DISSOLUTION FORMS OF POTASSIUM CHLORIDE CRYSTAL IN AQUEOUS SOLUTION

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Abstract. Using the apparatus for in-situ observation habit changes of KCl crystal in dissolution were studied in a wide undersaturation range controlled rigidly. It was found that PbCl₂ as an impurity has significant effects on the dissolution of the crystal surface. A mechanism for the dendritic dissolution form was elucidated.

1. Introduction

Many facts¹ seem opposed to strict reciprocity between the growth and dissolution processes. For example, there is little reciprocity in growth and dissolution velocities at the same degree of over- or under-saturation, that is to say, the velocities of growth are generally much less for most substance than those of dissolution. Speaking more precisely, the rate of growth and dissolution is different at parts of a crystal, especially corners and edges have generally larger dissolution velocity. The rate of the average for all faces becomes at most decouple in the case of K₂SO₄ at a certain condition. Therefore, it is a matter of course that the experiment of dissolution process needs more sufficient accuracy in the saturation control than that of growth process.

On the other hand, it is well-known that some kinds of impurity show dramatic effects on the change of the habit in the crystal growth from aqueous solution. It is naturally expected in the case of dissolution process too.

In the present paper, habit changes of KCl crystal in dissolution processes affected by an impurity are studied over a wide range of under-saturation using an apparatus for in-situ observation of crystal growth and dissolution from aqueous solutions.²

The experiment using aqueous solution at near room temperature and atmospheric pressure is of advantage to the rigid control of the saturation degree. Klein Haneveld H. B.³ found that the growth and dissolution rates of
KCl crystal in solution depend linearly on the supersaturation $\sigma$ down to $\sigma = 10^{-4}$ and the quadratic part of the $R(\sigma)$ curve must be situated at the lower supersaturation and the rate of dissolution is about 5.5 times as great as that of growth.

PbCl$_2$ are added to the solution as an impurity, which decrease the rate of both growth and dissolution. G. D. Botsaris et al.\textsuperscript{41} researched the effect of PbCl$_2$ concentration and supersaturation on growth rate on the \{100\} face of KCl crystal.

The dissolution experiments controlled rigidly are carried out on habit modifications of cube, cubo-octahedron and octahedron and reveal interesting habit changes in each undersaturation range. It is found that octahedron crystal develops into characteristic dendritic form in a fixed low undersaturation range. A mechanism for the dendritic dissolution is elucidated, in which the presence of the crystal face having extremely slow dissolution rate is an essential factor.

2. \textit{Experiment}

The cell for in-situ observation shown in Fig. 1 is mounted on a stage of a polarization microscope and dissolution features are photographed by a 35mm camera at every interval of the fixed time under the control of a micro computer. Thermomodules are used as temperature control power, which are possible to control both heating and cooling of the cell and to operate in wide temperature ranges. The temperature fluctuation is detected by a thermistor set at the corner of the cell near a thermomodule, where it is most sensitive for the temperature control. The set-up temperature is controlled by a regulator by P. I. D. method. The temperature of the dissolution is measured by a copper constantan thermo-couple set at the center of the cell near the crystal, which is connected with a digital voltmeter readable to 0.1 $\mu$V and is stored by a micro computer too. The temperature at the center of the cell is held constant to $\pm 0.005^\circ$C at near the room temperature. Both sides of the cell are covered with plate glass of 8mm in diameter for in-situ observation and the

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{The cell for in-situ observation. C: Growth Cell, M: Thermomodule, P: Cooling Pipe, G: Glass Window, F: Copper Frame}
\end{figure}
inside of the cell is coated by teflon to keep away the contact of the solution with a copper frame.

A seed crystal prepared in another vessel is enclosed in the cell with the KCl solution. The value of PbCl₂ added as an impurity is $2 \times 10^{-3}$ moles PbCl₂/mole KCl. The saturation temperature of the solution enclosed in the cell is determined by confirming no change of the crystal size under a microscope for several days and the value of the undersaturation $\sigma$ at the set-up temperature is calculated from solubility curve at each temperature.

