Transactions of the Materials Research Society of Japan 25 [1] 59-63 (2000)

Application of Magnetic Field to Reaction Control and Materials Processing

Ryoichi Aogaki

National Laboratory for Magnetic Science, Science and Technology Corporation, 1-1-56, Shibashimo, Kawaguchi, 333-0848, Japan

Fax: 81-48-265-8200, e-mail: aogaki@saitama.jst.go.jp

(Department of product design, Polytechnic University, 4-1-1, Hashimotodai, Sagamihara, 229-1196, Japan)

(Fax : 81-427-63-9219, e-mail: aogaki@uitec.ac.jp)

Abstract

Application of magnetic field to reaction control and materials processing in liquid phases is discussed. In energetics, usually the magnetic field yields not so much amount of energy as the electric field. In almost all cases, the magnetic field thus does not affect the electron transfer process of a reaction, but generates the magnetic force or Lorentz force to order the molecules or to move the material itself. Therefore, the magnetic field mainly changes the mass transfer processes of reactants in solution. In the present paper, some examples of the promotion and depression of the reactions are presented. The magnetic levitation of materials is also discussed from the viewpoint of the protection of the contamination from the vessel.

Key word: High magnetic field, Magneto-convection, MHD effect, micro-MHD effect, Magnetic force, Lorentz force

1. INTRODUCTION

Recent development of the superconducting technology has attracted many people's attention. As the application of this technology, superconducting magnets are now worldwidely spreading; especially, the invention of the liquid-helium-free type of superconducting magnet has accelerated such tendency. At the same time, various phenomena in high magnetic fields have been clarified by using the magnets.

Though magnetic field is often compared with electric field, there are great differences between them in the effects on the reaction and materials processing. From the energetics, the electric field can provide a reaction system with the energy equal to or more than the thermal energy, whereas even at the high magnetic field of 10 T, the system is supplied with at most only the order of the 1/1000 th of it. This means that the interaction between magnetic field and matter is weaker than that between electric field and matter. Magnetic field transmits the bodies of nonmagnetic materials such as water without strong interaction, while electric field vanishes at the quite short distance (several μm) because of the formation of an electric double layer. As a result, in an electrode reaction, the electric field affects the electron-transfer processes of the reactants adsorbed on an interface. Except for few cases, magnetic field does not change the electron-transfer processes, yielding the magnetic forces in the wide area. Therefore, the magnetic field induces the convection flows for gas and liquid phases[1-4], and levitates liquid spheres and solid materials[5,6]. On the other hand, just like the magnetic field effect on polymerization, the magnetic field improves the mechanical strength of materials by the magnetic orientation[7].

From these results, in solution phases, the magnetic field as a reaction field is expected to produce remarkable effects on the mass transfer processes. In fact, in various chemical processes, it has been reported that the reaction rates are varied by the magnetic fields, which, in almost cases, result from the mass transfer processes. In this paper, from the viewpoints of the reaction control and the application to the materials processing, the magnetic field effects are discussed, which are mainly based on the results of the author's laboratory.

2. MAGNETO-CONVECTION EFFECTS

It is well known that the dissolution rate of oxygen into water is enhanced by the magneto-convection[1]. Figure 1 shows the relationship between the total amount of dissolved oxygen and the intensity of the magnetic field. The cause of this phenomenon is that when oxygen with paramagnetism dissolves into water under the magnetic field gradient, a magnetic force acts on oxygen, so that the water surface moves to accelerate the mass transfer of the oxygen. Under the constant gradient of a magnetic field with an axial symmetry, the dissolution rate increases with the 1/4th order of the magnetic flux density[2,3]. Moreover, such promotion of the dissolution rate, as shown in Fig. 2, takes place also in the homogeneous magnetic field[4], which is formulated

