

Measurement of Crystal Formation in Supersaturated Solution

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Abstract: The degree of supersaturation is an important measure for the operation of crystallization processes, because it is directly related to the control of crystal size distribution and shape. A conventional technique utilizing solution composition and temperature has a variety of problems caused from the measurement error and the handling of analyzing samples.

A monitoring system of the supersaturation using a quartz crystal sensor is proposed here, and its performance is examined applying different manipulations of coolant temperature. The experimental outcome and photographic examination indicate that the measurements of resonant frequency and resistance of the sensor can be used for the prediction of the formation and growth of solid crystal from the crystallization process. The monitoring system eliminates the intrinsic error source of the conventional system to give the improved measurement and on-line application availability.

Keywords: : Crystallization, Super-Saturation, Quartz Crystal Sensor, Resonant Frequency, Solubility Monitoring

1. INTRODUCTION

The distribution of crystal size and shape is a key factor to determine the quality of crystal products, and its growth is controlled by the adjustment of the degree of supersaturation during the crystallization process. The seeding at the beginning of the crystal formation is also important, which is determined from the supersaturation degree. Though the supersaturation degree is very important property in the crystallization process, its determination is difficult with conventional analytical procedure. The measurement of solution concentration and physical property, such as temperature, is conducted to determine the degree, but an accurate prediction is not simple because the small variation of the measurements results in large difference of the degree. Therefore, a small measurement error induces erroneous prediction, which is not allowed in the control of crystal size and shape distributions.

In sugar industry, continuous measurement of sugar concentration using a refractometer has been implemented to predict the supersaturation degree by measuring the concentration [1]. When an accurate temperature measurement and control is available, the concentration measurement can be utilized to predict the degree. A clinical application of the supersaturation degree for the prediction of stone formation from urine was conducted to find that the measurement of cystine solubility improves clinical management of cystinuria [2].

A direct measurement of supersaturation using an interdigital transducer (IDT) and a surface acoustic wave (SAW) sensor was reported by Löffelmann and Mersmann [3]. By lowering temperature of the sensor surface, subcooling of sample solution is induced to produce crystal on the surface and to decrease the wave frequency of the sensor. The frequency reduction is proportional to the mass of the crystal formed on the sensor surface.

In the determination of nano-scale variation of mass and rheological property of a thin film, a quartz crystal sensor is widely used owing to its size and simplicity of the measurement. A mass variation associated with organic vapor adsorption was detected with the quartz crystal sensor [4], and a surface roughness caused by metal corrosion was also measured with the sensor [5].

In this study, a monitoring of supersaturation with the quartz crystal sensor is conducted with saturated sodium chloride and sodium nitrate solutions by cooling of the sensor surface for

crystal formation. The temperature control of the sensor surface is carried out with a cooling liquid flowing through the back of the sensor. For the on-line determination of the supersaturation in a practical crystallization process, a flowing sample system is implemented in this experiment. The performance of the sensor system is examined from applying various temperature variations of the cooling liquid and different flow rates of solution and coolant.

2. EXPERIMENTAL

2.1 Preparation of sensor module

Two flow systems of saturated NaCl salt solution and cooling ethanol are attached as shown in Figure 1. In the middle of the module, a quartz crystal sensor is placed and two polyethylene plates are used to build a housing for each sides of the sensor. The plates are square, and the thickness of the plates is 3 mm for inner side and 5 mm for outer side. In order to prevent from the breakage of quartz plate of the sensor, four bolts are placed four corners of the housing plates in parallel. Four o-rings are placed between the plates and the sensor. An AT-cut quartz crystal having base frequency of 8 MHz (Sunny Electronics Co., Korea) is utilized to prepare the sensor. The electrode of the crystal is silver finished.

By placing the sensor in vertical position, sedimentation of crystals and foreign suspended particles is eliminated. Because the cooling ethanol is in direct contact with the 0.2 mm thick quartz sensor plate, temperature near the surface of salt solution is close to the temperature of the coolant.

