investigate the usefulness of new developments in glass melting techniques. In the simulation, precise properties of glass melt are needed to get an accurate result. Surface tension is one of the important properties related to refining [1] or homogenizing.

The surface tension values have been measured in several silicate [2 to 6] and borosilicate [7] melts. For silicate melts, the values were around 300 mNm^{-1} and their temperature dependence was small. For borate, they were around 200 mNm^{-1} and had a greater temperature dependence. Recently, a new set of calculation parameters has been proposed by Kucuk et al. [8]. In that paper factors from several authors were summarized. According to those data, there are some discrepancies between the calculated values. In order to confirm the accuracy of the proposed values, one needs more precise data.

There are several ways to measure the surface tension. For glass melts, the sessile drop method [3, 5 to 7], pendant drop method [5 and 9], ring method [10] and maximum bubble pressure method [2 to 4] have all been used. Sessile drop and pendant drop methods are promising ways to get an accurate value since they are static ones and need not to consider a resistance from viscous flow. These methods need precise measurement of the drop shape if the liquid has high surface tension and density [11] like glass melts. The major problem for these drop and ring methods is a surface composition change by volatilization from the melt since large volume of air contacts to melt. Another problem for drop methods is a contamination by reaction between substrate and melt, which is more serious than when using other methods since the drop is not renewed. On the other hand, these

problems are not serious for the maximum bubble pressure method since the air volume contact to the bubble is small and the interface is refreshed for each bubble formed. Moreover, it needs a simple technique; just measuring pressure difference between internal bubble pressure and the atmosphere. The bubble formed at the tip of a capillary grows with increasing pressure and expands until it suddenly breaks free on passing a maximum pressure at time t_{max}. However, the shape and size of capillary must be determined precisely since too rapid bubble growth can cause large errors from viscous flow. Because of these problems the method has not often been used for glass melts except for Akhtar et al. in 1968 [4] though there have been some studies in slags [12]. The dependence of the surface tension on rate of bubble growth has been studied in the field of colloidal solution [13 and 14]. Surface tension was found to be related to the maximum bubble forming time t_{max} by the equation

$$\sigma = \sigma_s + C/t_{max}^{1/2} , \qquad (1)$$

where σ is the dynamic surface tension, σ_s the static surface tension, C a constant. Adsorption on the surface and diffusion affect the value of C. Exact σ_s value can be estimated from this relation by extrapolating $1/t_{max}$ to zero.

Another experimental problem arises from the wettability of capillary material with melt. If the wettability is high, the melt will rise in the capillary at the beginning of bubble formation because of the capillary action, which might change the effective inner diameter of the capillary. On the other hand, if the wettability is too low and the capillary tip does not have a thin sharp edge, it is not clear what value of radius should be used since bubble diameter would change before a perfect hemisphere is formed.

In this study, the effects of capillary material and shape were examined in relation with the bubble forming time.

2. Experimental

For bubble formation in melt, three types of platinum tubes were used. The outer diameter of each tube was 6 mm and a hole diameter at the tip of tube was ca. 1.0 mm. The diameters of the holes were measured with a microscope with a scale. The materials of the tube tips are (a) platinum(Pt)-13%rhodium(Rh), (b) Pt-20%Rh and (c) zirconia-dispersed Pt-5%Au (FKS Pt-5%Au, Furuya Metal). The tip shapes were flat for (a), cut to 45° but flat near the hole for (b), cut to 30° at outer side and 60° near the hole for (c). The hole shapes were slightly distorted circles and their radii were (0.50 ± 0.02) mm for (a), (0.486 ± 0.010) mm for (b) and (0.534 ± 0.010) mm for (c). The tube was connected to a microvalve and a digital manometer (co. DP-200A, Okano, Osaka (Japan)) and was in-

