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The Magnetic Field Effects on Electrolysis. II.[1)] The Anodic Surface Oxidation of Gold

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Synopsis. In the anodic oxidation of gold in an acidic solution, the electrode surface is covered with a black deposit. It dissolves immediately after the application of an external magnetic field (1 T). The results are discussed in terms of a magnetohydrodynamic mechanism.

In previous work,[1)] the magnetic field effects on the electrochemical reduction of hexacyanoferrate(II) and oxidation of hexacyanoferrate(III) were studied by means of potentiometry. It was shown that the magnetic field effects on these redox reactions can be interpreted in terms of a magnetohydrodynamic (MHD) mechanism in which an electrolyte flow near the electrode is affected by an external magnetic field.

In the present paper we report on magnetic field effects on the anodic surface oxidation of gold in an acidic solution.

Experimental

The experimental set-up was essentially the same as that described previously.[1)] An electrolytic cell and electrodes were placed between the pole pieces of an electromagnet (Tokin SEE-15). A magnetic field did not affect the potential of a saturated calomel electrode (SCE) used as a reference. One side of a gold plate electrode (5×10 mm) was covered with an epoxide glue. The electrode plate was always kept parallel to the magnetic flux.

Electrolysis was carried out by using a potentio/galvano stat (Hokuto Denko, HA-102). The purest grade sulfuric acid, sodium sulfate, and sodium chloride were used as received. Water was distilled twice before use.

Results and Discussion

Figure 1 shows the potential–current curves of a gold electrode in an acidic solution observed in the absence and the presence of a magnetic field (1 T). An electric current increases with the increasing electric potential and reaches a maximum at 1.2 V, a sudden drop of the current appearing at 1.23 V. By increasing the potential, however, the current again increases. Gas (probably O_2) evolves at higher potentials (>1.4 V).

The anodic behavior of Au in chloride solutions has been reported by several research groups.[2—5)] Concerning anodic oxidation of gold in $NaCl-H_2SO_4$ and $KCl-HClO_4$ solutions,[4,5)] the current increase with increasing potential in the range of 1.0—1.4 V was reported to be due to the dissolution of Au:

$$\mathrm{Au} + 4\mathrm{Cl}^- \longrightarrow \mathrm{AuCl}_4^- + 3\mathrm{e}^-. \qquad (1)$$

Thus, the current increase in the range of 1.0—1.2 V shown in Fig. 1, can be attributable to the Reaction 1 mentioned above. A sudden drop at 1.23 V is due to the formation of a passive oxide and/or adsorbed oxygen film on the Au electrode. In the presence of a magnetic field, the electrolytic current at 1.1—1.2 V increases by about 300% compared with the one in the zero field, as shown in Fig. 1. Judging from the results in a previous paper,[1)] this current increase is attributable to the MHD mechanism, since the MHD force is expected to affect the mass transfer near the electrode surface.

Upon electrolysis at an electric potential of about 1.2 V, the surface is covered with a black deposit in the absence of a magnetic field, as reported in the literature.[4)] By applying a magnetic field, the black deposit on the surface was found to dissolve, suggesting that the MHD mechanism is operative in the present reaction. In order to make this point clearer, the influence of the orientation of electrode

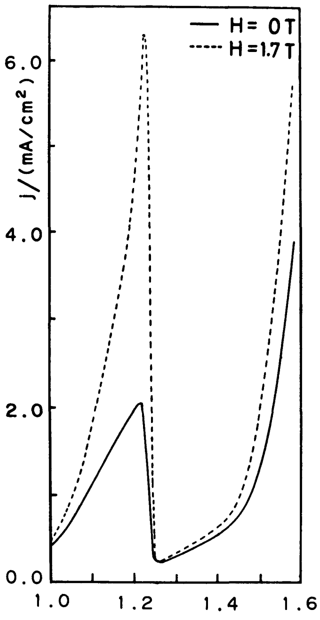

Fig.1 Mangetic field effects on the potential-current curves of the anodic surface oxidation of gold. Concentrations of Na_2SO_4, H_2SO_4, and NaCl are 0.1, 0.05, and 0.01 mol dm^{-3}, respectively.

