Hexagonal Corrosion Pattern upon Cleavage of a Zinc Single Crystal under a Vertical High Magnetic Field

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A two-dimensional hexagonal pattern was observed upon cleavage of a zinc single crystal after attack with sulfuric acid under a vertical high magnetic field. This phenomenon results from the formation of microscopic magnetohydrodynamic flow (micro-MHD flow) as microscopic vortexes, which interact with fluctuations of the reaction activity. The spatial pattern of the zinc surface is thought to be a result of the growth of fluctuation in the reaction activity about the zinc anodic dissolution, which was stabilized by the micro-MHD vortexes.

Studies designed to gain insight into nonequilibrium states of reactions have recently discovered a number of phenomena that are based on the effects of a magnetic field on metallic corrosion.[1–3] Specifically, a novel view of the effect of a magnetic field on metal corrosion has been introduced; that the micro-MHD effect is induced in the reaction interface by local Lorentz forces, which flowed in the interaction between the magnetic field and electrochemical corrosion current in the solution phase.[2] From a microscopic view, such a flow effect reflects fluctuations in the reaction activity, i.e., non-uniformity of the reaction rate density distribution. Therefore, if the micro-MHD and reaction fluctuations could fall into a feed back state, there exists a significant probability that stabilized fluctuation induces some traces on the reaction surface. In the usual case, however, perturbations from the interface will disturb or disallow fluctuations arising from the solution side. In the present experiment, the cleavage of a zinc single crystal was used to remove perturbations from the initial surface conditions. The remaining surface structure after chemical etching in dilute sulfuric acid was then observed.

A superconducting magnet was used to generate a magnetic field. This magnet was capable of generating magnetic fields up to 10 T at the center of a room temperature bore space 100 mm in diameter. Nonuniformity of up to 0.25% of the magnetic flux density within 25 mm from the center point was verified by hole-probe measurements.

The corrosion test piece was a zinc single crystal disk that was 8 mm in diameter and 3 mm in thickness. The test piece was heat shock cleaved using liquid nitrogen from a single crystal column, which was initially made by the Bridgman method from 99.99% zinc shots. In the test cell, which was a Pyrex grass beaker that was 30 mm in diameter and 40 mm in height, the sample was dipped in a 2 mol dm^{-3} sulfuric acid solution for 1 h under various magnetic flux densities. The experiments was done under the magnetic field from 0 T up to 10 T. The unit of magnetic flux density variation was 0.5 T. The sample was then washed with distilled water prior to observation of its surface with a scanning electron microscope (SEM) and laser surface profile micrometer.

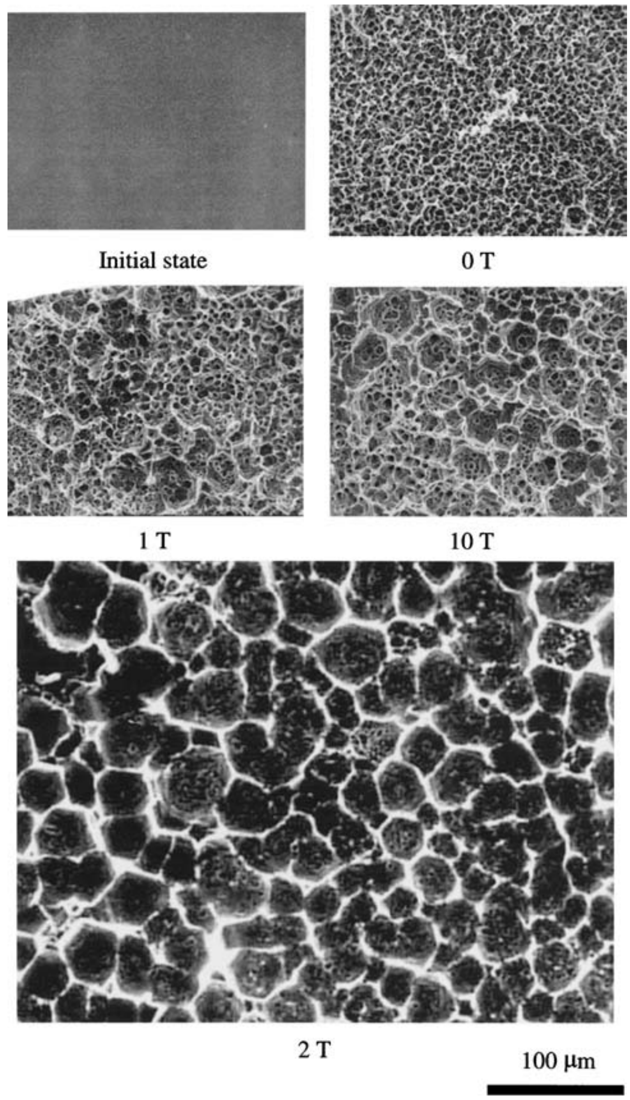

Figure 1. SEM images of the corroded zinc single crystal surface.

