High magnetic field effect on copper electrodeposition and anodic dissolution

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Magnetoelectrochemistry is the electrochemistry in magnetic field, which is characterized by a macroscopic solution flow called magnetohydrodynamic (MHD) flow induced by Lorentz force resulting from electrolytic current and magnetic field. Mass transport in magnetic field is strongly affected by MHD flow, so that in electrodeposition and anodic dissolution, surface morphology of electrode can be controlled by magnetic field.

Numerous microscopic flows called micro MHD flow spontaneously occur in MHD flow. In a vertical magnetic field, a macroscopic tornado-like vortex called vertical MHD flow emerges over an electrode called vertical MHD electrode (VMHDE). In electrodeposition and anodic dissolution, lots of vortexes of micro MHD flows create screw dislocations having chirality depending on the direction of magnetic field. According to this process, copper electrodes with high chiral catalytic activities have been fabricated and applied to enantiomeric reactions [1]. However, in general, because of viscosity, about 1 μm vortexes mentioned above are impossible to rotate. For such a high performance of catalysis, something to drastically decrease the viscosity is required. One question therefore arises; what is it?

Answer is ionic vacancy created as a byproduct in electrode reaction; a polarized spherical free space of the order of 0.1 nm surrounded by oppositely charged ionic cloud, which is produced by the conservations of linear momentum and electric charge during electron transfer [2]. The average lifetime is about 1 sec [3], which is extraordinarily long comparing with a collision period of 10^{-10} sec of solution particle. The most important point is its migration without entropy production, which implies that it does not interplay with other solution particles, providing inviscid flow without viscosity. In copper anodic dissolution on a copper VMHDE, microbubbles originated from ionic vacancies has been observed (Fig. 1) [4]. Furthermore, the micro MHD flows make ionic vacancies distributed in mosaic, so that on the patterned vacancy layer, drilling effect of micro MHD vortexes leads to characteristic pit formation with high aspect ratio on a copper electrode surface (Magneto-drill effect) (Fig. 2).

Electrodeposition is also strongly affected by magnetic field. Unrelated with hydrogen evolution, copper dendrites develop in high magnetic fields (Magneto-dendrite effect) (Fig. 3) [5], where in place of hydrogen molecules, nanobubbles from ionic vacancies adsorb on 3D copper nuclei, inducing remarkable dendritic growth.

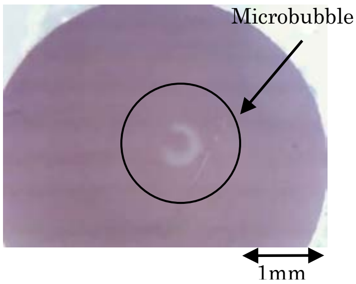

Fig 1. Microbubble globules on copper surface during copper dissolution at 8 T.

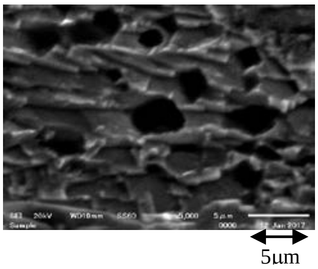

Fig. 2 Magneto-drill effect on a copper rod electrode at 10T.

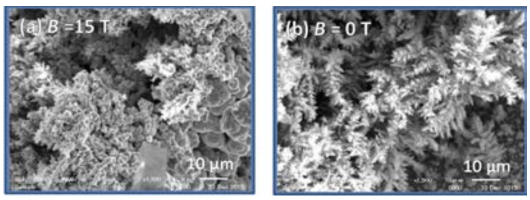

Fig. 3 Magneto-dendrite effect in copper deposition.
(a) B = 15 T without hydrogen gas evolution.
(b) B = 0 T with hydrogen gas evolution.

Reference

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