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Realtime observation of growing electrodeposits by quick XRF imaging

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Introduction

Electrochemical deposition of metals from aqueous solution is an operative way to study a variety of pattern formation observed in growth phenomena [1]. The growing zinc dendrites were dynamically observed using a non-scanning X-ray fluorescence (XRF) imaging technique [2], and the pattern formation process was examined. To perform quick imaging, the technique was combined with a multilayer monochromator [3] installed at BL-16A1.

Experimental

Electrolysis was performed using a compact cell with a copper ring anode (i.d. 16 mm) and a copper wire cathode (0.7 mm dia.) in the center of the ring. An electrolyte consisting of an aqueous solution of 360 mM zinc sulfate was put inside the ring and sandwiched by acrylic resin (bottom) and by a thin Mylar film (on the irradiation side) to form an about 200 µm thin layer. A DC voltage of 2.5 V was applied between the electrodes. Quick XRF imaging using quasi-monochromatic X-rays, the energy of which was above the Zn K-edge, commenced just after the applying voltage.

Results and Discussion

Electrodeposition started to grow from the cathode when the DC voltage was applied. Zinc dendrites with metallic luster branches grew two dimensionally in the cell. An XRF image of 12 mm × 12 mm (1000 × 1000 pixels) could be obtained in only 0.1 sec exposure, due to the strong photon flux of the multilayer monochromator, which irradiated the sample surface brightly enough despite the small-angle incidence. The 15 min movie of the growth process was composed of 600 frames in total. Although the potential capacity is 9,000 frames for 15 min, since 1 image was obtained in 0.1 sec, only limited frames were stored (1 image per 1.5 sec) in this study. Figure 1 shows four static images at 3.75 min intervals extracted from the 600 frames. Each image is of a 12 mm × 9 mm (1000 × 750 pixels) portion. In the images, it can be observed that some main stems formed and from these side branches emerged. The angle between stem and branches was about 60 degrees, which reflects the hexagonal symmetry of zinc crystal. In the images, the distribution of solute (Zn^{2+}) in the electrolyte is also observable as the contrast of medium. The concentration of the solute is higher on the outside of the growing deposits, and lower on the inside. It can be seen that the growing tips of the main stems touch the concentrated electrolyte and penetrate rapidly into the region. However, the side branches that emerge from the stems get a late start and have to proceed obliquely. If one of these side branches reaches this concentrated region exceptionally, it can become a thick stem (e.g. **A** in Fig. 1). But if it cannot, it falls behind with no chance of touching the fertile region. Therefore, it can only become a fine and short branch (e.g. **B**). Thus, zinc dendrites assume the pattern of a combination of thick main stems and fine branches. Using the quick XRF imaging technique, the changes in two-dimensional elemental distribution could be observed and the growth pattern formation could be understood. The authors gratefully acknowledge the kind assistance of Drs. H. Sawa, Y.Wakabayashi, Y.Uchida during the experiments.

References

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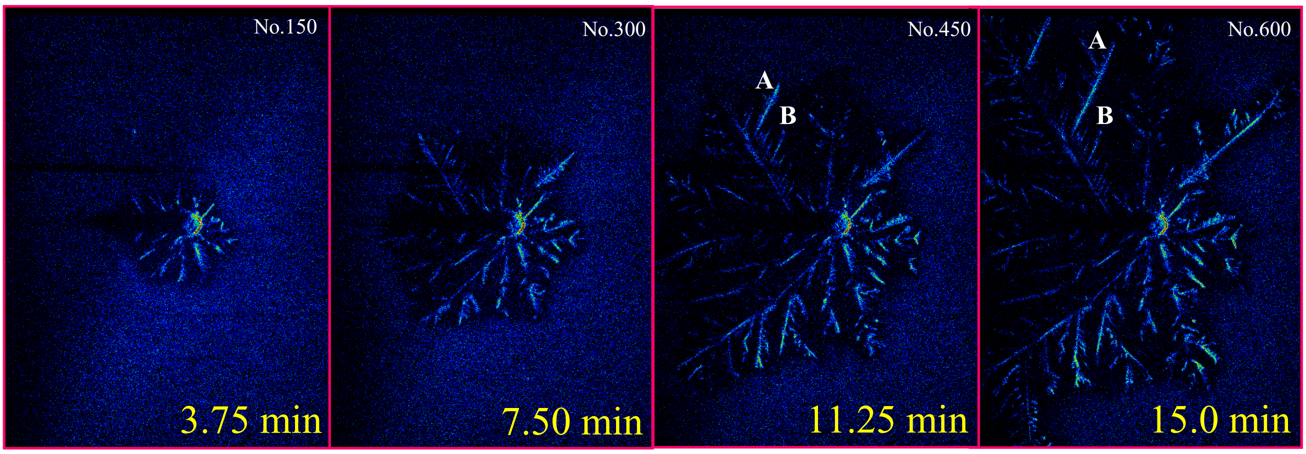

Figure 1. XRF images of growing zinc dendrites from 360 mM $ZnSO_4$ aqueous solution with 2.5V applied voltage. Incident energy, 9.8 keV (quasi-monochromatic), image size for each, 12 mm × 9 mm and, exposure time, 0.1sec / 1 image. Description of typical patterns A and B are given in the text.