Decoloration and Fining of Soda-Lime-Silicate Glass Melts by Direct Current Electrochemical Treatment

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Direct current electrochemical(DCEC) treatment was applied to iron oxide-containing soda-lime-silica glass melts, and its effects on the decoloration(the redox equilibrium of iron) and the fining of bubbles in glass were investigated. Soda-lime-silica glasses containing 0.05 and 0.15mol%FeOx were prepared by melting at 1500°C for 24h. The quenched glasses were remelted at 1250°C, and DC voltage of 1.35V was applied for 1-6h. The resultant glass samples were found to be decolorized well by the treatment for 1-2h. The optical absorption and electron spin resonance spectroscopies revealed that the redox equilibrium of iron shifted towards higher valence state, Fe^{3+}, and the fraction of Fe^{2+} causing blue color decreased below 5% by 2h-treatment. The direct observation of glass melts under DCEC treatment showed that the oxygen bubbles with a diameter 1-2mm were continuously formed on the anode electrode, and the convection of melt was caused.

The experiment on the glass melt to which a lot of fine bubbles were intensionally introduced using fine cullet of soda-lime-silica glass showed that the number of bubbles decreased fastly by 1h-treatment at 1250°C, and the effect of fining at low temperature was also observed. From these results, DCEC treatment was found to have high potential as a method to make the decoloration of glass without the decolorizing chemical additives like selenium compounds, and also refine the glass melt at low temperature.

Introduction

Transition metal ions with unfilled d-orbitals take several different valence states, and the redox equilibria between different valence states are formed in glass. Their equilibria are known to be affected by various kinds of factors. Melting temperature is the important one to define the redox equilibria of the transition metal ions in glass. The higher melting-temperature, the lower valency of the metal ions is taken in the glass melts.

The most typical case is iron in soda-lime-silica glass. Iron comes from the batch mixture of the raw materials as an impurity. The melting temperature over 1500°C increases the fraction of Fe^{2+} ions in soda-lime-silica glass melt and causes a blue coloration. The temperature of fining of glass melt is about 200°C lower than melting temperature, where the redox equilibrium of $Fe^{2+} \leftrightarrow Fe^{3+}$ tends to shift towards higher valence state. However, it can not be accomplished because the diffusion of oxygen which will be needed to oxidise Fe^{2+} into Fe^{3+} is quite low. In the case of soda-silicate glass, Paul and Douglas [1] reported that the equilibration between the melt and atmosphere required more than 70h at 1400°C even in the melt of the laboratory scale(30g, 1cm-depth). As a result, the redox equilibrium at high temperature is flozen in the obtained glasses.

In order to decolorize the iron-containing soda-lime-silica glass, the chemical agents like selenium compounds have been introduced into the batch, because Se forms colloides in the glass which absorb complementary color, and apparent decolorization can be carried out. However, most of selenium(about 90%) eliminate from the glass melts, because of their low vaporalization temperature and low solubility of selerium in the glass melt. The emitted selenium have been trapped in the equipment for the exhaust-gas purifier, and finally disposed as the waste of the glass production in the glass industry. From the point of view of

the recent movement towards zero-emission production and/or the process of low environment load, the utilization of selenium compounds is an unfavorable process, and an alternative process will be required.

In this study, we report the effect of direct current elechtrochemical(DCEC) treatment on iron oxide-containing soda-lime-silica glass melt at 1250°C. The induced physical and chemical behaviors are shown, where the decoloration of glass(the shift of the redox of iron) without selenium compounds has been obtained and, in addition, the effect on the fining of bubbles in the melt is also shown.

EXPERIMENTAL

Glass Preparation

The typical composition of soda-lime-silica glass, $13.3Na_2O$-12.1CaO-$74.6SiO_2$(mol%) was chosen. High purity raw materials, SiO_2, $CaCO_3$ and Na_2CO_3 were used as the starting materials. As an impurity, FeOx was introduced in two levels; 0.05 and 0.15mol% by using Fe_3O_4.

The mixed raw materials for 120g-glass were melted in a platinum crucible at 1500°C for 24h in air, in order to attain the equilibration with a partial pressure of O_2 in ambient atmosphere. The melt was once quenched below the glass transition temperature by casting into a graphite mold with the dimension, 23mmϕ x 80mm, followed by the annealing and rate cooling.

