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## Gas release phenomena in soda-lime-silica glass

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## ABSTRACT

Heterogeneous bubble nucleation during the production of commercial glasses is one of the negative factors affecting their technology and technical properties. In order to eliminate these bubbles, we conducted extensive research of bubble nucleation in soda-lime-silica glass melts at increasing temperatures and variable redox states of glass. Evolved gas analysis (EGA) coupled with gas chromatography and mass spectrometry were used to identify and evaluate crucial chemical reactions during the melting. The reactions were indicated also by the bubble compositions estimated from bubble contraction during the temperature drop. The fining action of sulfates in the reducing conditions was observed at temperatures between 1200 and 1300 °C using high temperature monitoring. This was confirmed by the relatively high average values of the bubble growth rates. In addition, extensive nucleation of bubbles took place at relatively low temperatures. The temperature region of nucleation was determined by monitoring bubble nucleation on the Pt wire immersed in the melt at increasing temperatures. The nucleation of the bubbles in variously reduced glasses has been observed at temperatures even lower than 1300 °C which further decreased with the increasing  $C/SO_4^{2-}$  ratio. Next, we tried to clarify whether the process of bubble nucleation at a low redox state of glass was caused by supersaturation of the glass melt by either physically dissolved or chemically bound gases. We suppose that the nucleation of bubbles  $SO_2$  around 1300 °C can be attributed to the reaction between the sulfate remaining in melts and sulfides which have been formed by reduction reactions.

## 1. Introduction

During the melting process a silicate melt formation is associated with the abundant production of gases. Because of vaporization, decomposition and chemical reactions releasing gases, bubbles form in the melt. In addition, gases also interact with the glass melt to form complexes or dissolve physically. These gases saturate the melt which is made more susceptible to the origin of new bubbles by the process of nucleation. In most laboratory and industrial glass melts, inhomogeneities are present which can be an initiating factor for heterogeneous bubble nucleation. The decisive impulse to bubble nucleation is supersaturation of the melt by a gas which occurs when the melt composition, temperature, pressure or electric potential are changing and are reaching the relevant values. There are several events in the glass melting process where we can expect extensive bubble nucleation. First new bubbles of  $CO_2$  emerge during the early stages of glass melting owing to the decreasing glass basicity. Afterwards, new bubbles are formed because of supersaturation by a fining gas. The optimal fining range of glass melts depends on the type of glass produced and can be specified by controlling the redox state [1–3]. In order to increase the

quality of the glass, both residual and newly formed bubbles must be removed and the melt has to be effectively degassed [4]. A lower amount of dissolved gases reduces the ability to originate new bubbles in a previously fined glass melt.

The initial composition of the bubbles, which have been nucleated at higher temperatures, depends on the kind of fining gas. The bubbles contain  $O_2$  if the glasses were fined by oxides. However, the majority of the world's glass productions use sodium sulfate as a fining agent (with or without a reducing agent) where different gases and different reactions cause bubble nucleation. The redox state of the glass melt has a crucial impact on the mechanisms of fining in sulfate-fined glasses and subsequently on the bubbles' nucleation. Previous studies have shown the existence of sulfate in more oxidizing conditions where nucleated bubbles then contain  $SO_2$  and  $O_2$ . The supersaturation of glass by the  $SO_3$  gas was the cause of bubble nucleation. In contrast, sulfide existence has been proved under more reducing conditions. Moderately reduced glasses contain both sulfate and sulfide [5]. Chemical reactions between both oxidation sulfur states can trigger bubble nucleation [5, 6]. The glass becomes supersaturated by  $SO_2$ , so  $SO_2$  bubbles are produced by the nucleation process.

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The commercial amber glasses are easy predisposed to supersaturation and bubbles in amber glasses have consequently a high content of  $\text{SO}_2$  [7, 8]. The significant effect of the sulfur reactions under reducing conditions is concentrated in the range of medium temperatures (1200 to 1300 °C). Besides the melt supersaturation by gases also the large number of nucleation sites dispersed in the glass melt plays an active role in the bubble nucleation process. The concentration of undissolved sand particles as the nucleation sites is high in this region of melting. Extensive bubble nucleation can be a source of microconvection in the melt [5]. This is a good opportunity for bubble nucleation to enhance the dissolution process.

The reappearance of bubbles in bubble-free melts is termed reboil. The most technologically significant is the thermal reboil. Both physical and chemical gas solubility play important roles in bubble nucleation processes. The chemical solubility of technologically significant gases ( $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ) is reduced with increasing temperature [8, 9]. These gases then supersaturate the glass melt. The physical solubility of gases in commercial glass melts is low and the subsequent bubble nucleation arises easily. The state when the supersaturation of the melt is sufficient to produce the first nuclei and consequently, nucleus growth, can be numerically expressed by the nucleation temperature [10, 11]. The glass homogeneity affects the value of the nucleation temperature therefore the values should be compared among glasses of the same type and melted under similar melting conditions. However, generally speaking, the value of the nucleation temperature decreases with the growing concentration of the complex ion binding the nucleating gas chemically and with the decreasing physical solubility of the gas in the melt with decreasing glass basicity [8, 10]. The chemical solubility of gas decreases with the decreasing basicity of glass [8, 10] and the physical solubility decreases with growing temperature [11]. Consequently, bubble nucleation becomes easy at high temperatures and in a glass melt with low basicity. The bubble nucleation temperature provides information that could adjust the fining process more precisely. The fining close to the bubble nucleation temperature ensures the rapid bubble growth and, consequently, their fast rising to the level. Fining above the nucleation temperature is accompanied by the formation of new bubbles [10].

