Oscillatory Circulation of Copper Particles during Silver-Displacement Plating in a High Magnetic Field

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(Received January 11, 2000; CL-000030)

Motion of copper particles during silver-displacement plating in a high magnetic field was investigated. Immediately after injecting a silver nitrate solution to a vessel filled with copper powder and suspending the powder in the solution, the particles start to circulate along a vessel under a vertical magnetic field with suddenly changing their directions. The velocity of the motion increased with the magnetic field strength though the deposition rate remained constant.

In recent years, following the development of the superconducting magnet, the magnetic field effects in various reaction processes have attracted many researchers' attention.[1] As a result, various phenomena have been reported in many fields.[2-6]

In electrochemistry, the MHD effect that a solution flow (the MHD flow) induced by the Lorentz force greatly affects reaction rates has been clarified.[7] For chemical dissolution of metals in magnetic fields, a new concept, i.e., the micro-MHD effect has been proposed.[8] In these reactions, without any external electrolytic current, a kind of MHD flow takes place on the metal surfaces.

If the metal is a particle suspending in a solution, there is a possibility that the Lorentz force makes it move. Actually, Shinohara et al. have found the gigantic circular motion of zinc particles under high magnetic fields.[9]

The micro-MHD effect can be also considered for other phenomena such as electroless plating and displacement plating.[10-13] From the viewpoint of materials processing, the functional electroless plating onto metal particles is an important method for the surface finishing of metal powder. Therefore, the aim of this paper is to examine a new possibility of the electroless plating by observing the behavior of copper powder during the displacement plating from a silver nitrate solution in a high magnetic field.

Figure 1 shows the schematic configuration of the apparatus. The magnet was a liquid-helium-free superconducting magnet (Sumitomo Heavy Industries Ltd., HF10-100VHF) with a bore space of 10 cm in diameter and the maximum magnetic flux density of 10 tesla (T). For a horizontally homogeneous magnetic field, the interface of the plating solution was placed at the distance of 11 cm from the top of the magnet, where the magnetic flux density was kept constant within the error of ± 0.01 T. Copper powder with the average diameter of 0.1 mm (99.9% pure) was used, and 0.3 mol dm^{-3} silver nitrate solution was prepared as the plating solution.

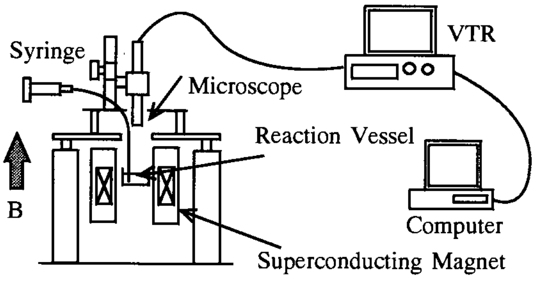
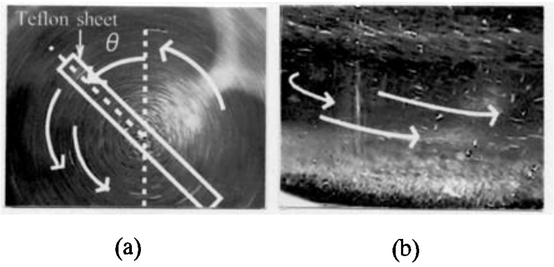


Figure 1. Schematic configuration of apparatus.

After settling in the bore a test vessel (1.7 cm in diameter) filled with 30 mg copper powder, the plating solution was injected into the vessel. The temperature of the solution was kept at 50 °C. The motion of the particles was monitored with a CCD camera through a microscope. The circulation velocity of the solution was measured by using a tetrafluoroethylene (Teflon ®) strip (0.2 cm × 1 cm) floating and rotating at the liquid interface during the reactions as shown in Figure 2. The circulation velocity of the particles was determined by measuring the angle θ of the strip from a standard lines. After the experiment, the plated powder was filtrated and supplied for determining the amount of the deposited silver with the inductive coupled plasma mass spectrometry (ICP-MS).

Figure 2 exhibits the photos of the surface of the plating solution and the inside of the solution; the solution together with the mass of the copper powder rotated along the inner wall of the test vessel, and the silver dendrites quickly developed. Needle-like dendrites repeatedly grew up and fell off. Simultaneously, as shown in Figure 3, the direction of the rotation was changed suddenly. Such abrupt change of the rotating direction seemed accidental and non-periodic, just like a chaotic oscillation. In spite of the chaotic motion, the velocity increased linearly with the magnetic field strength, and the deposition rate was kept constant (1.34×10^{-5} mol s^{-1}) independent of the magnetic field strength.



(a) (b)

Figure 2. Revolution of copper particles under the vertical magnetic field of 3.1 T. Photos were taken after 30 seconds from the starting of the reaction. Solution contained 0.3 mol dm^{-3} $AgNO_3$. Temperature was kept at 50 °C. (a) the surface of the plating solution. (b) the inside of the solution. The revolution velocity of the particles was determined by measuring the angle θ of a Teflon strip from the standard line (dotted line).

