～脱泡技術関連として～ An Overview of Gas－Injection Fining

Irene Peterson, Prantik Mazumder, Sue Schiefelbein, Traci Harding, Leilani Burdick－Burnett, Joe Matusick, Dave McEnroe, Michelle Wallen, Rich Curreri and Gary Squier

Abstract

The removal of toxic fining agents from glass compositions has renewed interest in alternative fining methods, such as gas-injection fining. This paper gives an overview of the causes of blisters and mechanisms of blister removal. Experiments demonstrating the successful use of gas-injection fining to reduce blister counts are discussed.

Introduction

Tiny bubbles, called blisters, can be trapped in glass for a variety of reasons. As the applications for glass become more demanding, the tolerance for these blister defects has decreased dramatically, both in the number density permitted and the maximum size of the blister permitted in the glass. Historically, a variety of chemicals have been added to the glass to help remove the blisters. Unfortunately, some of the most effective of these fining agents, such as arsenic oxide, are toxic to the environment. The desire to find a more environmentally-friendly method to remove blisters from the glass has led the glass industry to consider a variety of processing techniques. Among these methods is bubbling gases through the melt, a technique known as gas-injection fining. Experiments at Corning, Inc. have demonstrated the use of gas-injection fining to decrease blisters by two orders of magnitude.

Corning Incorporated Advanced Process Engineering Technology and Engineering　SP PR 13　Corning NY USA
TEL　1-607-974-0418　FAX　1-607-974-2925
Email : petersonim@corning.com

This paper will give an overview of the causes of blisters, discuss how gas-injection works to remove them, and show the results of some experiments demonstrating successful use of the technique.

Blister formation

Gas can be trapped in the glass during many stages of the glassmaking process. When the batch material is introduced to the melter, air or furnace gas can be trapped between the particles. As the batch materials decompose, they can release a variety of gases, including water vapor, carbon dioxide, sulfur compounds, oxygen and others. Fuel vapors or combustion products can be trapped in the glass as it melts. During melting, borders between glass regions of different compositions can result in sharp solubility gradients for different gases, leading to blister formation at the interfaces between them. Temperature gradients can also reduce the local solubility of gas, resulting in blister formation. Glass can react with the furnace materials, resulting in gas formation. During stirring processes designed to homogenize the glass, gas can also be stirred into the melt.

These gases can be dissolved in the glass melt both physically and chemically, and can precipitate out later in the process. All gases can physically dissolve in the melt, and some, such as O_2, CO_2, SO_2 and H_2O can also chemically dissolve. The physical solubility is higher the smaller the molecule[1], and the chemical solubility is much higher than the physical solubility. Analysis of gases trapped in the blisters can help determine the blister source. Gases commonly found in blisters include N_2, O_2, Ar, SO_2 and combustion products.[2]

Important properties of the gas

The behavior of the gas in the glass is determined by its solubility and its diffusivity, both of which depend on glass composition and structure. The solubility can either increase or decrease with temperature. Solubility is usually stated as the "Oswald solubility", $S_{i,Os}$:[3]

$$S_{i,0s}=\frac{C_i}{C_g}$$

where C_i is the concentration of gas in the glass and C_g is the concentration of gas in the atmosphere.

The diffusion behavior is characterized by the diffusion coefficient, D_i, which increases with temperature according to the Arrhenius relationship:

$$D_i=D_{0,i}\exp\left[\frac{-\Delta Q_{D,i}}{RT}\right]$$

where $\Delta Q_{D,i}$ is the activation energy for diffusion of species i, R is the universal gas constant and T is the temperature in degrees K.[4]

Removal of blisters from the glass

Blisters can be removed from the glass melt by rising to a free surface or by dissolution of the gas back into the melt. Blister dissolution occurs if the blister is smaller than a critical radius, r^*. This critical radius depends on many factors, but is typically less than 100 μm.

For a system with a single component gas present, the gas will diffuse out of the blister and the blister will shrink when the pressure inside the blister exceeds the partial pressure of the gas in the melt. The pressure inside the blister, P, can be calculated:

$$P=\frac{2\sigma}{r}+P_x+\rho gh$$

where r is the blister radius, σ is the surface tension in the melt, P_x is the external pressure, ρ is the density of melt, g is the acceleration of gravity, and h is the distance of the blister below the melt surface.[5] For the more general case of a multicomponent gas mixture, we have defined the critical radius as the initial radius of a bubble that will neither grow nor shrink in the melt.

