Fining of Flint Glass Melts Containing Blast Furnace Slag

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ABSTRACT

In this study, flint glass batches with blast furnace slag (BFS) were prepared and the contribution of the BFS to the fining of melts was studied through investigations of the melting and fining characteristics. Additionally, a sulfur redox reaction for BFS-doped melts was examined by square wave voltammetry (SWV). The results of the melting & fining test showed that BFS improved the fining of the melts. In a voltammogram of BFS-doped melts, two reduction peaks were shown at high frequencies while only one peak appeared at low frequencies. The peaks were located at a potential that was similar to those of melts fined by sulfate. From those results it was concluded that sulfide (S^{2-}) in BFS has effects in glass melts that are identical to those of sulfate (SO_4^{2-}).

Key words : Blast furnace slag, Sulfur, Sulfate, Sulfide, Fining, Square wave voltammetry

1. Introduction

I n relation to the use of blast furnace slag (BFS) as a raw material in the glass industry, many benefits have been reported, including an improvement of the melting and fining characteristics.[1-4] It is known that the decomposition of sulfate (SO_4^{2-}) by reacting with the sulfide (S^{2-}) in BFS improves fining of melts. Although it is known that sulfide alone can produce a fining action by reacting with oxygen and generating SO_2, detailed investigations regarding melts containing only BFS have not been performed.

In general, sodium sulfate (Na_2SO_4) is introduced into glass melts as a fining agent in the flint glass industry. The effectiveness of sulfur (S) in glass melts depends on its valence state, which can be S^{6+}, S^{4+}, S^0, or S^{2-} under a reduction or oxidation atmosphere.[5-6] In glass melts, various redox reactions of sulfur can be expected. Therefore, it is very interesting to investigate the redox behavior of sulfur in situ in glass melts with BFS and to compare the results to those of sulfate-doped melts[7] as a small amount of sulfide (S^{2-}) exists in BFS. In the present work, the fining capability was tested with soda lime silicate flint glass batch containing BFS and sulfur redox reactions were studied via square wave voltammetry (SWV).

2. Experimental Procedure

2.1. Glass preparation

The composition of blank flint (BF) glass in wt% was $74SiO_2$, $2Al_2O_3$, $10CaO$ and $14Na_2O$. The raw materials consisted of high purity sand (99.999 SiO_2 Iota USA) and reagent-grade chemicals. For BFS batches BFS2, BFS4, and BFS6 in this study, 2, 4, and 6 wt%, respectively, of the total sand content was replaced by BFS. Table 1 shows the compositions of the experimental glasses and BFS. The batches were melted at 1550°C in a Pt/Rh crucible and homogeneous glass melts were prepared. Viscosities (η) of the BF glass melts were determined using a rotating viscometer (RV30 Hakke, Germany) in a temperature range of 1000 to 1500°C.

2.2. Melting & fining test of the glass batches

Based on the viscosity value of the melts, the fining capability of each batch corresponding to the composition shown in Table 1 was estimated considering the first fining of the melts, which involved removing the bubbles via a growth and rise process. Batches of 300 g were melted in a 500 cc alumina crucible for 90 min at 1400°C corresponding to $10^{2.2}$ dPas, determined by viscosity measurement. The melts were then annealed at room temperature. A specimen was removed from the crucible using a diamond saw and both surfaces of the specimen were polished to mirror grade using CeO_2 slurry. Observations of the residual seeds in each polished specimen were performed by a stereomicroscopy coupled to a monitor via a CCD camera.

2.3. Square wave voltammetry (SWV) measurements

For the SWV measurements, the bubble-free melts that had been fined were transferred to another electric furnace. While the prepared melts were maintained at 1400°C in the furnace, the electrodes of an electrochemical cell were dipped into the melts to perform SWV measurements. The electrochemical cell consisted of three electrodes immersed into the melt along with a potentiostat (Model 273A, EG & G, USA)

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Table 1. Compositions (wt%) of Experimental BF Glass, Bfs-doped Glass and BFS

