Observation and Analysis of the Interface Between NaCl Substrate and KCl Deposit Crystal

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The solid-solid interface between NaCl substrate and KCl deposit crystals of a NaCl-KCl combined crystal which was created in the NaCl-KCl-H2O ternary system was observed. It was assumed that the NaCl-KCl interface had different physical properties from pure NaCl or pure KCl crystal. In order to discuss the formation process and the physical property of the NaCl-KCl interface experimentally, an atomic force microscope (AFM) was applied to observation and analysis. After cleaving the combined crystal, the influence of moisture in the air to the solid-solid interface between NaCl and KCl was examined by controlling humidity. The force-vs.-distance curve of AFM was measured as the line analysis on the cleaved crystal. As the result, it became clear that the NaCl-KCl interface was easily damaged by the moisture in the air. [DOI: 10.1380/ejssnt.2007.113]

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I. INTRODUCTION

When the nucleation of potassium chloride (KCl) was induced near the surface of the sodium chloride (NaCl) substrate crystal which was growing or dissolving in an aqueous solution, the phenomenon of deposition of KCl on a substrate crystal was observed in the NaCl-KCl-H2O ternary system [1]. The crystallographic faces of the KCl deposit crystals were assumed to be 100 and they settled in a manner parallel to the 100 face of the substrate NaCl crystal (Fig. 1(a)). From the observed phenomena of co-crystallization and the tests for the measurement of the bonding forces between the substrate and the deposit crystals, the growth process of such composite crystals was discussed. And, it was also reported that KCl crystals deposited on the NaCl substrate crystal while the NaCl crystal was dissolving in the NaCl-KCl-H2O system [2, 3]. According to phase equilibrium of the NaCl-KCl-H2O ternary system, the nucleation was caused by the local high supersaturation created by the dissolution of NaCl into the mother liquor [3]. The crystals created by these methods were named the combined crystals. The lattice constants of NaCl and KCl crystals are substantially different, so that lattice matching between the two crystal phases is hardly expected when the two phases have perfect structures upto the surfaces. And solid solution of those compounds does not form at ordinary temperature. We therefore assume an existence of a continuous interface layer between the NaCl substrate crystal and the KCl deposits where the crystal lattices may change gradually from those of NaCl to those of KCl. From those reasons, the conventional crystal growth theory for the solution could not explain the formation of a NaCl-KCl combined crystal. It is therefore interesting and important to investigate such phenomena of the combined crystal of multiple components which are basically immiscible each other in the solid state. And the physical properties of the NaCl-KCl interface were not also clear.

There are not so many researches of combined crystals under the aqueous solution conditions, and the formation process and the physical property of the solid-solid interface of a combined crystal are not investigated sufficiently.

The following phenomena were observed when combined crystals were created in the NaCl-KCl-H2O system and the interface between NaCl substrate crystal and KCl deposit crystal was exposed by cleaving. (1) After a combined crystal was cleaved in the air whose humidity was not controlled, the presence of the slight groove was observed with a differential interference microscope (Fig. 1(b)). (2) When the same place was observed after keeping it in a desiccator for several days, the groove had become wider (Fig. 1(d)).

FIG. 1: The differential interference photomicrographs of KCl deposit and NaCl substrate crystal (combined crystal). (a) Typical KCl deposit crystals on the NaCl substrate surface. (b) The cross section photomicrograph of the interface zone of the cleaved combined crystal soon after crystallization. (c) The illustrate of outline. (d) The interface zone of the cleaved combined crystal after several days.

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From these observation results, it was supposed that the physical property of the solid-solid interface of the combined crystal such as solubility differs from pure NaCl or pure KCl crystals. This paper reports the physical properties of the NaCl-KCl interface experimentally, and an atomic force microscope (AFM) was applied to the observation of a combined crystal by using the NaCl-KCl-H$_2$O ternary system.

II. EXPERIMENTAL

In order to observe the solid-solid interface between NaCl and KCl crystal with AFM and also to analyze the interface by using force-vs.-distance curves of AFM, the NaCl-KCl-H$_2$O ternary system was used for the experiments. Special grade NaCl and KCl crystalline reagents were purchased from Wako Pure Chemicals. The ultra pure water created by MILLIPORE (Japan Millipore, Inc.) was used as the solvent.

As an observation cell, a 40 ml acrylic vessel with a water jacket was used. The potassium chloride 26 mass% aqueous solution (KCl saturated solution) was prepared as the mother liquor and placed in the observation cell. Solution temperature was controlled at 298 K. Then, a single piece of NaCl substrate crystal about 3 mm in diameter was placed on the bottom plate of the cell, and this time was defined as 0 time, and elapsed time was measured. The mother liquor in the observation cell was not agitated, and the surface of the substrate crystal was observed with the optical microscope. Local supersaturation for KCl was generated near the NaCl crystal surface by NaCl dissolution, and the NaCl-KCl combined crystal was created because the primary nucleation of KCl was induced [3]. The crystal was taken out from the cell after 1 min, and adhering mother liquid on the surface was removed immediately by using wiper (KIMWIPER Kimberly-Clark).

