

# Laboratry investigation of oxy-fuel-firing atmosphere on soda-lime-silica melts

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Oxy-fuel firing of recycled cullets have attracted much attention in the glass industry. Although the firing has remarkable advantages such as fuel saving and  $\text{NO}_x$  reducing, the influence of high water vapor pressure (about 0.6 atm) over the melt makes change in the water content in glasses. On the other hand, the use of recycled cullets is usually accompanied by addition of  $\text{Na}_2\text{SO}_4$  as a fining agent to eliminate gas bubbles during the glass melting.

In this study, as the model of the cullet melting by oxy-fuel firing, soda-lime-silica glass cullets containing different  $\text{SO}_3$  content ( $\text{SO}_3$ -free and 0.6 wt%  $\text{SO}_3$ ) were remelted at 1350 °C and 1550 °C (below and above the dissociation temperature of  $\text{SO}_3$ ) under wet atmosphere ( $p_{\text{H}_2\text{O}} = 0.6$  atm). The OH concentration profiles of glass samples were measured by scanning a beam spot of 1mm diameter in the direction from their surface to inside using the FT-IR spectrometer. The  $\text{SO}_3$  profiles were also plotted by successively polishing and removing the surface layers of glass samples and measured the content by X-ray fluorescence. In the  $\text{SO}_3$ -free glasses, after melting, they showed the normal diffusion-controlled profiles of OH. In the glasses containing  $\text{SO}_3$ , after melting at 1550 °C, the OH content increased remarkably from 100 to 600 ppm along with decreasing of  $\text{SO}_3$  from 0.6 to 0.15 wt%. For comparison, after melting at 1350 °C,  $\text{SO}_3$  did not decrease.

## INTRODUCTION

Recentry, the oxy-fuel firing has been widely used in the glass industry for saving fuel and reducing  $\text{NO}_x$  emissions. The firing, however, makes change in the water content in glasses by the influence of high pressure of water vapor ( $p_{\text{H}_2\text{O}} = 0.6$  atm) over the melt. Generally, water incorporation influences the glass properties by lowering the viscosity and changing the redox state of the melts. On the other hand, recycled cullets are usually melted with  $\text{Na}_2\text{SO}_4$  as a fining agent to eliminate gas bubbles during the glass melting. The previous papers pointed out the close relation of water incorporation and  $\text{SO}_3$  in soda-lime-silica glass melts is one of the most important issues in the glass industry.

Alkali silicate glass cullets with 0.5 wt%  $\text{SO}_3$  were remelted and change in the foaming temperature was investigated with increasing the partial pressure of water vapor, (the temperature decreased from 1440 °C ( $p_{\text{H}_2\text{O}} = 0$ ) to 1410 °C ( $p_{\text{H}_2\text{O}} = 0.6$ ) for 20 $\text{Na}_2\text{O}$ -80 $\text{SiO}_2$  melt)<sup>1</sup>. In soda-lime-silica glass cullets containing  $\text{SO}_3$ , increasing the partial pressure of water vapor also lowered the foaming temperature. The  $\text{SO}_3$  content decreased at 1300 ~ 1400 °C, along with the increase of water content up to 1000 ppm. Thus, water vapor in the firing atmosphere enhanced the sulfate dissociation<sup>2</sup>. Since the measurements of OH and  $\text{SO}_3$  concentration profiles need the elaborate techniques, the content data of the samples were always the average values in these previous papers.

In this study, as the model of the cullet melting by oxy-fuel firing,  $\text{SO}_3$ -containing soda-lime-silica glass cullets were remelted under wet atmosphere ( $p_{\text{H}_2\text{O}} = 0.6$  atm). After remelting concentration profiles of OH and  $\text{SO}_3$  were measured in these samples. The relation of the oxy-fuel-firing atmosphere and the water incorporation into the  $\text{SO}_3$ -containing soda-lime-silica glass melt was investigated.

## EXPERIMENTAL

The  $\text{SO}_3$ -free and 0.6 wt%  $\text{SO}_3$ -containing soda-lime-silica glasses were prepared by the conventional melting and quenching technique. Glasses were prepared from reagent grade  $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$ . For the 0.6 wt%  $\text{SO}_3$ -glass, 10 % of  $\text{Na}_2\text{CO}_3$  was substituted for  $\text{Na}_2\text{SO}_4$ . The batches were melted in Pt crucibles at 1450 °C under dry atmosphere to lower the OH content. The compositions of obtained glasses are listed in Table 1.