Glass code \ Component	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	Fe_2O	MnO	SO_3	TiO_2	Remarks
BF	74	2	10	14					·		Blank Flint
BFS2	73.9	1.99	9.99	13.98	0.008	0.066	0.044	0.004	0.012	0.013	2% Slag/Sand
BFS4	73.8	1.99	9.97	13.97	0.017	0.127	0.088	0.008	0.024	0.026	4% Slag/Sand
BFS6	73.8	1.99	9.96	13.96	0.025	0.188	0.131	0.012	0.036	0.040	6% Slag/Sand
BFS	33.9	16.3	42	0.28	0.58	4.22	0.3	0.28	0.84	0.92	Blast Furnace Slag

connected to a computer. A platinum plate and a wire were used as a counter electrode and a working electrode, respectively. Another platinum wire serving as an reference electrode was connected with O^{2-} conducting Y_2O_3-stabilized ZrO_2 (YSZ) ceramic, which was in contact with the melts and flushed by reference air at a known oxygen partial pressure (0.21 bar) during the SWV experiment. Details regarding the SWV process are described in the literature.[8,9] The SWV measurements in the present work were performed under the following conditions: an applied potential of 0~-800 mV and a frequency range of 5~1000 Hz. A final voltammogram for each BFS-doped melt in the temperature range of 1000-1400°C was obtained by subtracting the values of the BF glass melt from the original recorded voltammogram.

3. Results and discussion

3.1. Fining capability

Fig. 1 shows the results of the melting & fining test for the BF batch and the BFS-doped batches. According to the state of the residual seeds shown in the polished specimens, no non-melted solid particles are visible in the glasses. In addition, for BFS 6, no seeds were found. In a comparison of the state of the BFS-doped melts to that of the BF melt, the number of residual seeds decreases as the BFS content increases. As the test for the batches was performed under the same viscosity, it can be assumed that the physical fining condition for the buoyant rise of bubbles, here termed the first fining, is identical for all melts. The increase of the BFS content, however, indicates a pronounced change of the chemical fining condition, including SO_2 generation, by the following oxidation of sulfide, as expressed by $2S^{2-}+3O_2\rightarrow 2S^{4+}+4O^{2-}$ during the batch melting process. The influence of the concentration of the chemical agent on the fining of melts is well known.[10] Considering the difference of the sulfur content shown in the BFS series in Table 1, the dependence of the chemical fining on the BFS content can not be negligible. Therefore, the decrease in the number of remaining seeds with the increase of the BFS content is due to the increase of fining gas (SO_2) contributing to the growth of bubbles.


(a) BF   (b) BFS2

(c) BFS4   (d) BFS6
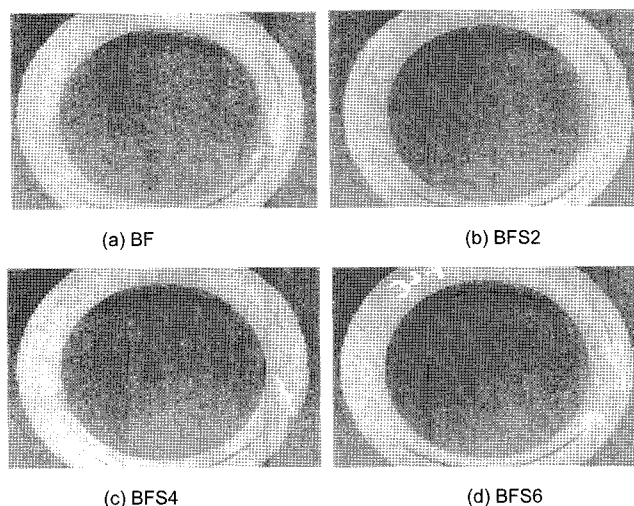
Fig. 1. Results from the melting & fining test for the BF batch and the BFS-doped batch.