Blisters rise in the glass melt at a rate V_s, according to Stokes' Law:

$$V_s=\frac{2}{9}\,\frac{gr^2\Delta\rho}{\eta}$$

where g is the gravitational acceleration, r is the blister radius, $\Delta\rho$ is the difference in density between the blister and the glass melt, and η is the viscosity of the glass melt. The larger the blister size, the faster it rises out of the melt.

Chemical fining agents operate by releasing a burst of gas into the melt, which diffuses into the pre-existing blisters to increase their size (and therefore increase their rise velocity). However, in recent years there has been renewed interest in removing chemical fining agents from the glass. This has brought new attention to processing methods to remove blisters, including gas-injection fining, ultrasonic fining and low pressure (vacuum) fining.[6]

Most reports of gas-injection fining focus on inert gases, such as helium.[2,6,7]. However, it is also possible to use a gas which reacts with the glass chemistry, such as oxygen. In this work, combinations of helium and oxygen were studied to determine the effects of different gas types on fining.

Experiment

Two different batch compositions in the CaO–Al_2O_3–SiO_2 system, called compositions A and B, were used in this study. The batch material was poured into a platinum crucible, which was placed inside a liner inside the induction melting unit. A platinum tube could be inserted through a two-piece refractory lid on top of the liner A cover gas was introduced over the melt by placing the tube between the lid and the surface of the glass melt. The

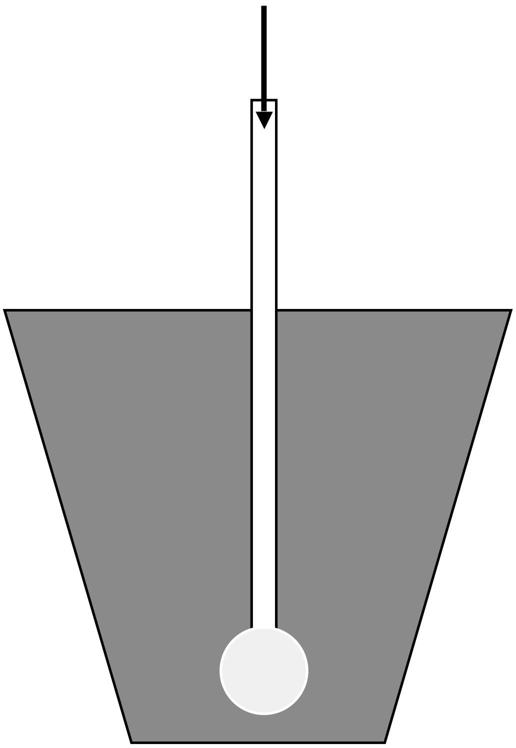

Fig. 1. Schematic of bubbler tube inside crucible

Fig. 2. Induction melter with platinum bubbler tube.

tube could also be lowered into the glass melt to bubble gas into the melt.

Gas pressure and flow were controlled using a low-pressure regulator and a low pressure flowmeter. During the experiment, bubble formation and release could be verified by periodic changes in flow rate, as indicated by the flowmeter. A schematic of the bubbler tube inside the glass is shown in Figure 1. The induction unit is shown with the bubbler tube in Figure 2.

Effect of bubbling and gas composition

The goal of the first set of experiments was to determine the effect of gas atmosphere and bubbling on blister concentration in glass composition A. Gas was introduced either over the melt (as a cover gas) or bubbled through the melt. Gas compositions are shown in Table I.

The goal of the second set of experiments was to determine the effect of the helium to oxygen ratio on blister concentration in glass composition B. The gas compositions are shown in Table II. Gas was bubbled into the glass during all the experiments in Table II.

A three step thermal schedule was used. The first step was melting, followed by a hold or bubbling step. The third step was for fining.

When a cover gas was used, it was introduced before melting, and turned off after the fining step. During bubbling experiments, the bubbler was lowered into the glass after the batch materials had melted, and raised out of the melt before the fining step.

To determine the oxidation state of the glass, samples were removed from the melt using a platinum spoon at various stages of the process and quenched in air. After the fining step, the glass was quenched to room temperature, annealed and then core drilled from the crucible.

Table I. Gas compositions for bubbling and cover gas in composition A

Gas composition	**Bubbled or cover gas?**
Air (79% N_2, 21% O_2)	Cover gas
Air (79% N_2, 21% O_2)	Bubbled
80% He, 20% O_2	Cover Gas
80% He, 20% O_2	Bubbled
95% He, 5% O_2	Bubbled

Table II. Gas compositions for bubbling in composition B

Gas Composition	**Bubbled or cover gas?**
80% He, 20% O_2	Bubbled
50% He, 50% O_2	Bubbled
100% O_2	Bubbled

Characterization techniques

The oxidation state of the glass was determined from a redox indicator, M, inside the glass composition. The $M^{reduced}/M^{total}$ ratio was measured using the Inductively Coupled Plasma (ICP) technique for M^{total}, and titration for $M^{reduced}$.

