수정진동자를 이용한 결정생성의 측정

최희석, 정옥진, 김영한*, 김상렬
동아대학교 화학공학과
(yhkim@mail.donga.ac.kr*)

Crystallization Measurement Using a Quartz Crystal Sensor

Hee Seok Choi, Ok Jin Joung, Young Han Kim* and Sang Yeul Kim
Dept. of Chemical Engineering, Dong-A University
(yhkim@mail.donga.ac.kr*)

Introduction

Because the introduction of seed material to a quasi-stable supersaturated solution induces the initiation of crystallization, monitoring the state of crystallization solution is an important job to find the optimum moment of the seed introduction. The moment controls the size distribution and shape of crystal product, which are prime factors of the product quality. The solution monitoring is mostly conducted indirectly by detecting solution temperature and analyzing its chemical composition. However, the indirect measurement is prone to make errors from sample handling and inaccurate chemical analysis.

A direct measurement technique of supersaturation with an interdigital transducer and a surface acoustic wave sensor was developed by Löffelmann and Mersmann[1,2]. By lowering temperature of the sensor surface, subcooled solution produces crystal on the sensor surface to result in the decrease of the wave frequency of the sensor. It was found that the frequency reduction is proportional to the mass of the crystal formed on the sensor surface. A similar technique using a quartz crystal sensor was utilized in the monitoring of crystal formation[3]. The initiation temperature of crystal formation is found with the sensor.

In this study, the direct monitoring technique using the quartz crystal sensor is applied to the crystallization process of potassium bromide to monitor the crystallization and dissolution of solute and to measure hysteresis between the temperatures of the crystallization initiation and the end of crystal dissolution. The behavior of supersaturated solution near the temperatures of crystallization and dissolution is important to determine the moment of seed introduction for the control of crystallization product quality and to find the optimum condition for mother solution preparation.

Experimental

1. Experimental setup

Two sets of liquid circulation systems for salt solution and coolant are installed in the experimental apparatus as shown in Figure 1. The solution temperature is maintained in a thermostat, and the solution is circulated through the left hand side of the sensor module demonstrated in Figure 2. The coolant flows to the right hand side of the module where a

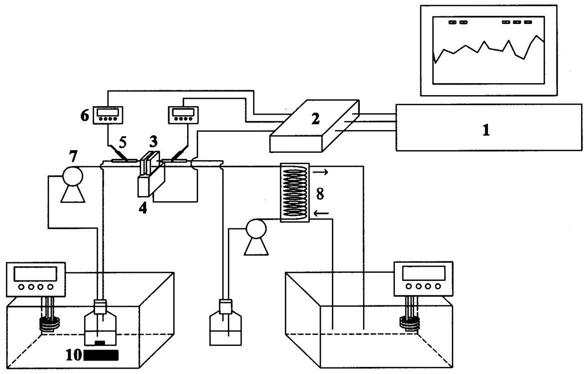

Fig. 1. Experimental setup.

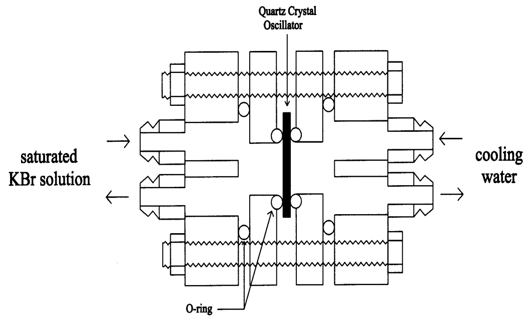

Fig. 2. Schematic diagram of sensor module.

quartz crystal sensor is installed in the middle. The coolant temperature is adjusted in a heat exchanger cooled by cooling water drawn from another thermostat. The temperature is manipulated by controlling the flow rate of the cooling water. Reason to utilize the heat exchanger is that coolant temperature control is easier than direct temperature adjustment using the thermostat due to the large heat transfer area of the heat exchanger. An oscillation circuit contained in the box beneath the sensor module is directly connected to the quartz crystal sensor to prevent possible weakening of the electric signal from the sensor. Temperatures of the salt solution and the coolant are measured with a platinum resistance thermometer of 1 mm in diameter (Okazaki, Japan, model PT100). The measured temperature is displayed with an indicator, and electric temperature output is provided to an A/D converter for the transmission of temperature data to a PC. The oscillation is counted using a home-made frequency counter, and resonant resistance is measured with a built-in amplifier in the counter. The digital signals of resonant frequency, resonant resistance and two temperature measurements are provided to a PC for data processing.

