

Liquid Inclusion Formation in a Sodium Chloride Crystal Caused by Contacts of a Stainless Steel Rod*

M. Yokota, N. Saito, A. Sato and N. Kubota

Department of Applied Chemistry and Molecular Science, Iwate University,
4-3-5 Ueda, Morioka 020-8551, Japan.

Conclusive evidence of the formation of liquid inclusions caused by contacts of a stainless steel rod with the surface of a sodium chloride crystal is shown. Contacts with the rod caused formation of macro steps at the non-contacted area. The shape of the macro steps gradually changed during growth of the crystal. After a while, a new growth layer passed over the macro step, and liquid inclusions were formed. Additionally, we confirmed that contacts are the main cause of the formation of liquid inclusions in a suspension crystallizer. Total volume of the liquid inclusions per crystal grown in suspension, V [μm^3], was successfully correlated with the size of the crystal, L [μm], as: $V = 4.0 \times 10^{-6} L^4$.

1. INTRODUCTION

In an industrial crystallizer, a large number of crystals are suspended. These crystals collide with each other, an impeller and the wall of a crystallizer. Although the effect of a contact on secondary nucleation and crystal growth have been recognized, we believe that the quality of a crystal will also be influenced by contacts. Indeed, we can find some photographic pictures in literature that show how the quality decreases by liquid inclusions caused by contacts. To our knowledge, Garside and Larson [1] are the first who showed the contact effect on the quality of a crystal. They showed a picture that revealed the occurrence of liquid inclusion formation when a steel rod was contacted with a crystal. Another cause of liquid inclusion formation was found by Toyokura et al [2]. When a small crystal was adhered to another large crystal and subsequently buried into the crystal, liquid inclusions were formed. Other research groups also recognized the liquid inclusion formation caused by these two events of mechanical impacts and adhesion of small crystals [3, 4]. However, no mechanism of liquid inclusion formation was proposed in such previous reports.

In our previous studies [5, 6], a process of liquid inclusion formation caused by adhesion of small

crystals was examined in detail and a mechanism was explained as follows. When adhesion of small crystals occurs, some mechanical stress may be induced in the crystal due to the mismatch of lattice orientation, etc. Hence, microscopic cracks can be formed on the surface of the crystal. From the cracks, new growth steps are generated. This change in the step pattern leads to the formation of liquid inclusions. The most important point of this mechanism is that the mechanical stress created in the crystal should be sufficient to cause a change in the growth step pattern. We believe that this hypothesis can also be applied to explain the liquid inclusion formation caused by mechanical impacts.

In this paper, a stainless steel rod was contacted repeatedly with the surface of a sodium chloride crystal growing in an aqueous solution, and the seed crystal was observed under an optical microscope. In addition to this in-situ observation experiment, an agitation crystallization experiment was performed to study the mechanism of liquid inclusion formation in an actual crystallizer.

2. EXPERIMENTAL

2.1. In-situ observation of liquid inclusions caused by mechanical impacts onto a seed crystal

* Financial support by the Salt Science Research Foundation (No.9704) is gratefully acknowledged.

Since details of experimental apparatus and procedure are described elsewhere [7], only a brief description is given here.

A seed crystal (1 to 3 mm in size) of sodium chloride was fixed in a flow cell (Figure 1). The flow cell was equipped with a stainless steel rod (400 μm in diameter) so that contacts of the rod with the crystal can be done by manipulating the rod by hand.

At first, the seed crystal was grown in a solution of sodium chloride without any mechanical impacts (supercooling = 5 K, solution temperature = 308 K). The linear growth rate of the front surface (see Figure 1) of the seed crystal was measured and the top surface was observed. After a while, the rod was contacted with the seed crystal several times (Figure 1) and changes in surface topography and growth rate were observed.

2.2. Measurement of the amount of liquid inclusions in crystals produced from a batchwise operated agitated crystallizer.

The agitated vessel used in this investigation is a 2-L flask equipped with an impeller. Using the vessel, crystallization of sodium chloride was carried out as follows.