Direct Current Elechtrochemical(DCEC) Treatment

A 100g-glass rod was settled in the crucible of alumina(99.9% purity) or silica glass for DCEC treatment. The apparatus is illustrated in Fig. 1. A couple of Pt elements was used as the electrodes. The anode was settled at the bottom of the crucible, and the cathode was inserted into the melt surface so that the surface area of the electrode in the melt became almost constant. The glass in the crucible was heated in the electric registance furnace up to 1250°C of the fining temperature. When the tempeature reached to the desired temperature, the cathode was immersed into the melt, and DC voltage 1.35V was applied between the electrodes. The conditions of DCEC treatment are summarised in Table 1.

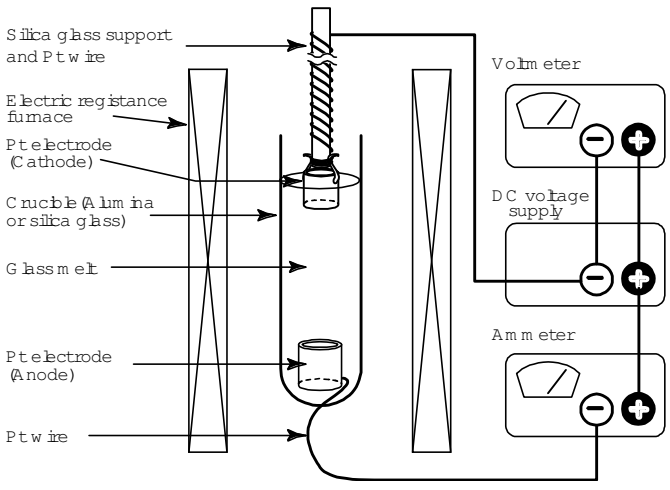

Fig. 1 Schematic illustration of the equipment of DCEC treatment on the glass melts.

A silica crucible was used for the direct observation of the melt between the electrodes. The changes occurring in the melt under DCEC treatment were monitored by a video camera through a glass window of the furnace.

Optical Measurement and Evaluation of Fe^{2+}/Fe^{3+} ratio

Optical absorption spectra of the glass samples with a thickness of 1cm were recorded in the wavelength region between 200-2500nm. Electron spin resonance(ESR) spectroscopy was used to determin the concentration of Fe^{3+} ions in the glass samples. In order to evaluate the concentration of Fe^{3+} in the glass samples, the signal intnsity at g=4.3 which is attributed to Fe^{3+} ion in tetrahedral form, was used. Fe^{2+}/Fe^{3+} ratio was finally determined from the changes in both the absorption band at 1100nm and ESR signal intensity at g=4.3. Total Fe concentrations before and after DCEC treatment were checked by X-ray fluorescence(XRF) spectroscopy analysis.

Table 1. Condition of DCEC treatment on the glasses and the lists of the fraction of Fe^{n+} in the samples.

	Initial(1500°C,24h		**DCEC(1250°C,1h)**		**DCEC(1250°C,2h)**		**DCEC(1250°C,6h)**	
	Fe^{2+}(%)	**Fe^{3+}(%)**	**Fe^{2+}(%)**	**Fe^{3+}(%)**	**Fe^{2+}(%)**	**Fe^{3+}(%)**	**Fe^{2+}(%)**	**Fe^{3+}(%)**
0.05mol%FeOx	**24**	**76**	**8**	**92**	**3**	**97**	**---**	**---**
0.15mol%FeOx	**14**	**86**	**7**	**93**	**---**	**---**	**2**	**98**

RESULTS

Figure 2 shows the changes of DC current during DCEC treatment on the glass melts containing 0.05 and 0.15mol%FeOx. Just after DC voltage was applied, the current about 20-30mA was observed and steeply decreased. After 20min, the current saturated near 10-15mA. The saturated current values were almost constant irrespective to the content of FeOx.

