The Effect of Temperature, Cooling and Surface Tension on the Fining in Alkali-Alkaline Earth-Silica Glassmelts Containing ZnO

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The effects of temperature, cooling and surface tension on the fining were studied in alkali-alkaline earth-silica TV screen glassmelts containing ZnO. Sodium antimonate ($Na_2OSb_2O_5$) was used as a fining agent. Viscosity and surface tension of the melts were determined. On the basis of these properties, fining tests for several batches were performed by "MF" (Melting and Fining) and "PMF" (Profiled Melting and Fining) methods. The results of these tests showed an opposite behavior each other with increase in ZnO content. This behavior has been discussed in terms of two fining processes - growth of bubbles and shrinkage of seeds.

Key words : Fining, Viscosity, Surface tension, Bubble growth and shrinkage

I. Introduction

The most frequent defects found in TV screen glasses are bubbles (blister and seed). Especially, as recent display technology is improved the quality control concerning bubble size is becoming stricter for display glasses, for example computer monitor glasses. As a source of bubble it is generally divided into four catagories; air inclusion in batch, batch reactions, interaction of the glassmelt and refractories, and others (reboil etc). Once a bubble is generated it disappears or stays in molten glass irrespective of its source during manufacturing process, in other words melting, conditioning or forming. Therefore, glass composition is very important factor for controlling the generated bubbles. Theoretically, glass fining consists of two main processes,[1-4] 1) enlarge exiting bubbles, rise to the surface and break 2) bubbles that do not reach the surface dissolve during cooling. In spite of those two processes the most attempts have focused on the fining behavior due to the former.

Alkali-alkaline earth-silica is the basic system of the commercial TV screen glasses. In the whole world there are about 6 great TV glass makers and Table 1 contains their composition ranges and x-ray absorption coefficients. Several common minor components as ZrO_2, TiO_2, CeO_2, Al_2O_3, Sb_2O_3 and the existence of ZnO are founded in Table 1. In order to maintain optimal properties of TV screen glasses and their good productivity, these minor components are introduced and, thus each component plays a specific role. The role of the minor components except ZnO in TV glass product or their manufaturing process is well known to us. For example, Sb_2O_3 is a chemical fining agent and ZrO_2 gives a great con-

tribution to the x-ray absorption coefficient of TV glass inspite of its small amount. In order to prevent from the solarization and the browning effect TiO_2 and CeO_2 are introduced respectively. But in the case of ZnO, although its small amount is introduced to the glass deliberately, its role in TV glasses is not known clearly. The present work has originated from this point.

ZnO is one of components frequently used in many technical glasses and affects several glass properties, especially viscosity and surface tension of glassmelts[5-8] as a network former or modifier.[9] In the present work, from the viewpoint of above two basic fining mechanisms the effect of temperature, cooling and surface tension on the fining was studied in alkali-alkaline earth-silica glassmelts in which SiO_2 is replaced by ZnO up to 0.4 wt%.

Table 1. Composition Range and X-ray Absorption Coefficient of Commercial TV Screen Glasses

Components & x-ray absorption coefficient		Composition range (wt%)
Components	SiO_2	60.0-61.5
	Na_2O	7.4-8.0
	K_2O	7.0-7.6
	MgO	0-0.4
	CaO	0-1.5
	SrO	8.1-9.0
	BaO	9.0-9.6
	ZnO	0-0.5
	ZrO_2	1.5-2.5
	TiO_2	0.4-0.5
	CeO_2	0.3-0.4
	Al_2O_3	2.0-2.2
	Sb_2O_3	0.2-0.4
X-ray absorption coefficient (/cm)		28.6-29.1