troduced into an electric furnace. The manometer had a measuring range from 0 to 2000 Pa with 0.2 % of precision and 0.02 s in response. A platinum crucible was set in the furnace. An alumina cover with a hole was put on the crucible to avoid contamination by dust from upper hole of the furnace. After temperature was raised to a measuring point, the tube was moved down in 0.02 mm steps by using a screw with scale. Contact between the glass melt and tip was detected electrically using an LCR meter (hp 4262A, Hewlett-Packard (USA)). A small amount of dry air (80 % N_2-20 %O_2) was introduced into the tube at a rate about $5 \cdot 10^{-4}$ cm³/s, and a rise of the pressure was confirmed at the time of contact. The tube was then moved down slowly to a predetermined position. The bubble generation rate was adjusted with the microvalve. The rate of gas flow was in the range from $2 \cdot 10^{-4}$ to $5 \cdot 10^{-2}$ cm³/s. The difference in pressure between the inside of the tube and atmosphere was recorded on a chart or stored in a computer allowing measurement of the maximum differential pressure ΔP_{max} and bubble forming times. When the bubble generation rate was slower than 0.2 min⁻¹, a shortcut method was adopted to save the experimental time, in which excess air was passed at first to about two thirds of the maximum value and then at a normal rate. In this case, the value of t_{max} was extrapolated as shown in an insert in figure 1.

The surface tension σ was calculated with the equation

$$\sigma = f \cdot r_0 (\Delta P_{max} - \varrho g h)/2 \qquad (2)$$

where ϱ is the density of melt, g the gravity constant, h the depth of the tip below the surface of melt, r_0 the radius of the platinum capillary, which was corrected for the thermal expansion of platinum, and f the bubble-shape correction factor which is smaller than unity. The factor is a function of r_0, ϱ and σ itself and was calculated according to the table by Sugden [15]. Since r_0 was small and the surface tension high, the correction factors were from 0.99 to 0.995.

Because of the thermal expansions of melt and platinum tube, the depth h, which was nominally 5 mm by the scale, could change with temperature. In order to calibrate h, a glassy carbon or an FKS Pt-5% Au tip, which were less wettable by the melt was attached at the end of the platinum tube with platinum wire. The position of the surface was determined at each temperature with the electrical contact method. The glassy carbon tip was used in an N_2 atmosphere. Reproducibility of the surface position was within 0.3 mm against heating and cooling cycle, which corresponded to 0.6 % of error at most.

Two glass compositions, $20Na_2O-10CaO-70SiO_2$ and green float glass (Nippon Sheet Glass Co., Itami (Japan)) were used. The composition of green float glass is shown in table 1 [16]. The latter sample was used as a standard sample in a project of characterization of glass melt performed by New Glass Forum Japan. The

Table 1. The composition of the green float glass in mass% [16].

SiO$_2$	Al$_2$O$_3$	MgO	CaO	Na$_2$O	K$_2$O	Fe$_2$O$_3$	TiO$_2$	SO$_3$
70.9	1.6	3.9	8.8	13.3	0.7	0.5	0.04	0.2
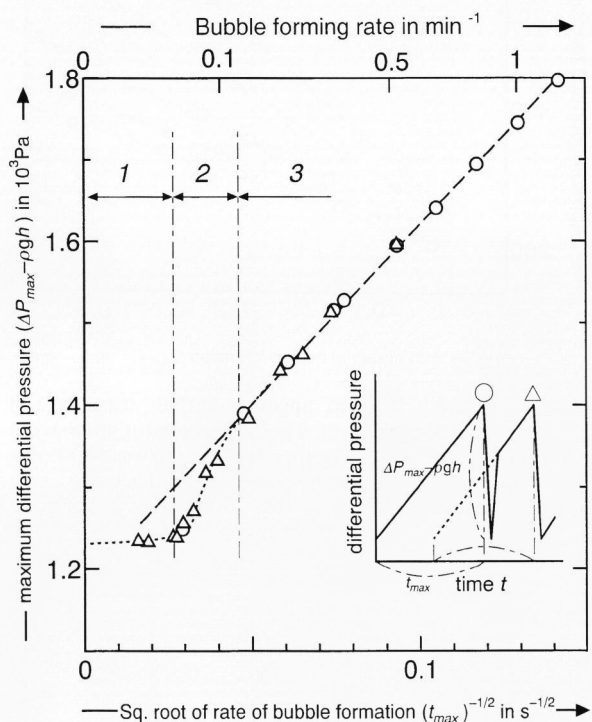
Figure 1. Relation between the bubble forming time t_{max} and the maximum differential pressure ΔP_{max} for 20Na$_2$O$-$10CaO $-$70SiO$_2$ glass melt and the comparison of values with shortcut ($\triangle$) and normal ($\bigcirc$) methods. From dependence of ΔP_{max} on t_{max}, the measured values can be separated to three regions.

