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Crystal shape monitoring and supersaturation measurement in cooling crystallization with quartz crystal oscillator

Byoung Chul Kim, Hyun Woog Kang and Young Han Kim†

Dept. of Chemical Engineering, Dong-A University, Busan 604-714, Korea
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Abstract–A crystallization monitoring system using a quartz crystal oscillator was utilized to predict different shapes of crystal formation by measuring crystal growth rate and to measure supersaturation. Applying different rates of cooling, crystal formation of different shapes was induced, and the frequency variation of the oscillator and the crystal shape observed with an SEM were compared to determine how the frequency variation can be interpreted for the prediction of produced crystal shape. The experimental results obtained from the crystallization of potassium nitrate and cupric sulfate solutions showed that the proposed frequency measurement technique could be applied in the prediction of crystal shape of cooling crystallization processes. In addition, supersaturation was determined from the measurements of solution and coolant temperatures.

Key words: Crystallization, Crystal Shape, Quartz Crystal Oscillator, Crystallization Monitoring

INTRODUCTION

The shape of a crystallization product is a key factor in controlling crystallization processes, because the shape determines the product quality. The shape disparity often incurs a large difference in the product price. Though the product shape and growth are controlled by the introduction time of seed crystals and the temperature adjustment of crystallization solution in cooling crystallization, the control for a desired crystal shape largely depends upon the experience of an operator, because the measurement of solution state is difficult for the prediction of the product shape. In practice, the solution concentration and temperature are measured to determine the seed introduction moment and the cooling rate of solution, but accurate determination is not simple because a small error in the concentration and temperature measurements leads to a large difference of the product quality.

A direct monitoring system of the crystallization processes using an interdigital transducer (IDT) and a surface acoustic wave (SAW) sensor was introduced by Löffelmann and Mersmann [2002a, b]. By lowering temperature of the sensor surface, a cooling crystallization of sample solution was induced to form crystals on the surface and to reduce the wave frequency of the sensor. The frequency decrease is proportional to the crystal mass formed on the sensor surface, which can be utilized in the temperature control of the crystallization solution. Similarly, a quartz crystal oscillator has been widely used owing to its size and simplicity of the measurement in the determination of nano-scale variation of mass and rheological property of a thin film contacting the oscillator surface. The quartz crystal oscillator has also been implemented in the monitoring of crystal formation at the beginning stage of cooling crystallization processes [Kim et al., 2003; Joung et al., 2005a, b].

In this study, the monitoring system of the quartz crystal oscillator was employed in the prediction of crystal shape from two crystallization processes of potassium nitrate and cupric sulfate. A controlled cooling crystallization was induced on the oscillator surface, and the frequency variation was measured and compared with the result of microscopic observation of produced crystals. From the experimental outcome, the availability of the crystal shape prediction using the oscillator system was examined here. Also, it was indicated that the supersaturation of crystallization solution could be determined from the monitoring system.

†To whom correspondence should be addressed.
E-mail: yhkim@mail.donga.ac.kr

EXPERIMENTAL

1. Preparation of Sensor Module

A schematic diagram of the sensor module is demonstrated in Fig. 1. Two rooms of salt solution and cooling ethanol were separated with a quartz crystal oscillator, and two polyethylene plates and two o-rings were used to build a room on each side of the oscillator. Two pumps provided separate flows of saturated salt solution and cooling ethanol to the rooms. The plates were square, and their thicknesses were 3 mm for inner side and 5 mm for outer side. An AT-cut quartz crystal oscillator having a base frequency of 8

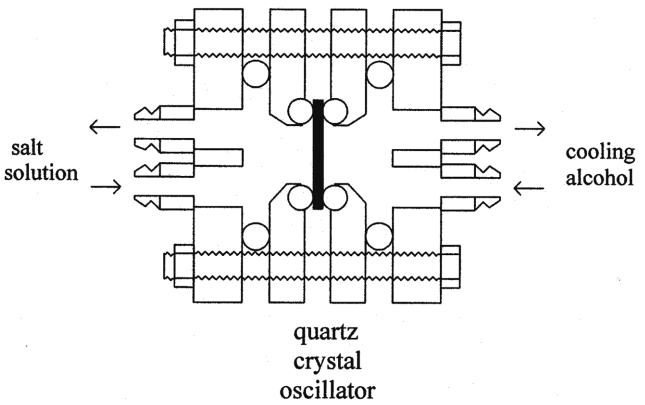

Fig. 1. A schematic diagram of the sensor module for in-line measurement.