2.2 Experimental setup

Two separate temperature control and liquid circulation systems for salt solution and coolant are installed in the experimental apparatus as illustrated in Figure 2. The sensor module locates in the middle of the setup and the salt solution is fed from the left hand side as indicated in Figure 1. The cooling ethanol is provided from the right hand side. The temperature of the saturated NaCl solution is maintained with a water bath having a temperature controller. By keeping solid salt on the bottom of the beaker containing the salt solution, the saturation of the solution is assured during the experiment. Two peristaltic pumps are utilized for liquid flowing. Because the temperature of the cooling ethanol needs to be raised and

lowered, both heating and cooling systems are installed in the container of the coolant. The heating is from a hot plate heater and stirrer, and tap water is used for cooling. A solenoid valve activated by a temperature controller controls the cooling water flow.

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. Temperature of the salt solution and the coolant is 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 illustrated in Figure 1, 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 the frequency count and resistance are provided to a PC for data processing.

2.3 Experimental Procedure

Sodium chloride (Junsei Chemical Co., Ltd., Japan, special grade reagent) is dissolved into distilled water of 250 mL contained in a 300 mL beaker. While the solution is heated at 70 °C, the solid salt is added until no more is dissolved and rest of the solid salt is kept on the bottom of the beaker. Then, the beaker is placed at the water bath to be maintained at 40 °C. The cooling ethanol (Hayman Limited, U. K., 1st grade reagent) is put in a 100 mL beaker and its temperature is adjusted at 25 °C. The coolant temperature is manipulated according to experimental procedure. Sodium nitrate (Junsei Chemical Co., Ltd., Japan, special grade reagent) is also used to examine the role of solubility difference.

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. While the measured frequency and resistance are collected to a personal computer, the cooling ethanol is provided to the right hand side of the module with a peristaltic pump at the flow rate of 8 mL per minute. After the flow settles, the salt solution is provided to the left hand side of the module at the rate of 5.5 mL per minute. The temperature of the coolant is adjusted for different experiments, but the temperature of salt solution and the flow rates are kept constant. During 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 computed as frequency shift from the base frequency of a quartz crystal sensor and displayed in the upper left diagram in Figure 3. That of resonant resistance and two temperatures of the solution and coolant are also illustrated in the figure. All four are simultaneously measured and shown in the same time scale. After 445 seconds of blank run, the coolant is provided, which is indicated with EtOH. The indications of alcohol and salt in the upper left figure are of the moments of beginning of coolant and salt solution flow. When the coolant is introduced to the module, the sudden decrease of the frequency indicates the moment. At the same time, the resonant resistance is abruptly

raised because of the coolant contact on the sensor surface. After another 312 seconds, the salt solution is fed to show the variations of the frequency and the resistance. Applying a sufficient temperature difference between the solution and the coolant, the formation of NaCl crystal is induced. The solution temperature is controlled between 36.3 °C and 37.5 °C, and the coolant is between 24 °C and 25 °C. The average difference of 12.4 °C is large enough to produce solid crystal salt on the sensor surface. The steady decrease of the resonant frequency tells that the crystal is formulated on the sensor surface and it is growing. The increase of the resonant resistance implies an increased surface roughness yielded from the crystal growth. Figure 4 is a SEM photograph of the surface, which is taken two minutes after the salt solution is provided. In order to avoid the crystal formation from drying the remaining solution, the surface is gently rinsed with alcohol to remove the solution. The particles of 1 to 2 micron shown in the picture are the crystals. After the experiment of Figure 3 is done, the sensor surface is observed as seen in Figure 5. Distinct crystals shaped cube of as large as 5 micron are the result of crystal growth. The comparison between the measurements and photograph observation gives that the frequency variation of a quartz crystal sensor used in this experiment is useful to indicate the formation of solid crystal from a supersaturated solution under a certain temperature difference. The smaller the temperature difference without crystal formation is, the higher the supersaturation is.

