Atomistic Mechanisms of Habit Modification of Alkali Halide Crystals. 2. Cases of NaCl Tube Whiskers.

H. Shindo[a], M. Kwak[b], T. Igarashi[b], W. Karino[b] A. Ito[b] and T. Kose[b],
The Institute of Science & Engineering a Graduate School of Science & Engineering b
Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Summary

NaCl whiskers grown from the surface of cellophane in contact with saturated aqueous solution on the other side were observed by means of optical microscopy and scanning electron microscopy (SEM). Square tube whiskers, often tapered at the top, were commonly observed. In situ observation revealed that the growth occurred at the base, not at the tip. Tapered whiskers were also formed starting at the tip. Characteristic structures were found with SEM at the bases of well-developed tube whiskers, namely, macro-steps growing horizontally around the outer surface, smooth bottom face presumably in contact with the cellophane surface, and a duct connecting the inside to the outside of the tube. The lowest part of the whisker was covered with water on the outside. The tube size changes depending on the balance between the growth rates in horizontal and perpen-dicular directions. Presence of rough parts at the inner surface suggests that the sidewalls were not necessarily in contact with water.

Addition of $[Fe(CN)_6]^{4-}$ with various concentrations markedly changed the whisker growth patterns by suppressing horizontal step motions on the (100) surface. At concentrations of 1-80 μmol/L, whiskers started to grow as thin solid pillars. Horizontal connections were, then, gradually made at the base between the pillars, finally bunching into a common base. When two pillars having the same crystallographic orientation combined horizontally, a whole tube having a square cross section was generated. This explains how tube whiskers are formed. At a concentration of 0.5 mmol/L, tiny single crystals in the forms of tubes having rectangular cross sections, rectangular plates and blocks were formed. Among them, the tubes would have better chances of growing bigger in wet conditions in the absence of $[Fe(CN)_6]^{4-}$. At 1 mmol/L concentration, tiny sharp cones were formed due to growth inhibition to all directions except along the crystal axes.