II. Theory of Fining

It is well known that there are two basic processes in glass fining, namely, remove of bubbles from molten glass, and each process consists of chemical and physical mechanisms.[1-4] In the upper part of Fig. 1 a typical TV glass melting tank is described with major convection flow of glassmelts and in the lower part the coresponding fining processes are summarized. The first step of fining is growth of bubbles, their buoyant rise and collapse. The second step called refining is shrinkage of bubbles and their dissolution into melt. The former called primary fining is most effective at high temperature, namely, in hot spot area. In this area the oxygen gas generated by the reduction of chemical fining agent (Sb_2O_5) diffuses into and enlarges existing bubbles due to the decrease of gas solubility. According to the general relationship for the thin flow melts under $10^{2.6}$ dPas the bubble rise velocity (v) in a melt is proportional to the square of its radius (R^2) and the reciprocal of viscosity ($1/\eta$) as follows, $v=R^2/\eta$. Hence, the redox reaction and melt viscosity play important role in the growth of bubbles and their buoyant rise. On the other hand, at low temperature, namely, in front area and conditioner the glass temperature is normally too low and viscosity too great to allow smaller bubbles (seeds) to rise to the surface and break. Because antimony ion shifts from the lowest valency state (Sb^{+3}) to a higher valency state (Sb^{+5}) and gas solubility generally increases in this temperature range, the gases dissolve into the glassmelts and, thus the shrinkage of seeds occurs. In this stage, there is also internal pressure of bubble as an another factor to shrink the bubbles. The more the internal pressure in bubble increases, the greater the possibility of bubble shrinkage becomes. The internal pressure of bubble (P_{bubble}) in the melt is as follows: $P_{bubble}=P^0+\rho gh+\sigma/R$, where P^0 is the atmospheric pressure, ρgh is the hydrostatic pressure and σ is the melt surface tension. The internal pressure of bubble increases with decrease of bubble size. In the refining zone the dissolution of bubbles is hence a dominant process in which the redox reaction and the internal pressure in seeds are essential parameters for bubble shrinkage and, thus surface tension of glassmelt becomes an important property. The above processes can be summarized as follows: as the chemical fining mechanism the redox reaction of fining agent and the gas solubility take part in growth and shrinkage of bubbles through gas diffusion between bubbles and molten glasses, the bubble rise due to the melt viscosity and the bubble shrinkage caused by increased internal pressure in seed belong to the physical fining mechanism.

III. Experimental

1. Glass preparation and measurement of melt property

The base glass composition in wt% was $62.2SiO_2$, $15R_2O(Na_2O+K_2O)$, $18RO(SrO+BaO)$ and others as ZrO_2, TiO_2, Al_2O_3 in which only SiO_2 was replaced by ZnO up to 0.4 wt% and the concentrations of the other components were fixed. The raw materials consist of sand and industrial carbonate chemicals etc. 2.7 wt% of total alkali oxide content is supplied as KNO_3. Sodium antimonate ($Na_2OSb_2O_5$) as a fining agent used routinely in TV glass industry was selected to minimize the volatilization of antimon oxide. Table 2 shows the compositions and the raw materials of the experimental glasses. The batches
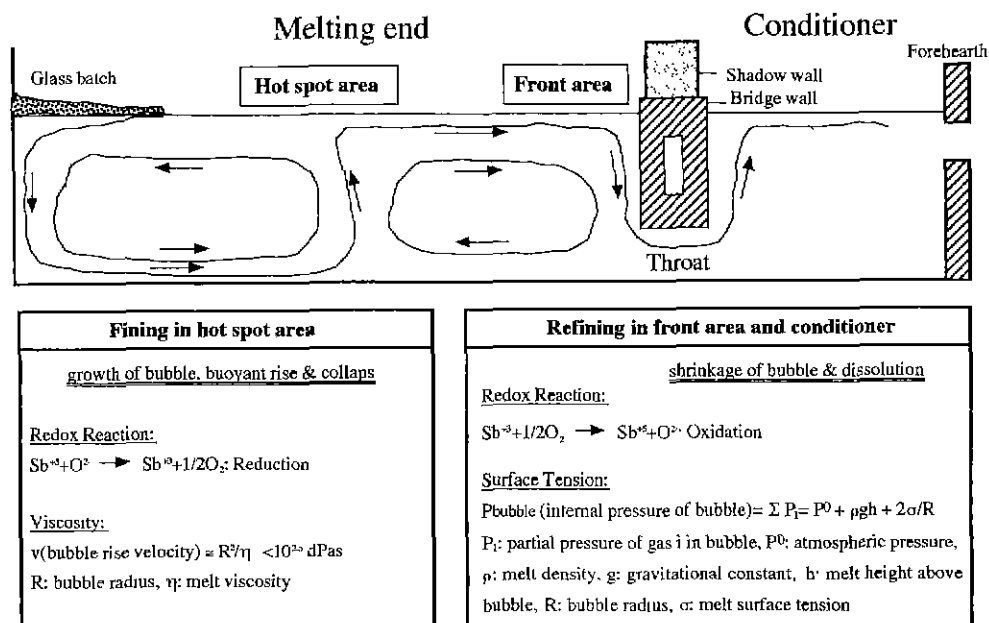

