Reaction of soda–lime–silica glass melt with water vapour at melting temperatures

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ABSTRACT

The soda–lime–silica glass melt was exposed to an atmosphere with a high water vapour partial pressure at temperatures of 1400–1500 °C and the processes in the melt were observed and monitored using the high temperature observation method. The glass batch containing sulfates with carbon – so that the molar ratio between the carbon and sulfate ions in the batch varied between 0 and 9 – the batch without any fining agent and the batch with the addition of antimony oxide were prepared. The foaming and bubble nucleation on the level of the molten glass were observed in glasses with sulfate additions when the water vapour partial pressure in the atmosphere exceeded 50 kPa, but the bubble nucleation in the reduced glass was observed also at a lower partial pressure. The bubble nucleation intensity increased with temperature. No bubble nucleation was observed in the melts with antimony oxide or in the melt without any fining agent. The bubbles nucleated on the glass level in both the oxidized and reduced melts with sulfate additions grew by a growth rate exceeding the bubble growth rate in the volume of glass by almost one order of magnitude. The unstable but rapidly renewed foam subsequently spread over the glass level. The most intensive foaming was observed in the glass melt without carbon and in the slightly reduced glass. The mechanism of the reaction between water vapour and glass is discussed in terms of a controlling process as well as its impact on the glass melting process.

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1. Introduction

Water vapour easily reacts with silicate and boric glasses under the formation of OH groups bonded to either silicon or boron atom [1]. Under glass melting conditions, the source of water is batch and atmosphere humidity. The content of the OH groups in the melt during the melting process often attains equilibrium with the water vapour partial pressure in the atmosphere due to the rapid transport of water vapour through the batch and OH groups through the melt [2]. Consequently, the water vapour diffuses in bubbles and plays a useful role during glass fining [3], but it also influences the glass properties at higher concentrations of OH groups in the glass [4]. Another reaction between the water vapour and glass melt takes place in those glass melts containing sulfate ions. The reaction between both components leads to the formation of OH groups in the melt and to the decomposition of sulfate ions producing sulfur dioxide and oxygen [5,6]:

$$SO_4^{2-}(l) + H_2O(g) \rightarrow SO_2(l,g) + 1/2O_2(l,g) + 2OH^-(l). \qquad (1)$$
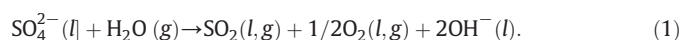
The amount of released gases frequently exceeds the gases's physical solubility in the melt and produced bubbles or regions of continuous foam on the melt level. This is an industrial experience especially from oxy-fired melting. The foam worsens the fining process and slows the heat transfer from the combustion space into the glass melt. The resistance of the melt to foam formation and foam stability in an atmosphere containing water vapour has been studied in several works. Kappel [7] found that the foam decays more easily if there is water vapour in the atmosphere. This probably occurs owing to a decrease of glass viscosity containing an increasing amount of OH groups and easier drainage of foam lamellas. Leimböck [8] presents the s.c. dilution model which explains the foaming of the melt with sulfates being in contact with an atmosphere containing water vapour: water vapour diffuses quickly into the glass and owing to its high solubility in the melt and mentioned rapid diffusion affects even deeper regions of the melt. The water dissolved in the form of OH groups then diffuses into rising bubbles, dilutes the fining gas inside and enhances bubble growth. The growing bubbles form the foam layer after reaching the melt level.

The goal of this work is to reveal in detail the mechanism of foam formation on the melt level in the presence of a high concentration of water vapour in the atmosphere, its quantitative evaluation and an appraisal of the relative importance of the reactions of water vapour with a glass melt containing sulfates for the glass melting process.

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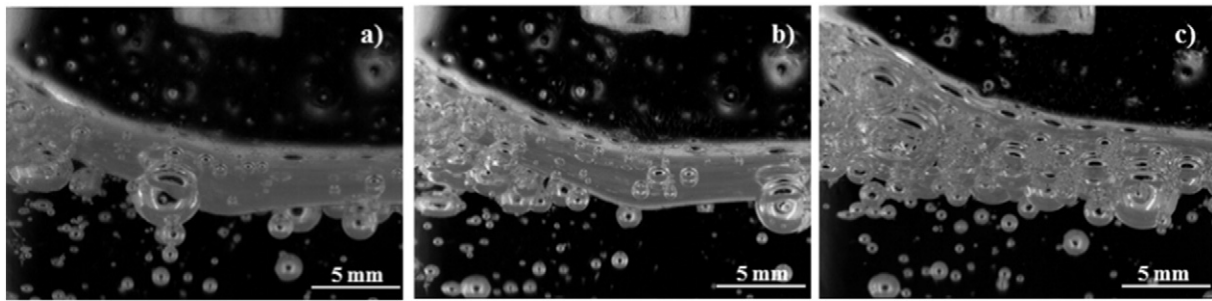*E-mail address:* Jaroslav.Klouzek@vscht.cz (J. Kloužek).