An aqueous solution of sodium chloride (saturation temperature = 333 K) was quickly cooled to 293 K (250 rpm) to commence crystallization by a primary nucleation mechanism. Two hours after the crystallization was started, all the crystals were separated by filtration (final suspension density = 0.004 [-]) and the crystals were heated in an oven (323 K) for 24 hours. In the oven, originally irregular-shaped liquid inclusions (typical example can be seen in Figure 2) changed to cubic shaped inclusions. This allows us to measure the volume of liquid inclusions easily using an optical microscope.

The crystals obtained were classified into appropriate size groups depending on their overall size range. The average size in each class was taken as characteristic size for each class. From 15 to 120 crystals in each size class were selected randomly and volume of total liquid inclusions contained in a crystal was measured.

To clarify the effect of the mechanical impacts, non-agitation crystallization experiment was also performed. Since no stirring was done, crystals were crystallized in the bottom of the crystallizer.

3. RESULTS AND DISCUSSION

3.1. Mechanism of liquid inclusion formation caused by contacts

Figures 2.(a)-(c) are typical microscopic pictures showing topographic changes in the crystal surface caused by contacts of the stainless steel rod. The crystal had a clear surface before contacts (Figure 2.(a)). About one minute after (a), the rod was contacted with a corner of the crystal. By these contacts, the contacted area was slightly damaged. It is acceptable to assume that liquid could be trapped into the cavities formed by the damage. However, the point we want to stress here is that the liquid inclusion was formed even at a non-contacted area (Figure 2.(b) and (c)). That is, some macro steps were generated on the top surface just after the contacts as can be seen in Figure 2.(b). Some of the macro steps stopped moving after a while and newly generated active steps overcame the previous macro steps and some liquid inclusions were formed (see Figure 2.(c)). Although we could observe only the top surface, the same kind of surface topographic change must have occurred at the other surfaces. This can be recognized more easily by seeing the growth rate of another (front) surface (Figure 3). Before the contacts, no change in growth rate was observed, however, the growth rate increased rapidly just after the contacts (22 min). Here we must say, that the contacts did not always cause an increase in growth rate and that the increase in growth rate was not always followed by liquid inclusion formation. Liquid inclusion formation was thought to occur periodically.

The phenomena observed in Figures 2 and 3 were essentially similar to the previously reported phenomena (liquid inclusion formation caused by adhesion of small crystals) [5, 6]. Therefore, the previously proposed mechanism [5, 6] described in the introduction can be applied to this (contact) case. The most important thing in forming liquid inclusions is the occurrence of instability of the growth rate. It is reasonable to consider that instability of the growth rate can occur even without mechanical impacts and/or adhesion of small crystals. Indeed, we sometimes observed instability of the growth rate followed by the formation of liquid inclusions under mechanical impact-free conditions.

3.2. Amount of liquid inclusions in a crystal

obtained from suspension crystallization

The total volume of liquid inclusions per crystal, V , was plotted against the average size, L , of crystals in Figure 4 (\square mark). From the plot, we found that V can be correlated with the average size as

$$V = 4.0 \times 10^{-6} L^4. \quad (1)$$

Mark \times in the figure shows plant data [8] obtained from a Krystal-Oslo crystallizer. It is interesting to point out that, although crystallizer scale and crystallization conditions such as temperature and suspension density of the plant crystallizer were much different from ours, the plant data can be plotted almost on the line extrapolated from our data. This is an interesting result. However, crystal size range of our data and the plant data are different. Therefore, additional data should be collected before discussing the reason of the interesting result.

In the case of non-agitation crystallization (\blacksquare), the total volume of liquid inclusions per crystal was correlated with the size of crystal size as:

$$V = 9.1 \times 10^{-5} L^3. \quad (2)$$

We need more data to explain the physical meaning of Equations (1) and (2). One of the important points obtained from Figure 4 is that the total volume of liquid inclusions per crystal (\blacksquare) was much lower than that of agitated crystal (\square). This fact brings us to a conclusion that contacts of the crystal with other solid bodies is the main cause of the liquid inclusion formation in a suspension crystallizer.