Fig. 1. Major convection flows in a fuel-fired tank furnace (upper part)[3] and the corresponding two fining processes (lower part).

Table 2. Compositions for the Experimental Glasses in wt%

Glass No. Components	Z0	Z1	Z2	Z3	Z4	Raw Materials
SiO_2	62.2	62.1	62.0	61.9	61.8	Sand
ZnO	0	0.1	0.2	0.3	0.4	ZnO
R_2O (Na_2O+K_2O)	15					Alkali carbonates, 2.7 wt% of alkali : KNO_3
RO (SrO+BaO)	18					Alkaline earth carbonates
Sb_2O_3	0.4					$Na_2OSb_2O_5$
Others : CeO_2, ZrO_2, TiO_2, Al_2O_3	4.4					CeO_2, Zircon, TiO_2, $Al(OH)_3$

were melted at 1550°C in a Pt/Rh crucible and homogeneous glassmelts were prepared to measure their viscosity and surface tension.

The measurements of glass properties in the molten state were carried out by using a vertical tube furnace (KFGM-60, Korea Furnace Development Co., Korea) on which viscometer and microbalance are installed. Viscosities (η) of glassmelts were determined by the rotating viscometer according to Searle principle. Based on the dimensions of Pt/30Rh-crucible and -spindle, the viscometer (RotoVisco "RV30" Hakke Co., Germany) was calibrated using DGG (Deutsche Glastechnische Gesellschaft) standard glass I in the temperature range 1000~1450°C. An apparatus constant was determined at the immersion depth of spindle of 30 mm. The viscosity of each glass melt was measured every 100°C interval within the temperature range 1500 to 1000°C.

The surface tension of glassmelts in the viscosity range between 10^2 and 10^3 dPas was determined by the maximum pull-on-cylinder method. The over-all design of the present apparatus is similar to that of the previous.[10] The apparatus consists of a Pt/20Rh-cylinder connected with a digital recording microbalance (D-101, Cahn, USA) by platinum wire and an alumina crucible filled with glassmelt. The measuring system for surface tension was at first calibrated direct at high temperature between 1400~1100°C with $7.5Na_2O17.5Rb_2O$ $75SiO_2$ (mol%) glassmelt of which surface tension values at high temperature were already determined by Frischat[10] and the correction factor was applied to the measured temperature range. The maximum force (F_{max}) was detected by a microbalance while descending the alumina crucible after the melt in alumina crucible had been in contact with the bottom of the platinum cylinder. The surface tension (σ) of glassmelt was calculated by the equation, $\sigma=F_{max}/4\pi rg$, where r is the radius of the platinum cylinder and g is the gravitational constant.

2. Fining test of glass batches

On the basis of the above two melt properties, a fining capability of each batch in Table 2 was estimated by so called MF (Melting & Fining) and PMF (Profiled Melting & Fining) test.[11] Fig. 2 and Fig. 3 show the temperature-time profile for those tests and, sample preparation process for image analysis and seed counting, respectively. For the MF test the batches of 700 g were melted in 900 cc Pt/20Rh crucible for 3 hours between temperatures corresponding to 10^2 and 10^{23} dPas and, then the glasses were directly quenched and annealed. In the case of PMF test the batches were melted also in MF test range, subsequently refined for 2 hours at 1200°C and annealed. After annealing a vertical core of 3.5 cm in diameter was
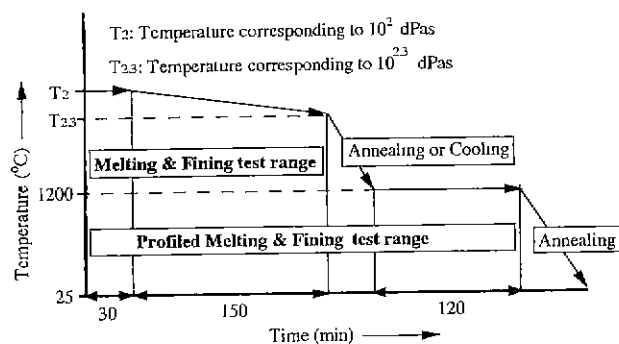

