Evaluation of reaction rate of refining agents

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To elucidate the thermal decomposition behavior of antimony oxide which is added to promote (re)fining of bubbles in TV glass, an evolved gas analysis (EGA) was conducted using a newly designed device for detecting the gases from the glass batch at increasing temperatures. Furthermore, a mathematical formulation was made to describe the above behavior. From the results of the EGA measurements, three parameters, which govern the reaction rate constant, viz. reaction order, activation energy and frequency factor, were decided. By coupling this mathematical model and the thermal fluid model of glass melts in tank furnaces, it is possible to simulate the conditions of generating refining oxygen in the furnace.

Abschätzung der Reaktionsgeschwindigkeit von Läutermitteln

Zur Klärung des Wärmezersetzungsverhaltens von Antimonoxid, das in Fernsehglasschmelzen als Läutermittel eingesetzt wird, wurde eine Gasanalyse (EGA = Evolved Gas Analysis) durchgeführt. Hierzu wurde für den Nachweis der bei ansteigender Temperatur aus dem Gemenge freigesetzten Gase ein neues Gerät entwickelt. Außerdem wurde ein mathematisches Modell entwickelt, um das obige Verhalten zu beschreiben. Aus den Ergebnissen der Gasanalysemessungen wurden drei Parameter ausgewählt, die die Reaktionsratenkonstante, d.h. die Reaktionsreihenfolge, die Aktivierungsenergie und den Häufigkeitsfaktor, bestimmen. Durch eine Verbindung dieses mathematischen Modells und des Wärmeflußmodells von Glasschmelzen in Schmelzöfen ist es möglich, die Bildungsbedingungen von Läuteroxiden im Schmelzofen zu simulieren.

1. Introduction

The authors in earlier papers [1 and 2] proposed a methodology that systematically evaluated bubble removing performance of a glass melting furnace by numerical simulation and clarified the role of refining agents in a tank furnace. Refining agents have been used for many years in the glass industry to promote the fining and refining of bubbles: many academic research studies have tried to explain the fining phenomena from the viewpoints of equilibrium and structure of glass melts. Up to now, various methods such as differential thermal analysis (DTA), thermal gravimetry (TG), evolved gas analysis (EGA), high-temperature microscopic observation and so forth have been used to study the glass-forming reaction mechanism of glass batch at high temperatures. There are few studies approaching fining from a kinematic perspective which can be applied to glass production in a real furnace. This paper shows the results of the measurement of the gas evolution rate generated from the refining agent in TV glass batch by using an evolved gas analysis method. A mathematical reaction model which can be coupled with the thermal fluid model of a glass melt is proposed. In this paper, EGA, i.e. gas profile measurement, will be used to directly observe the gases generated by the decomposition of glass batch and refining agents.

As is common practice, a batch sample is heated at the rate of several kelvins per minute and the decomposing behavior is quantitatively measured. However, in a real furnace the batch is charged into a furnace kept at around 1600 °C from room temperature. Consequently, the batch is heated at a rate of several 100 kelvins per minute. The initial glass is formed under these conditions in a real furnace. It was observed that the batch actually disappeared about 30 min after being charged into a TV glass furnace [2]. Therefore, gas profile measurement data obtained by heating at a rate of several kelvins per minute can not be used directly to describe the decomposing behavior of refining agents in a real furnace. Development of a mathematical model based on the gas profile measurements is clearly required for a quantitative evaluation of refining in a real furnace.

Krämer [3] conducted important research regarding the reaction behavior of glass batch at high temperatures using gas profile measurement. Sample batch was placed

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in a platinum boat and heated in a microwave furnace. The gases generated as the temperature increased were introduced into a gas-chromatograph with the carrier gas and the evolved gases were quantitatively measured. Krämer [3] describes the refining mechanism of antimony and arsenic oxides in soda-lime-silica and TV glasses. Moreover, the effect of nitrate used together with these refining agents was evaluated. Detailed discussions were presented concerning the reaction mechanism of the batch based on the measurement results. However, the gas profile measurement was stopped at 1500 °C. Recent glass furnaces are operated at temperature around 1600 °C, so the elucidation of the refining behavior above 1500 °C is indispensable. Furthermore, Krämer's paper did not deal with the results of the gas profile measurement to make the mathematical formulation needed for the simulation of the bubble removing process. This paper will describe the refining gas evolution in mathematical formulation.