Before DCEC treatment, the glass samples had blue color, especially the glass containing 0.15mol%FeOx showed deep blue. After 1h-DCEC treatment, the samples showed the progress of the decoloration. The longer DCEC treatment time, the more the samples were decolorized. Figures 3 and 4 show the absorption spectra of the samples containing 0.05 and 0.15mol%FeOx, respectively. DCEC decreased the absorption band around 1100nm assigned to $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} ions, while the absorption near 380nm by $^6A_1 \rightarrow {}^4T_2$ in Fe^{3+} ion[2] increased. The decrease of 1100nm-band decreased the absorption tail in the visible wavelength region, and decreased the blue color of the sample glasses.

Table 1 summarizes the fractions of Fe^{2+} and Fe^{3+} ions in the glass samples, and their dependence on the treatment time are plotted in Fig. 5. X-ray fluorescence spectroscopy revealed that the total amount of iron in the glass samples did not change before and after DCEC treatment. As seen in this figure, first 1-2h treatment is effective to shift the redox equilibrium of iron in the melts. In the case of 6h treatment on the melt with 0.15mol%FeOx, the fraction of Fe^{2+} decreased to 2%, which corresponds to Fe^{2+}-concentration much less than that of the initial glass containing 0.05mol%FeOx before DCEC treatment.

The direct observation of the melt under DCEC treatment using a silica glass crucible manifested that the bubbles with a diameter 1.5-2mm were continuously formed on the anode electrode and rised up towards the melt surface. The observed behavior of the bubbles

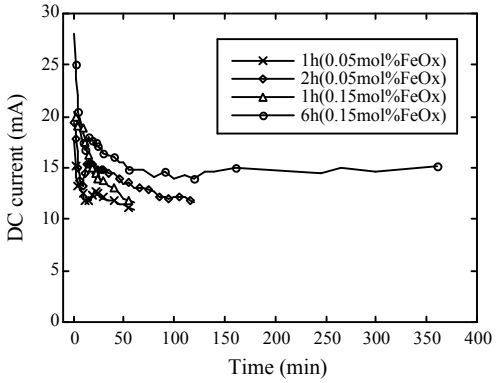

Fig. 2 Plots of DC current during DCEC treatment with 1.35DCV on the glass melts containing 0.05 and 0.15mol% FeOx at 1250°C.

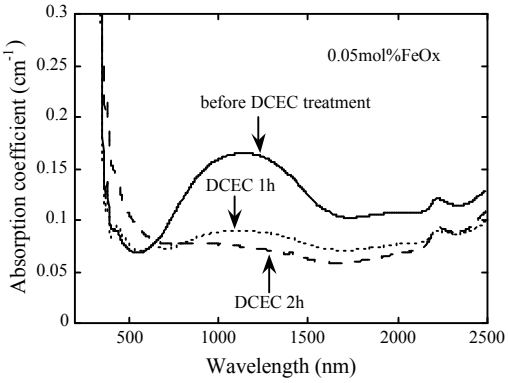

Fig. 3 Absorption spectra of the glass samples with 0.05mol%FeOx before and after DCEC treatments.

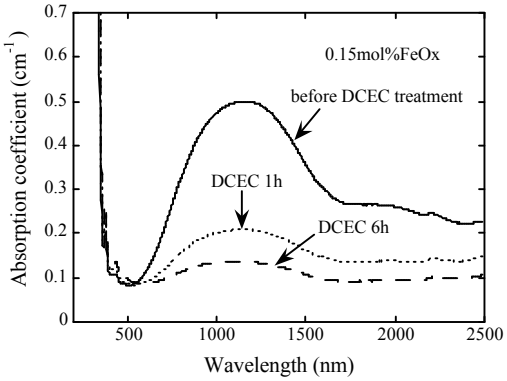

Fig. 4 Absorption spectra of the glass samples with 0.15mol%FeOx before and after DCEC treatments.

in the glass melt are illustrated in Fig. 6. The initial bubbles, which were formed immediately within 1min after the application of DC voltage, rised in the velocity of 5.4mm/min. They reached to the melt surface within 5min and the following bubbles with almost the same size rised at about 7.4-9.9mm/min. A 10min DCEC treatment caused bubble layer on the melt surface, where the bubbles had almost uniform daimeter about 1.5mm. The continuously formed and rising bubbles from the anode have been inducing the convention of the melt until the DC voltage was turned off.