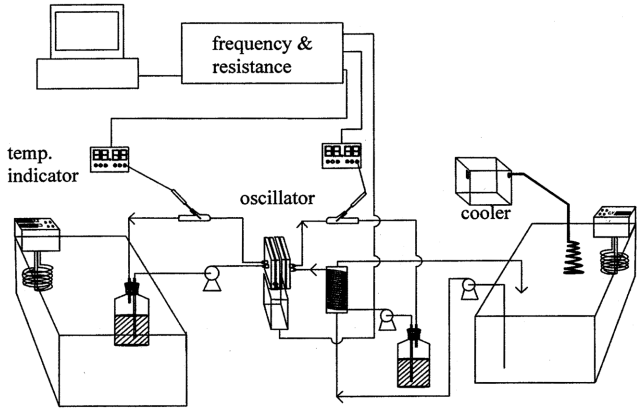

Fig. 2. A schematic diagram of the experimental setup with liquid flows and electrical wiring.

MHz (Sunny Electronics Co., Korea) was utilized in this experiment. The electrode of the crystal was silver finished. The oscillator was placed in vertical position in order to prevent the sedimentation of floating crystals and foreign suspended particles.

2. Experimental Setup

Two sets of temperature control and liquid circulation systems for salt solution and coolant were installed in the experimental apparatus as shown in Fig. 2. The oscillator module located in the middle of the setup and the salt solution was fed from the left hand side, and the coolant was provided from the right. Two thermostats were utilized for the control of temperatures of the solution and coolant. For fast manipulation of coolant temperature a glass heat exchanger was used, and a water containing thermostat supplied temperature adjusted water to the heat exchanger. The temperature of cooling ethanol was manipulated by the water temperature. The temperature of the thermostat was controlled with a programmable temperature controller.

An oscillation circuit contained in the box beneath the sensor module was directly connected to the quartz crystal oscillator to prevent possible weakening of the electric signal from the oscillator. Temperatures of the salt solution and coolant were measured with a tiny platinum resistance thermometer of 0.9 mm in diameter and 15 mm long (Konics Instrument, Korea, Model C100/09158). The oscillation frequency was counted by using a home-made frequency counter, and resonant resistance was measured with a built-in amplifier in the counter. The digital signals of resonant frequency and resonant resistance were provided to a PC for data processing.

3. Chemicals

Two salts, potassium nitrate (Katayam Chemical, Japan, Code No. 24-5020) and cupric sulfate (Shinyo Pure Chemicals, Japan, 1st grade) were used as received in this experiment. Ethanol (Hayman, U. K., Code No. 200-578-6) were utilized as a coolant.

4. Experimental Procedure

An amount of 11.7 g of potassium nitrate was dissolved into distilled water of 300 mL contained in a 500 mL glass bottle to saturated concentration at 25 °C. The bottle was placed in a thermostat to be maintained at the temperature. The sensor module was assembled, and the electric wires were connected to make the signal steady. A bottle of cooling ethanol was prepared, and the ethanol was pumped to the glass heat exchanger. The water from the other thermostat was supplied to the heat exchanger with a pump. The