It is an advantage claimed for this apparatus that experimental runs can be made again and again using the same mother solution and a seed crystal. It means that the mother solution enclosed in the cell satisfies exactly the same condition in every run.

3. Observation Results and Discussion

The dissolution experiments are carried out on habit modifications of cube, cubo-octahedron and octahedron respectively, because it is expected that the end shape largely depends on that of the original crystal.

The presence of lead chloride as an impurity causes the development of octahedral face at a lower supersaturation growth range, which plays an important role to grow a transparent, perfect octahedron crystal. Furthermore, it has more significant effects upon the dissolution rate of each crystal face as follows.

Dissolution of cube and cubo-octahedron

In both cube and cubo-octahedron modifications, the dissolution forms have a similar tendency to develop {100} face. The experiment in a low undersaturation range shows new crystal facets appearing at crystal edges. The relative velocity of their dissolution rates determines the final crystal habit.

Figure 2 shows changes on the crystal surface of a cubo-octahedron at the undersaturation $\sigma=2.54\%$. Figure 2(a) indicates the difference of the resistance against dissolution between {111} and {100} faces, which elapses about 10 minutes in dissolution process, that is to say, {111} faces show no change in its smoothness, on the other hand, {010} faces turn into rough surfaces in a macroscopic view. Features of second stage is the appearance and the development of the facets as shown in Fig. 2(b), which was photographed 30 minutes later. Two kind of facets appears. Facet "a" at the edge of two {111} faces can divide into two parts of the same rank, (hh1), (hh1). Facet “b”, (hkk) at the edge of {111} and {100} face develops more rapidly. It encroaches steadily on {111} face and facet “a” and the crystal shape is replaced by {100} face in the last stage. Cubic crystal essentially keeps the original shape regardless of the undersaturation ranges.
Fig. 2. The crystal surface of a cubo-octahedron at $\sigma=2.54\%$. a, b: crystal facets.

Dissolution of octahedron

The crystal of octahedron dissolves to unusual skeletal form in low undersaturation ranges, though cubic form seems to be stable finally in all undersaturation ranges.

Figure 3 shows a series of microphotographs representing the habit.
change into the characteristic dissolution form at undersaturation $\sigma = 1.04\%$. The elapsed time from Figs. 3(a)–(d) is 73 hours. First, two crystal facets "a" appear at the edge of the octahedron as shown in Fig. 3(b). At vertices of the octahedron, where facets of different direction intersect, concave parts "c" develop and precipices "d" become steep and deep (Figs. 3(c) and (d)). \{111\} face has strong resistance against the dissolution, as the result it survives as a projection. Facets "c" developing larger corresponds to the direction of \{100\} face (Fig. 3(d)). The shape of the final stage is shown in Fig. 4. Crystal of Fig. 4(a) is projected perpendicular to \(\langle 111 \rangle\) face and has 3-fold symmetry and Fig. 4(b) projected perpendicular to \(\langle 100 \rangle\) face shows 4-fold symmetry. The direction of elongated branches is parallel to \(\langle 111 \rangle\) and \{100\} face develops into large face in the last stage.

The impurity added in this experiment has significant effects upon the dissolution of the crystal surface. The property of Pb\(^{++}\) to retard the growth rate operates more conspicuously on the retardation of the dissolution rate and this facilitates the close observation of the dissolution process.

It is true that in the dissolution the crystal form is determined by the

Fig. 4. The dissolution form of octahedron. 3-a: perpendicular to \(\langle 111 \rangle\) face. 3-b: perpendicular to \(\langle 100 \rangle\) face.
difference in the dissolution rate of respective face\(^5\), that is to say, the crystal face dissolving at high rate develops larger in contrast with the growth process, but the face of low dissolution rate does not always disappear easily.

Microphotographs indicate that \{100\} face is readily attacked and develops large, on the other hand, \{111\} face is highly resistant to attack and the dissolution rate is extremely low compared with that of \{100\} face. The large difference of the dissolution rate between crystal faces causes the formation of the dendritic crystal.

REFERENCES