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

Measurement of Supersaturation with a Quartz Crystal Sensor

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

1. Introduction

In crystallization, introduction of seed material and manipulation of solution temperature depend mainly upon supersaturation degree of the salt solution. The quality of crystallization product is determined from the size distribution and shape of crystal, which are resulted from the process manipulation.

Though the supersatuaration is an important operating variable in the crystallization, its direct measurement is unavailable with the conventional equipments of process measurement. The concentration and temperature of the solution have been being utilized to indirectly determine the supersaturation. Yet an accurate evaluation with the measurements is not simple because small variation of the measurements leads to large error in the supersaturation determination. Therefore, an in-line measurement technique is preferred for the elimination of possible state variation while transporting the sample solution to be measured. In sugar industry, for instance, an in-line refractometer has been implemented for the continuous measurement of the sugar concentration to predict the supersaturation degree.

A direct measurement technique of supersaturation with an interdigital transducer (IDT) and a surface acoustic wave (SAW) sensor was proposed by Löffelmann and Mersmann [1]. By lowering temperature of the sensor surface, subcooling of sample solution is induced to produce crystal on the sensor surface resulted 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 [2]. The determination of nano-scale mass variation and micro-scale variation of rheological property of a thin film on the sensor surface is available with the quartz crystal sensor. A mass variation from organic vapor adsorption was detected with the quartz crystal sensor [3], and a micro-variation of surface roughness caused by metal corrosion process was also determined with the sensor [4].

In this study, the monitoring procedure of crystal formation using a quartz crystal sensor is extended to directly measure the supersaturation degree. The measurement with the quartz crystal sensor is conducted with saturated potassium chloride, potassium bromide and potassium nitrate solutions by cooling the sensor surface to induce crystal formation. Temperature of the sensor surface is controlled with cooling liquid flowing through the back of the sensor. For the in-line application of the sensor in a practical crystallization process, a flowing sample system is developed and utilized in this experiment. The crystal formation is detected with the variation of resonant frequency, and the sensor surface with the crystal is observed with a scanning electron microscope for the analysis of experimental outcome. The supersaturation degree is obtained from the temperature at the moment of the initial crystal formation and saturation solubility.

2. Experimental

2.1 Preparation of Sensor Module

In the middle of the module, a quartz crystal sensor is placed and two polyethylene plates are installed to build a housing for each sides of the sensor. Two separate flow systems of saturated salt

solution and cooling ethanol provide liquid flow to the chambers. The plates are square, and the thickness of the plates is 3 mm for inner side and 5 mm for outer side. Four o-rings are placed between the plates and the sensor. 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 placed in vertical position in order to prevent the sedimentation of crystals and foreign suspended particles.

2.2 Experimental Setup

Two sets of temperature control and liquid circulation systems for salt solution and coolant are installed in the experimental apparatus. The sensor module locates in the middle of the setup and the salt solution is fed from the left hand side, and the cooling ethanol is provided from the right. Two thermostats are utilized for the control of temperatures of the solution and coolant.

An oscillation circuit contained in the box beneath the sensor module is directly connected to the quartz crystal to prevent possible weakening of the electric signal from the sensor. Temperatures of the salt solution and the coolant are measured with a tiny platinum resistance thermometer of 0.9 mm in diameter and 15 mm long (Konics Instrument, Korea, Model C100/09158). The prepared sensor is installed in a specially designed sensor module, and two leads of the sensor are directly connected to an oscillation circuit for the minimum noise to the signal. 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 and resonant resistance are provided to a PC for data processing.