An AT-cut quartz crystal having a base frequency of 8 MHz (Sunny Electronics Co., Korea) is utilized in this experiment. The electrode of the crystal is silver finished. The sensor is a circular disc of 9 mm in diameter and 0.2 mm in thickness. The sensor is placed in vertical position in order to prevent the sedimentation of crystals and foreign suspended particles. Potassium bromide (Kanto Chemical Co., Inc., Japan, special grade reagent) is used as crystallization solute, and ethanol (Kanto Chemical Co., Inc., Japan, special grade reagent) is utilized as a coolant.

2. Experimental procedure

Saturated solution of potassium bromide is prepared at the temperature of 20℃ in a glass bottle of 500 mL in volume, and is put in a thermostat. Though the saturation temperature of the solution is 20℃, the experiment is conducted at the temperature of 22℃ in order to prevent crystal formation in connecting tubes. The bottle is placed on top of an immersion-type magnetic stirrer to agitate the solution. After the solution temperature settles down, it is introduced to the left room of the sensor module. When the sensor frequency is stable, the coolant is fed to the right room of the module. The flow rates of solution and coolant are the same at 7 mL/min. While the solution temperature is maintained at 22℃, the

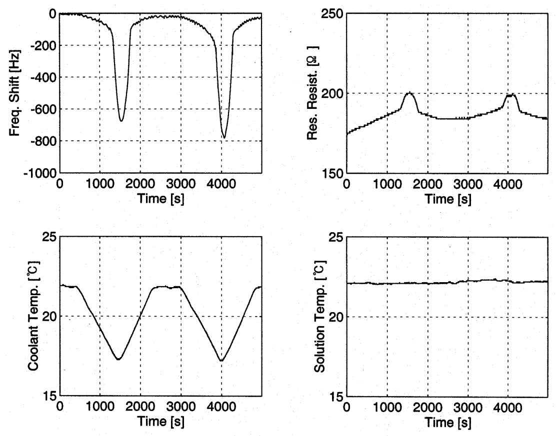

Fig. 3. Variation of resonant frequency and resistance with temperatures of coolant and potassium bromide solution.

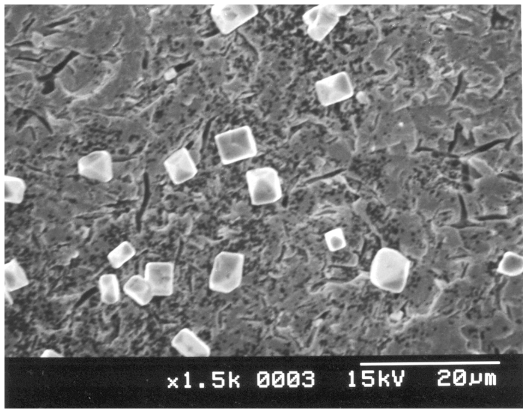

Fig. 4. An SEM photograph of potassium bromide crystals on sensor surface.

coolant temperature is lowered about 5 degrees from 22℃ at the rate of 0.5 degrees per minute and raised back to the initial temperature. This procedure is carried out twice. Along with the measurements of resonant frequency and resistance of the sensor, temperatures of the solution and coolant are collected and stored to a PC for the data analysis of the experiment.

Results and discussion

The variation of resonant frequency with coolant temperature is described in the left two plots in Figure 3. While the solution temperature is maintained at 22℃ as shown in the bottom of right hand side, the coolant temperature is lowered by 4.6℃ and raised back and the same procedure is applied again. As the coolant temperature is reduced, the surface temperature of quartz crystal sensor decreases and crystallization occurs on the surface. The quartz sensor is so thin that the solution in contact with the sensor is readily cooled to produce the crystal. When the crystal is formed on the sensor surface as illustrated in Figure 4, the resonant frequency drops and is raised back with the elevation of coolant temperature due to crystal dissolution. The resonant resistance increases as the crystal is produced, but the variation is not much because the crystal is so sparsely located on the sensor surface that the horizontal movement of the quartz plate of the sensor is partly restricted.

