Electrochemical Approach in Plasma Display Panel Glass Melts doped with Sulfate and Sulfide I. Oxygen Equilibrium Pressure

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ABSTRACT

The oxygen gas behavior in PDP (Plasma Display Panel) glass melts doped with sulfate (SO_4^{-2}) or blast furnace slag (BFS, S^{2-}) or both by means of yttria-stabilized zirconia (YSZ) electrodes was observed after the first fining. The temperature dependence of oxygen equilibrium pressure (P_{O2}) in each melt showed typical behavior, namely P_{O2} decreased as temperature decreased. This suggests that an oxidation of S^{4+} to S^{6+} took place. However, the P_{O2}-value at constant temperature increased in the following order: BFS < sulfate + BFS < sulfate. Of particular note, the P_{O2} of the melt doped with sulfate + BFS was much lower than that of the melt with only sulfate, although only 10% of sulfur was added by the BFS. This behavior can be explained by the redox reaction between sulfide ions in the BFS and dissolved oxygen ions in the melt during the first fining.

Key words : Oxygen equilibrium pressure, Sulfate, Sulfide, Redox reaction

1. Introduction

During the melting of glass, batch gases are released by dissociation of carbonate raw materials and a large amount of bubbles are generated in glass melts. These bubbles are regarded as defects harming the optical and mechanical quality of the final products. Therefore, the bubbles must be removed by a physicochemical fining process consisting of two stages: 1) growth of bubbles, buoyant rise and collapse at high temperature, 2) shrinkage of bubbles and dissolution into the melt at low temperature.[1] The fining process is enhanced by chemical agents and various chemicals are used depending on the composition of the glass.

In manufacture of glass substrate for plasma display panels (PDP) by the float process, chemical fining is particularly important because such display glasses permit almost no bubble-induced optical defects. In general, the chemical fining at the first stage in PDP glass manufacture is completed by a redox reaction of sulfate ions (SO_4^{2-}) supplied from Na_2SO_4 under oxidation atmosphere. Fig. 1 shows gas release due to sulfate decomposition in the course of a batch melting performed by Kraemer.[2] During increase of melt temperature, the first amount of both SO_2 and O_2 denoted as ① is already released in the rough melt within the temperature range around 1100°C. This low-temperature gas release is the result of the reaction between sulfate and sand, $Na_2SO_4 + SiO_2 \rightarrow Na_2SiO_3 + SO_2 + 1/2O_2$. The dissolution of the sand is accelerated by means of this reaction.

The release of the actual fining gas is observed at higher temperatures (1400°C < T < 1500°C) denoted as ② and leads to considerable bubble growth. During the actual fining process the bubbles theoretically undergo the following reduction from S^{6+} to S^{4+} by generation of SO_2 and O_2, which participate in bubble growth.[3-6]

$$SO_4^{2-}(\text{melt, } S^{6+}) \rightarrow SO_2 \,(\text{gas, } S^{4+}) + \frac{1}{2}O_2 \,(\text{gas}) + O^{2-}(\text{melt}) \qquad (1)$$
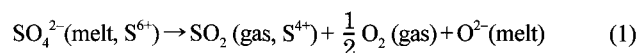
It has been demonstrated in several studies[7-9] that sulfide ions (S^{2-}) contained in blast furnace slag (BFS) can contribute to fining during batch melting by reacting with free or non-bridging oxygen to produce SO_2. Redox behavior of sulfur ions in fined melts has been studied qualitatively by square wave voltammetry for soda lime silica glasses.[10-13] There is another electrochemical method called oxygen equilibrium pressure (OEP) by which oxygen generation during fining of melts can be detected quantitatively.[14-17] However, there have been no studies in which using OEP for sulfur-doped melts has been attempted.

In the present work, electrochemical measurements of glass in the melt state were performed by means of zirconia solid electrodes. The measurements of OEP for the PDP display glass melts containing sodium sulfate, or BFS with sulfide or a mix of both materials were conducted at temperatures ranging from 1400 to 1000°C. The redox reaction of various sulfur ions is discussed in the results.