To show the application for the supersaturation measurement, the same procedure as explained for Figure 3 is applied with varying coolant temperature, and the outcome is shown in Figure 6. In this case, the coolant temperature is decreased to make gradually large temperature gap between the solution and the coolant. The crystal formation begins at about 41 minutes after the solution is applied, when the temperatures of the solution and coolant are 34.3 °C and 25.4 °C, respectively. The difference is 8.9 °C and it is the measure of the supersaturation. In a practical application this measurement can be utilized to determine the supersaturation degree and to find a proper seeding time for the initiation of crystal formation. In addition, the manipulation information of the solution temperature for the control of crystal size distribution and growth is found from the degree.

The relation between crystal formation and the measurements of resonant frequency and resistance is demonstrated in the next experiment of Figure 7. In this run, the coolant temperature is lowered first and then raised back to the initial temperature to examine the reproducibility of the sensor. While maintaining the solution temperature, the coolant temperature is dropped from the temperature of the solution to 26.1 °C and increased until the resonant frequency restores the initial value. While the coolant temperature decreases, the frequency begins to fall in about 17 minutes after the solution is provided to the sensor module. This indicates that the crystal is formulated and grows until the coolant temperature reaches the lowest. Then the frequency rises until the original frequency is recovered while the coolant temperature is elevated. The frequency variation points out that the solid crystal is formulated as the temperature difference between the solution and the sensor surface is raised. By reducing the difference the crystal dissolves into the solution again until the solid crystal disappears. The variation of the resonant resistance has the same pattern as the frequency. The crystal deposited on the sensor surface induces the drop of the frequency and increases the resistance. The frequency reduction is from the crystal mass

buildup, and the increase of surface roughness from the crystal growth causes the resistance rise. The outcome of this experiment shows the formation of the solid crystal can be monitored from the measurement of resonant frequency and resistance.

While sodium chloride has near flat solubility with varying temperature, sodium nitrate has a moderate increase of solubility with raising temperature. A couple of experiments using the sodium nitrate are conducted to examine the role of solubility in the monitoring of crystallization process. A constant temperature difference is applied in the similar manner as given in Figure 3, and the variations of resonant frequency and resistance are illustrated in Figure 8. The pattern of the variations in the two figures shows no significant difference to indicate that the solubility does not affect the monitoring process. A V-shape temperature variation as demonstrated in Figure 9 leads to similar outcome as seen in Figure 7 having the same pattern of temperature variation.

In order to investigate the role of flow rates of supersaturated solution and coolant, three different flow rates of sodium nitrate solution in 5 mL/min, 8 mL/min and 9 mL/min are applied with constant temperature difference between the solution and coolant, and the variations of resonant frequency are exhibited in Figure 10. As the solution flow is elevated, more reduction of the frequency is observed. Because more fresh solution is provided with the high, more crystal is produced on the sensor surface to give higher shift of the frequency. With different flow rates of the coolant between 6.2 mL/min and 14.5 mL/min, the frequency variation is shown in Figure 11. The higher the flow is, the more reduction the frequency has. The high flow of coolant increases cooling rate on the sensor surface to induce fast crystallization.

The flow cell measurement system of this study has several advantages over conventional monitoring of a crystallization process which relies on the solution composition. Though the impurities contained in the solution greatly affects the supersaturation and crystal growth, an accurate determination of the chemical composition is difficult to lead to the obstacle for the supersaturation measurement. The sampling for the composition analysis causes another complexity because the temperature variation from the sample dislocation alters the supersaturation measurement. Measurement error and lag of the solution temperature incurs another difficulty in the conventional method of supersaturation determination. Because the proposed system of this study directly measures the supersaturation from the solution, the detection error of impurity composition and the temperature variation in the process of measurement are not included in the analysis. In addition, its on-line applicability makes fast process monitoring and automatic process control available.

4. CONCLUSION

A monitoring technique for the crystallization in supersaturated solution using a quartz crystal sensor is proposed and its performance is examined by applying different cooling to the sensor surface. By employing direct monitoring, problems associated with the conventional method implementing solution composition and temperature are eliminated.

