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Morphology and compositional distribution of Cu-Zn growing electrodeposits

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Introduction

Electrochemical deposition of metals from an aqueous solution is an operative way to study a variety of pattern formations observed in growth phenomena [1]. In this study, electrodeposits of a binary system composed of copper and zinc were observed and the relationship between composition and pattern was examined. A non-scanning X-ray fluorescence (XRF) imaging technique [2,3] effective for the 2-dimensional analysis of chemical composition was employed for the dynamical observation of the growing electrodeposits.

Experimental

Electrolysis was performed using a compact cell with a copper wire cathode (0.7mm dia.) and a copper ring anode (i.d. 16mm). An electrolyte of an aqueous solution of copper sulfate and/or zinc sulfate, of which the initial concentrations were 6 ~ 250 mM $CuSO_4$ and 180 ~ 350 mM $ZnSO_4$, respectively, was covered by thin Mylar film and forms a 100~200 m thin layer inside the ring. The DC voltage applied was fixed at 2.5 V in all growing runs.

Results

When the Cu/Zn ratio in the electrolyte is rather large (1/6~3/2), a ramified deposit of short branches similar to pure copper deposits was observed (1). As the Zn concentration increases, the pattern changes gradually: bent branches (2), fine straight branches grown parallel and densely (3), and finally zinc dendrite (4). It was observed from XRF images that both copper and zinc were distributed in branches. Figure 1 shows a typical XRF image of deposits. Pattern (2) can be seen to the left of the cathode (located almost center), and pattern (3) in a limited area to the right. Pattern (1) is also observed in the outer edges. Such differences are due to the inhomogeneous Cu/Zn ratio. Copper ions from the ring anode contributed to such a complex distribution.

The relationship between the chemical composition of the electrolyte (corresponding to 4 types of patterns) and that of the deposits is summarized in Fig.2. When pure copper deposit-like pattern (1) is observed, the compositions are in the region of the α (copper and solvent solution by adding zinc), β' or γ phases. A typical powder XRD pattern (inserted in Fig. 2) indicates the existence of each phase of α, ε and η. On the other hand, for the bent deposits (2), both the XRD pattern and the chemical composition agree well with the hexagonal ε phase (represented as $CuZn_4$ or $CuZn_5$). The authors would like to thank Prof. A. Iida for his valuable discussions and kind assistance during the experiment.

References

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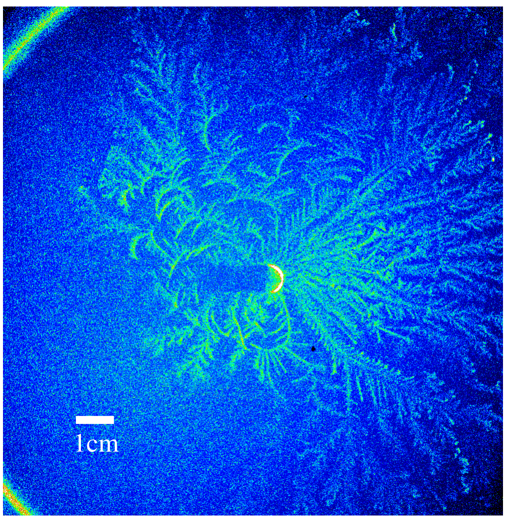

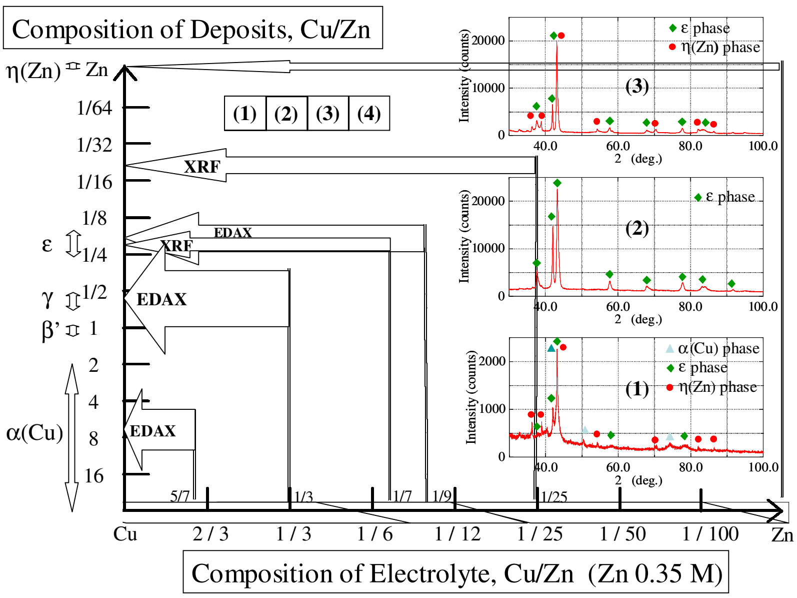

Fig.1 (left) XRF image of electrodeposits from 300 mM $CuSO_4$ and 350 mM $ZnSO_4$ aqueous solution. The pattern started from the cathode (located almost center). Incident energy : 8 keV. Exposure time, 2 min.

Fig.2 (right) Summary of crystal phases of Cu-Zn binary deposits. Four types of phases were obtained for different chemical compositions.