The process of glass melting with sulfur compounds embraces thus several phenomena which character, intensity and mutual relations are determined by the time-temperature regime and oxidation-reduction state of glass. The consonance between phenomena is extremely welcome because the course of the entire group of phenomena finely leads to the homogeneous glass melt. Gases either dissolved physically and chemically or as a separate phase (bubbles, foam, atmosphere) play here a serious role, particularly bubbles which participate in chemical reactions, mass transfer, nucleation and foaming. The appreciation of their complex role is especially demanding. Naturally the application of one method or approach to this problem can provide only restricted picture of the process. The parallel application of more relevant experimental procedures seems to be a suitable way to move from the clarification of single aspects of gas phenomena to appreciation of their complex role in the melting process. Here the questions are to be solved as the real existence of assumed chemical reactions, the temperature regions of glass saturation and bubble nucleation with respect to evolution of gases by these reactions, the behavior of bubbles and melt fining ability, as well as the melt foaming in the melts with variable temperature regime and redox state. Clarification of introduced questions by parallel use of more experimental methods, as well as precision of beneficial conditions of the glass melting process, are the aim of this work.

## 2. Experimental

All the experiments were carried out in soda-lime-silica glass melts with the standard experimental composition  $74\text{SiO}_2\text{-}16\text{Na}_2\text{O-}10\text{CaO}$ , wt%. The glass batches were mixed, which contained the following

constituents: sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), calcium carbonate ( $\text{CaCO}_3$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) all of purity per the analysis.  $\text{SiO}_2$  was dosed by using silica sand of commercial purity (0.015 wt% of  $\text{Fe}_2\text{O}_3$ ). Organic contaminations may lead to fluctuations during the fining process thus the silica sand was annealed for 1 h at 1000 °C before its using in glass batches. Sodium sulfate was added to the batches to promote the removal of bubbles from the glass melt (as a fining agent). Fine-ground coke of commercial purity was used as a reducing agent. The reducing agent contained 85% of C and is referred to as carbon in this paper. The initial content of  $\text{SO}_3$  as sulfate was 0.5 wt% in all the glasses. The addition of the reducing agent was varied to control the redox state. The molar ratio  $\text{C}/\text{SO}_4^{2-}$  ranged between 0 and 9. Therefore, the redox state of the batches involved the region between oxidized, medium reduced and reduced glasses.

The standard experiment of glass observation to specify the bubble nucleation temperature was the following one:

The glass batch for 50 g of glass was thoroughly mixed and charged into a specially shaped silica glass tube. The tube was inserted into a vertical electric laboratory furnace at 700 °C. The high temperature observation of processes in the melt was facilitated by the furnace side window and its monitoring by the camera. The glass batch was heated by the heating rate 10 °C/min to the glass-tempering temperature (1100 °C and 1300 °C). Two sets of tempering experiments were performed to get rid of most bubbles present in the glass melt. In the first set of experiments, each sample was held at a constant temperature of 1100 °C for 24 h. This low temperature was chosen because abundant bubble nucleation took place in the preliminary experiments already at temperatures lower than 1300 °C and under reducing conditions [10]. In the second set of experiments, the tempering temperature was 1300 °C with tempering times ranging from 135 to 210 min. After the melting and tempering, the substantial part of the bubbles was removed and the glass melts were ready for observation of the bubble nucleation and determination of the bubble nucleation temperature.

The determination of the bubble nucleation region and nucleation temperature was performed by high temperature observation and monitoring of the process. A platinum wire with a diameter of 1 mm was used as a supporting material for nucleation. The wire was cleaned by ethylalcohol and distilled water before the experiment. Subsequently, the wire was annealed above a Bunsen burner and tempered above the glass level (in the furnace) for about 10 min. The Pt wire was then cautiously immersed into the glass melt to avoid contact between the metal and silica because the contact between the Pt wire and the silica tube could cause the formation of an electrochemical cell. Afterwards the recording of the experiment by CCD camera started and the temperature during the experiment was raised by 2 °C/min from the glass tempering temperature to 1520 °C. The formation of bubbles on the support material was observed and the size of a few initial growing bubbles, arisen by nucleation along the Pt wire, was evaluated by using the image analyzer. The nucleation temperature was specified by the linear extrapolation of the bubbles' size of the first nucleated bubbles to the zero value. After the final upper temperature was achieved, the contraction of the last nucleated bubbles during the temperature drop from 1520 °C to 1250–1300 °C was studied to assess their composition.

The following experiments and measurements were further implemented to complete the results of the previous nucleation study:

1. The method of evolved gas analysis coupled with gas chromatography and mass spectrometry was used to analyze the gases evolved during the heating of the 1 g glass batches and to study the sulfur reactions in the early stage of the melting process. The evolved gases were examined during melting at temperatures increasing by a rate of 10 °C/min from 700 °C to 1500 °C.
2. The average bubble grow rates have been specified by high temperature observation and monitoring from the linear dependences between the bubble diameter and time at the higher tempering temperature of 1300 °C.

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