Table 1. Compositions of glass cullets determined by X-ray fluorescence.

	$\text{SiO}_2$ (wt%)	$\text{Na}_2\text{O}$ (wt%)	$\text{CaO}$ (wt%)	$\text{SO}_3$ (wt%)	OH (ppm)
$\text{SO}_3$ -free	80	11	9	0	90
0.6 wt% $\text{SO}_3$	80	11	9	0.6	100

Glass cullets of 12 g in weight were remelted in an alumina crucible using an apparatus as shown in Fig. 1. The glass melt in the crucible was 9 mm in depth. Temperature programs are shown in Fig. 2. The remelting temperatures were chosen to be 1350 °C or 1550 °C (below and above the dissociation temperature of  $\text{SO}_3$ ). Glass cullets were heated up to 1350 °C (or 1550 °C) under dry atmosphere and kept for 10 min. Then the atmosphere changed to wet ( $p_{\text{H}_2\text{O}} = 0.6$  atm) at the same temperature for 2 hours (or 30 min), and the melt was allowed to cool in air. The obtained glass samples were cut and polished for the measurements.

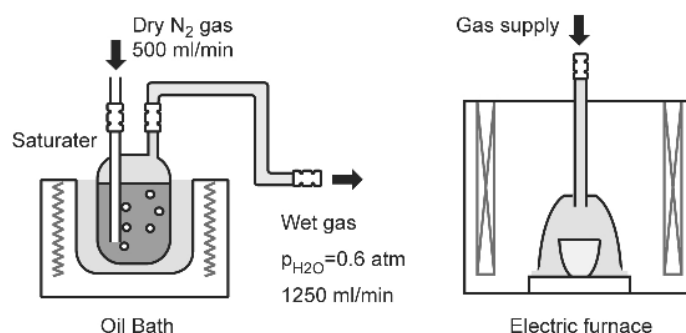


Fig. 1. Schematic illustration of the apparatus for controlling gas supply.

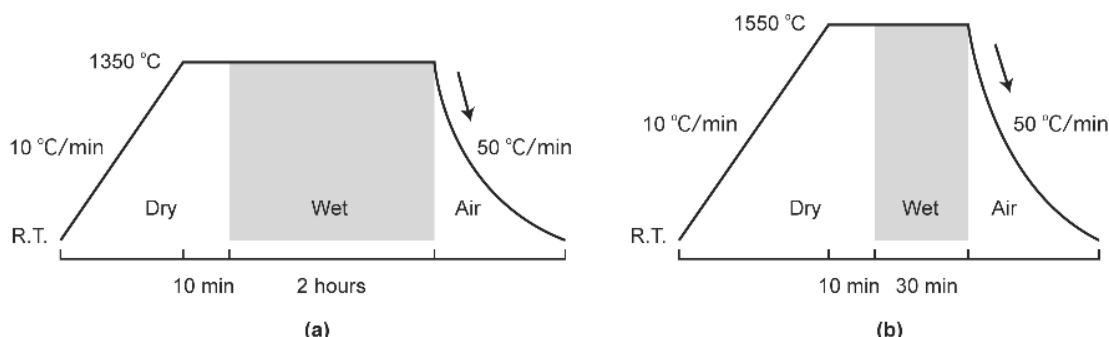


Fig. 2. Temperature programs.

The concentration of water (OH) in glass was determined by the optical absorption spectrum in the infrared wavelength region measured by FT-IR spectrometer (SHIMADZU, Model FT-IR8000PC). Following the procedure recommended by TC14 of ICG<sup>3</sup>, the concentration of water in glass  $C$  (mol/l) was determined by the equation (1):

$$C = \frac{1}{d} \left( \frac{A_{2.8} - A_{2.5}}{\epsilon_{2.8}} + \frac{4}{3} \frac{A_{3.6} - A_{2.5}}{\epsilon_{3.6}} \right) \quad (1)$$

where  $A_i$  is the optical absorbance,  $d$  is the sample thickness,  $\epsilon_i$  is the extinction coefficient. Subscripts present the wavelength in micrometer. To obtain the OH profiles of glass samples, FT-IR measurements were carried out moving a beam spot of 1 mm diameter in the direction from their surface to inside. The glass samples were polished to remove the surface layer and then measured by wavelength dispersive X-ray fluorescence (PHILIPS, Model PW2404). Concentration profiles of  $\text{SO}_3$  in glasses were determined by repeating the polish-measure procedures.