Because the decrease of resonant frequency indicates crystal formation, monitoring the frequency gives the temperature of crystallization initiation. The behavior of subcooled solution is directly observed from the frequency measurement. As the coolant temperature is lowered, the frequency decreases as shown in Figure 5. The section marked "A"of slow variation indicates the frequency drop caused by sensor cooling. When the crystallization begins, fast decrease denoted with "B"of the frequency occurs to demonstrate large buildup of crystal mass on sensor surface. On the other hand, the frequency of section C increases with rise of the coolant temperature, which means that the formed crystal on the sensor surface dissolves back in the solution. After the completion of the crystal dissolution, the slow increase of frequency in section D is of sensor temperature variation.

The intersection of two straight lines drawn from sections A and B gives the initiation temperature of crystal formation. Likewise, the intersection of lines of sections C and D

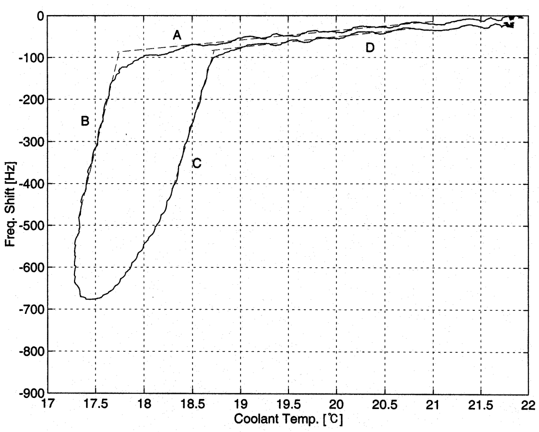

Fig. 5. Resonant frequency variation curve with coolant temperature and hysteresis measurement of the first cycle of experiment.

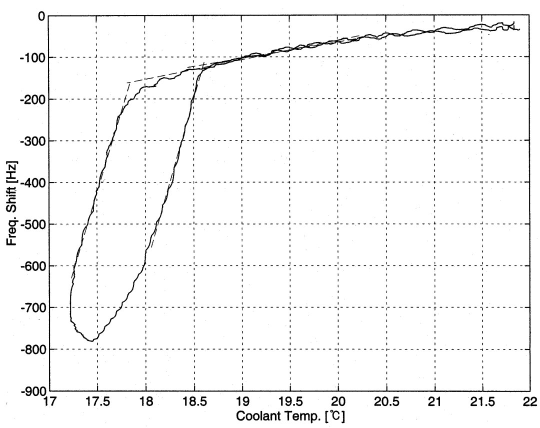

Fig. 6. Resonant frequency variation curve with coolant temperature and hysteresis measurement of the second cycle of experiment.

shows the completion temperature of crystal dissolution. The difference between two temperatures, which is 0.98℃ in this case, is a measure of the hysteresis in the process of crystallization and dissolution. This information is useful to manipulate solute concentration and temperature of mother solution in crystallization process. The same analysis is applied to the second cycle of coolant temperature manipulation, and the outcome is described in Figure 6. The shape of the curve is similar to the previous result, but the hysteresis is 0.76℃ in this cycle. The smaller hysteresis is due to the faster temperature variation than the first cycle.

Conclusion

A direct monitoring technique using a quartz crystal sensor is applied to monitor crystal formation and dissolution in potassium bromide solution and to measure hysteresis between the initiation temperature of crystal formation and the completion of dissolution. The experimental outcome indicates that the monitoring shows a detailed process of crystallization, and hystereses of 0.98℃ and 0.76℃ depending on the rate of temperature change are yielded. In other words, the direct monitoring technique can be utilized to manipulate the temperature and solute concentration of the mother solution in a crystallization process for high quality crystal products. It is also shown that the proposed sensor is simple and efficient to be employed in practical crystallization processes.

References

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