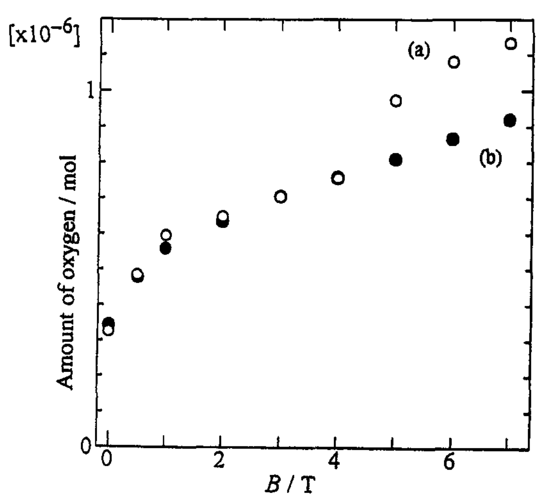

Figure 1. The relationship between the total amount dissolved oxygen and the intensity of the magnetic field in the absence (a) and presence (b) of absorbent cotton in the bore.

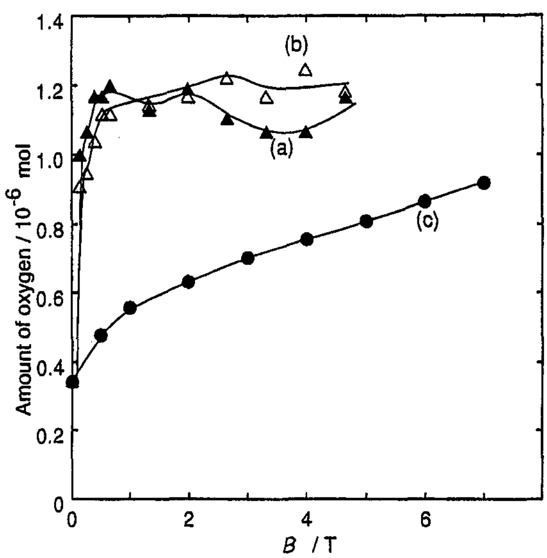

Figure 2. The relationship between the total amount dissolved oxygen and the intensity of the homogeneous (a, b) and heterogeneous (c) magnetic field.

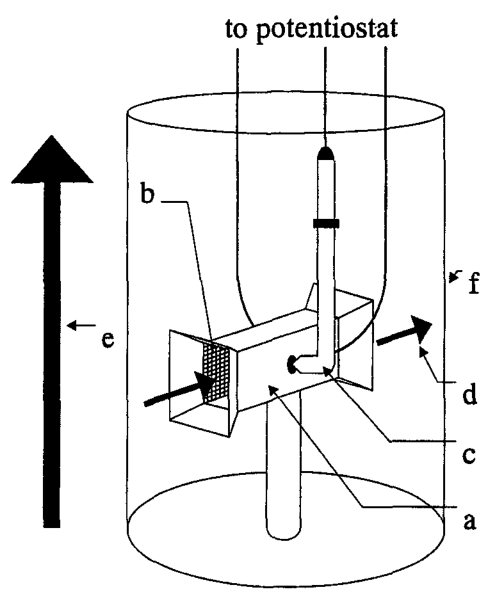

Figure 3. Magnetohydrodynamics electrode. a; working electrode, b; counter electrode, c; Luggin capillary connected with the reference electrode, d; MHD flow, e; magnetic flux density, f; vessel filled with solution.

by the nonequilibrium fluctuation theory. These experimental results suggest the possibility of the mass transfer rate control with the magnetic field.

3. MHD AND MICRO-MHD EFFECTS

As a different type of magnetic force mentioned above, we can consider the Lorentz force. In electrochemical systems, the Lorentz force generated by the interaction between the electrolytic current and the magnetic field drastically changes the reaction rate. For example, with an electrolytic cell called the MHD electrode shown in Fig. 3, a remarkable increase of the electrolytic current is observed. Figure 4 represents the plots of the current vs. the 1/3rd order of the magnetic flux density, which follow straight lines[8]. This can be elucidated by the fact that the Lorentz force induces a solution flow which enhances the mass transfer of active ions. This magnetic field effect is called the magnetohydrodynamic (MHD) effect. If we tentatively call such enhancement in reaction rate "the positive catalytic effect", we can also find "the negative catalytic effect" where the reaction rate is depressed.