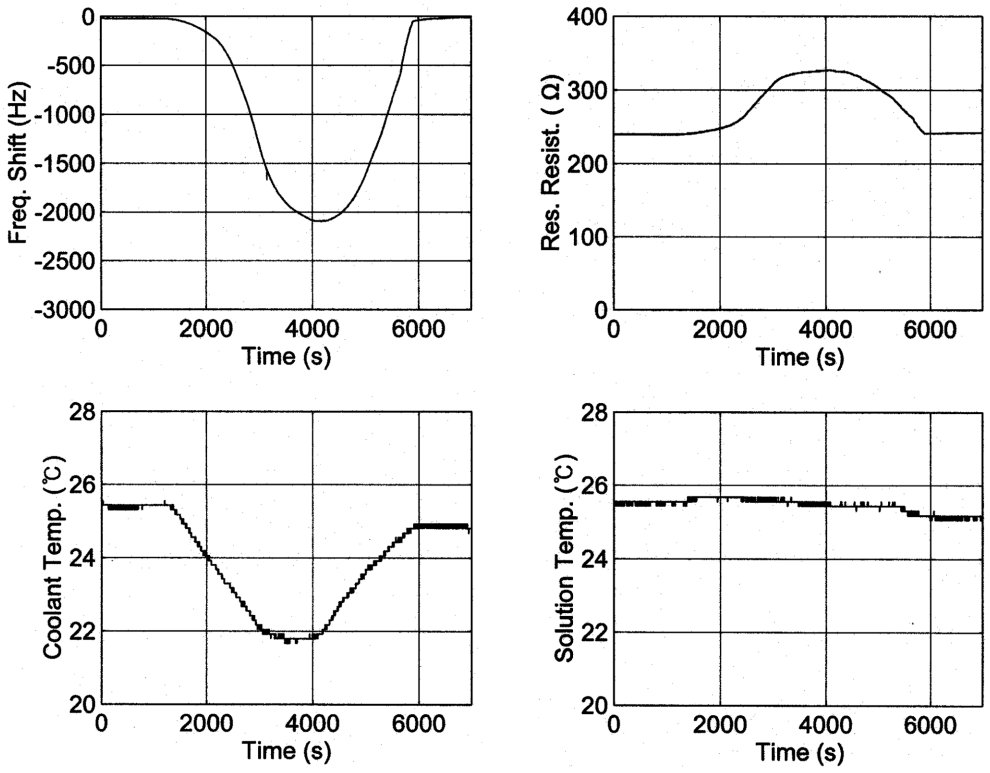

Fig. 3. Variations of resonant frequency and resistance, and coolant and solution temperatures in a slow cooling crystallization of potassium nitrate (Run-1).

temperature adjusted ethanol from the exchanger was supplied to the sensor module at a flow rate of 7 mL/min after half an hour settlement of the sensor module. When the oscillation frequency was steady, the saturated potassium nitrate solution was provided to the left hand side of the sensor module at a rate of 7 mL/min. When the oscillation frequency was stable again, the programmable temperature controller for coolant temperature adjustment was activated and the measurement of resonant frequency and resistance was initiated. The manipulation of coolant temperature was determined at the beginning of the experiment, and the resonant frequency and resistance, and the temperatures of solution and coolant were stored in a PC for the analysis of experimental result. The experiment was conducted again with cupric sulfate by the same procedure explained above.

After the experiment the sensor module was disassembled to take out the oscillator with crystals on it for the observation of crystal shape. The oscillator surface was carefully rinsed with ethanol, and dried to observe the surface with a scanning electron microscope (Hitachi High-Technologies, Japan, Model S-2400). In cases of experimental run-1 and run-2, the produced crystal was dissolved to inspect the oscillator stability by checking the initial frequency and resistance. Therefore, the same experiment of crystal production was conducted again to obtain the oscillator with the crystal. The cooling rate was adjusted at the same as the frequency measurement until sufficient crystals were made on the oscillator, which was taken for the microscopic observation.

RESULTS AND DISCUSSION

The variations of resonant frequency and resistance are shown in the top two figures of Fig. 3. While the temperature of potassium nitrate solution was maintained the same, the coolant temperature was reduced to induce the crystal formation and raised to dissolve the crystal. The frequency decrease indicates the crystal formation, and the elevation of resonant resistance demonstrates the increase of surface roughness due to the formation. As the crystals dissolve, the frequency and resistance return to the initial values. The cooling rate and frequency dropping rate are listed in Table 1. A similar experiment was conducted with higher rate of coolant temperature variation, and the outcome is described in Fig. 4.