Klouzek [4 and 5] analyzed the thermal behavior of TV glass batch using the same method as Krämer [3]. The focus of his study was the batch decomposing reaction at comparatively low temperatures, below 1500 °C. Accordingly, the effect of the refining agent between 1000 to 1600 °C, necessary for describing the fining and refining behavior of a bubble in glass, was not reported.

Stelzner et al. [6 and 7] and Hartman et al. [8] executed an experiment to heat a glass sample melted in an actual glass tank and measured the evolved gas in the vacuum with a mass spectrometer. In their released gas spectrum, many spike signals corresponding to the bubble explosions at glass surface, at which point the dissolved gas component became a bubble and was buoyed to the surface, were clearly observed, but the continuously released gas components were disregarded. In contrast to this measurement, Imagawa et al. [9] succeeded in developing their vacuum extraction and mass spectrum device in which the ratio of "volume of the heating furnace to the exhaust speed" was enlarged and gave a high signal/noise ratio. This equipment could catch the pulse component due to the explosion of bubbles and sufficient amounts of gas components released from the glass melt. Their research clarified the amount of refining oxygen from antimony and cerium oxide in the soda-lime-silica glass as a function of temperature.

The use of a mass spectrometer by Stelzner et al. [6] and Imagawa et al. [9] means that the gas is released in a high vacuum, which is feared to lead to a very different condition from actual production furnaces. Furthermore, there is also anxiety as to whether the glass sample measured represents the characteristics of the whole mass of the glass melt, because the glass melt tends to be heterogeneous when melted at low temperature and the mass of the glass sample used for the measurement was in the range of tens of milligrams by virtue of the constraints of their equipment.

2. Decomposing reaction rate equations for refining agents

2.1 Frequency factor, activation energy and reaction order

Assuming refining agents decompose according to the chemical reaction such as $M_2O_5 \Rightarrow M_2O_3 + O_2\uparrow$, the reaction rate of the agents under isothermal conditions is expressed in the following equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)\,(1-\alpha)^n \tag{1}$$

where α denotes the yield defined as the ratio of a refining agent which has decomposed by time t, T the absolute temperature, and n the reaction order. Here, $k(T)$ is the reaction rate constant, depending only on temperature, and it is assumed to follow Arrhenius' equation, given in equation (2):

$$k(T) = A\,\exp\left(\frac{-E}{RT}\right) \tag{2}$$

where A is the frequency factor, E the activation energy, and R the gas constant.

This study utilizes "non-isothermal analysis", where the glass sample is heated at a constant rate. Assuming $\beta = 1-\alpha$, β is the ration of the refining agent which has not decomposed at time t. Differentiating both sides of this relationship with respect to time t

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = -\frac{\mathrm{d}\alpha}{\mathrm{d}t}\,. \tag{3}$$

When equation (3) is substituted for equations (1) and (2), the following equation is obtained:

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = -A\,\exp\left(\frac{-E}{RT}\right)\beta^n\,. \tag{4}$$

Applying the Freeman and Carroll method [10], the following three parameters are determined: frequency factor A, activation energy E and reaction order n. The procedure is as follows: Taking the natural logarithm of equation (4), the following equation is obtained:

$$\ln\left(-\frac{\mathrm{d}\beta}{\mathrm{d}t}\right) = \ln A + \left(\frac{-E}{RT}\right) + n\ln\beta\,. \tag{5}$$