Figure 7(a) shows the photograph of the glass sample after 1h-DCEC treatment at 1250°C. This glass initially contained a lot of fine bubbles by the remelting fine cullets shortly. Figure 7(b) is that of the glass samples, which was remelted of the glass containing a lot of fine bubbles at the same temperature for 1h without DCEC treatment. The latter one still contains a lot of bubbles with a diameter ranging from less than 1mm to 2mm, which was almost the same as those of the initial glass before DCEC treatment. On the other hand, the fining of bubbles was found to be improved well by DCEC treatment as in Fig.7(a).

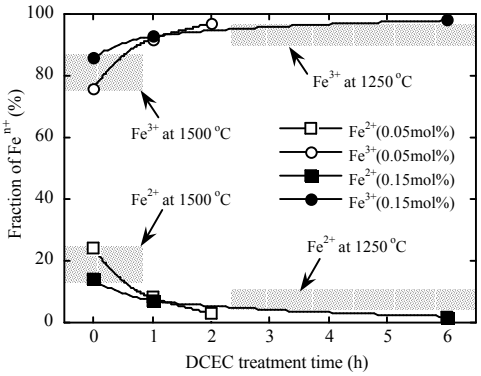

Fig. 5 Changes of the fraction of Fe^{n+} ions in the glass samples by DCEC treatment for various periods of time. Shadow areas represent the range of Fe^{n+} in the literatures for soda silicate and soda-lime silicate glass melts equilibrated at (a)1500°C and (b)1250°C.

DISCUSSION

Redox equilibrium of iron in soda-lime-silica glass melt has been investigated by a lot of authors. Paul [3] reported the equilibrium constants of iron in various kinds of alkali silicate and soda-lime-silica glass melts. In Fig. 5, the fraction range of Fe^{n+} in soda silicate and soda-lime-silica glass melts equilibrated at 1500°C and 1250°C are also shown. Taking into account the results by Paul and Douglas[1], the equilibration of whole of 100g-melt(6-8cm in depth) with the atmosphere would take more than 1week by just melting. However, DCEC is found to shift the redox of iron in the glass fastly from the equilibrium point at 1500°C to that at 1250°C fastly.

Factors causing this fast shift of redox should be the continuous formation of bubbles at the anode electrode during DCEC. Continuous and constant DC current during DCEC(over 6h) reveals that electron charges(most probably alkali ions) would be moved towards the cathode while the negative ones(most probable one would be expressed as O^{2-} apparently) towards the anode. The electrochemical reaction should also progress to cause the bubbles at the anode. In addition, the oxidation of the melt should progress, because XRF analysis showed that DCEC did not change the total amount of iron in the glasses between before and after the treatment. Most probable reactions at the electrodes under DC-voltage application would be expressed apparently as follows;

$$2O^{2-} = O_2 + 4e^- \quad (1)$$

$$Fe^{2+} = Fe^{3+} + e^- \quad (2)$$

At the anode, the reaction(1) is considered to progress towards right hand side, while opposite on the

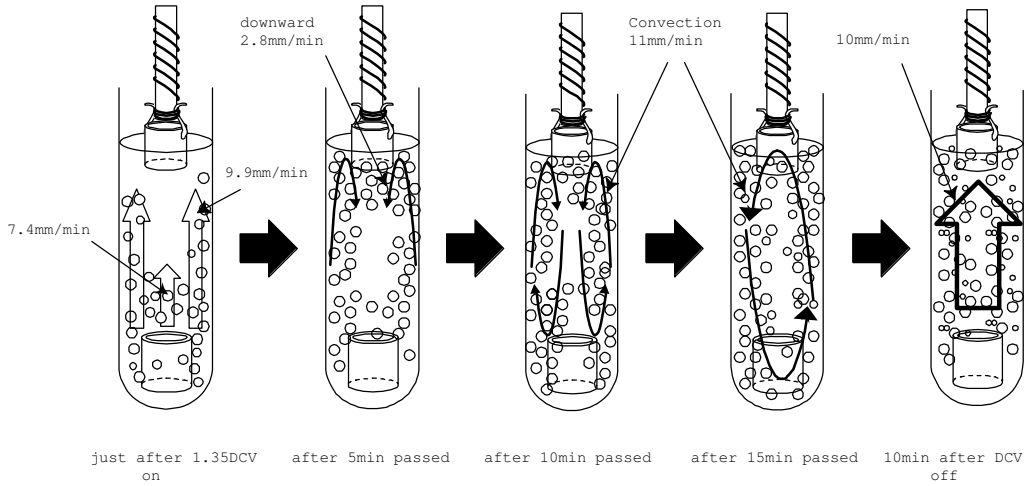

Fig. 6 Illustration of the behavior of bubbles in the melts during DCEC treatment. Silica glass crucible was used for observation.