Figure 1 shows SEM images of the zinc surface. In the absence of an applied magnetic field, the corrosion was fine and complex. In contrast, under a 1 T magnetic field, a relatively large degree of geometric order in the hexagonal shape was observed. Under a 2 T magnetic flux density, a very clear two dimensional hexagonal pattern arose on the zinc surface. Under an even higher magnetic flux density, this clear pattern degenerated to an indeterminate state similar to that observed with the lower magnetic flux densities, i.e., 1 T. Figure 2 shows the cross section

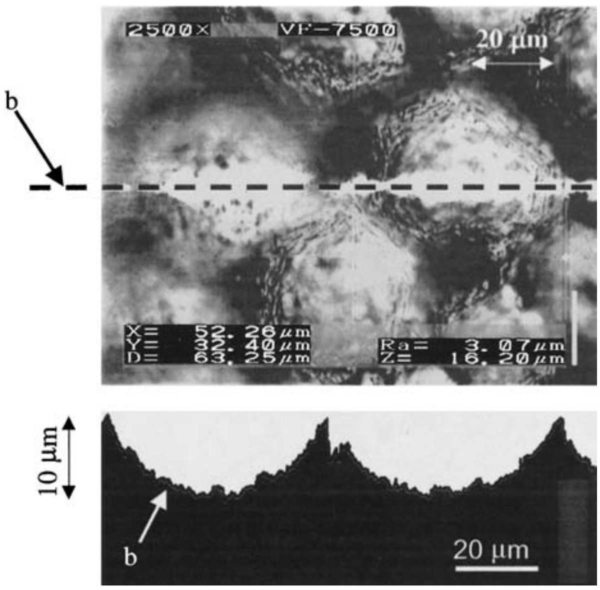

Figure 2. Cross section profile measured by a profile micrometer. Black zones indicate the zinc phase, and a; measured line, b is zinc surface.

profile of the sample at 2 T, revealing a shallow rounded crater. The basis for forming this specific structure is explained in the following discussion.

Zinc corrosion in sulfuric acid is represented electrochemically as:[4]

i) anodic reaction

$$Zn \rightarrow Zn^{2+} + 2e \quad (1)$$

ii) cathodic reaction

$$2H^{+} + 2e \rightarrow H_2 \quad (2)$$

The corrosion pattern follows the distribution of anodic current density, while the anodic reaction rate is controlled by the potential difference between the metal sample and solution.

Even at a uniform interface, the reaction current density fluctuates randomly from the thermal motion of active species.[5] Usually, this fluctuation remains small, and thus uniformity in the reaction is maintained. Under a vertical magnetic field, however, this fluctuation may increase and become stable with micro-MHD flow. This is illustrated schematically in Figure 3. At the interface with a fluctuating current density, there are parallel components of the current flux that can generate Lorentz forces, which circulate around the current density peak, leading to the induction of a circulating fluid flow. The radial component of flow will occur by centrifugal force. From mass conservation, the fluid will flow in a downward motion to the current peak point.

In the schematic illustration of Figure 3, products of the reaction are transported from the center point, resulting in the formation of concentration and activity gradients. Therefore, fluctuation of the current density may be stabilized with vertical magnetic flux density under the state where balance of fluid dynamics and local Lorentz force field was maintained self-consistently. Thus, for the present case, only at 2 T, such fluctuation may increase and be maintained by the balance between these parameters. In other cases, local Lorentz force may be too high or low compared with other functions. The hexagonal pattern is thus considered to be the order of the two-dimensional reaction activity fluctuation from balancing the micro-MHD flow and the activity gradient.

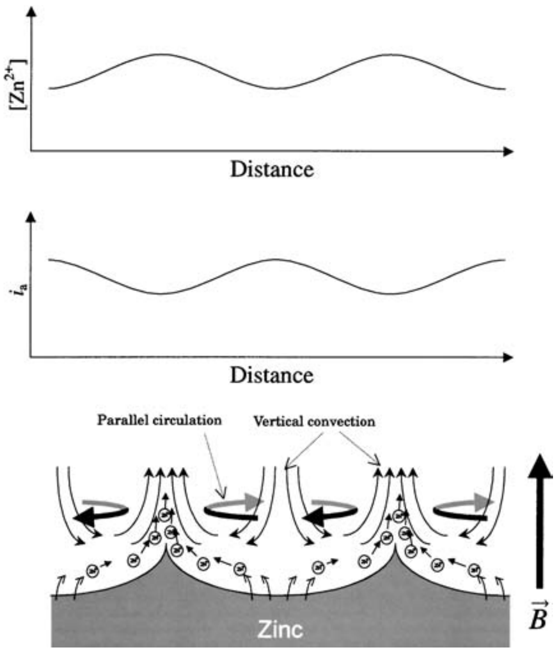

Figure 3. Schematic illustration of the ordering effect in zinc anodic dissolution under a vertical magnetic field.

Under a vertical magnetic field, a hexagonal corrosion pattern was observed upon cleavage of a zinc single crystal. The pattern is thought to be a result of micro-MHD flow. In other words, perturbation from the applied magnetic field led the reaction system to a new orientation including large scale ordering of convection, reaction activity, and current density. This phenomenon is a dissipative system, similar to previously found self ordered convection structures, such as the Benard convection.[5,6]

References

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