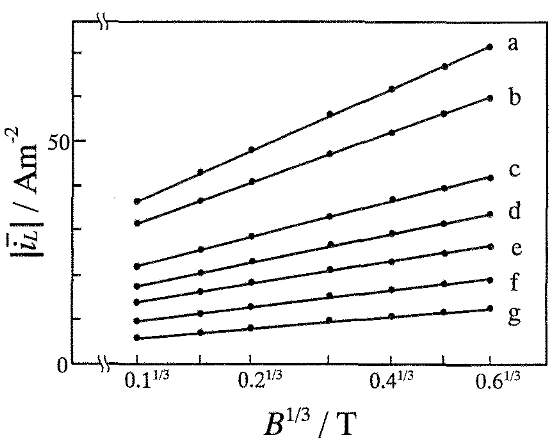

Figure 4. Enhancement of diffusion current by magnetic flux density. Diffusion current was measured for copper electrodeposition in copper sulfate solution with 0.5 mol dm^{-3} sulfuric acid.
a; C_0 = 7.6×10 mol m^{-3}, b; C_0 = 6.8×10 mol m^{-3}, c; C_0 = 5.2×10 mol m^{-3}, d; C_0 = 4.4×10 mol m^{-3}, e; C_0 = 3.6×10 mol m^{-3}, f; C_0 = 2.8×10 mol m^{-3}, g; C_0 = 2.0×10 mol m^{-3}.

Figure 5 exhibits the experimental results of the copper chemical dissolution in nitric acid. As shown in this figure, the dissolution is hindered by the high magnetic field[9]. In this case, apparently no electrolytic current flows, which however, actually exists to generate the Lorentz forces. As well known, a lot of electrochemical local cells are formed on the copper surfaces, and circulating currents flow among anodic and cathodic active points. Therefore, the localized Lorentz forces stir the solution with local convection flows. On the other hand, the copper dissolution autocatalytically develops with the nonequilibrium concentration

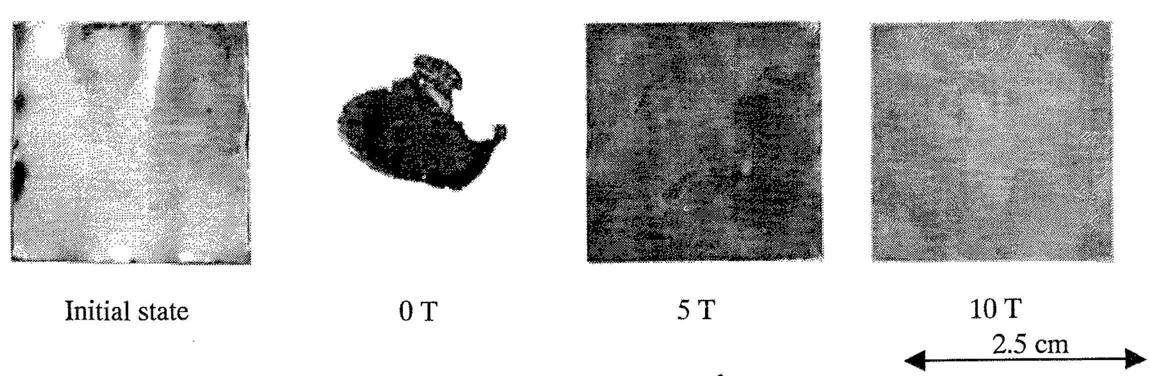

Figure 5. Photos of copper sheets after 20 minutes immersion in 3 moldm^{-3} nitric acid at the magnetic flux densities of 0T, 5T and 10T. The sample is copper sheet (99.7% in purity) with 2.5x2.5cm^2 in area and 0.1mm in thickness. Temperature is 11±1℃.

fluctuation[10]. As shown in Fig. 6, the local convection flows thus blow off the fluctuation from the reaction sites, so that the autocatalytic process is blocked, and the dissolution rate is resultantly suppressed[11]. Since the convection cells have the dimensions of the order of the electrochemical local cells (several 10 μm), this phenomenon is called the micro-MHD effect. When the magnetic field is vertically applied to the metal surfaces, these convection flows take the forms of microscopic vortexes, and a pair of macroscopic rotations is predicted to emerge by associating the vortexes. In Fig. 7, the schematic configuration of these two types of motions is exhibited[11]. Figure 8 is an example of the flow-visualization for the solution over the copper surface; as expected above, the rotations can be seen in the neighborhood of the surface[12].