3.3. Mechanism of liquid inclusion formation in an industrial crystallizer

Before talking about the mechanism of liquid inclusion formation in a suspension crystallizer, let us observe crystals formed in suspension. Figure 5 shows a schematic illustration of the inside of a (large size) crystal generated in this study. There are two regions in the crystal. One is a liquid inclusion-containing region and the other is an inclusion-free region. An inclusion-free region exists in the central part and at the edges of the crystal. In other parts of the crystal, liquid inclusions can be found. In the liquid inclusion-

containing regions, the liquid inclusions were observed to be aligned in rows and the rows were parallel to the crystal surface. This arrangement of the liquid inclusions is a characteristic phenomenon that occurred when liquid inclusions were formed by adhesion of small crystals [6] and by mechanical impacts [7].

From these results described above, a possible mechanism for liquid inclusion formation in a suspension crystallizer can be schematically drawn as shown in Figure 6. Case 1 shows the previously reported mechanism [5, 6]. Adhesion of small crystals and mechanical impacts cause formation of a macro step followed by the formation of a liquid inclusions. Additionally, we can not ignore the other two mechanisms (Cases 2 and 3) that are widely accepted phenomena. Case 2 shows the formation of a cavity and a crack when an agglomeration or a mechanical impact occurs. The liquid is trapped into them. In cases 1 and 2, liquid inclusions can be formed over a wide range of surface and not only at the contact site. Case 3 shows trapping of a liquid inclusion among crystals that form an agglomerate. A common factor found in cases 1-3 is that the first step of the formation of a liquid inclusion is the contact of a crystal with other solid bodies (crystal, impeller, etc.).

4. CONCLUSIONS

1. Contact of the stainless steel rod with a crystal causes liquid inclusion formation not only at the contact site but also at the non-contacted area. The mechanism of liquid inclusion formation caused by the mechanical impacts was essentially the same with that of previously reported liquid inclusion formation caused by adhesion of small crystals.
2. In an agitated crystallizer, mechanical impacts are the main cause of liquid inclusion formation.
3. Total volume of liquid inclusions per crystal for those produced from an agitated crystallizer was correlated with the crystal size by Equation (1).

REFERENCES

1. J. Garside, and M. A. Larson, *J. Cryst. Growth*, **43**, (1978) 694.
2. K. Toyokura, H. Sakai and R. Uchida, Proc. of the 10th symposium Industrial Crystallization, J.

- Nyvtl and Zacek (eds.), Bechyne, (1987) 215.
3. K. Shimizu and N. Kubota, *Kagaku Kogaku Ronbunshu*, **12** (1986) 388.
 4. T. Shimaoka, H. Takiyama and M. Matsuoka, *Kagakukogaku symposium series*, **49** (1995).58.
 5. M. Yokota, N. Saito, J. Hirai, A. Sato and N. Kubota, *AIChE J.*, **43** (1997) 3264.
 6. N. Saito, M. Yokota, A. Sato and N. Kubota, *Kagaku Kogaku Ronbunshu*, **24** (1998) 486.
 7. N. Saito, M. Yokota, A. Sato and N. Kubota, *AIChE J.*, **45** (1999) 1153.
 8. L. Ehara, S. Kowaki, M. Sasaki and A. Otsubo, *Bulletin of the Society of Sea Water Science, Japan*, **50** (1996) 77.