Adopting the values of the neighboring two measured points in the gas profile data, which correspond to two different temperatures, β and $\mathrm{d}\beta/\mathrm{d}t$ can be calculated and the difference of these values is shown as Δ in the following equation (6):

$$\Delta \ln\left(-\frac{\mathrm{d}\beta}{\mathrm{d}t}\right) = -\frac{E}{R}\,\Delta\frac{1}{T} + n\,\Delta\ln\beta\,. \qquad (6)$$

If equation (6) is divided by $\Delta\ln\beta$, equation (7) is derived.

$$\frac{\Delta\ln\left(-\dfrac{\mathrm{d}\beta}{\mathrm{d}t}\right)}{\Delta\ln\beta} = \frac{-\dfrac{E}{R}\,\Delta\dfrac{1}{T}}{\Delta\ln\beta} + n\,. \qquad (7)$$

This equation denotes a first-degree function with the intercept n and the gradient E/R to variable $\Delta(1/T)/\Delta\ln\beta$. When the values of $\Delta(1/T)/\Delta\ln\beta$ and $\Delta\ln(-\,\mathrm{d}\beta/\mathrm{d}t)/\Delta\ln\beta$ are respectively plotted on horizontal and vertical coordinates, E and n are determined, and if these values are substituted into equation (4), A is evaluated.

2.2 Nonreaction ratio after a lapse of time *t*

Where T_0 is the initial temperature, setting the heating rate as h, the temperature T after a lapse of time t is given as follows:

$$T = T_0 + h\,t\,. \qquad (8)$$

When equation (8) is differentiated by t, it will become:

$$\mathrm{d}T = h\,\mathrm{d}t\,. \qquad (9)$$

Equation (9) is substituted for equation (4), and the following equation (10) is derived:

$$\frac{\mathrm{d}\beta}{\mathrm{d}t} = -\frac{A}{h}\,\beta^n \exp\left(\frac{-E}{RT}\right). \qquad (10)$$

Since analytical integration of the equation (10) is not possible, it is converted into the following differentiated equation (11):

$$\frac{\beta_j - \beta_{j-1}}{T_j - T_{j-1}} = -\frac{A}{h}\,\beta_{j-1}^n \exp\left(\frac{-E}{R\,T_{j-1}}\right). \qquad (11)$$

Equation (11) is transposed, and β_j equals equation (12):

$$\beta_j = (T_j - T_{j-1})\left\{-\frac{A}{h}\,\beta_{j-1}^n \exp\left(\frac{-E}{R\,T_{j-1}}\right)\right\} + \beta_{j-1}\,. \qquad (12)$$

Equation (12) makes it possible to obtain the value of β at each time step.

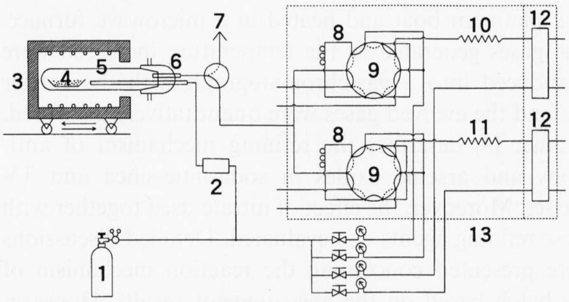

Figure 1. Block diagram of gas profile measurement; 1: helium gas cylinder, 2: precise flow controller, 3: electric furnace, 4: platinum boat, 5: vitreous silica tube, 6: water cooled jacket, 7: exhausting tube, 8: gas sampling loop, 9: 10-way valve, 10: column – Porapak Q, 11: column – Molecular Sieve 5A, 12: thermal conductivity detector, 13: constant temperature oven.