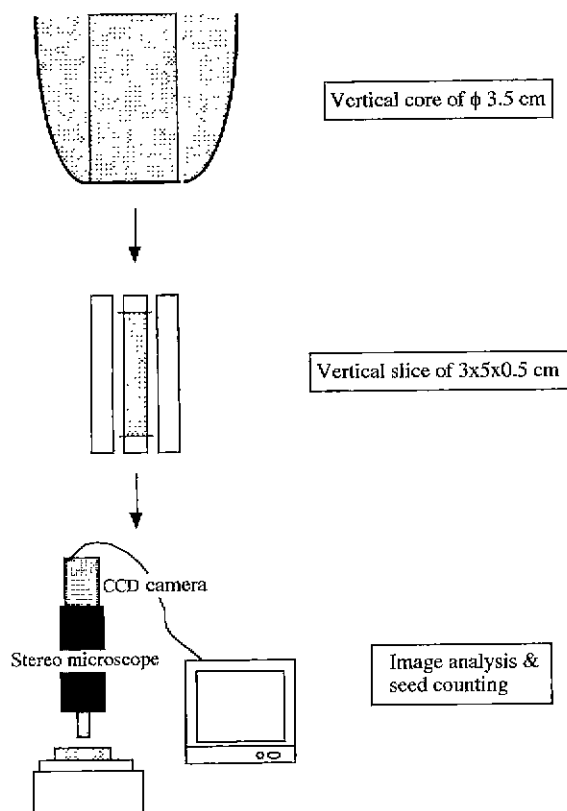**Fig. 2.** Temperature-Time profile for MF & PMF test.

Fig. 3. Sample preparation process for image analysis and seed counting.

removed from the each melt and a vertical slice approximately 5 mm thick with dimension of 3×5 cm was cut from the center of the core. A seed counting in each polished slice was performed by a stereo microscope coupled to a monitor via CCD camera and the number of remaining seeds per in^3 was determined statistically.

IV. Results and Discussion

In Fig. 4 the isokom temperatures at 10^2 and 10^4 dPas are presented as function of ZnO content. With small replacement of SiO_2 by ZnO the isokom temperature decreases, in other words the decrease of melt viscosity occurs. On the other hand, the isothermal surface tension of glassmelts in Fig. 5 increases as ZnO content increases and temperature decreases. The results of viscosity and surface tension show a similar tendency to those
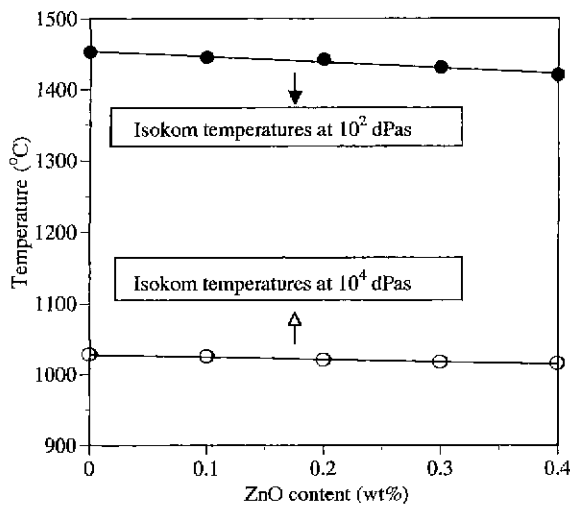
of previous studies.[5,8] According to Rosenthal etal,[9] it has been found that ZnO can play a network former as ZnO_4 tetrahedra at its low concentration, but acts to disrupt the silica structure. The increase of the surface tension by introduction of ZnO is explained by the low polarizability of ZnO due to its high field strenth.[6]