Top view of the flow cell

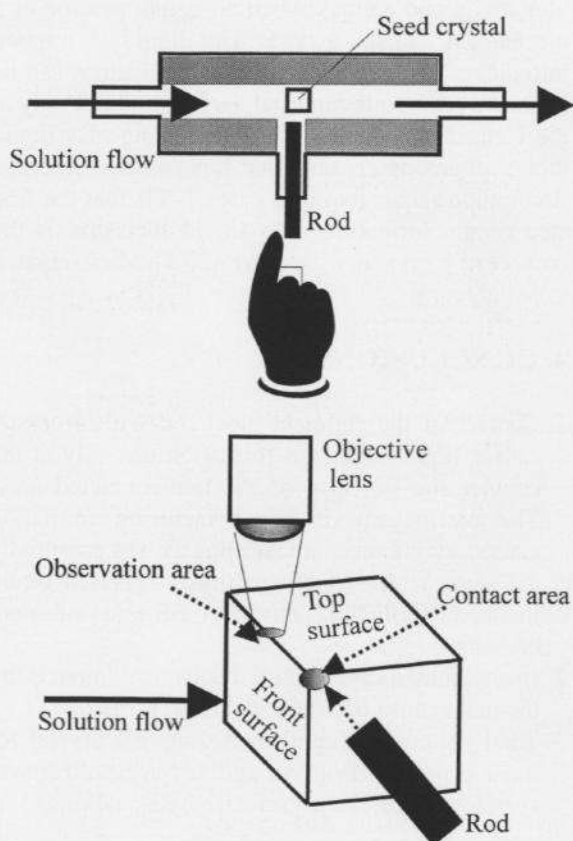


Figure 1. Schematic illustration of the flow cell used for in situ observation experiments of liquid inclusion formation caused by contact of a stainless steel rod with a sodium chloride crystal.

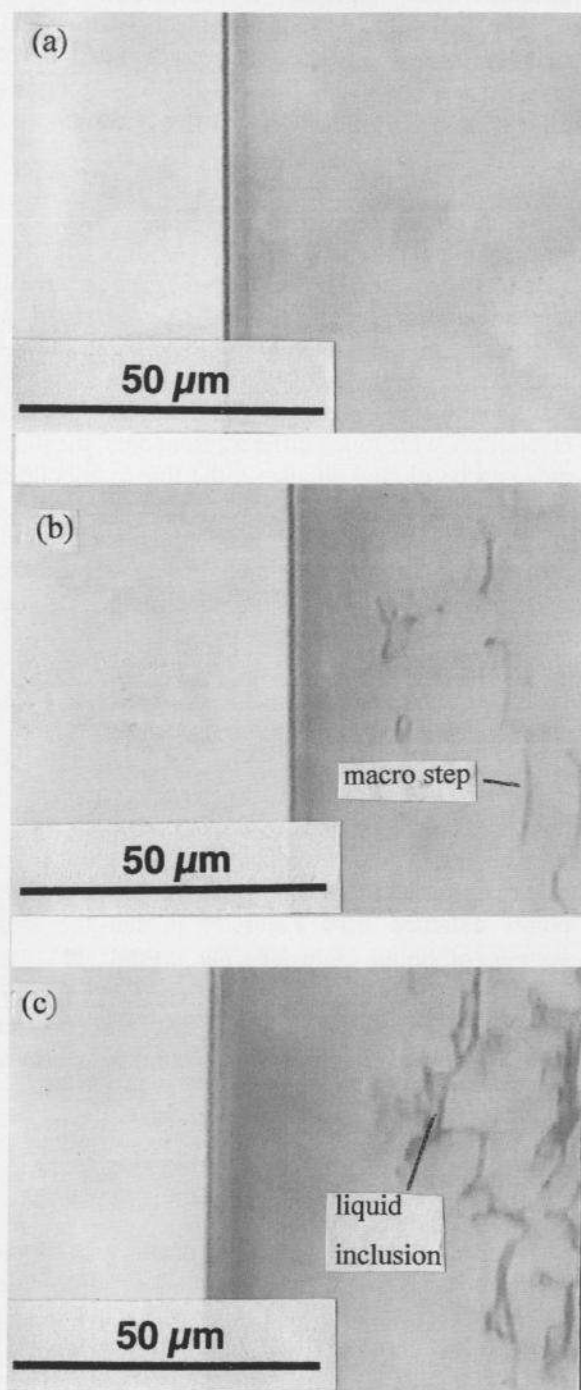


Figure 2. Optical microscopic pictures showing change in crystal surface topography before and after the contacts. (a): before contacts, (b): 12 sec after contacts, (d): 1 min after contacts.

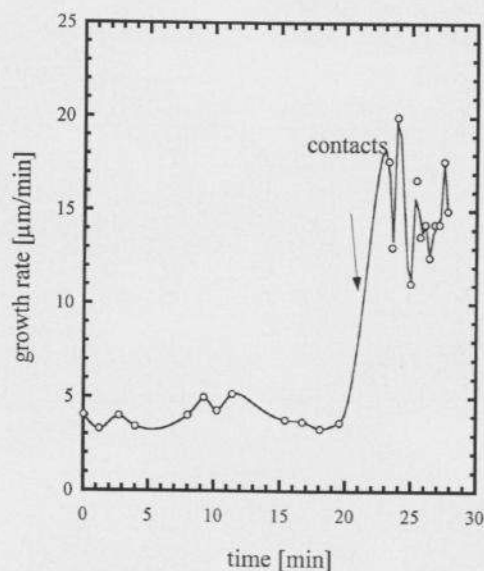


Figure 3. A typical example of transient growth rate of the front surface of the seed crystal before and after contacts.