3. Gas profile measurement

3.1 Measurement device and temperature conditions

Figure 1 is a block diagram of the measuring equipment used for this research. The basic function of this device is to measure the generated gases quantitatively by means of gas chromatography by heating the glass batch in a carrier gas (helium). The furnace is heated with silicon carbide elements. The sample temperature is usually raised up to 1600 °C at the rate of several kelvins per minute. However, it is also possible to heat the sample rapidly by inserting it into an operating furnace kept at high temperature as shown in figure 1. Helium with 99.9999 % purity is introduced into the sample room at the rate of 55 ml/min adjusted with a precise gas controller. A platinum boat containing the sample whose carrying part consists of a vitreous silica tube is placed in the heated part of the furnace. The vitreous silica can be kept sufficiently airtight up to 1600 °C. The tube breaks into pieces because of crystallization once it returns to room temperature. Accordingly, the tube must be renewed after each measurement.

The platinum boat has the capacity of about five grams to enable the measurement of the glass raw materials with the same grain size as used in the real production. The gas generated from the sample is carried to the gas chromatograph with the carrier gas. The carrier gas is divided into two lines, one of which is packed with Molecular Sieve 5A and the other is filled with Porapak Q as a gas-separating material. The purpose of the former line is to separate O_2, N_2, and NO and the latter one is for CO_2 separation. The detection of these gases is conducted with thermal conductivity detectors. The gas sampling cycle for each measurement is 11 min. The temperature control of the oven, the carrier gas control and the recording of measured data are carried out by a computer which controls the whole system.

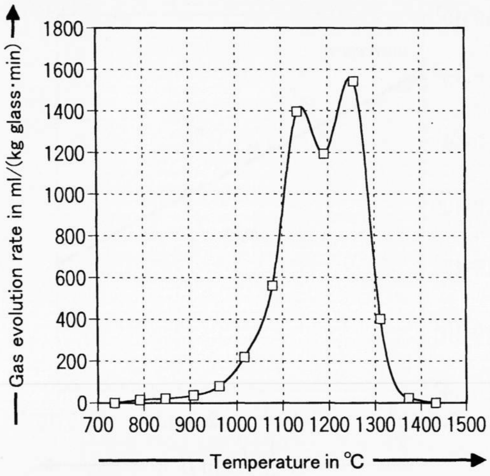

Figure 2. Gas profile of barium carbonate.

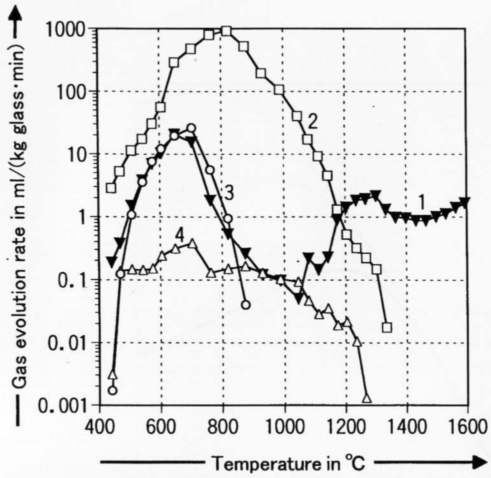

Figure 3. Gas profile of TV glass batch; curve 1: O_2, curve 2: CO_2, curve 3: N_2, curve 4: NO.

3.2 Performance test of equipment

For the purpose of investigating the reliability of the gas profile equipment, the following performance test was executed using calcium carbonate and barium carbonate. They were heated at the rate of 2.9 K/min, and CO_2 gas generated by the decomposition of the carbonate was measured as a function of temperature. The gas evolution from barium carbonate is illustrated in figure 2. Assuming that both chemicals completely decompose, this equipment could detect 94 % of the CO_2 from calcium carbonate and 98 % of the CO_2 from barium carbonate against theoretically obtainable value.

It was also confirmed by nonload test that the vitreous silica tube which is used to support the platinum boat filled with the chemical specimen could maintain a gas-tight condition up to 1600 °C and the gas evolution from the tube material was less than the detection limit of the measuring device.