2. Experimental Procedure

2.1 Preparation of glass melts

The blank composition of the PDP glass in mol% was $69.1SiO_2$, $9.0(Na_2O + K_2O)$, $13.0RO(MgO + CaO)$, $5.3SrO$,

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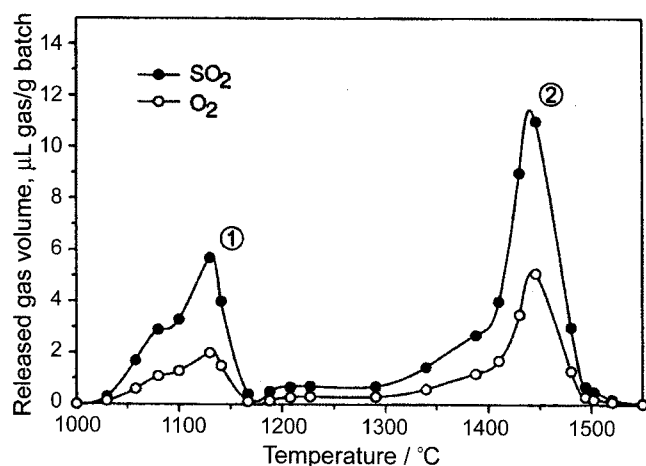 Tel : +82-63-469-4737 Fax : +82-63-469-4731

Fig. 1. Gas evolution during batch melting of CRT glass containing sulfate under oxidizing conditions as a function of temperature.[2]

1.1BaO and a small amount of ZrO_2, Al_2O_3 in which the Na_2O/K_2O and the MgO/CaO mole ratios were fixed at 1.[18-20] Three melts with different sulfur supplies were studied in the present work. The blank melt was doped with 0.4 wt % SO_3 supplied from Na_2SO_4, with 0.03 wt % SO_3 from 6% BFS (corresponding amount to 6 wt% of sand in the glass batches) and with a mix of both materials. Table 1 contains the compositions of four experimental glass melts (PDP blank, sulfate, BFS6 and sulfate+BFS6) and the BFS. High-purity raw materials were used to exclude the effect of another polyvalent impurity such as Fe or Ti. The glass batches of about 300 g were melted at 1550°C in a Pt/Rh crucible for 60 min in an electric furnace and the melts were stirred by Pt/Rh rod for 60 min for homogenization. The crucible with bubble-free homogeneous glass melts was transferred to another electric furnace to conduct the OEP measurements. In order to examine the thermal behavior of the BFS, a thermal analysis was conducted by TG-DTA (TG-DTA 2000, MAC Science, Japan)

2.2 OEP measurement

The electrochemical cell for OEP measurement consisted of three electrodes immersed into the melt in the Pt/Rh crucible. Platinum plate was used as a counter electrode. The other platinum wire, called the reference electrode, was connected with an O^{2-} conducting Y_2O_3-stabilized ZrO_2 (YSZ) material which was in contact with the melts and flushed by
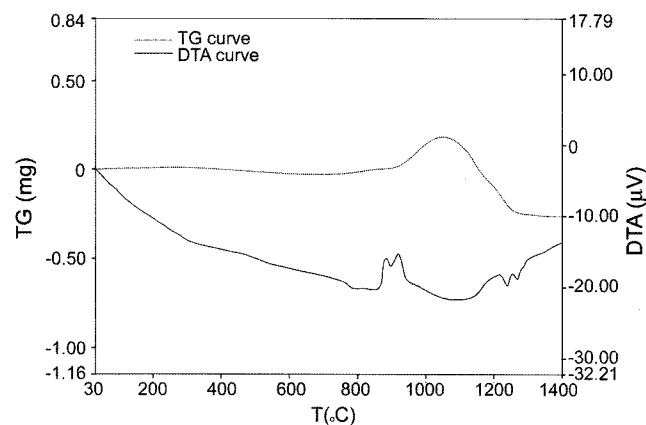

Fig. 2. TG-DTA curve of the powdered BFS. Heating rate : 10 °C/min.