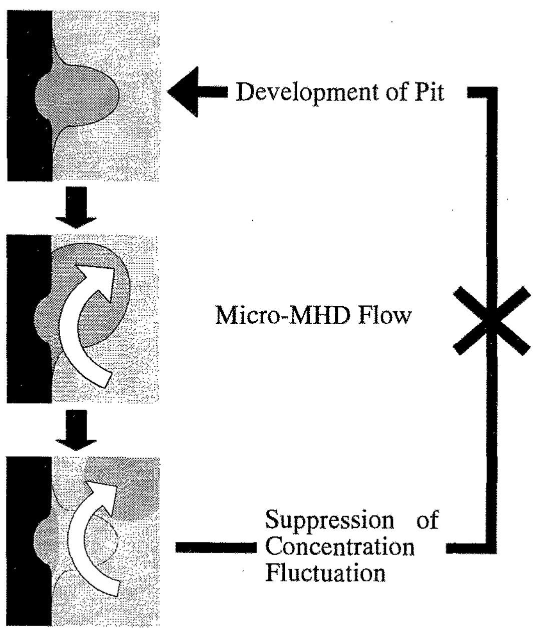

Figure 6. Suppression of unstable growth of concentration fluctuation by MHD flow.

4. MAGNETO-LEVITATION EFFECTS

By using the magnetic fields, it is possible to levitate a matter in the space against the gravity force. These methods are also classified into two cases, i.e., one comes from the Lorentz force and another is attributed to the magnetic force by the magnetic field gradient. Among them, the cold crucible levitation method has most

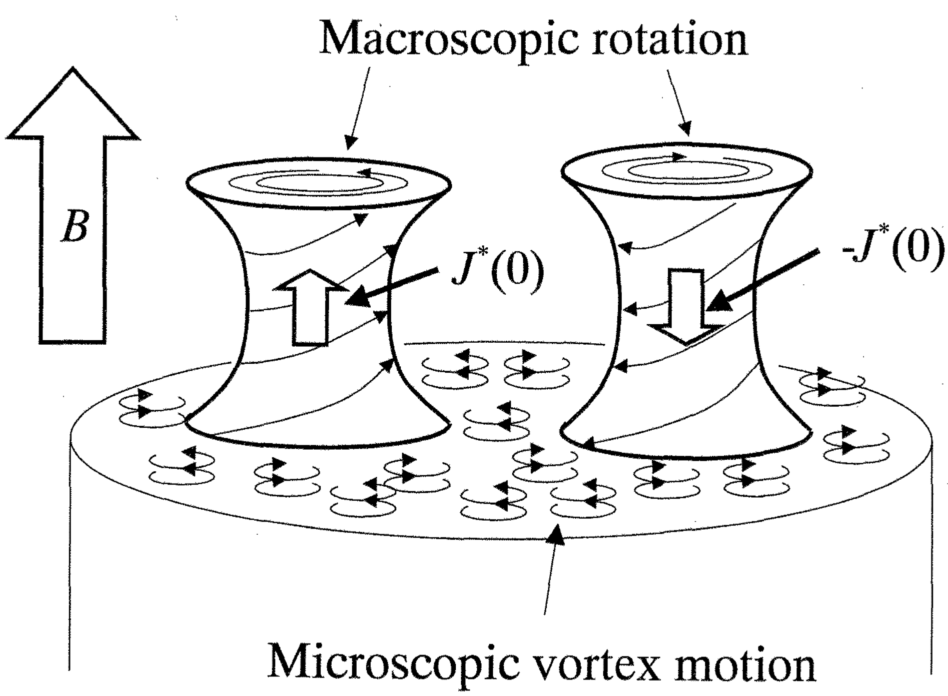

Figure 7. Schematic illustration of macroscopic solution flow induced by micro-MHD flow cells.