4. Measurement conditions, results and analysis of TV glass batch

4.1 Measurement conditions

The glass sample used for the measurement had the following oxide composition (in wt%) $61SiO_2$, $2Al_2O_3$, 8BaO, 10SrO, $8Na_2O$, $8K_2O$ and other. Antimony trioxide (0.3 wt%) was used as the refining agent, when converted to net glass weight. In addition, sodium nitrate (1.5 wt%) was added to oxidize the antimony trioxide into antimony pentaoxide during the process of increasing the temperature. The measurement was run under the conditions described in section 3 and the sample was heated from 400 to 1600 °C at the rate of 2.9 K/min.

4.2 Measured results

The gas volume of CO_2, O_2, NO, and N_2 released from the TV batch per unit time and per unit weight during the process of increasing temperature is illustrated in figure 3. The horizontal axis is the temperature and the vertical axis is the released gas volume expressed in logarithmic scale. It indicates that the decomposition of carbonates used as raw materials began from about 450 °C, formed a peak at 800 °C and ended at 1300 °C. CO_2 was evolved at a rate about 100 times that of O_2 and NO because carbonates were used in large quantity as batch materials. On the other hand, the peaks of O_2 gas in the chart are thought to stem from three different causes of gas generation. Namely, it is presumed that the peak of about 700 °C was caused by the decomposition of the nitrate, the peak from 1150 to 1350 °C was attributed to the decomposition reaction ($Sb_2O_5 \Rightarrow Sb_2O_3 + O_2\uparrow$) of antimony pentaoxide which acted as the refining agent, the continuous increase of oxygen gas towards 1600 °C after the bottom curve made at 1350 °C might be due to the decomposition of metallic oxide at higher temperatures. This third peak was not discussed in the papers of Krämer [3] and Klouzek [4 and 5]. The amount of NO gas release was almost as much as that of O_2 at about 700 °C but NO generation stopped at 900 °C. N_2 gas started to decompose from about 450 °C and continued up to 1250 °C, but the released gas volume was not as abundant as that of other gases.

4.3 Computation of reaction rate parameters

The gas profile of the identical batch composition containing the refining agents was measured three times and O_2 gas evolution at beyond 1000 °C was also detected. In addition, a similar gas profile measurement was executed on the batch which did not contain any refining agents. The value, the latter profile value was subtracted from the former value, is regarded as the refining oxygen purely generated by the refining agents and is depicted in figure 4.

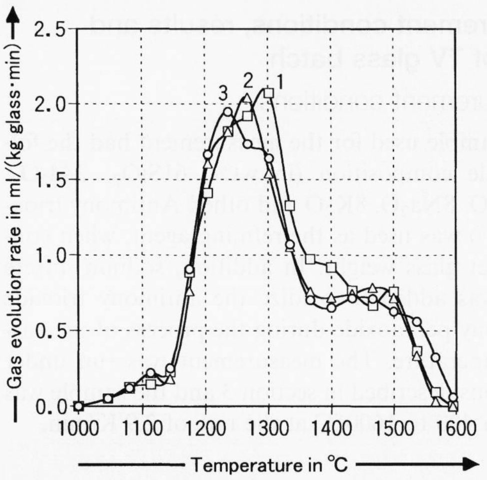

Figure 4. Oxygen gas evolution from TV glass batch. The gas profile measurement of the identical batch composition was repeated three times for accuracy.

The data were analyzed by the Freeman and Carrolls' method and the summary of their analysis by equation (7) is given in figure 5. As the results, the following parameters were confirmed:

- reaction order: $n = 3.868$,
- activation energy: $E = 4.248 \cdot 10^5$ J/mol.

In the next step, the above-calculated reaction order, activation energy and the measured data were substituted in equation (4) and averaged, which derived the frequency factor with the following value:

- frequency factor: $A = 2.347 \cdot 10^{11}\ \mathrm{s}^{-1}$.