For blister measurements, a vertical cross section was cut from the center of the core drilled section and polished to an optical finish, as shown in Figure 3. Automated blister count measurements were made to determine the number, size, and location of each blister in the glass.

Results and Discussion

Figure 4 shows the results of calculated blister rise and dissolution times as a function of the processing conditions (4 A) and the photographs of the glass cross-sections (4 B) after helium/oxygen bubbling (left) and after an air cover gas (right). The model predicts that

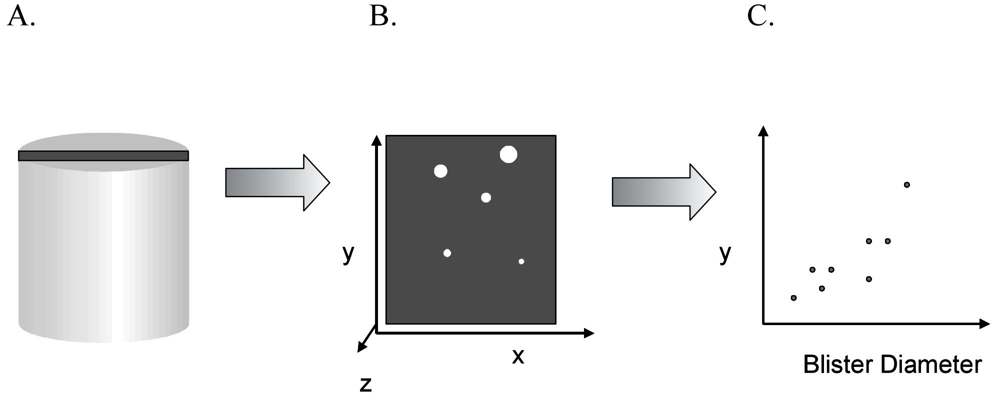

Fig. 3. Blister count measurements. A. Location of cross section; B. Schematic of blisters inside cross section; and C. Graph of blister vertical location (y) as a function of blister diameter.

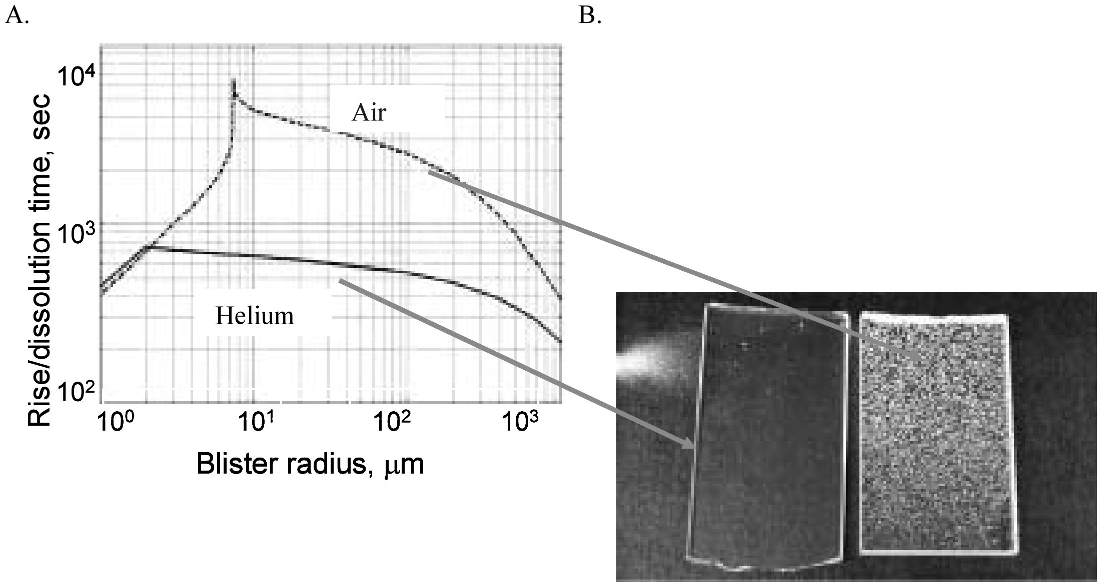

Fig. 4. A. Predicted reduction in blister rise/dissolution time under different processing conditions; and B. Corresponding glass cross sections in bubbled sample (left) and sample which was prepared using an air cover gas (right).

that blisters disappear more quickly in the bubbled melt, which is consistent with the decrease in blisters observed in the bubbled sample.