1. Influence of temperature on the primary fining

Fig. 6 shows results of MF and PMF test according to the schedule of Fig. 2. After tests the melts do not have any nonmelted particles and the size of bubbles lies between 20 and 50 μm in both cases. But they show an opposite behavior each other as ZnO content increases. In Fig. 7 the MF test temperature (or isokom temperature) and the number of remaining seed per in^3 by

Fig. 6. Number of remaining seeds per in^3 after MF(■) and PMF(○) test as function of ZnO content.
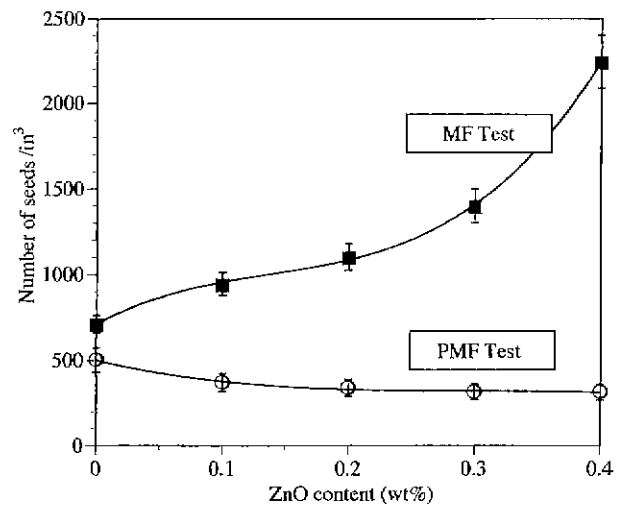
Fig. 4. Isokom temperatures at 10^2(●) and 10^4(○) dPas as function of ZnO content.
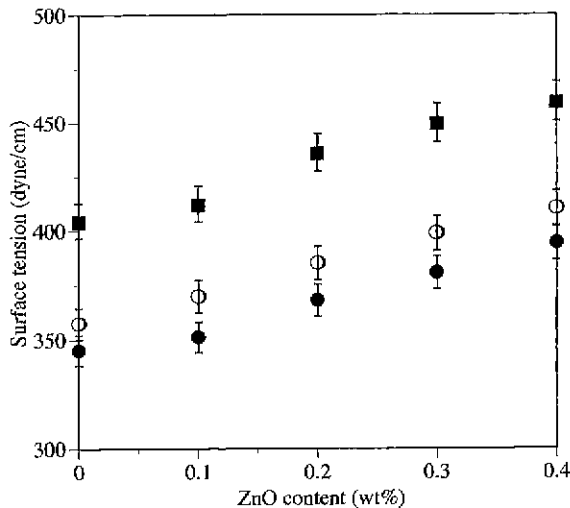
Fig. 5. Surface tension at 1200(■), 1300(○) and 1400°C(●) as function of ZnO content.
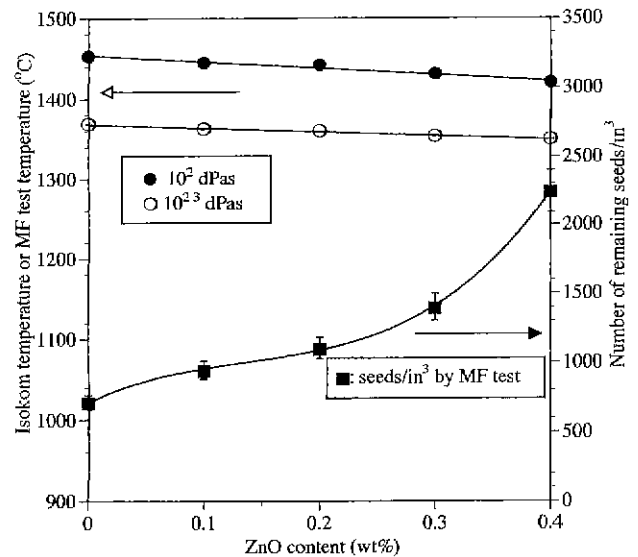
Fig. 7. MF test temperature at 10^2(●), $10^{2.3}$(○) dPas and number of remaining seeds/in^3(■) after MF test as function of ZnO content.