The measurements of resonant frequency and resistance and the microscopic observation of solid crystal formed during the experiments explain the relation between the sensor measurement and actual crystal growth and prove that the measurements give useful information in the process of crystal formation and growth. Therefore, monitoring the variation of the frequency and resistance can be utilized in the determination of supersaturation degree and seeding time for the initiation of crystallization. The specially designed sensor module handles flowing sample to be applied for the on-line measurement and the automatic control of crystallization processes.

ACKNOWLEDGMENT

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REFERENCES

- [1] L. Rozsa, The SeedMaster device – For on-line supersaturation measurement and automatic crystalliser seeding, *Int. Sugar J.*, 100 (1998) 601-607.
- [2] Y. Nakagawa, J.R. Asplin, D.S. Goldfarb, J.H. Parks and F.L. Coe, Clinical use of cystine supersaturation measurements, *J. Urology*, 164 (2000) 1481-1485.
- [3] M. Löffelmann and A. Mersmann, A new method for supersaturation measurement: Idea, implementation and results, *Int. J. Modern Physic, B* 16 (2002) 391-398.
- [4] Y.H. Kim and K.J. Choi, Fabrication and application of an activated carbon-coated quartz crystal sensor, *Sensors and Actuators, B* 87 (2002) 196-200.
- [5] K.J. Choi, Y.H. Kim, S.M. Chang, A. Egawa and H. Muramatsu, Characterization of aluminum corrosion with a quartz crystal analyzer, *Anal. Chim. Acta*, 386 (1999) 229-236.

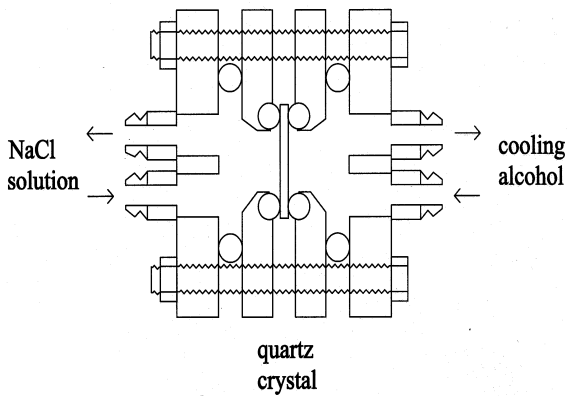


Figure 1. Schematic diagram of sensor module.

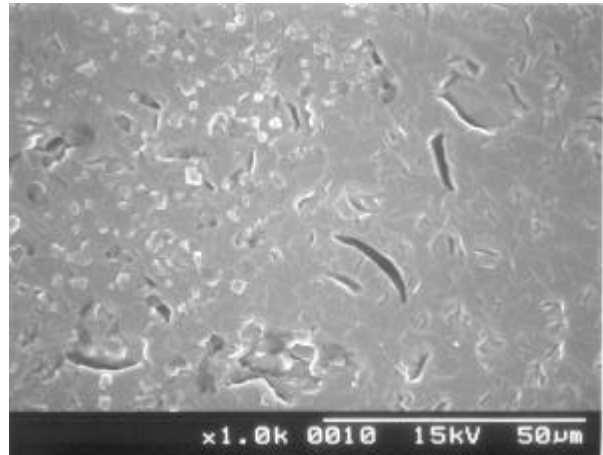


Figure 4. SEM photograph of early-stage sensor surface.

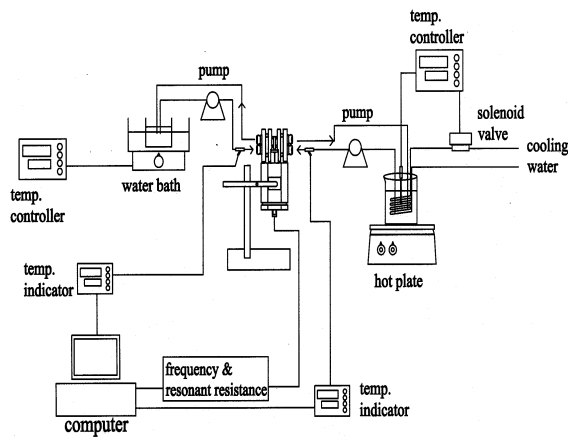


Figure 2. Schematic diagram of experimental setup.