3.2. Voltammetry

Voltammograms of the BF melt are presented in Fig. 2. As the BF melt does not contain multivalent ions, the voltammograms show no characteristic peaks but instead show a typical current-potential curve; in other words, at a high negative potential region, the resulting current increases with the frequency increase and the temperature decrease due to the reduction of Si ion to silicium.[11] Voltammograms of BFS-doped melts of different frequencies at 1200°C were produced, as shown in Fig. 3. One or two peaks were found due to the reduction of sulfur ions. The occurrence of these peaks depends on the frequency and the sulfur concentration. In particular, frequency dependence is shown clearly in Fig. 3(c). Here, the BFS6 melt with the highest sulfur concentration is shown. At a low frequency, only one reduction peak, the first peak, can be observed at approximately - 500 mV. However, from 200 Hz, another peak (second peak) begins to occur at approximately – 400 mV. Fig. 4 shows voltammograms of the BFS melts in the present work as well as the flint glass melts produced from batches containing sulfate (supplied by Na_2SO_4) in a previous work.[7] Although the peak current of the BFS melts shows a strong dependence on the sulfur concentration, the two peaks observed in the voltammogram of each BFS melt are located at a similar potential to those of the sulfate-doped melt. As mentioned above, the melts for the SWV measurements
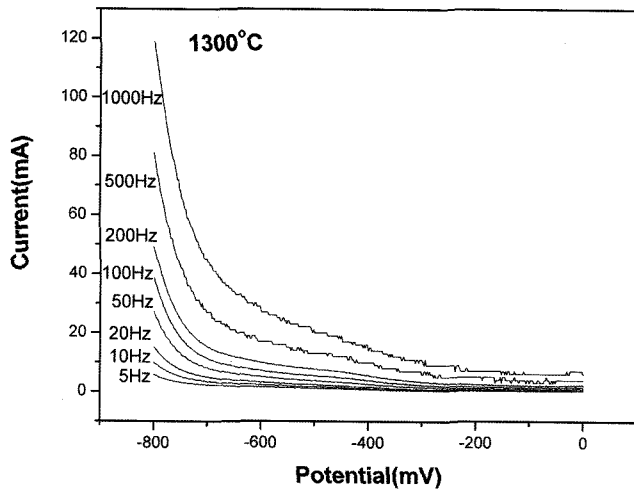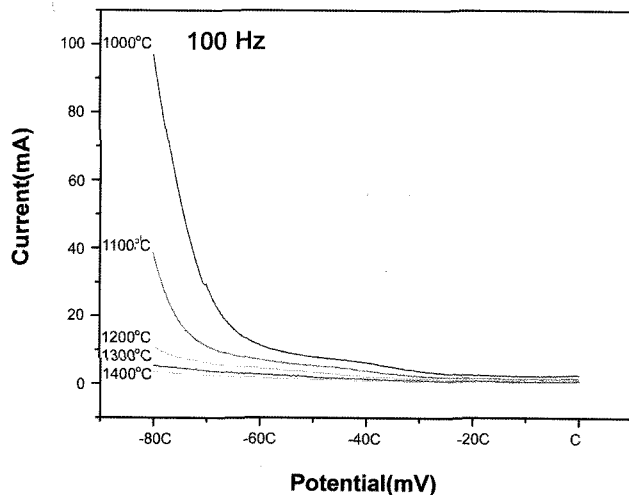
**Fig. 2.** Voltammogram of BF melts (a) at 1300°C in a frequency range of 5~1000 Hz (b) at 100 Hz in a temperature range of 1000~1400°C.

underwent their first fining under an oxidation atmosphere. Therefore, it can be assumed that most sulfur ions exist as S^{4+} or S^0 in the melts through the oxidation of the sulfide ions (S^{2-}) contained in the BFS. This assumption is supported by the observation of the same voltammetry behavior between the BFS-doped melts and the sulfate doped melts, as shown in Fig. 4.