Fig. 1. Photographs of bubble foam development on the level of the soda–lime–silica glass with the addition of carbon and sulfate ions in the molar ratio of $C/SO_4^{2-} = 9$ between 1300 and 1450 °C and $pH_2O = 80$ kPa. a) 1301 °C and 0 s, b) 1353 °C, 318 s, c) 1451 °C, 895 s.
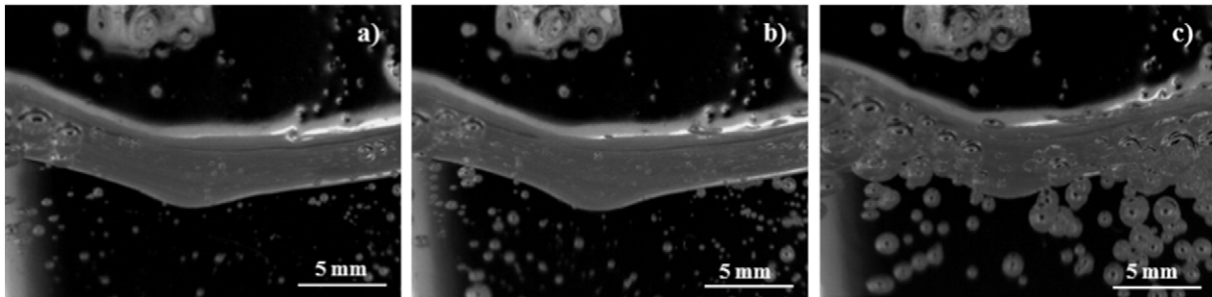

Fig. 2. Photographs of the foam development on the level of the soda–lime–silica glass with a molar ratio of $C/SO_4^{2-} = 0$ at temperatures increasing from 1400 °C to the final temperature of 1500 °C and at $pH_2O = 80$ kPa. The rate of heating is 10 °C/min. a) 1450 °C, b) 1475 °C, c) 1500 °C.

2. Experimental

The glass batch was prepared from commercial chemicals, namely soda and calcium carbonate of per analysis purity, and glass sand with the maximum content of Fe_2O_3 being 0.015 mass%. The sand was annealed for 1 h at 1100 °C before each experiment. The glass batch was prepared to provide glass of a composition of 16% of Na_2O, 10% of CaO and 74% of SiO_2 (mass). The sodium sulfate was added replacing the adequate amount of Na_2O from soda to the batch to attain theoretically 0.5 mass% of chemically dissolved SO_3 in the melt. The carbon was used in the form of fine coke particles and added to the batch to attain a molar ratio between the coke and SO_4^{2-} ions in the glass in the range of 0 to 9. Thus, the glass batches were prepared with molar ratios of C/SO_4^{2-} 0, 0.5, 1, 1.5, 2, 3, 6 and 9. Most experiments were performed with glasses characterized by the C/SO_4^{2-} ratios 0, 2 and 6. Antimony oxide with sodium nitrate replacing a part of the Na_2O from soda was also used as a fining agent. An amount of antimony oxide was added to the glass batch to attain theoretically a 0.5 mass% of Sb_2O_3 in the glass and a 1 mass% of Na_2O was added as $NaNO_3$ replacing the adequate amount of the Na_2O from soda in the batch.

The high temperature observation (HTO) method was used to follow the phenomena in the melt and on the glass level. The experiment was opened by a system calibration to obtain the real size of the etalon. Subsequently, 15–25 g of the batch was inserted into a silica glass cell with parallel walls in the lower part of the cell. The cell was inserted in a vertical electric laboratory furnace heated to 700 °C, the batch was heated by the heating rate 10 °C/min to the temperature of partial fining at 1400 °C and kept there for 30 min to remove most of bubbles from the glass melt (but the temperature was increased up to 1450 °C in the sample with the molar ratio of $C/SO_4^{2-} = 0$, designated for the foaming experiment at 1500 °C, then decreased back to the standard initial temperature of 1400 °C). When conducting foam observation at 1300 °C, the glass was standardly heated to 1400 °C to remove the substantial part of bubbles from the melt and then cooled to the experimental temperature of 1300 °C. If the experimental temperature was 1500 °C, the melt was heated at the rate of 10 °C/min. The observation experiments at the partial pressure of water vapour of 80 kPa were performed at experimental temperatures of 1300, 1400 and 1500 °C for the samples with the ratio of $C/SO_4^{2-} = 0$–9 whereas the experiments at $pH_2O = 11$, 50 and 100 kPa were performed only at 1500 °C for the
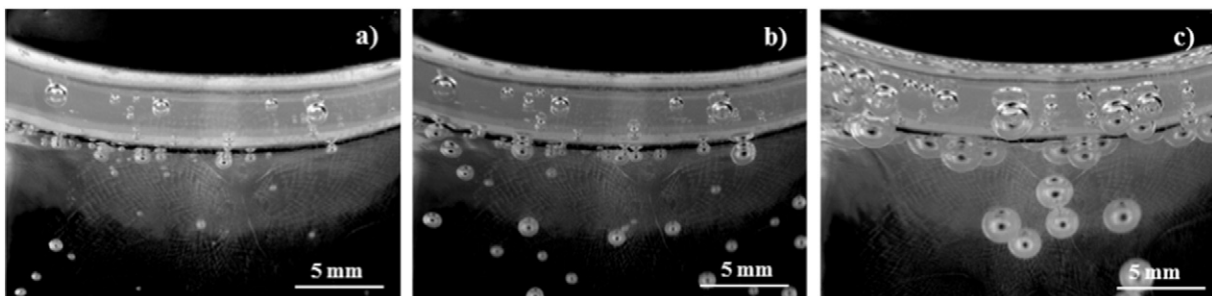

Fig. 3. Photographs of the glass level of the soda–lime–silica glass with the molar ratio of $C/SO_4^{2-} = 0$ at temperatures increasing from 1400 °C to 1500 °C and without water vapour exposition. a) 1450 °C, b) 1475 °C, c) 1500 °C.