reference air with a known oxygen partial pressure (P_{rO2}:0.21 bar) during the OEP experiment. Details regarding the OEP measurement are described in the literature.[17]

When the OEP (P_{O2}) in the glass melts is different from the oxygen partial pressure (P_{rO2}) of the reference air, a potential difference (ΔE_m) between the counter and reference electrodes arises. OEP (P_{O2}) in the glass melts at T is given as follows:

$$P_{O2} = P_{rO2} \cdot \exp\left[\frac{4 \cdot F \cdot \Delta E_m}{R_g \cdot T}\right] \qquad (2)$$

Here, R_g is the gas constant and F is the Faraday constant.

While the prepared glass melts were maintained at 1400°C in the furnace, the electrodes were dipped into the glass melts. The potential difference between both electrodes was measured continuously by voltmeter (34401A, Agilent, USA) and then converted to OEP through an equation (2). In order to exclude atmospheric influence from affecting the OEP, an alumina lid was used as a crucible cap and N_2 gas was flushed into the crucible during measurement.

3. Results and Discussion

Fig. 2 exhibits traces of DTA and TG for BFS under oxidation atmosphere. In the DTA-run, exothermic peaks occurred around 870~910°C due to crystallization, and endothermic peaks at 1220~1270°C indicate melting of crystalline phase. In the case of the TG-run, the weight began to increase at 910°C and then from 1050°C the weight decreased until 1270°C. The final weight was lower than the

Table 1. Compositions (mol %) of Experimental Glass Melts and BFS

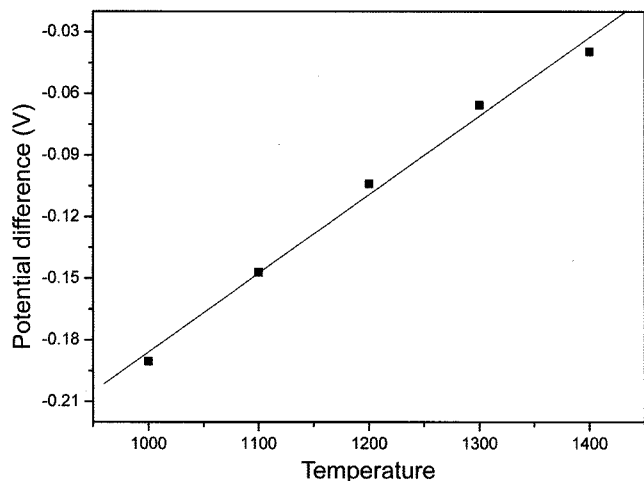| component glass code	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	SrO	BaO	ZrO_2	Fe_2O	MnO	TiO_2	SO_3
PDP blank	69.1	0.4	4.5	4.5	6.5	6.5	5.3	1.1	2.1				
Sulfate	68.9	0.4	4.5	4.5	6.5	6.5	5.3	1.1	2.1				0.3
BFS6	66.2	4.6	4.7	4.9	3.4	6.1	4.6	3.6	1.7	0.005	0.008	0.03	0.03
Sulfate+BFS6	66.1	4.6	4.7	4.8	3.4	6.1	4.6	3.6	1.7	0.005	0.008	0.03	0.33
BFS	33.9	16.3	0.28	0.58	4.22	42.0			0.3	0.28	0.92	0.84	

Fig. 3. Measured potential difference between counter electrode and reference electrode in sulfate melts containing 0.3 mol% SO_3.

initial one. On the basis of the TG-run, the reaction of S^{2-} in BFS between 910°C and 1050°C can be expressed as follows.

$$S^{2-}(melt) + 2O_2 \rightarrow SO_4^{2-}(melt, S^{6+}) \tag{3}$$
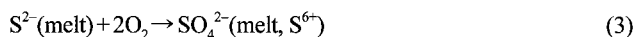
The weight increase was due to oxidation from S^{2-} to SO_4^{2-} and the subsequent weight decrease at 1050°C was related to decomposition of SO_4^{2-}, as described in reaction (1). The decomposition finished at about 1270°C.