The combined crystal created by above method was cleaved with a scalpel under the humidity conditions shown in Table I. The hygrometer (SHINYEI TRH-CA) was used. Run B and Run C were carried out within glovebag (CHELTENHAM-PENA). NaCl-KCl interface which appeared in a cleavage surface was observed by AFM, and the tip-sample interactions was measured by the force-vs.-distance curve with AFM (Digital Instrument Nano Scope IIIa). The probe used for this AFM measurement was cantilever with integrated tips of Si$_3$N$_4$, and their elastic spring constant was 0.12 N/m. All AFM measurements were carried out in the contact mode. After the crystals were measured by AFM, they were also analyzed with the EPMA (JEOL JXA-8900) to identify the chemical component.

| Run No. | Condition | Humidity  |
|---------|-----------|-----------|
| A       | air       | RH 60%    |
| B       | air       | RH 25%    |
| C       | dry nitrogen | RH 10%  |

III. EXPERIMENT RESULTS AND DISCUSSION

When the combined crystal cleaved in the air was observed, there was a groove at the interface. The shape of the groove was changing during several days (Fig. 1). Then, the influence of the moisture on the solid-solid interface between NaCl and KCl crystals was examined by controlling the humidity during the combined crystal was cleaved. Figure 2 shows the observed interface of the combined crystal which was cleaved under the humidity condition at RH 25%. The position of the cantilever was
depicted by the CCD image as shown in Fig. 2(a). The triangular shade is the cantilever. From the result of the EPMA analysis, it became clear that the cubic shaped KCl crystal had grown on the projection of NaCl substrate crystal. The shape of the interface was able to be explained by the process with the dissolution of NaCl and the nucleation of KCl crystals. The schematic image for the formation mechanism of the NaCl-KCl interface was illustrated in Fig. 3. According to phase equilibrium of the NaCl-KCl-H$_2$O ternary system, the solution concentration on the dissolving surface of NaCl must be on the extended solubility curve of NaCl. This solution concentration shows supersaturated condition for KCl. So the nucleation was caused by the local high supersaturation created by the dissolution of NaCl. The crystallization phenomena were reported by using phase equilibrium for NaCl-KCl-H$_2$O ternary system in detail [3].

The cracks which probably occurred in the cleavage were also observed in Fig. 2. These cracks passed through the solid-solid interface between NaCl substrate crystal and KCl deposit crystal. Therefore, just after the cleavage, it was considered that there was crystal structure to bond the NaCl substrate to the KCl deposit crystals. Figure 2(b) shows the AFM height image at the interface after 17 min from the cleaving. The groove was already formed between NaCl and KCl. This crystal was kept in the container of which relative humidity is about 20%, and the same part was observed at periodic time with AFM. The AFM observation result of the interface four days after cleaving is shown in Fig. 2(c). It was observed that the groove became wider and deeper. It was considered that the moisture absorbed to the grooves by the capillary tube effect. However, it seemed that the degree of damage caused by crystal dissolution on the groove of NaCl-KCl interface was larger than the grooves of the cracks. The inclusions were observed in KCl deposit crystals because deposit crystal growth rate was fast. However, the NaCl-KCl interface was damaged by the moisture compared with bulk KCl deposit crystal. And, the tip-sample interactions of NaCl, KCl, and the NaCl-KCl interface were measured by using the force-vs.-distance curve of AFM. The force-vs.-distance curve is one of the functions of AFM analysis. The overall tip-sample interactions force such as meniscus force for the adsorption layer of water and van der Waals force are able to be measured by using the force-vs.-distance curve [4]. The line analysis result of the attractive force is shown in Fig. 4. The analyzed spots are along the broken line A-B shown in Fig. 2(c). The value of the force around the interface between NaCl and KCl was larger than the force of pure NaCl or KCl. Since observation and cleavage were carried out in the air, it was considered that the interface was influenced by moisture.

Then, in order to discuss the effect of moisture, the combined crystal was cleaved under the low humidity condition under nitrogen atmosphere condition (Run C). The CCD image of the interface just behind cleaving crystal is shown in Fig. 5(a). It was observed that the KCl crystals were deposited on the NaCl substrate crystal, but there was not always a groove near the solid-solid interface of a combined crystal under the low humidity conditions. However, the groove was always formed if the NaCl-KCl interface was exposed into the air (Fig. 5(b)). In the case of NaCl crystal it was reported that if humidity became about 47% [5, 6], the steps on the crystal surface began to move by the influence of the water which was absorbing to the crystal surface. From these reasons, it was considered that the NaCl-KCl interface of combined crystal had the different physical properties from pure NaCl or pure KCl crystal and the interface became unstable caused by moisture existence. It was suggested that the influence of moisture is large especially near the interface.
IV. CONCLUSIONS

In order to discuss the physical property of the solid-solid interface between NaCl substrate and KCl deposit crystals in detail, the following conclusions were obtained as the results of observation and analysis by using AFM. When the overall tip-sample interactions of NaCl, KCl, and the NaCl-KCl interface were measured by using the force-vs.-distance curve, the value of the force was high especially near the interface. The NaCl-KCl interface tended to be damaged with the moisture absorbed on the crystal.

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