density of the latter glass was measured in this project; 2.441 g/cm^3 at 1200 °C and 2.426 g/cm^3 at 1300 °C [17]. That of the former glass is adopted from a data book [18]. These values affect only $\varrho\,g\,h$ values.

3. Results

Figure 1 shows the relation between bubble forming time and the maximum differential pressure for the 20Na$_2$O$-$10CaO$-$70SiO$_2$ glass melt measured with the Pt-20%Rh tip (b). The figure also compares the shortcut and normal methods. The x axis is the square root of the rate of bubble formation ($t_{max}^{-1/2}$), see equation (1). The data by shortcut method ($\triangle$) agreed with that by normal method ($\bigcirc$) in this case. Hence the appropriateness of the shortcut method was confirmed in the region of long bubble forming time t_{max}. That is not true for short t_{max} due to the viscosity of the glass, as discussed later. The pressure $-t_{max}$ curve in figure 1 can be separated into three regions. In region 1 where the $t_{max}^{-1/2}$ is
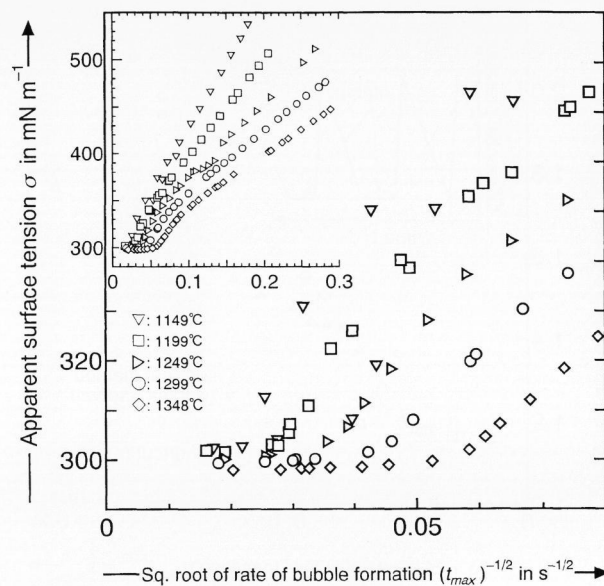

Figure 2. Relation between apparent surface tensions and $t_{max}^{-1/2}$ at regions 1 and 2 at various temperatures. The melt composition was 20Na$_2$O$-$10CaO$-$70SiO$_2$ and tip (b) was used. The insertion is the relation for wider range of t_{max}.

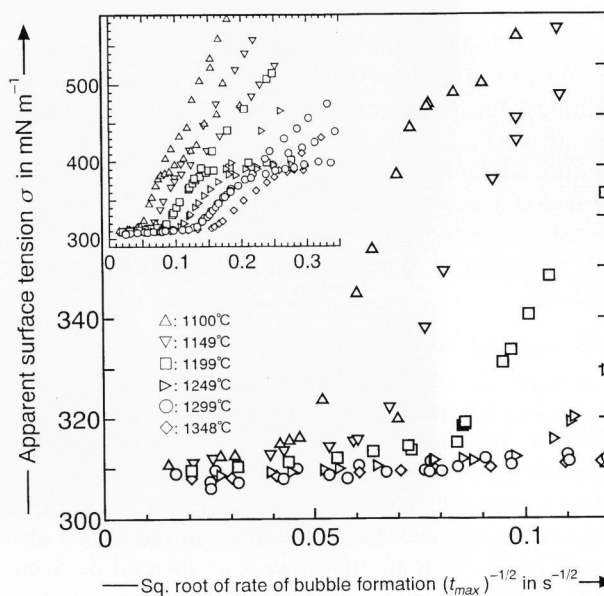

Figure 3. Relation between apparent surface tensions and $t_{max}^{-1/2}$ at regions 1 and 2 at various temperatures for the same melt as in figure 2 using tip (c). The insertion is the relation for wider range of t_{max}.