5. Influence of heating rate

In actual production the glass batch is charged into a furnace kept at high temperature and is heated at a very high speed as described previously. Introducing the parameters into equation (4), the evolution rate of the refining gas at different heating rates was calculated. The results are shown in figure 6. As is obvious from the figure, although the position of maximum gas generation is about 1250 °C at a heating rate of 2.9 K/min, it is calculated that the peak shifted to 1380 °C at 29 K/min and to about 1500 °C at 290 K/min. Additionally, it is predicted that the gas generation rate increases by one digit as the heating rate increases by a factor of 10.

When the above methodology is applied to a glass furnace simulation that can trace the glass flow starting from the glass batch, the evolution distribution of the refining gas in the glass melts can be obtained as reported in a previous paper [2]. That indicates the situations that rapidly released the refining gas under the glass batch and then the gas evolution rate at once moderates as the glass flows through the lower temperature zone. The gas generation becomes violent again as the glass flow approaches the glass surface. Such results explain various phenomena experienced in actual furnace operations.

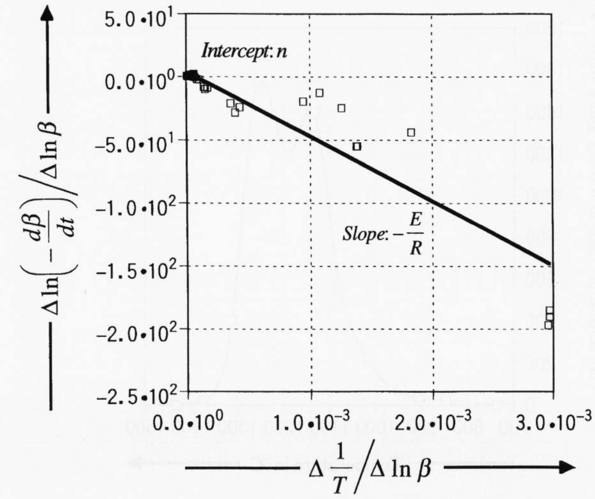

Figure 5. Analytical results for O_2 gas by Freeman and Carrolls' method.

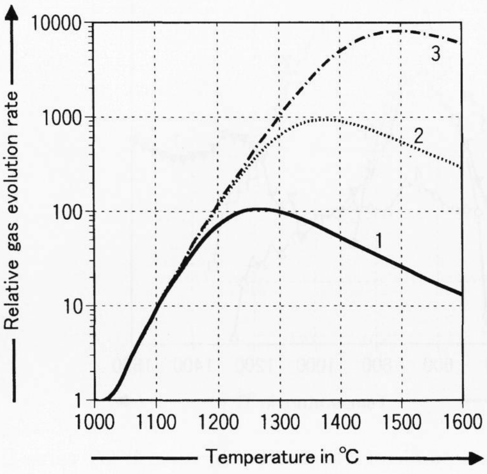

Figure 6. Oxygen gas evolution at different heating rates; curve 1: 2.9 in K/min, curve 2: 29 in K/min, curve 3: 290 in K/min.

6. Conclusion

Gas profile measurement equipment was developed to measure the glass batch used in real production and to measure the gas volume generated during the melting process from room temperature up to 1600 °C. In particular, priority was given to applying the measured result to the description of the characteristics of the thermal reaction of refining agents. Then, a mathematical model was proposed. The gas profile measurement for TV glass batch was executed, and the values of the three parameters which characterized the mathematical model were provided. If these results are utilized together with a thermal fluid analysis of a glass melting furnace, the concentration distribution of refining gas can be predicted, as it was applied in the authors' previous papers [1 and 2].

7. Nomenclature

A	frequency factor in s^{-1}
E	activation energy in J/mol
h	heating rate in K/s
$k(T)$	reaction rate constant in s^{-1}
n	reaction order
R	gas constant in J/(mol · K)
T	temperature in K
T_0	initial temperature in K
t	time in s
α	reacted ratio against whole amount
β:	non-reacted ratio against whole amount $(1-\alpha)$

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