Fig. 3 shows the temperature dependence of measured potential difference for the sulfate melt containing 0.3 mol% SO_3. The BFS6 and the sulfate+BFS6 showed similar behavior. The calculated P_{O2} is presented as a function of temperature in Fig. 4. P_{O2} in the measuring temperature range was lower than the atmospheric pressure. Since the glass batch in the present work was melted at 1550°C and the resulting glass melt was then chemically homogenized by stirring, the first fining stage must have already been complete. At the first fining stage for the sulfate melt, O_2 and SO_2 gases were generated by reduction from S^{6+} to S^{4+} as shown in reaction (1). For the BFS6 melt, SO_2 gases were generated by the decomposition of the SO_4^{2-} produced by the oxidation of S^{2-} as described in reaction (3). For the sulfate+BFS6 melt reaction, (1) and (3) may take place simultaneously. The decomposition of sulfate (SO_4^{2-}) through reaction with the sulfide (S^{2-}) in BFS generates a large amount of SO_2 gas, as indicated in reaction (4),[4] and a violent degassing resulting from such a reaction was directly observed during batch melting of the present work. After the first fining there is no possibility for the existence of S^{2-} in BFS6 melt or sulfate+BFS6 melt under oxidation atmosphere.

$$3SO_4^{-2}(melt) + S^{2-}(melt) \rightarrow 4SO_2(gas, S^{4+}) + 4O^{2-}(melt) \tag{4}$$
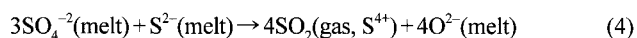
At the second stage the physically-dissolved oxygen gases are primarily converted to chemically-dissolved free oxygen ions ($O_2 \rightarrow O^{2-}$), resulting in a complete dissolution into the melt and then a decrease of P_{O2}. SO_2 gas may undergo a conversion similar to that of the oxygen; namely, physically-dis-
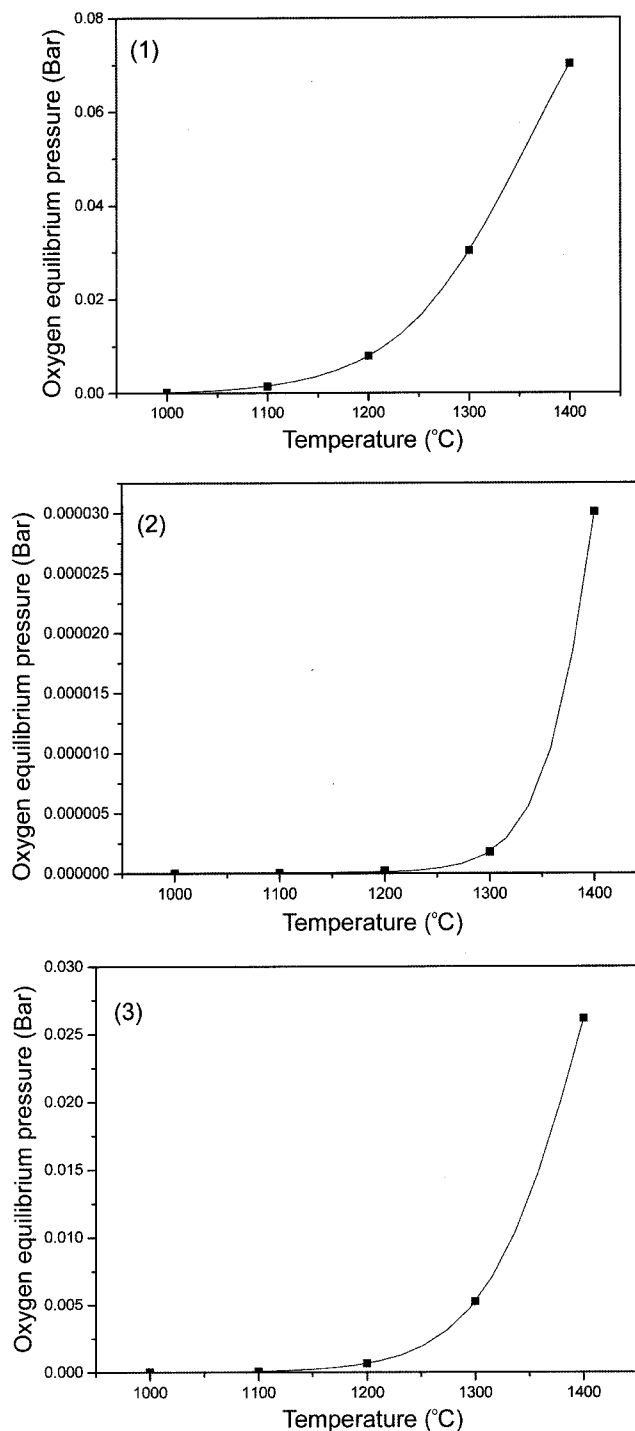