less than 0.02 ($t_{max} > 2500$ s), slope of the curve is small and the static value of σ could be calculated by extrapolating ΔP_{max} curve to zero rate, hence this region was the most important one for the surface tension measurement. In region 2, the slope is much steeper. In region 3 where the rate was greater than 0.05, the maximum pressure increased proportionally to $t_{max}^{-1/2}$, which was similar to colloid solutions [13 and 14].
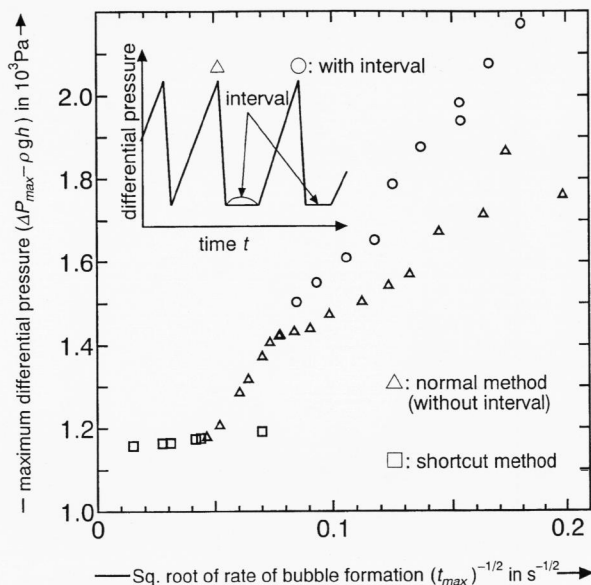
Figure 4. Difference between the ΔP_{max} value from continuous normal method and that obtained by a method with some interval after the last bubble rupture.
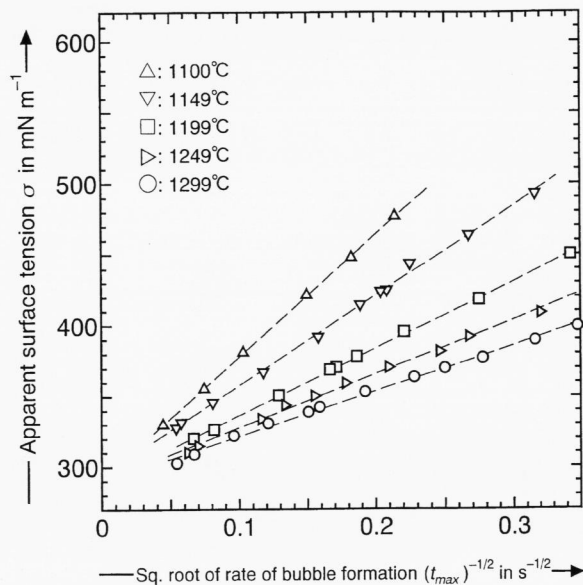

Figure 5. Relation between apparent surface tensions and $t_{max}^{-1/2}$ at various temperatures. The melt composition was the same as in figures 2 and 3. The tip of Pt-Rh tube was Pt-13%Rh (a). A longer t_{max} region was not measured in this case.

Figure 2 shows the apparent surface tension value for $20Na_2O - 10CaO - 70SiO_2$ glass melt at various temperatures. Each apparent σ value was calculated from measured ΔP_{max} value using equation (2). At high temperature where the viscosity of the melt becomes lower, the region 1 becomes wider and the static σ_s value can be easily obtained. Also the slope for the short t_{max} region is smaller at high temperature than at lower temperatures.

