Analysis of bubble gas composition by Raman spectroscopy

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1. Introduction

Bubbles in glass products are one of the major defects in glass manufacturing. The technology for removing bubble defects has been advanced day by day. At the same time, the demand for higher glass quality is increasing. Therefore, reducing bubble defects has been a long-standing problem for glass engineers. One way for reducing bubble defects is analyzing bubble gas composition and optimize the conditions of glass manufacturing process based on the results. So, it is essential technique for glass manufacturing engineers to identify the bubble gas composition.

2. Analyzing the bubble gas composition by mass spectrometry

Generally, the bubble gas composition is analyzed quantitatively by mass spectrometry. This analysis method is that gas in a bubble is released by breaking the bubble in a vacuum chamber, and the gas is detected by a mass spectrometer. However, the analysis method is not suitable for tiny bubbles. One of the reasons is that it is extremely difficult to break a tiny bubble in the chamber. In general, the diameter of a bubble that can be broken is about 50 μm. Another reason is that the amount of gas released from a tiny bubble is very small. The gas volume of a bubble is proportional to the cube of the diameter. Therefore, as the bubble becomes smaller, it becomes difficult to detect the released gas by a mass spectrometer drastically. In addition, a part of the released gas is adsorbed on the fracture surface of a glass sample and on the inner surface from the bubble breaking chamber to the detector.

3. Analyzing the bubble gas composition by Raman spectroscopy

In order to solve these problems, we analyzed a gas composition of tiny bubbles using a Raman spectrophotometer. Analysis of bubble gas composition in glass by Raman spectroscopy has been attempted for decades and it has reached a practical level due to the recent improvement of the analysis apparatus. Raman spectroscopy is a non-destructive analysis. Therefore, it solves the problems of bubble gas analysis related to breaking a tiny bubble and gas adsorption on active fracture surface by mass spectrometry. We succeeded in analyzing the gas composition of the bubble with a diameter of about 25 μm by Raman spectroscopy (Figure 1).

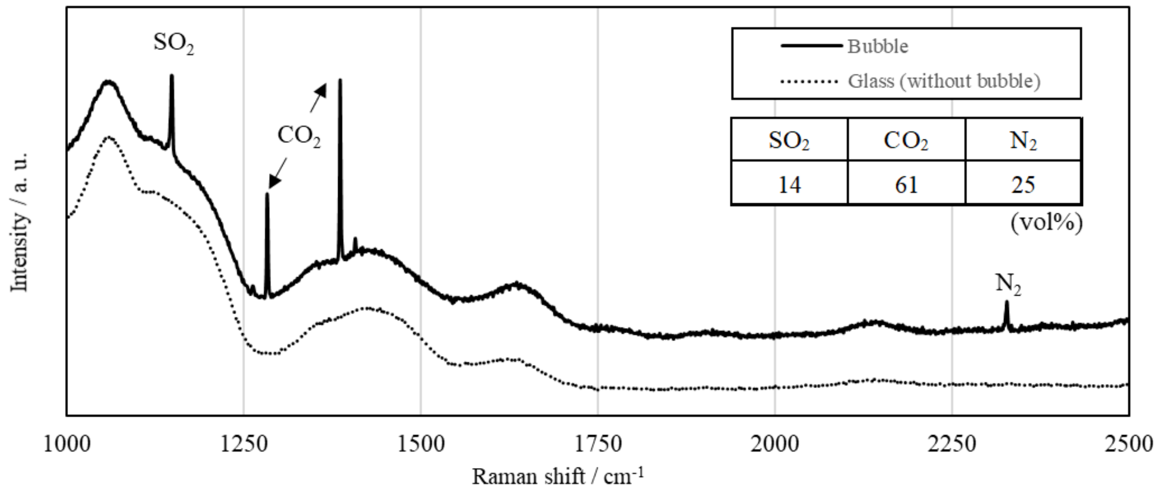

Figure 1. Raman spectrum of bubbles with a diameter of about 25 μm and the gas composition ratio.

4. Bubble gas change experiment using Raman spectroscopy

One of the advantages of Raman spectroscopy is non-destructive analysis. Therefore, analysis more than once can be performed on a same bubble. Heat treatment and analysis were carried out repeatedly for specific bubbles in soda lime glass. We will introduce the results of the gas composition change and the bubble size change during the heat treatment (Figure 2). Information on changes in the gas composition and diameter of bubbles in the glass melt is very useful for estimating the source of bubbles.

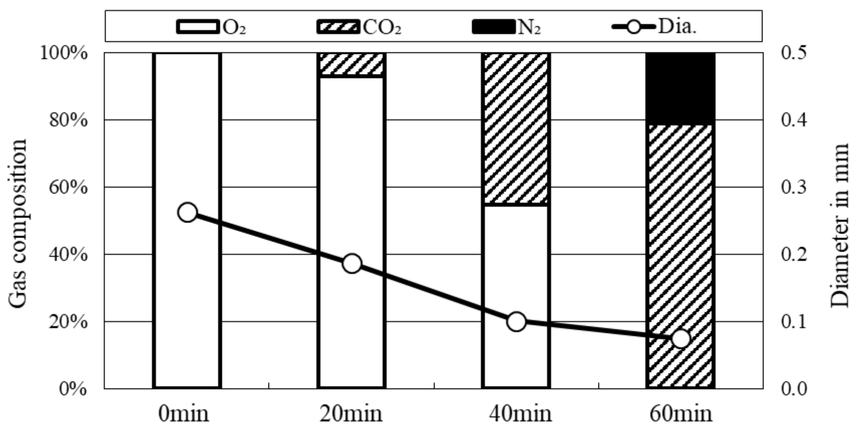

Figure 2. Changes in gas composition and size of a bubble in soda lime glass with a heat-treatment at 1250 °C.