2.3 Experimental Procedure

Patassium chloride (Kanto Chemical Co., Inc., Japan, special grade reagent) is dissolved into distilled water of 300 mL contained in a 500 mL glass bottle to the saturated concentration at the temperature of 30 °C. The bottle is placed in a thermostat to be maintained at the temperature. Two bottles of the cooling ethanol (Kanto Chemical Co., Inc., Japan, special grade reagent) are prepared, and one is put in the thermostat of the salt solution and the other is in a separate thermostat adjusted for cooling at lower temperature. The coolant temperature is manipulated according to experimental procedure. Potassium bromide and potassium nitrate (Kanto Chemical Co., Inc., Japan, special grade reagent) are also used for different experiments with the same experimental procedure.

The sensor module is placed on top of the oscillator and the two conductors of a quartz crystal sensor are attached to the connector of the oscillator in vertical position. In the beginning, the saturated solution is fed to the left chamber of the module at the flow rate of 5.5 mL per minute. To the right chamber, the coolant is provided from the bottle stored in the same thermostat that holds the solution bottle at the flow rate of 8 mL per minute. After the flow settles, the coolant of lower temperature kept in the other thermostat is supplied by rotating two three-way valves. The temperature of the coolant is lowered in the first half of the experiment and is raised back for the dissolution of the produced crystal. The temperature of salt solution and the flow rates of the salt solution and coolant are kept constant during the experiment. In an experimental run, resonant frequency and resistance of the sensor and temperatures of the solution and coolant are continuously measured and collected by a PC for data analysis.

3. Results and discussion

The variation of frequency is represented as frequency shift from the base frequency of a quartz crystal sensor and displayed in the upper left diagram in Figure 1. That of resonant resistance and two temperatures of the coolant and potassium chloride solution are also shown in the figure. All four are simultaneously measured and illustrated in the same time scale. When the flows of the salt solution and coolant of the same temperature are settled, the coolant of lower temperature is applied as indicated in the lower left picture of Figure 1. As the coolant temperature drops, the resonant frequency decreases to indicate the crystal formation on the sensor surface. The mass buildup from the

crystal deposit on the sensor surface causes the frequency reduction, and therefore the frequency change indicates the crystal formation. The photograph of a scanning electron microscope demonstrates the crystal particle in Figure 2. The formation induces the elevation of surface roughness to result in the increase of resonant resistance as given in the upper right figure in Figure 3. When the coolant temperature is raised back, the produced crystal is slowly dissolved to raise the frequency and to lower the resistance to the initial values. For the close examination of the beginning of crystal formation, the variation of resonant frequency along with temperature difference between the salt solution and sensor surface is illustrated in Figure 3. The initial formation is observed at the moment in 562 seconds from the drop of the frequency. The drop indicates that a small amount of crystal is formulated on the sensor surface. Though the variation is not steady in the early stage due to the unstable formation of the crystal, the frequency reduction is continued and finally decreases in high rate.

The measurement shows that the initial formation is yielded with temperature difference of 1.7 °C at the cooling rate of about 3°C per minute. When the supersaturation is expressed as a difference in concentration, its computation formula is

$$\Delta c \;=\; c - c^* \tag{1}$$

where c is salt concentration in g/L and c^* is saturation concentration at the same temperature. Therefore, the saturation concentration, 365.2 g/L, at the initial temperature of crystal formation of 28.3°C and the saturation concentration, 370 g/L, at the solution temperature of 30°C give the supersaturation of 4.8 g/L for the potassium chloride solution with the cooling rate of 3 °C per minute. It means that the solution can be supersaturated up to 4.8 g/L at the temperature of 28.3°C when the cooling rate of 3 °C per minute is applied. This information is useful to manipulate the solution temperature in a crystallization process where the prediction of crystal formation and the control of crystal growth are necessary for the control of product quality.

For the inspection of the outcome, the crystallization is conducted in a glass beaker and observed the crystal formation with a naked eye. The formation is detected when the solution is cooled to the temperature of 27.4 °C. In this case the cooling is maintained at the rate of 3 °C per minute as in the sensor measurement. The experimental results are summarized in Table 1. In order to observe the crystal formation with an eye, the crystal size has to be much larger than that on the sensor surface, and therefore the temperature in the beaker test is lower than that in the sensor experiment. In other words, an early determination of the crystal formation is possible with the sensor, and an accurate measurement of the supersaturation is available.