Figure 3 shows the surface tension for the same glass as in figure 2, but measured with FKS Pt-5%Au tip (c). On comparing these results with those in figure 2, it is seen that, although the general trends are similar, there are some differences. In particular, the static values are a little higher. There is some possibility that the wetting of the tip by the melt has some effect on the results obtained. Figure 4 shows that leaving an interval between the formation of successive bubbles gave rather higher values of σ at higher rates of formation, but almost identical values for almost static conditions.

Figure 5 shows the same kind of figure as figures 2 and 3 measured with Pt-13%Rh tip (a). In this case, the slopes of σ versus $t_{max}^{-1/2}$ curves are much smaller than that in figures 2 and 3. Since the σ's were not measured at longer t_{max} region in this experiment, accurate static values could be obtained. Once again the material used for the tip might affect the results.

Figures 6 and 7 show the results for green-float glass measured with Pt-20%Rh (b) and FKS Pt-5%Au (c) tips. Similar trends as in figures 2 and 3 are observed. In figure 7, the region 1 is clearly observed so that σ_s's are

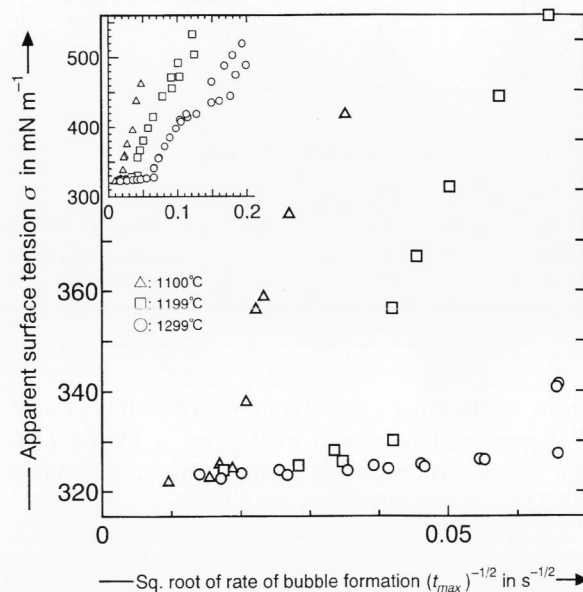Figure 6. Relation between apparent surface tensions and $t_{max}^{-1/2}$ at regions 1 and 2 at various temperatures for green float glass with tip (b). The insertion is the relation for wider range of t_{max}.

easily estimated at each temperature. The viscosity of the melt is 3300 dPa s at 1100 °C [16].

Figures 8 and 9 show the dependence of static surface tension on temperature for the two kinds of glasses. Each value was derived from an extrapolation of measured values to zero rate of formation. In figure 8, the straight line is the data by Badger et al. [2] for a similar composition.
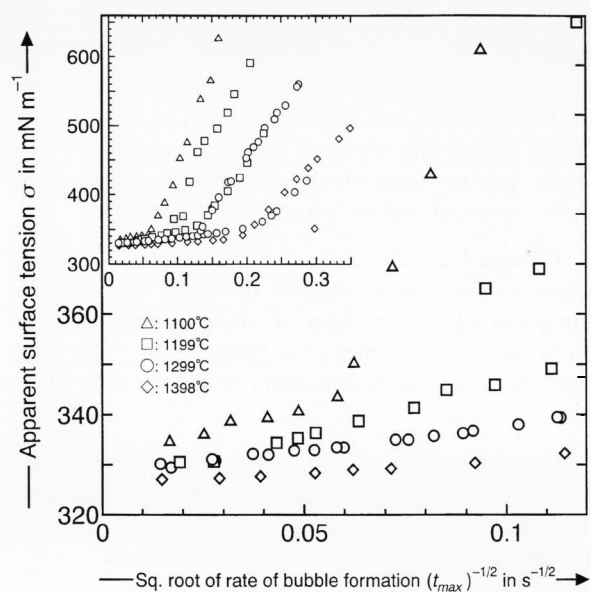
Figure 7. Relation between apparent surface tensions and $t_{max}^{-1/2}$ at regions 1 and 2 at various temperatures for the same green float glass as in figure 6. Tip (c) was used. The insertion is the relation for wider range of t_{max}.
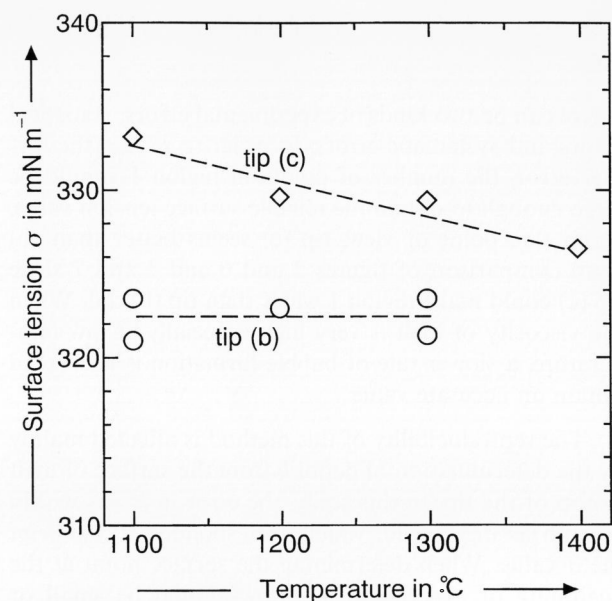