Table 1. List of cooling rate and frequency decreasing rate

Run	Salt	Cooling rate (°C/min)	Frequency drop (Hz/min)	Crystal shape
1	KNO_3	0.11	114	orthorhombic
2	KNO_3	0.29	176	cubic
3	$CuSO_4$	0.25	154	triclinic
4	$CuSO_4$	0.31	183	acicular

One can predict that a slow cooling crystallization of salt solution produces crystals of its intrinsic shape, but the critical cooling rate is hard to determine. By monitoring the resonant frequency variation of a quartz crystal oscillator the crystallization rate can be determined because the frequency reduction is proportional to the mass increase of the crystals produced. To compare the crystallization product of potassium nitrate in two different rates of cooling, the cooling crystallization having the same profile of cooling as shown in Figs. 3 and 4 was conducted and the oscillator was taken at the

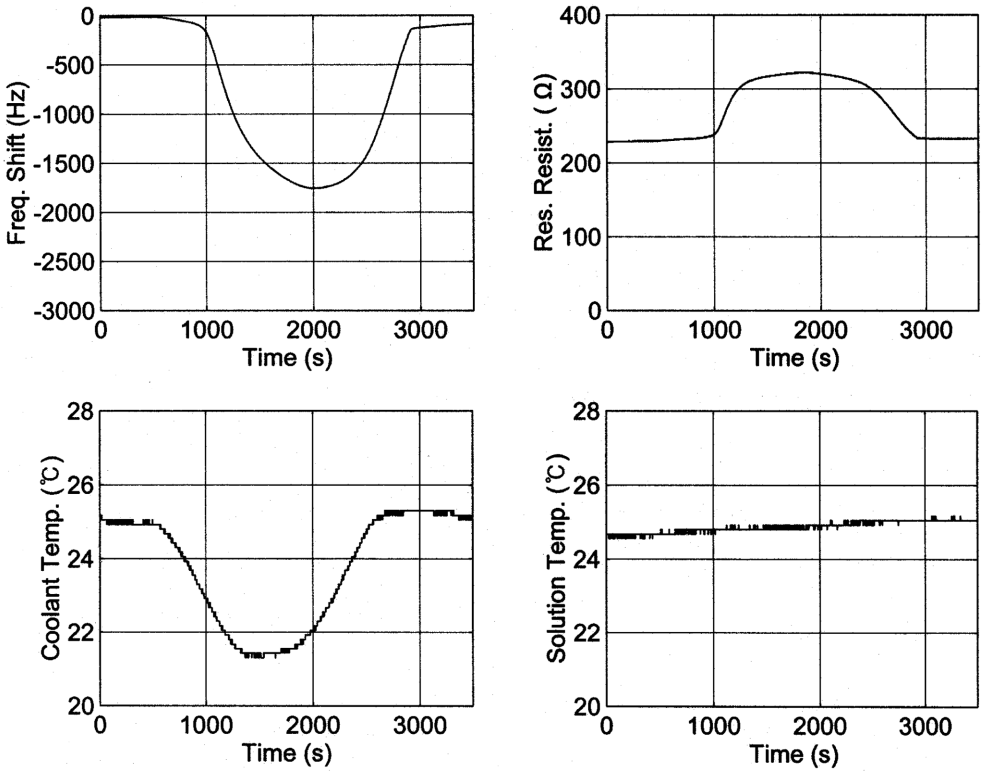

Fig. 4. Variations of resonant frequency and resistance, and coolant and solution temperatures in a fast cooling crystallization of potassium nitrate (Run-2).

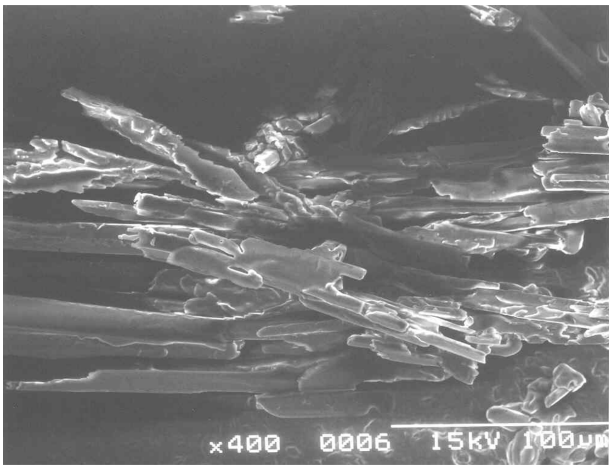

Fig. 5. A SEM photograph of orthorhombic crystalline formed from a slow cooling crystallization of potassium nitrate (Run-1).