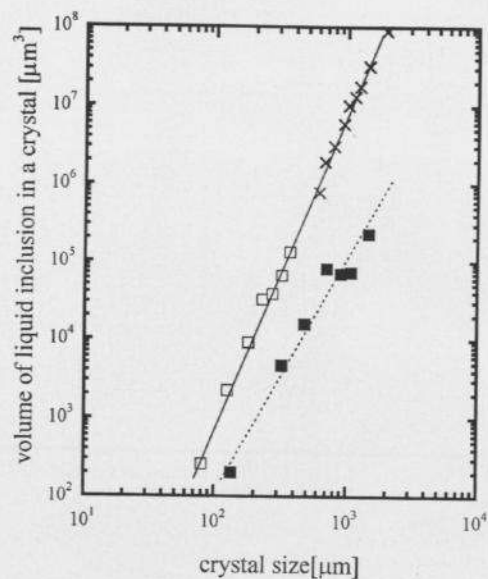


Figure 4. Volume of liquid inclusions per crystal as a function of the crystal size (\square : agitation crystallization, \blacksquare : non-agitation crystallization, \times : plant data [8])

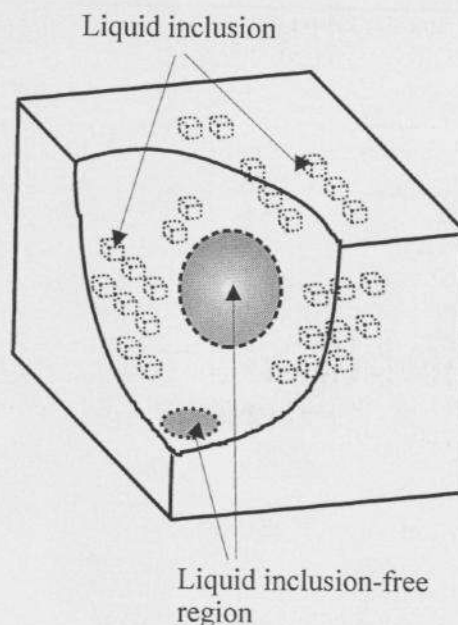


Figure 5. A schematic illustration of a large crystal produced in a suspension crystallizer.

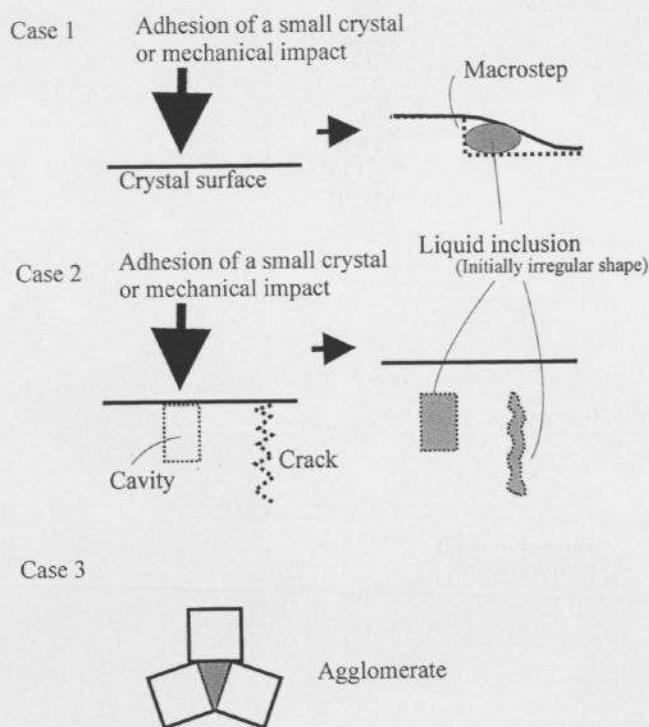


Figure 6. Possible formation mechanisms of liquid inclusions.