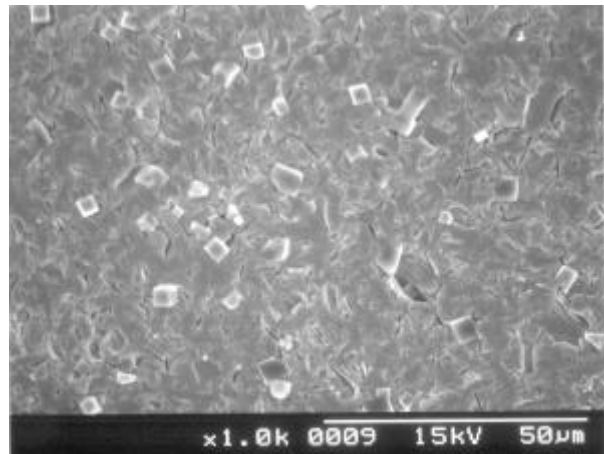


Figure 5. SEM photograph of sensor surface with grown crystals.

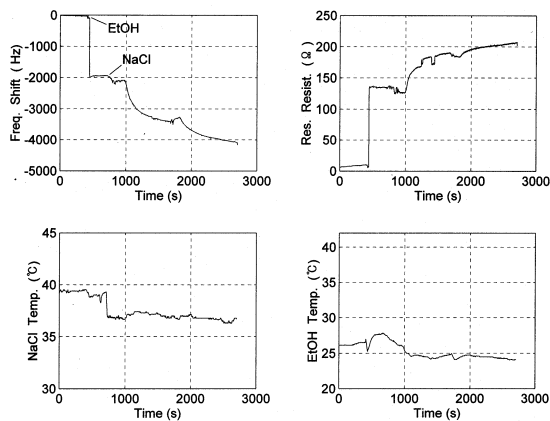


Figure 3. Variation of frequency shift and resonant resistance along with temperatures of solution and coolant in the experiment of constant coolant temperature. The indication NaCl is for supersaturation solution and EtOH for coolant.

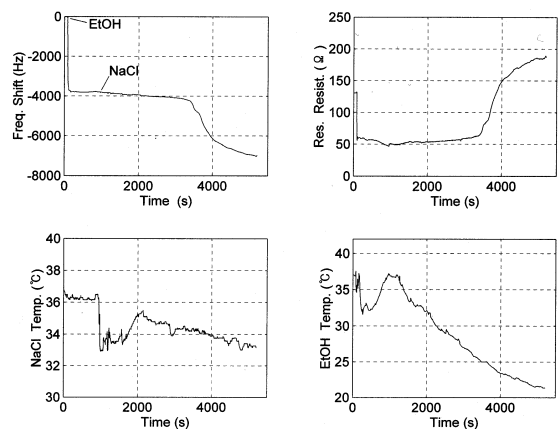


Figure 6. Variation of frequency shift and resonant resistance along with temperatures of solution and coolant in the experiment of decreasing coolant temperature. The indication NaCl is for supersaturation solution and EtOH for coolant.

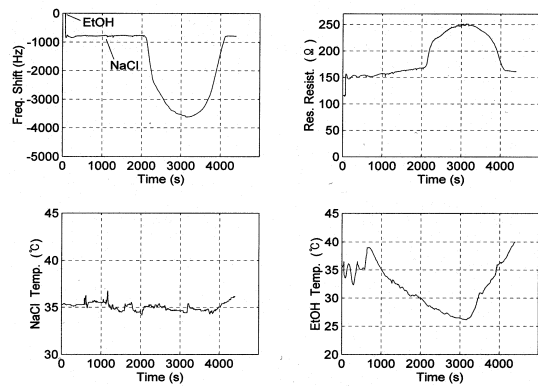


Figure 7. Variation of frequency shift and resonant resistance along with temperatures of solution and coolant in the experiment of V-shape coolant temperature manipulation. The indication NaCl is for supersaturation solution and EtOH for coolant.