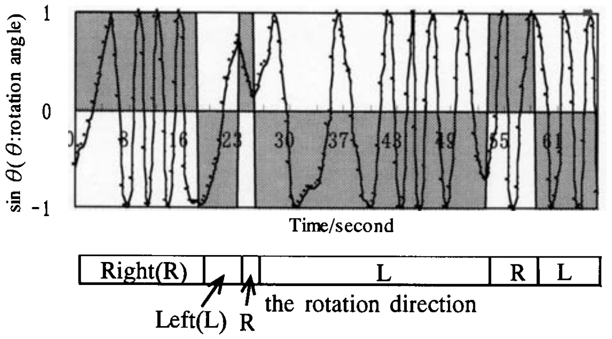


Figure 3. Time dependence of the rotation angle and the rotation direction. The angle was measured as shown in Figure 2, and all the conditions were the same as Figure 2.

In this plating, it is thought that an electrochemical local cell is formed between the following anodic and cathodic reactions,

$$1/2\ \mathrm{Cu} \rightarrow 1/2\ \mathrm{Cu}^{2+} + e^{-} \qquad (1)$$

$$\mathrm{Ag}^{+} + e^{-} \rightarrow \mathrm{Ag} \qquad (2)$$

As mentioned above, the dendrites are rough and eager to fall off from the copper substrate. From these experimental results, as shown in Figures 4 and 5, we can suppose the mechanism of this phenomenon as follows: Assuming that this motion comes from a cooperative effect of a lot of particles, we can pick up one particle as the representative of all other particles. Figure 4 indicates how the particle moves, i.e., inside the particle, from the cathodic site to the anodic site, an electrolytic current flows, so that in the magnetic field, a localized Lorentz force is produced, and the particle moves to the right side. As explained in Figure 5, after a certain time elapses, the cathodic portion is roughly covered with silver dendrites, and the silver ions are depleted in the solution near the dendrites. Therefore, the whole reaction rate decreases and finally the motion ceases (b). On the anodic side, however, the silver ions can be sufficiently supplied, so that the reduction of silver ions starts at the former anodic site (c). On the former cathodic side, among the roots of the dendrites, the copper substrate dissolves because of the anodic dissolution of copper (d).

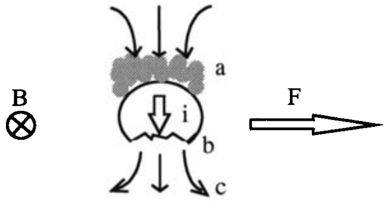


Figure 4. Schematic illustration of a moving copper particle. B, magnetic field; i, current density; F, Lorentz force; a, cathodic site; b, anodic site; c, current line.

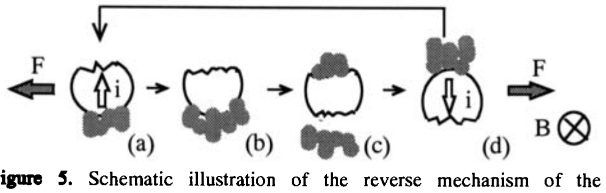


Figure 5. Schematic illustration of the reverse mechanism of the moving direction. B, magnetic flux density; i, current density; F, Lorentz force; (a), Initially, silver dendrites deposite at the bottom side.; (b), Because of depletion of silver ions, deposition rate decreases, and motion finally ceases.; (c), Reduction of silver ions startes at the top side which abounds in silver ions. As the dissolution of the substrate at the bottom progresses, the silver dendrites begin to fall off.; (d), At the top side, silver deposition prodeeds, and the particle moves in the direction opposite to (a).

Namely, the cathodic and anodic sites are exchanged, so that the current in (a) and (d) flow in the opposite directions, and the Lorentz forces operate reversely. This is the reason why the rotation changes the direction. As the reactions proceed, at the new cathodic site, silver dendrites grow, whereas the silver dendrites at the new anodic site are removed by the dissolution of the copper substrate. Because the dendrites tend to fall off, the period of each state of the plating becomes uncertain.

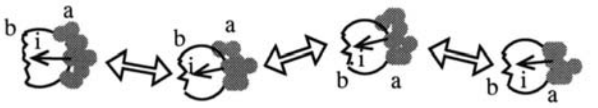


Figure 6. Schematic illustration of the cooperative plating of the copper particles. i, current density; a, cathodic site; b, anodic site;

In an actual system, all the particles behave cooperatively just like one gigantic particle. This is because the particle density is so high that the neighboring particles have the great probability to contact each other. Figure 6 schematically represents such effect; an electrolytic current penetrates all the ordered particles in one direction. The anodic and cathodic sites of each particle go hand in hand with those of the neighbor particle. Therefore, according to the mechanism mentioned above, if one particle changes the current direction, all other particles also change the directions. This situation in Figure 6 is similar to the phase transition represented by the Ising model for ferromagnetism materials.[14]

This is only a qualitative elucidation, so that we are now attempting to quantitatively examine the oscillatory behavior of this rotation.

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