Though it is difficult to monitor the early stage of crystallization process with conventional techniques due to tiny size of the produced crystal and difficulty to maintain the supersaturated state, the detection using a quartz crystal sensor provides a good means of the monitoring of the crystallization and supersaturation measurement. The sensor system is relatively simple to be implemented in practical processes, and it has in-line availability for the continuous monitoring and direct control of the processes. In addition, the elimination of sampling process required in the conventional measurement method of the supersaturation reduces a possible error in temperature measurement and the chance of impurity contamination. This increases the measurement accuracy of the proposed sensor system.

4. Conclusion

A measurement technique of supersaturation for crystallization processes using a quartz crystal sensor is proposed, and its performance is examined by applying to the crystallization of three different salt solutions. Direct cooling of the sensor induces crystal formation on the sensor surface. When the beginning of the formation is detected with the variation of resonant frequency, the solution and sensor temperatures are utilized to calculate solubility difference, i.e., supersaturation.

For the performance evaluation of the proposed system, it is applied to the crystallization of three different salt solutions and the supersaturation is measured. The experimental outcome is examined with eye observation result, and is analyzed with the microscopic photograph of the produced crystal. The application indicates that the proposed technique is effective and useful to the microscopic monitoring of crystallization in early stage and supersaturation measurement. The system also has the availability of in-line application for the continuous and computerized measurement and control of crystallization processes.

Acknowledgment

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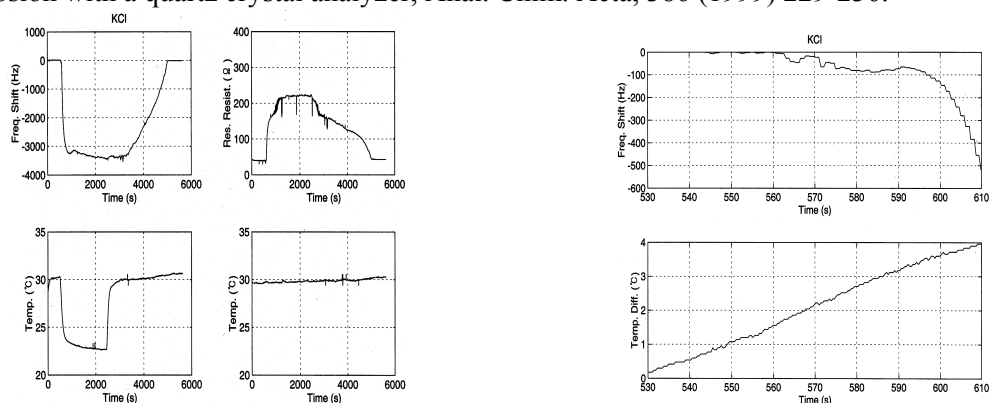

Figure 1. Variation of frequency shift and resistance. Figure 3. Frequency shift and temp. difference.
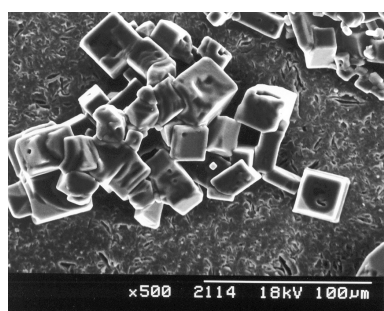

Figure 2. An SEM photograph.

Table 1. Comparison of sensor measurement and observation result of the initial temperature of crystallization and calculated supersaturation for the salt solution at the temperature of 30°C.

salt	initial temperature (°C)		cooling rate (°C/min.)	supersaturation (g/L)
	sensor	observation		
KCl	28.3	27.4	3	4.8
KBr	29.1	27.2	3.5	9.6
KNO3	29.0	26.5	2.5	13.9