Figure 5 shows the number of blisters/cm^3 in composition A produced using the different processing conditions listed in Table I. The best condition for blister removal was to bubble a mixture of 80% helium／20% oxygen through the glass.

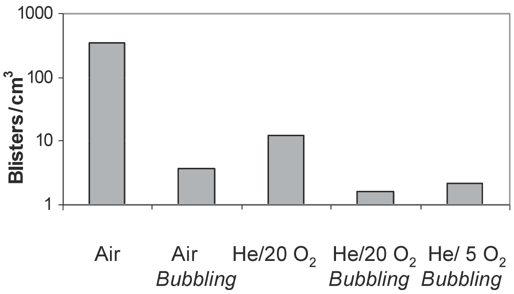

Fig. 5. Effect of bubbling and gas composition on blisters in composition A

The effect of the helium to oxygen ratio in the bubbling gas on the blister density in composition B is shown in Figure 6. The higher the concentration of oxygen in the gas, the lower the resulting blister count.

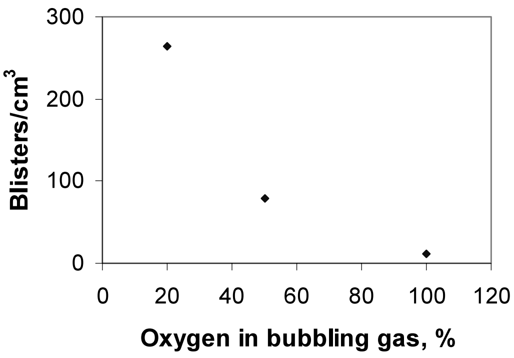

Fig. 6. Effect of the helium to oxygen ratio in the bubbling gas on blisters in composition B

The effect of the oxygen concentration in the gas mix on the oxidation state of the glass after bubbling is shown in Figure 7. As expected, as the proportion of oxygen in the gas mix increased, the glass became more oxidized, as indicated by a falling level of M ^{reduced} in the redox indicator.

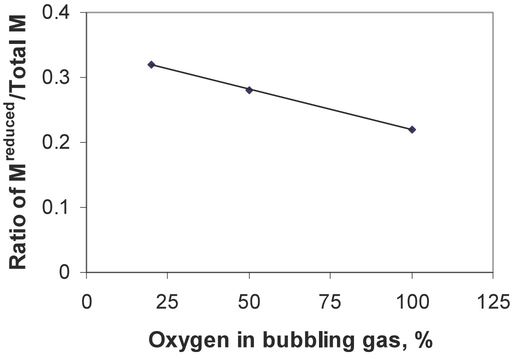

Fig. 7. Effect of bubbling gas composition on glass oxidation

Conclusions

Gas can be trapped inside glass during many different steps in the glass melting process. Blisters can be minimized by removing the causes of blister formation, and developing processes to remove blisters after they form.

This paper showed promising results for using gas-injection fining to minimize blisters in two glass compositions. By proper choice of bubbling gas, the blister count was decreased by two orders of magnitude. The observed trends in blister count agreed well with predicted rise and dissolution times.

Acknowledgements

The authors gratefully acknowledge the assistance of their colleagues, especially Dan Sternquist, Charles Blackwell and Philip Kwasney.

References

1 . H. Scholze, Glass Nature, Structure and Properties, 3 rd Ed. , Springer, Berlin 1991.
2 . J. Shelby, " Handbook of Gas Diffusion in Solids and Melts" ASM International (1996) Materials Park, OH.
3 R. H. Doremus J. Am. Ceram Soc. 43 (1960) 655.
4 . N. P. Bansal, R. H. Doremus, Handbook of Glass Properties, Academic, 1986.
5 . M. Cable, J. Am. Ceram. Soc. 49(8)436-411966.
6 . RGC Beerkens, " Analysis of Advanced and Fast Fining Processes for Glass Melts" ; pp 27-30 in Cermaic Transactions, Vol 141 Advances in Fusion and Processing of Glass III (July 2003, Rochester, NY) Edited by J. Varner, T. Seward, H. Schaeffer, American Ceramic Society, Westerville OH 2004.
7 . N. Yoshida, M. Kawaguchi, M. Tkagi and S. Aoki, " Advanced Fining Technology for Glass Melts" Proceedings 20 th International Congress on Glass Kyoto Japan Sept 27-Oc 112004 Ceramic Society of Japan Tokyo, Japan.