cathode. Cyclic voltanmetory and chronopotentiometric study by Maric *et al.*[4] revealed that

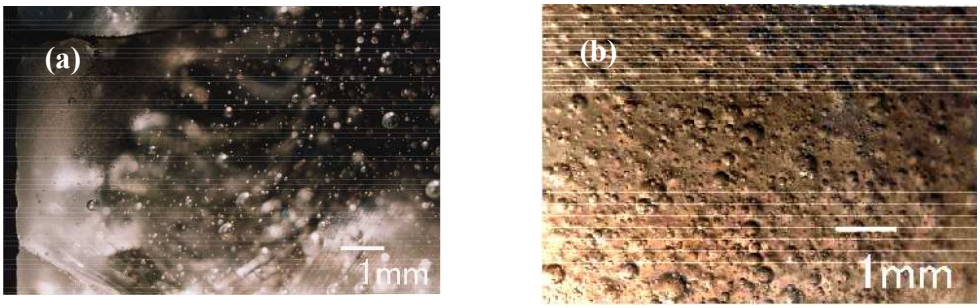

Fig.7 Optical micro-photographs of the glass samples after remelting at 1250°C (a)with DCEC treatment for 1h followed by 10min holding and (b)without DCEC for 1h10min. Both samples were cooled to room temperature at a rate of 7-8K/min.

platinum oxide layer on the electrode is deeply related to the evolution and formation of oxygen molecules;

$Pt + O^{2-} \rightarrow Pt{-}O + 2e^- \rightarrow Pt + 1/2O_2(g)$ and/or $Pt{-}O + O^{2-} \rightarrow Pt + O_2(g) + 2e^-$. (3)

Continous formation of oxygen bubbles are considered to be partly consumed to oxidize Fe^{2+} by interacting with the melt during their rise towards the melt surface. On the other hand, the further oxygen introduction from outside the melt should be considered because the equilibrium(2) shifted to higher valence side totaly. The reverse reaction of (3) would be one of the appropriate mechanisms as cathode reaction. During treatment, the melt surface around cathode was found to be surrounded by a lot of bubbles(foam layer). The rapid transport(drainage) of melt at the bubble boundary in foam[5] would be one of the important factors to enhance it. Therefore, decoloration in DCEC-treated glass can be said to be due to the shift of redox by the effective dissolution of oxygen from atomsphere by electrochemical process. The rapid attainment to the equilibrium point at low temperature even in the melt with high level iron impurity is important to consider the cost of raw materials. Furthermore, in glass industry, decoloration using selenium compounds has become one of the problems

for reduction of the environmental load and the cost of glass production. This results would give some information to consider an alternative process of Se-free colorless glass.
Concerning the fining effects found in DCEC treatment, convection of bubbles in the melt should be taken into account. Detailed mechanism how the rising bubbles interacted with a lot of fine bubbles which had already been contained in the glass melt has not been clarified yet. However, the fining of bubbles at low temperature would be a fascinating feature to lower the melting temperature. Detail analysis on the behavior of bubbles in the melt should be important to consider the mechanism.

CONCLUSION

DCEC treatment has been applied on soda-lime-silica glass melts containing FeOx as an impurity. Oxidation of Fe^{2+} causing an absorption of visible light to colorless Fe^{3+} was observed, and decoloration without chemical additives has been accomplished in short period of time 1-2h. It was also shown that DCEC has a potential to refine the glass melt containing a lot of fine bubbles in it. The continuous formation of oxygen bubbles and introduction of oxygen from atmosphere via electrochemical reaction at the electrodes were considered to cause these phenomena.

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