Figure 9. Dependence of surface tension values on temperature for green float glass melt.
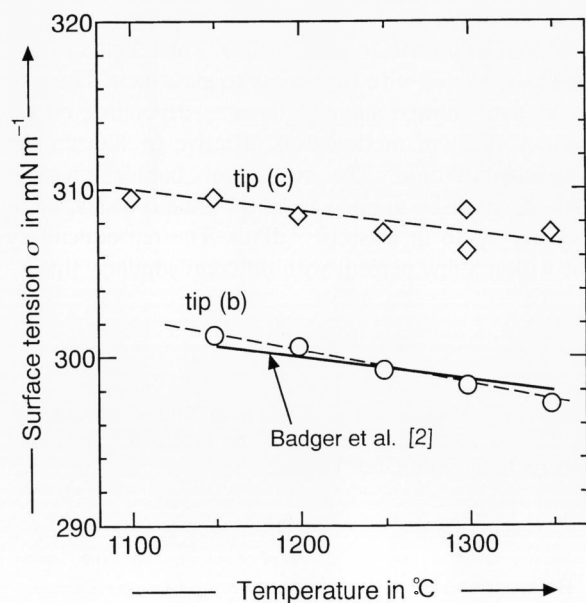

Figure 8. Dependence of surface tension values on temperature for $20Na_2O-10CaO-70SiO_2$ glass melt. The value for each temperature was obtained from an extrapolation of apparent surface tensions to infinite bubble blowing time.

Figure 10. Case where the values from normal method and shortcut method disagreed.

4. Discussion

4.1 Validity of the shortcut method

As shown in figures 1 and 4, the values from the shortcut method agreed with those from normal method when the bubble forming time was long and temperature was high. The values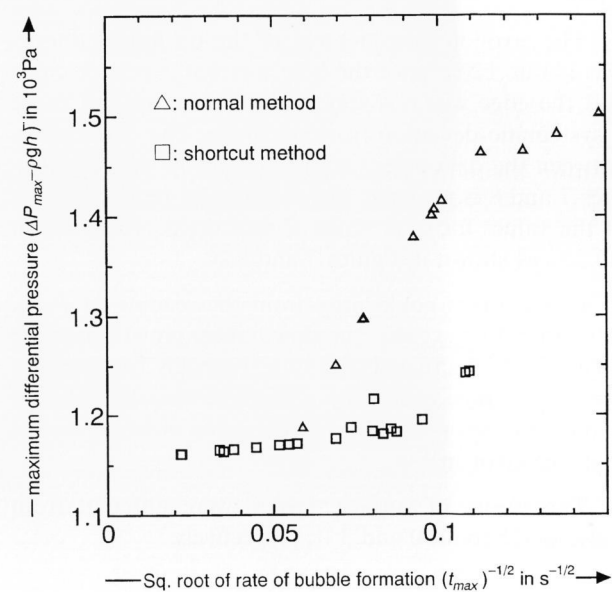 at much longer time agreed within an experimental error though they are not shown in figures. In the short time region at low temperature, deviations sometimes occurred between the shortcut method and normal method as shown in figure 10. The points from the shortcut method, however, fit with the straight line from region 1. Hence the shortcut method is thought to be useful to obtain an extrapolated static surface tension value. This method would also be useful to reduce a composition change from volatilization.