## RESULTS AND DISCUSSION

The concentration profiles of OH and  $\text{SO}_3$  in remelted glasses are shown in Fig. 3. As shown in Fig. 3 (a) and (b), the OH profiles of the  $\text{SO}_3$ -free glasses remelted at both 1350 °C and 1550 °C were fairly fitted with the semi-infinite diffusion model described as

$$\frac{C(x,t)}{C_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{Dt}}} \exp(-\lambda^2) d\lambda = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (2)$$

where  $C(x,t)$  is the concentration at depth  $x$  after time  $t$ ,  $C_0$  is the concentration at surface, and  $D$  is the diffusion coefficient. The diffusion coefficients derived from the fitting technique with the equation (2) are shown in Fig. 4 (the results of McGinnis and Shelby<sup>4</sup>, which were estimated from the total OH content as a function of the exposure time, are also involved in the figure). The diffusion coefficients of  $\text{SO}_3$ -free glasses agree well with those in the ref. 4. Therefore, the water incorporation from the oxy-fuel-firing atmosphere into  $\text{SO}_3$ -free glass melts can be considered to follow the diffusion model even at 1550 °C. It should be noted that the OH content values at very near the surface of the glasses (remelted at 1550 °C) did not fitted the diffusion curve. The plausible explanation is that the dehydration occurred while cooling process. Thus, the high content OH near the surface incorporated from water vapor is easily evacuated when the melt is kept in dry atmosphere.

In Fig. 3 (c) and (d), the profiles for 0.6 wt%  $\text{SO}_3$ -glasses are shown. The shapes of OH profiles of the 0.6 wt%  $\text{SO}_3$ -glasses remelted at 1350 °C and 1550 °C were remarkably different from those of  $\text{SO}_3$ -free glasses. After 1350 °C remelting for 2 hours, the total OH content in the 0.6 wt%  $\text{SO}_3$ -glass was two times as high as that of  $\text{SO}_3$ -free glass. The concentrations of  $\text{SO}_3$ , however, did not decreased compared with the initial value. The data shows that  $\text{SO}_3$  influenced the OH penetration into the melt even below the dissociation temperature of  $\text{SO}_3$ .