Fig. 4. The oxygen equilibrium pressure in PDP glass melts. (1) Sulfate, (2) BFS6, and (3) Sulfate+BFS6.

solved SO_2 gases may be converted to chemically-dissolved free sulfite ions ($SO_2 \rightarrow SO_3^{2-}$). Therefore, at this stage SO_3^{2-} (or SO_2, S^{4+}) and SO_4^{-2} (S^{6+}) are in a state of equilibrium. With temperature decrease, an oxidation from S^{4+} to S^{6+} takes place; namely, the reaction (1) proceeds to the left hand side.

As mentioned already, a P_{O2}-decrease with temperature decrease means that during cooling of melts the redox reac-

tion proceeds preferably to oxidation and the oxygen solubility into the melts increases. Comparing the OEP curves in Fig. 4, sulfate melt shows the highest oxygen equilibrium pressure at all temperatures. P_{O2} of the sulfate melt at 1400°C, 0.07 bar, is much higher than the 0.3×10^{-4} bar of the BFS6 melt. As temperature decreased, P_{O2} of the BFS6 melt decreased and then approached a zero value at 1200°C. By contrast, P_{O2} of the sulfate melt decreased continuously and finally approached a zero value at 1000°C. P_{O2} behavior in the sulfate+BFS6 melt was a little surprising. The concentration of dissolved oxygen (O^{2-}) in the melt after first fining was calculated theoretically based on reactions (1) and (4). The theoretical concentration of O^{2-} in the sulfate+BFS6 melt was calculated to be 1.1 times as great as in the sulfate melt. Hence, the OEP of the sulfate+BFS6 melt should have been higher than that of the sulfate melt. However, the P_{O2} of the sulfate+BFS6 melt was much lower than the expected value. This means that in the sulfate+BFS6 melt the dissolved oxygen ions (O^{2-}) were already consumed during the first fining. Considering that oxygen is necessary for oxidation from S^{2-} to SO_4^{2-} in melts containing BFS as described in reaction (3), there are two possibilities for oxygen supply during the first fining: one is atmospheric oxygen gas and the other is dissolved free oxide ions in the melt. In the case of the sulfate+BFS6 melt, oxygen can be provided sufficiently from dissolved oxygen ions produced by sulfate decomposition as described in reaction (1). The low concentration of dissolved oxygen in the melt may explain the low OEP of the sulfate+BFS6 melt in Fig. 4 (3).

4. Conclusions

Oxygen equilibrium pressure (P_{O2}) measurements were conducted in three plasma display panel glass melts doped with 1) sulfate, 2) BFS6, and 3) sulfate+BFS6 during the second fining stage. Based on the temperature dependence of the P_{O2}, the redox reaction of sulfur ions during the first and second fining processes was examined for each melt. The temperature dependence of the P_{O2} showed expected behavior, decreasing as temperature decreased. However, comparing P_{O2} curves, the value of the melt doped with BFS was much lower than that of the melt doped with sulfate. It is supposed that the dissolved oxygen ions produced by sulfate decomposition contributed to oxidation of sulfide ions during the first fining.

Acknowledgments

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