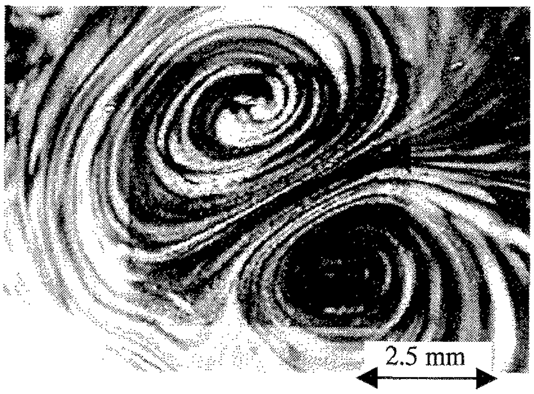

Figure 8. Photo of visualized solution flow. Electrode 5×5 mm^2 copper (99.9% in purity), solution 3 mol dm^{-3} nitric acid, solution depth 1mm, temparature 300±1 K, flow tracer is carbon colloid.

progressed; a melting metal is levitated by means of the Lorentz force to protect the contamination from the inner wall of the crucible[13]. On the other hand, non-magnetic materials such as water and glass are levitated by the magnetic force for materials processing[14].

5. CONCLUSIONS

For the application of the magnetic field to the materials processing, as represented by the magnetic orientation of polymers, it is reasonable to pay attention to the magnetic force itself. However, it is also important to consider the fact that the magnetic field transmits without reduction for a long distance. For example, as the application, the reaction control of reactants in a completely sealed vessel can be pointed out. Since it has been found that the crystal sizes in copper electroless plating decrease in the high magnetic field[15], we will be able to use such phenomenon for the micro-fabrication on surfaces in various shapes. For the materials processing by the magnetic levitation, though there are various problems to be solved, it is quite useful to utilize micro-gravity-like conditions for the processing.

Since this scientific field is anyway a new area that has just been born, we can expect a bright prospect in near future.

REFFERENCES

1. H. Uetake, J. Nakagawa, N. Hirota and K. Kitazawa, "Proceedings of The 1st Symposium on New Magneto-Science", p. 43, JST, Kawaguchi (1998).
2. S. Kishioka and R. Aogaki, *Chem. Lett.*, p.91 (1998).
3. S. Kishioka and R. Aogaki, "Proceedings of The 2nd Symposium on New Magneto-Science", p. 315, JST, Kawaguchi (1999).
4. S. Kishioka and R. Aogaki, Chem. Lett. p.473 (1999).
5. E. Beaugnon and R. Tournier, *Nature*, **349**, 470 (1991).
6. Y. Ikezoe, N. Hirota, J. Nakagawa and K. Kitazawa, *Nature*, **393**, 749 (1998).
7. H. Ezure, T. Kimura, S. Ogawa and E. Ito, *Macromolecules*, **30**, 3600 (1997).
8. R. Aogaki, K. Fueki and T. Mukaibo, *Denki Kagaku* (presently *Electrochemistry*), **43**, 509 (1975).
9. K. Shinohara and R. Aogaki, *Electrochemistry*, **67**, 126 (1998).
10. R. Aogaki, "Modern Aspects of Electrochemistry No. 33", p. 217, edited by R. E. White, J. O'M. Bockris and B. E. Conway, Plenum, New York (1999).
11. R. Aogaki, *J. Surf. Sci. Soc. Jpn*, **20**, 752 (1999).
12. K. Shinohara, K. Hashimoto and R. Aogaki, to be submitted.
13. M. Nagano, I. Muramatu, A. Awazu and T. Takahashi, "Proceedings of The 2nd Symposium on New Magneto-Science", p. 346, JST, Kawaguchi (1999).
14. M. Hamai, M. Tagami, I. Mogi, K. Watanabe and M. Motokawa, "Proceedings of The 2nd Symposium on New Magneto-Science", p. 150, JST, Kawaguchi (1999).
15. M. Hashiride, Y. Suzuki and R. Aogaki, "Proceedings of The 2nd Symposium on New Magneto-Science", p. 346, JST, Kawaguchi (1999).

(Received December 17,1999 ; Accepted February 15,2000)