MF test are plotted together as a function of ZnO content. As shown in MF test results, the number of remaining seeds increases with increase of ZnO content, namely, poor fining occurs. In Fig. 8 the fining process inclusive the redox reaction of antimony ion is qualitatively expressed by modification of reference.[12] Because the MF tests for all the batches were carried out in the temperature range corresponding to the viscosity between 10^2 and 10^{23} dPas it can be assumed that the physical fining condition for the buoyant rise of bubbles is same for all glasses. The decrease of MF test temperature or the isokom temperature with increase of ZnO content, however, means a pronounced change of chemical fining condition such as oxygen generation by redox reaction and gas solubility. It is already well known the influence of temperature and composition (especially, concentration of chemical fining agent) on the fining, namely, the dependence of the redox reaction $(Sb^{+5}+O^{-2}=Sb^{+3}+1/2O_2)$ and the gas solubility in glassmelts on temperature and composition.[13,14] Considering the fixed concentration of antimonate and the small difference of ZnO content in the present compositions, the dependence of chemical fining on the composition may be negligible. Therefore, the increase of remaining seed number with increase of ZnO content in MF test (Fig. 7) seems to be due to the decrease of MF test temperature by which the above redox reaction proceeds preferably on the left hand side and the gas solubility into melts increases. This behavior may give little chance to enlarge the existing bubbles.

2. Cooling effect on the refining

The results of PMF test in Fig. 6 show that the number of seeds is lower than that of MF test irrespective of

composition. From these results it can be postulated, while the glassmelts are cooled and maintained at 1200°C after passing through the MF test range as shown in Fig. 8, a part of the remaining seeds in MF test may be removed. Such a cooling effect on the refining of glassmelts was experimentally approved in another TV glass compositions and, explained by shrinkage and dissolution of bubbles due to the oxidation from Sb^{-3} to Sb^{+5} [14] and the increase of the gas solubility[15] at low temperature. Beyond this chemical process, as a physical parameter for the refining an increase of melt surface tension during cooling can be considered. It is discussed in the next section.

3. Effect of surface tension on the refining

As mentioned above and described qualitatively in Fig. 8, when the glassmelt cools, namely, at low temperature the shrinkage of seeds and their dissolution into melts become a major mechanism of seed removal. In this stage, beyond the chemical refining process via the redox reaction and the gas solubility, it is theoretically well known that the increase of internal pressure (P_{bubble}) of seeds with a radius (R) accelerates the diffusion of gases from the seed into the glassmelt and results in shrinkage and dissolution of seeds. Accordingly, the internal pressure becomes physically important parameter in seed removal. P_{bubble} is expressed as follows, $P_{bubble} \cong 2\sigma/r$. From this equation it can be suggested that surface tension (σ) of glass melt is important, especially more important as the seed diameter decreases.[16] Because the melt surface tension increases with decreasing temperature as shown in Fig. 5, the effect of surface tension on the refining at fixed composition may be included in cooling effect explained above. However, this cooling ef-
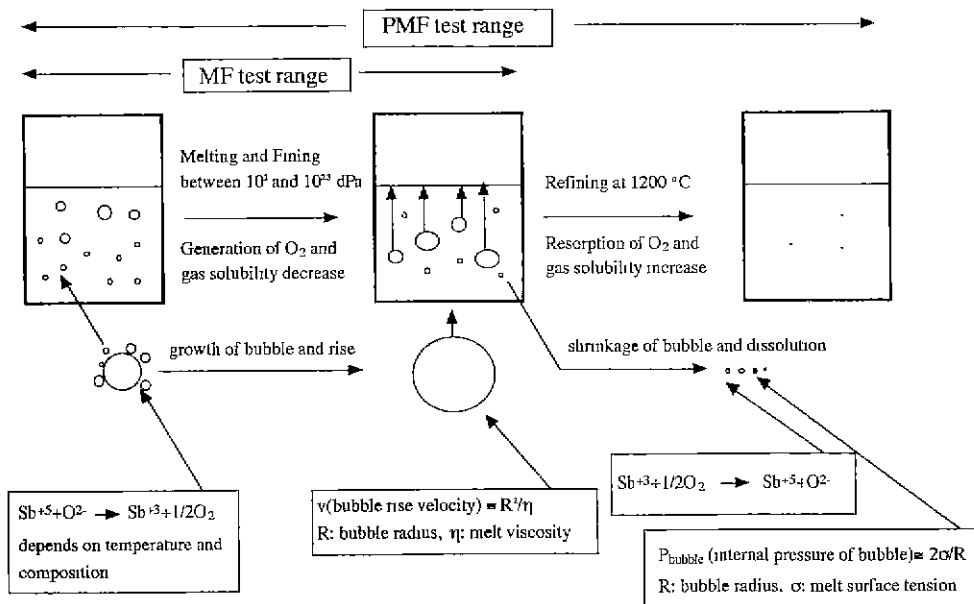