In relation to the identification of the two peaks shown in the voltammogram in Fig. 4, several voltammetric studies[6, 12-15] on sulfur-doped melts have been conducted. However, there has been no agreement regarding the interpretations of the redox pair (S^{4+}/S^0, S^0/S^{2-} etc) reduced at both peaks of the voltammogram. Some works[13,14] have suggested that the second peak located at the lower negative potential is due to S^{4+}/S^0; the first peak located at the higher negative potential is attributed to S^0/S^{2-}. Recently, it was proved that the second peak occurring at the lower negative potential results from the adsorption of sulfur (S^0) from the relationship
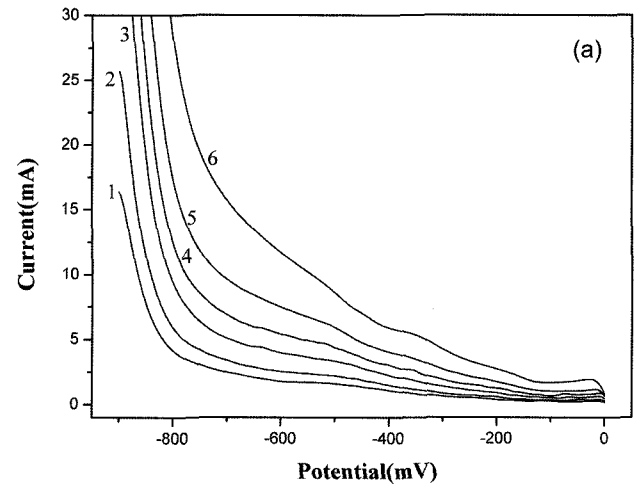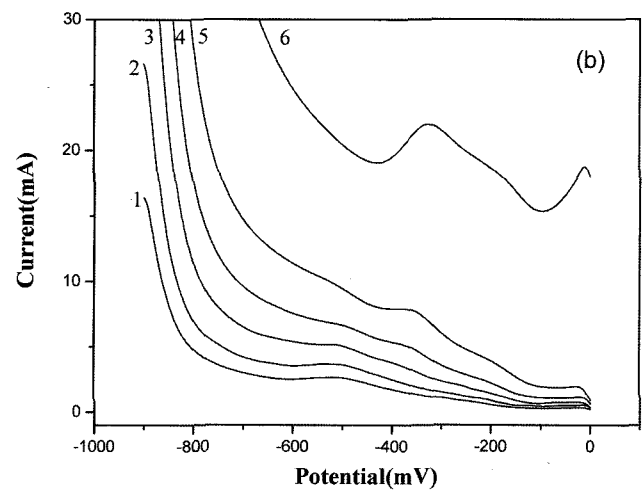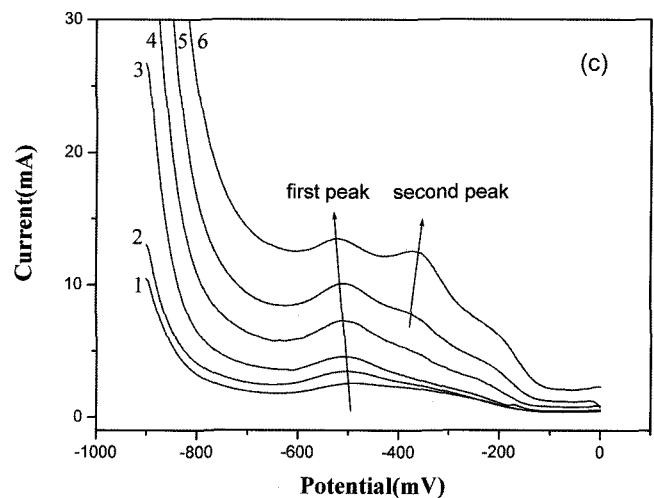
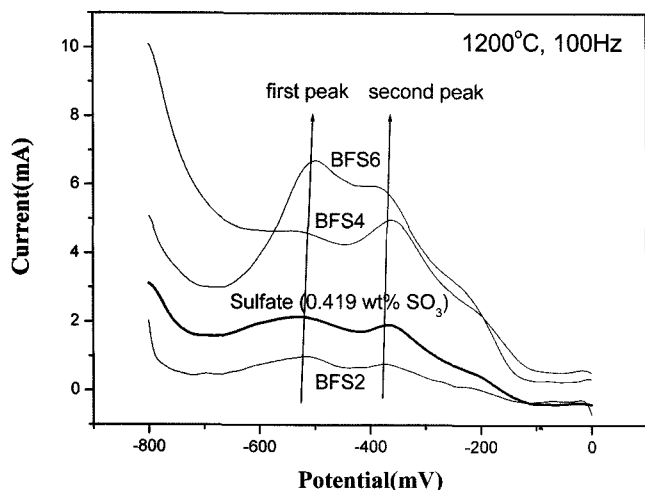**Fig. 3.** Voltammogram of (a) BFS2, (b) BFS4 and (c) BFS6 melts at 1200°C. 1: 10 Hz, 2: 20 Hz, 3: 50 Hz, 4: 100 Hz, 5: 200 Hz, 6: 500 Hz.

between the double-layer capacitance and the potential.[15] As the redox reaction is controlled by diffusion, it is also possible to identify the peak of the voltammogram using the relationship between the peak current (I_p) and the square

Fig. 4. Voltammogram recorded in flint glass melts containing BFS (BFS1: 0.012 wt% SO_3, BFS2: 0.024 wt% SO_3, BFS3: 0.036 wt% SO_3) and sulfate (0.419 wt % SO_3) at 1200°C and 100 Hz.

root of the reciprocal frequency $(\sqrt{1/f})$.[16,17] According to works performed with sulfur-doped melts,[7,14] the dependence of I_p on $\sqrt{1/f}$ for the second peak showed no clear linearity. In other words, the reaction at the second peak was not controlled by diffusion. Therefore, the second peak in the present work is not related to S^{4+}/S^0. The first peak appears to be related to the reduction of S^{4+}/S^0.

4. Summary

A melting & fining test and SWV measurements were carried out for a flint glass batch and melts containing BFS, respectively. The results of the melting & fining test indicated that the doping of BFS into the batches contributed to the fining of the melts. The location of the peaks shown in a voltammogram of the BFS-doped melts was very similar to that of the sulfate-doped melts. Based on results of the melting & fining test and the SWV measurements, it was concluded that sulfide in BFS contributes to fining through oxidation and behaves in the melts as as does sulfur from sulfate.

Acknowledgment

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