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X-Ray Fluorescence Movie of Cu-Zn Electrodeposits

Hiromi EBA and Kenji SAKURAI*
National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047 Japan

Introduction

Electrodeposits of metals form several interesting fractal patterns, which are sensitive to applied voltage and/or the concentration of solute [1]. In this study, growing patterns for a Cu-Zn system were observed as an X-ray fluorescence movie to investigate the morphology as well as the elemental distribution.

Experimental

A non-scanning XRF imaging technique [2] was employed for the dynamic observation of growing electrodeposits, using monochromatic radiation at BL-4A. The electrolysis cell used is a thin-layer vessel 100~200 μm thick, one side of which has a Mylar window of 6μm for XRF observation. An aqueous solution of $CuSO_4$ (0.003 ~ 0.5M) and $ZnSO_4$ (0.18 ~ 0.35M) was sealed in the vessel. A constant DC voltage of 2.5V was applied between the anode (copper ring, i.d. 16mm) and the cathode (copper wire, 0.7mm dia.) placed axially at the center of the ring.

Results and Discussion

Fig.1 shows the deposition process for 0.25M $CuSO_4$ and 0.18M $ZnSO_4$. The pattern indicates a ramified deposit of short branches. Incident X-ray energy was switched below and above the Zn K-edge to distinguish elements. While (a) and (c) show only Cu distribution, (b) and (d) show both Cu and Zn distribution.

Fig. 2 shows the change of electric current during the deposition. In the earlier stage (~ 10min.), Cu and Zn seem to be co-deposited, because the radius of the Cu distribution (a) and that of the Zn distribution (lighter parts of (b)) overlap. However, when the current increases rapidly (13 ~ 15min.), the Cu distribution (c) spreads to the outer region near the anode compared with the Zn distribution (d). This means that branches, mainly composed of Cu, started to grow, though there is little change in the morphology of the pattern. In this way, the use of XRF imaging clarifies the transition of the growing mode as changes in elemental distribution, corresponding to the increase in electric current.

As the $CuSO_4$ concentration in the electrolyte decreased, the growing pattern changed stepwise. First, curly branches were shown and then, fine straight branches grew parallel and densely. It was observed as XRF images that both copper and zinc were contained in the branches, but Zn concentration was much higher in those patterns.

References

[1] Y.Sawada et al., Phys. Rev. Lett. 56, 1260 (1986); L M.Sander, Sci. American Jan 81-88 (1987).
[2] K.Sakurai and H.Eba, PF Activity Report #17, 321 (1999); K.Sakurai, PF Activity Report, this issue.

* sakurai@yuhgiri.nims.go.jp

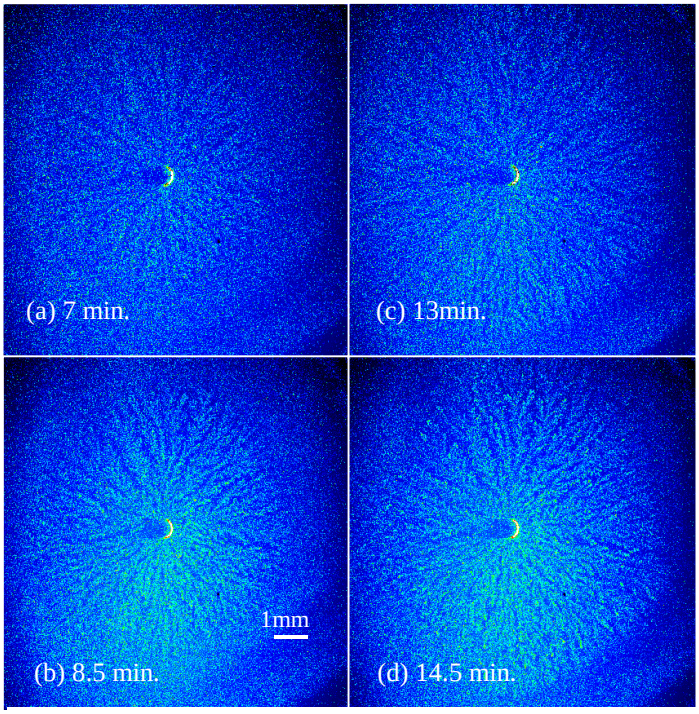

Fig. 1 XRF images obtained during the electrodeposition: (a) and (c) 9.3 keV irradiation (below Zn K-edge), (b) and (d) 9.8 keV irradiation (above Zn K-edge). Exposure time for each image is 1 min.

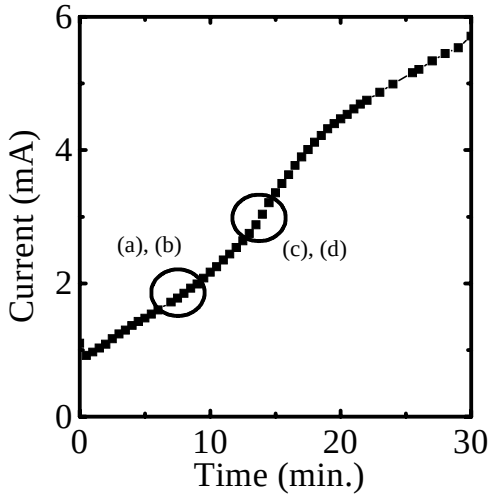

Fig.2 Time dependence of the electric current of electrolysis cell.