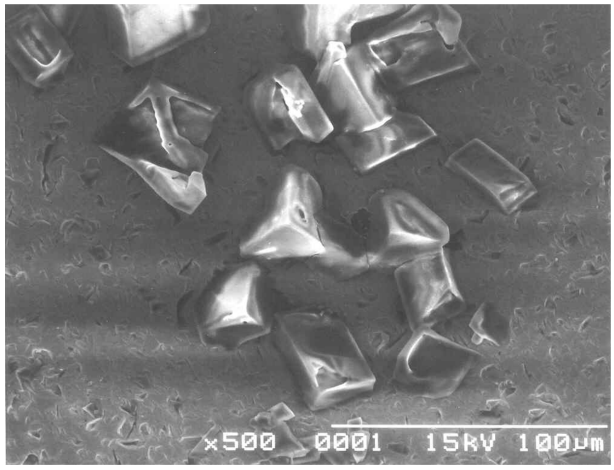

Fig. 6. A SEM photograph of crystalline formed from a fast cooling crystallization of potassium nitrate (Run-2).

lowest coolant temperature for the microscopic observation of the crystals formed. Fig. 5 illustrates the crystals from slow cooling of run-1, whereas Fig. 6 does those from fast cooling of run-2. The intrinsic crystal shape of potassium nitrate is orthorhombic, and the SEM photograph of slow cooling crystallization shows the shape. However, the fast cooling crystallization produces a different shape of product as demonstrated in Fig. 6.

The measurement of resonant frequency with a quartz crystal oscillator indicates the difference of crystal growth rate, which can be used to predict the shape of crystallization product. In Table 1, the frequency decreasing rate is given to show the difference of crystal shape. While the slow cooling leads to a rate of 114 Hz/min, the fast does to a rate of 176 Hz/min. Therefore, the crystal shape can be predicted by monitoring the frequency variation of a quartz crystal oscillator in cooling crystallization.

The same procedure of the cooling crystallization and monitoring explained above was implemented to cupric sulfate solution. The monitoring results of resonant frequency and resistance along with temperatures of salt solution and coolant are shown in Figs. 7 and 8, which demonstrate crystallization process for slow and fast cooling, respectively. The cooling rates and frequency decreasing rates are summarized in Table 1. As explained above, the slow cool-