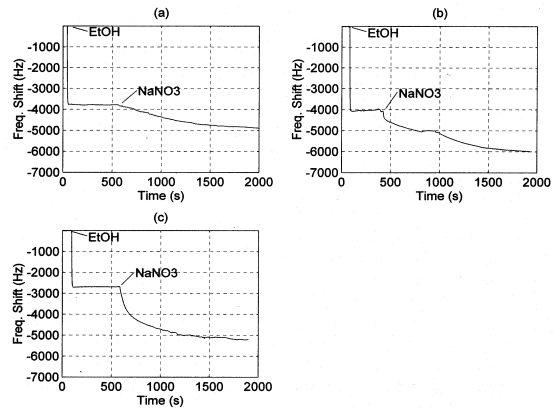


Figure 10. The effect of solution flow rate on crystallization monitoring. The flow rates are 5 mL/min (a), 8 mL/min (b) and 9 mL/min (c) with constant coolant flow of 11.5 mL/min..

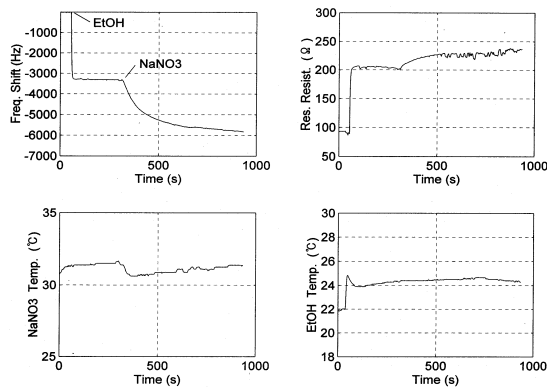


Figure 8. Variation of frequency shift and resonant resistance along with temperatures of sodium nitrate solution and coolant in the experiment of constant coolant temperature. The indication NaNO₃ is for the supersaturation solution and EtOH for coolant.

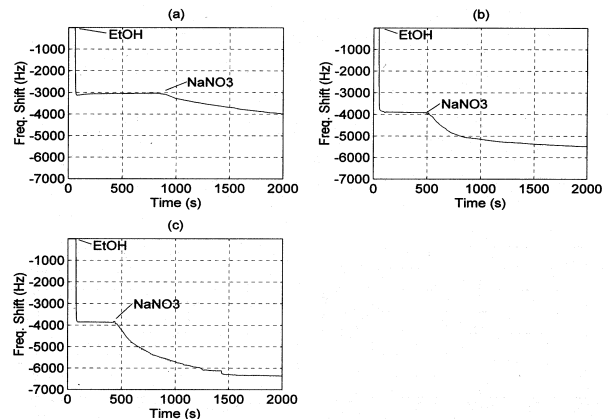


Figure 11. The effect of coolant flow rate on crystallization monitoring. The flow rates are 6.2 mL/min (a), 11.5 mL/min (b) and 14.5 mL/min (c) with constant solution flow of 7 mL/min..

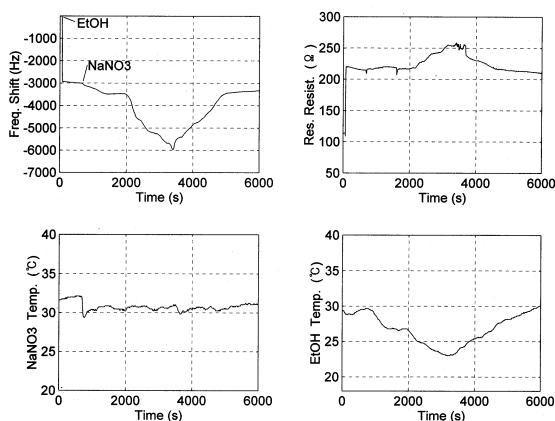


Figure 9. Variation of frequency shift and resonant resistance along with temperatures of sodium nitrate solution and coolant in the experiment of V shape coolant temperature manipulation. The indication NaNO₃ is for the supersaturation solution and EtOH for coolant.