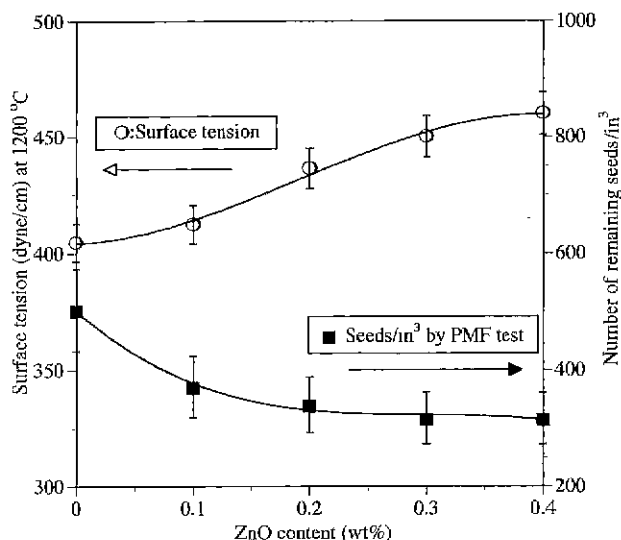Fig. 8. Qualitative description for the chemical and physical fining mechanism (Ref 12 modified).

Fig. 9. Surface tension (O) at 1200°C and number of remaining seeds/in³(■) after PMF test as function of ZnO content.

fect on the refining, as shown at the gap between the results of MF and PMF test in Fig. 6, becomes greater with increase of ZnO content. Therefore it must be considered as the effect of ZnO on the surface tension of glassmelt. In Fig. 9 the surface tension of glassmelts at 1200°C is presented with the number of remaining seeds by PMF test as a function of ZnO content. Concerning the results of PMF test to those of the melt surface tension under the theoretical consideration of physical refining process, an improved refining as the increase of ZnO content can be deduced from the increase of the melt surface tension. There are also another minor components as MgO and CaO which affects the viscosity and surface tension of glassmelts similarly to ZnO,[8] although their effect on the fining of glassmelt has not been investigated. But their contribution to x-ray absorption coefficient at 0.06 nm that is the most important property for TV screen glass is very small comparing with that of ZnO.[17]

V. Summary

It was investigated the effect of temperature, cooling and surface tension on the fining of TV screen glasses with small replacement up to 0.4 wt% of SiO₂ by ZnO. Sodium antimonate was used as a chemical fining agent. Based on theory of fining and two melt properties (viscosity and surface tension), the fining tests of several batches were carried out by MF (Melting & Fining) and PMF (Profiled Melting & Fining) methods. The results of both tests showed an opposite behavior each other as ZnO content increases. The number of remaining seeds by the MF test increases with increase of ZnO content. On the other hand, the results of the PMF test in which the refining is considered indicated decrease of re-

maining seeds. The gap between both test results becomes greater with increase of ZnO content. The MF test results were explained by temperature dependence of antimony redox reaction and gas solubility, under assumption that the physical fining condition is same. The difference between MF and PMF test results was explained by cooling effect on the refining which is determined by temperature dependence of redox reaction, gas solubility and surface tension. Finally, the effect of ZnO content on the refining or PMF test results was discussed on the basis of the melt surface tension.

Acknowledgment

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