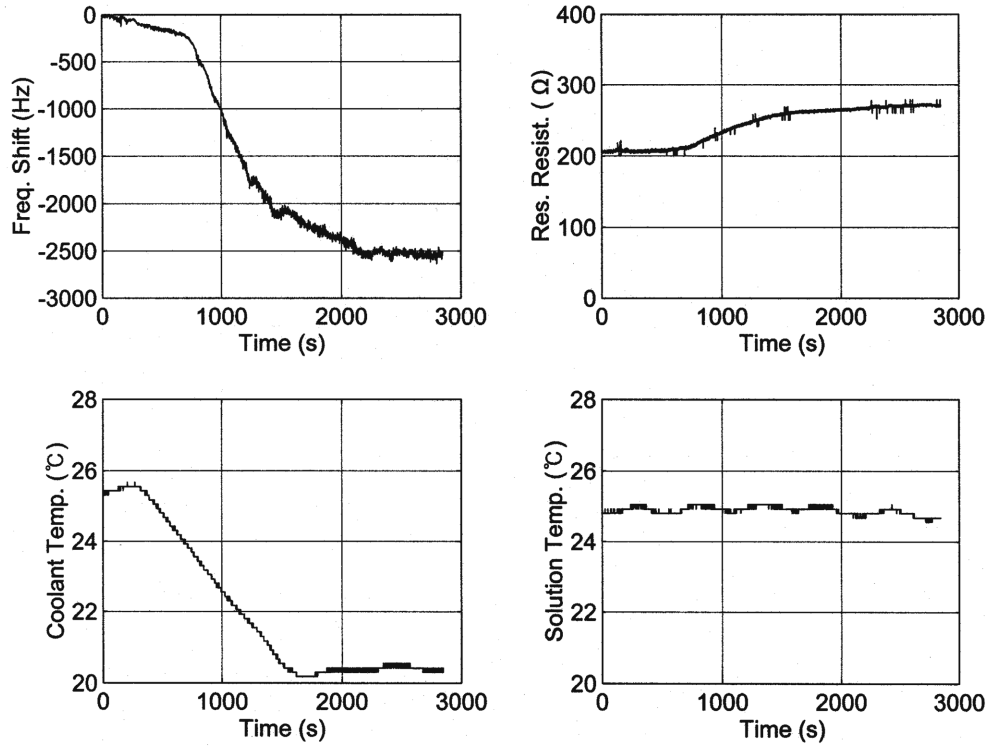

Fig. 7. Variations of resonant frequency and resistance, and coolant and solution temperatures in a slow cooling crystallization of cupric sulfate (Run-3).

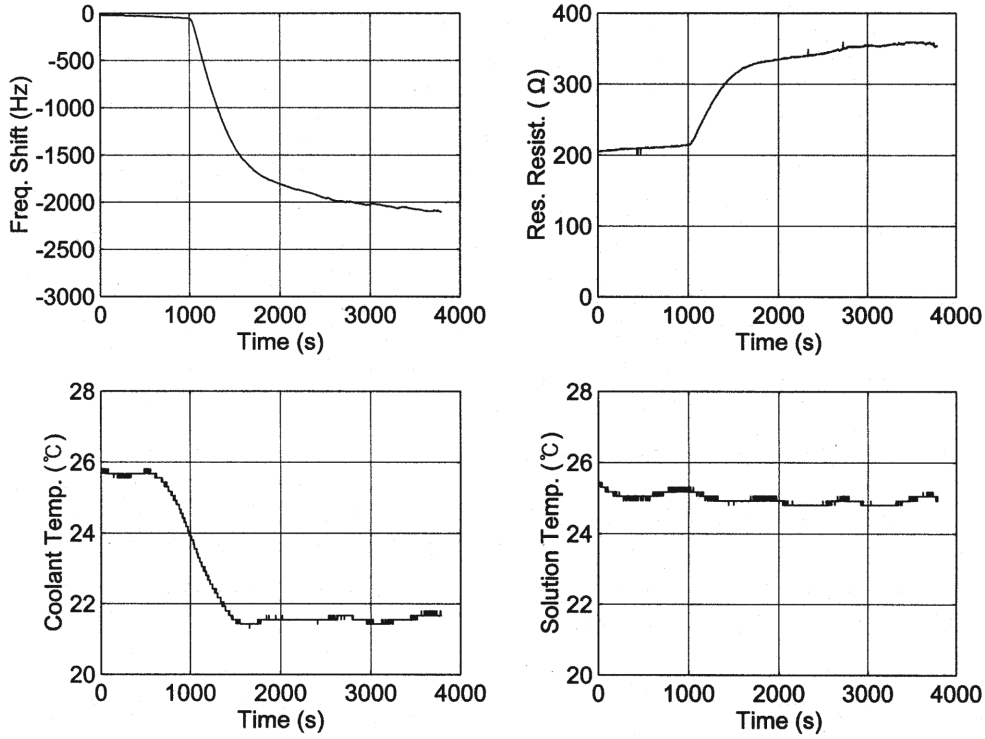

Fig. 8. Variations of resonant frequency and resistance, and coolant and solution temperatures in a fast cooling crystallization of cupric sulfate (Run-4).

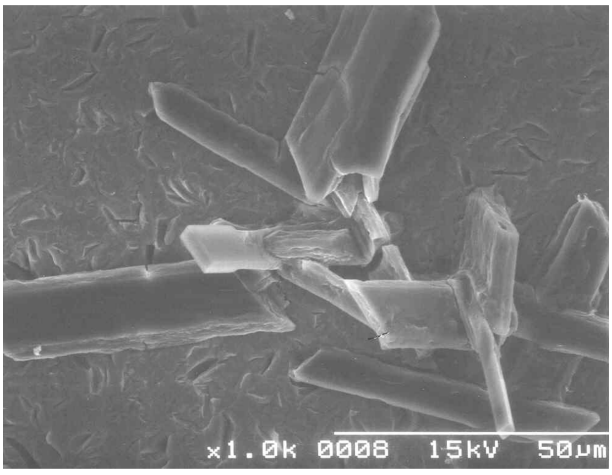

Fig. 9. A SEM photograph of triclinic crystalline formed from a slow cooling crystallization of cupric sulfate (Run-3).