4.2 Accuracy and reproducibility of the static value

There can be two kinds of experimental errors; statistical errors and systematic errors. In order to reduce the former error, the number of points in region 1 should be large enough to obtain the reliable surface tension value. From this point of view, tip (c) seems better than (b) from comparison of figures 2 and 6 and 3 and 7 since tip (c) could make region 1 wider than tip (b) did. When the viscosity of melt is very high especially at low temperature, a slower rate of bubble formation is needed to obtain an accurate value.

The reproducibility of this method is affected mainly by the determination of depth h from the surface of melt to top of the tip. In this study, the error in h was within 0.3 mm as mentioned, which corresponded to 0.6 % of the σ value. When determining the surface point at the beginning of experiment, air flow should be small or stopped since the flow would depress the melt surface just before contact and give a false position. The volume of the tube dipped in the melt could be ignored in this study since the diameter ratio of the tube/crucible was 0.1 corresponding to only 0.05 mm in h when h was 5 mm.

The error in measurement of the tip hole radius r_0 was about ±2 % since the hole was not a perfect circle and the edge was not very sharp. This error can cause a systematic deviation from tip to tip. The discrepancy between the data values with different tip shown in figures 7 and 8 is probably due to this. The reproducibility of the values for each series of measurement was about ±0.5 % as shown in figures 7 and 8.

Other errors could arise from the reading of P_{max}, estimation of t_{max}, etc.; for slow bubble growth pressure occasionally fluctuated with time, probably because of a pressure change caused by a slight temperature fluctuation. This error would be of the same order as or less than the error in h.

The values of surface tension were different from those in [2] about 0 and 3 %, respectively.

4.3 Effect of tip shape and wettability on the dynamic value

Depending on tip, the σ versus $t_{max}^{-1/2}$ curves differ as seen on comparing figures 2, 3 and 5. The slope at large $t_{max}^{-1/2}$ is similar in figures 2 and 3, while it is much smaller in figure 5. This tendency was reproducible for other glasses. The tip (a) used in figure 5 had a different shape from other tips and seemed to have higher wettability than those. If the wettability of tip is high, capillary action might affect the "dynamic" property.

In figures 2 and 3, the apparent σ values are less dependent on t_{max} in region 1 and then the values be-

came larger with decreasing t_{max} in regions 2 and 3. The border between regions 1 and 2 shifts to short t_{max} side with increasing temperature. The differences in these tips are the materials and hole diameter. The tip (c) has a slightly bigger hole diameter and lower wettability than tip (b). It is not clear which factor has the greater effect on the apparent surface tension.

Figures 4 and 10 mean that interference can occur before a perfect hemispherical bubble is formed if the rate is too high. From figure 4, allowing an interval between successive bubbles gives better results. This effect might be related with wettability or the viscosity of the melt.

Concerning the tip shape, its edge should be sharper if the contact angle between the tip and melt was large. However, too sharp edge might not be appropriate since it might become deformed at high temperature.

5. Conclusion

The surface tension of two glass melts was measured by the maximum bubble pressure method. The static value could be obtained by extrapolating apparent values at slow rates of growth to infinite time. Three kinds of tips were used related with wettability to glass melt. The estimated data showed slight differences depending on tip used. A shortcut method was effective to shorten the experimental time. The maximum bubble pressure method could be applied to fairly viscous melts, i.e. a viscosity up to at least $10^{3.5}$ dPa s. The reproducibility was within a few percent with different capillary tips.

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6. References

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