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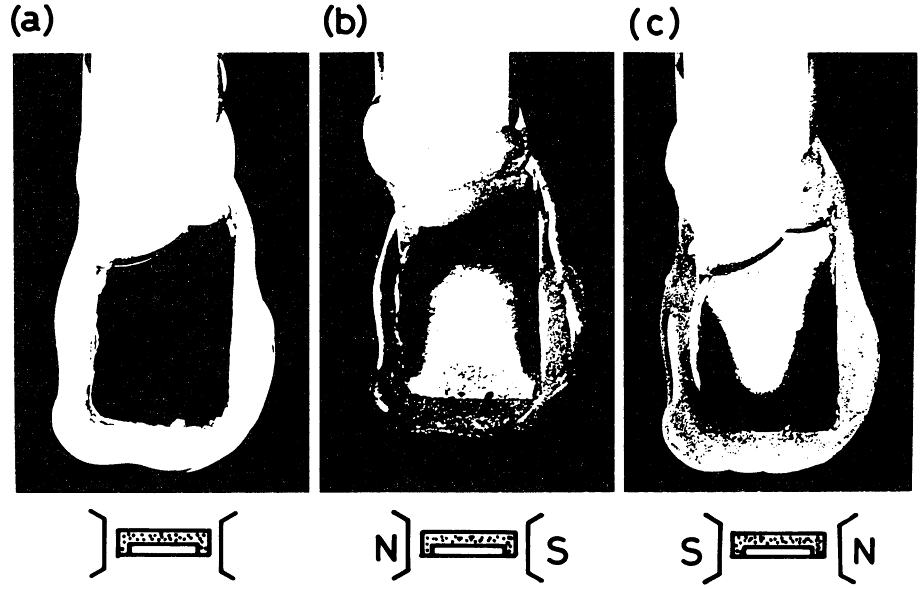

Fig. 2. Magnetic field effects on the deposit on a gold electrode in the absence (a) and in the presence ((b) and (c)) of a magnetic field (1 T). Electrolysis is carried out at 1.2 V vs SCE. Concentrations of Na_2SO_4, H_2SO_4, and NaCl are 0.1, 0.05, and 0.2 mol dm^{-3}, respectively. Top views of two magnetic field orientations with respect to the electrode are also illustrated in the figure. Dotted area indicates the epoxide glue and the rest is the gold electrode.

with respect to a magnetic field on the dissolution of the black deposit was examined.

Figure 2 shows the effects of a magnetic field (1 T) on the black deposit on the Au electrode. In the absence of a magnetic field, the surface of the Au electrode is covered with a black deposit 2—3 min after the start of electrolysis (a). Then, a magnetic field is applied in the direction shown in (b). The deposit immediately starts to dissolve from the bottom of the electrode. On the other hand, when a magnetic field is applied in the opposite direction, as shown in (c), after the electrolysis at zero field, dissolution of the deposit occurs from the top of the electrode.

Electrochemical corrosion and passivation of metal electrodes are affected by various experimental factors such as composition and concentration of electrolyte, current density, pH, and temperature. Taking into account the reports on the deposit on an Au electrode[2,4,6] and others,[7] the black deposit observed in the present study may be a hydrated oxide of Au, though its chemical composition has not yet been determined. According to the literature,[8—10] halogen ions, such as Cl^- and Br^-, attack the oxide film on metal electrodes, resulting in a dissolution of the oxide film. Therefore, the magnetic field effects on the dissolution of the black deposit can be interpreted in terms of the MHD mechanism as described below.

The MHD force $\boldsymbol{F}$ to the electrolytic current $\boldsymbol{j}$ in the magnetic field $\boldsymbol{H}$ can be given by

$$\boldsymbol{F} = \boldsymbol{j} \times (\mu \boldsymbol{H}), \qquad (2)$$

where μ is the magnetic permeability. In the orientation of the electrode with respect to the magnetic field shown in Fig. 2 (b), the MHD flow of the electrolyte occurs upward. This means an increasing supply of Cl^- from the bulk solution to the electrode surface, leading to an upward dissolution of the hydrated oxide deposit on the electrode. Similarly, in the orientation shown in (c), the electrolyte flows downward, resulting in a downward dissolution of the deposit.

In the absence of a magnetic field, Cl^- ions are supplied from a bulk solution to the electrode surface by such mass-transport processes as diffusion, convection, and electrophoretic migration. In the presence of a magnetic field, they are further supplied by the MHD flow. This efficient and orientation-dependent mass-transport process is observed as a dissolution of the black deposit (Fig. 2). Furthermore, an enhanced dissolution of the deposit by the MHD flow was also observed as an increase in the electrolytic current in the potential–current curve (Fig. 1).

It is noteworthy that the MHD flow of the electrolyte has no influence on the electrolytic current in the passive state around 1.35 V (Fig. 1). This fact suggests that bonding of the passive oxide film to the metal surface is probably strong, as the passive film might be quite thin.[11,12] On the other hand, the black (hydrated oxide) deposit appearing arround 1.2 V may loosely cover the electrode surface. Therefore, we may conclude that the external magnetic field significantly affects the mass-transport processes near the electrode surface, while it seldom influences those inside the surface. Thus, the present results *visually* demonstrate the importance of the MHD-induced flow for the mass-transport process near the electrode, though quite a few are reported for the magnetic field effects on the electrolytic current.[13]

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