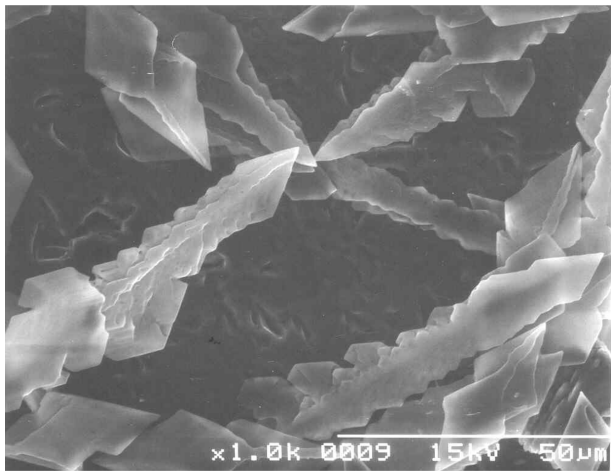

Fig. 10. A SEM photograph of crystalline formed from a fast cooling crystallization of cupric sulfate (Run-4).

ing leaves the intrinsic shape of triclinic crystals demonstrated in Fig. 9, whereas acicular crystals formed from fast crystallization are shown in Fig. 10. The frequency decreasing rate indicates the difference of crystal shapes, which again proves that the monitoring the frequency variation can predict the shape of crystallization product. The variation of resonant frequency does not directly predict the crystal shape from a cooling crystallization process. However, the crystal shapes yielded from a practical crystallization process are known, and the manipulation of solution temperature is necessary to obtain the crystallization product of a desired shape. The proposed device can be utilized in the direct monitoring of crystal growth, which leads to the prediction of a crystal shape from the known shapes of a crystallization process.

When crystallization begins, the resonant frequency of a quartz crystal oscillator drops fast due to the mass loading of the produce crystal on the oscillator surface. The frequency curve indicates the initiation moment of crystallization, and the temperatures of solution and coolant at the moment found as described in Joung et al. [2005b] are listed in Table 2. Because the crystallization initiation gives a change in the frequency curve, the initiation moment is obtained from the two asymptotes of the curve. The supersaturation was calculated from the difference of equilibrium solubility at the

Table 2. List of solution and coolant temperatures at the beginning moment of crystallization and supersaturation

Run	Salt	Solution temp. (°C)	Coolant temp. (°C)	Supersaturation (g/L)
1	KNO_3	25.7	23.3	33.7
2	KNO_3	24.8	22.9	26.6
3	$CuSO_4$	25.1	23.4	7.0
4	$CuSO_4$	25.2	23.8	5.9

temperatures, and the result is summarized in the table. As the cooling rate increases, the crystallization begins early leading to low supersaturation. In case of potassium nitrate a cooling rate of 2.5 °C/min was applied and the supersaturation was 13.9 g/L in the previous study [Joung et al., 2005a]. Compared with the result of run-2, the supersaturation decreased by a half as the cooling rate was raised by 8.6 times the rate of run-2.

In a practical application of the proposed device of crystal shape prediction, the manipulation scheme of solution temperature for a desired crystal shape can be obtained from the result of the prediction. Otherwise, the experimental operation has to be carried out to get the information in the field, which requires a significant amount of time and expense.

CONCLUSION

A monitoring system to predict the crystal shape from cooling crystallization was proposed and utilized for the crystallization of potassium nitrate and cupric sulfate solutions. The system was composed of a measurement device using a quartz crystal oscillator and an in-line solution flow and coolant flow systems. By applying two different cooling rates, different shapes of crystallization product were yielded, while the resonant frequency variation was monitored to compare with the microscopic observation of the crystals formed. The experimental results indicate that the proposed monitoring system can effectively predict the crystal shape produced from practical crystallization processes. Also, the supersaturation of crystallization solution was determined from the monitoring frequency variation.

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