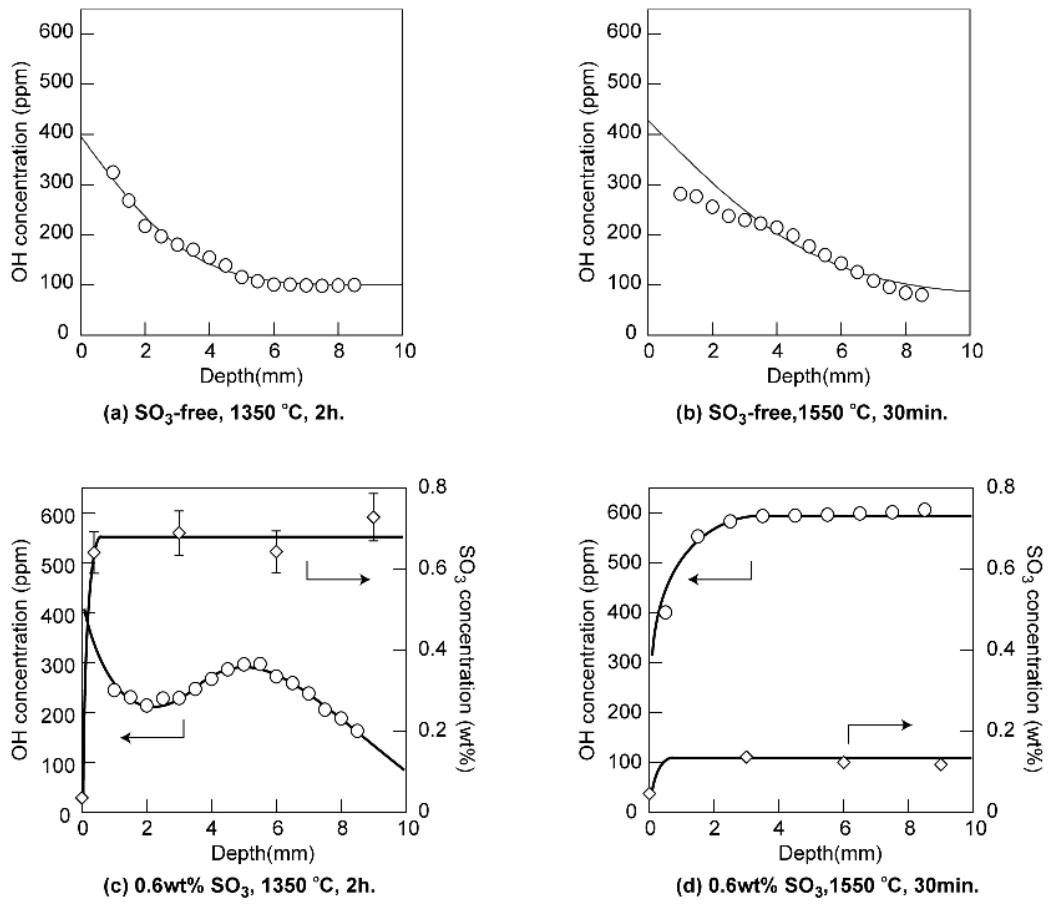


Fig. 3. Concentration profiles of OH and SO<sub>3</sub> in remelted glasses.

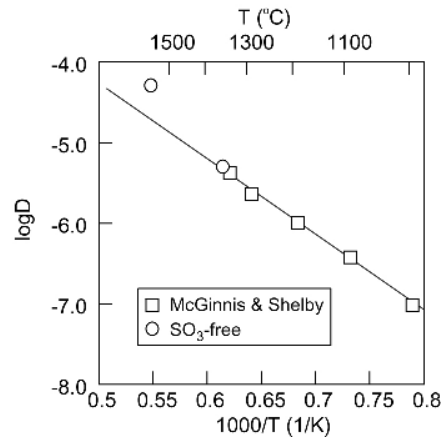


Fig. 4. Diffusion coefficients of OH.

After 1550 °C remelting for 30 min, the total OH content in the 0.6 wt% SO<sub>3</sub>-glass increased remarkably to seven times as high as those of SO<sub>3</sub>-free glass, along with the decrease of the SO<sub>3</sub> from 0.6 to 0.15 wt%. In additional experiment, in the glass remelted at 1550 °C for 30 min under dry atmosphere, SO<sub>3</sub> content decreased to 0.4 wt%. Thus, above the foaming temperature, SO<sub>3</sub> evolved from the melts anyway. Fig. 3 (d) also shows that the oxy-fuel firing cause noteworthy water penetration into the glass melts and the high water contents in the melts promoted the dissociation of SO<sub>3</sub>. Several explanations for the remarkable water incorporation are possible: strong bubbling of SO<sub>2</sub> accelerate the stirring, boundary of the bubble is easily OH penetration as suggested by Beerkens and Laimböck<sup>5</sup> and so on. It should be noted that the steep decrease of OH at the near surface was also observed in SO<sub>3</sub> containing glass (Fig. 3 (d)).

As pointed out in the ref. 2, and the data in the experiments, in melting of soda-lime-silica glass cullets by the oxy-fuel firing, an addition of Na<sub>2</sub>SO<sub>4</sub> results in the drastic increase of the water content in glass melts. Especially, above the foaming temperature, the water-rich layer (> 600 ppm) is formed on the surface of the melts. The increase of OH content would make undesirable influence on the properties of resultant glasses from the industrial viewpoint. By plotting the OH and SO<sub>3</sub> profiles using new technique, the differences between SO<sub>3</sub>-free (diffusion-controlled physical phenomena) and SO<sub>3</sub>-containing glasses (involving the chemical reaction) can be highlighted. The reason why such an OH increase occurred below and above the foaming temperature is still unsolved, but the profile-plotting techniques will contribute to give answer. Bonus results were also obtained: after firing process using Na<sub>2</sub>SO<sub>4</sub>, if melts flow to dry atmosphere section, the OH content decreased rapidly, as shown in Fig. 3 (d).

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