MAGNETOHYDRODYNAMIC AND PARAMAGNETIC GRADIENT EFFECTS DURING ELECTROCHEMICAL PROCESSES AT MICROSTRUCTURES

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Introduction. It is widely accepted that a magnetic field turbulences can enhance the mass transport in electrochemical reactions [1, 2]. Beside this Lorentz force induced effects, Eq. (1) the magnetic gradient forces, Eq. (2) are to small to affect measurable influences on mass transport:

$$\mathbf{f}_{\text{L}} = \mathbf{j} \times \mathbf{B}\,, \tag{1}$$

$$\mathbf{f}_{\text{P}} = \chi_m \mathbf{B}^2 \nabla \mathbf{c}/(2\mu_0)\,; \tag{2}$$

j – current density, B – magnetic flux density, χ_m – molar susceptibility, ∇c – concentration gradient, μ_0 – magnetic field constant.

There were some semi-empirical equations which attempt to describe the interplay of limiting current density, j_{L}, with the magnetic flux density [3, 4]. For macroscopic electrodes a linear dependence of j_{L} with $B^{1/3}$ is found in most cases [3] whereas for microelectrodes a proportionality of j_{L} to B is reported [5]. Nevertheless it is hard to predict the magnitude and sometimes even direction of a magnetic field effects at macorsized electrodes [2]. The investigations at micro electrodes were mainly performed with disk electrodes. However, from a hydrodynamic point of view recessed microstructures are more interesting.

Therefore, the aim of this paper was to study systematically the influence of a parallel arrangement between current lines and the applied magnetic field for copper and silver dissolution.

1. Experimental. The electrolytes were prepared from p.a. grade chemicals and doubly distilled water. All measurements were performed under thermostatic control at room temperature.

Arrays of six copper micro disk electrodes were prepared by embedding copper wires (diameter 100 μm) in epoxy resin. After curing of the resin the resulting blocks were cut and polished yielding two arrays of six micro disk electrodes. Embedding copper foils (diameter 30 μm) in the same manner produced vias of about 1cm length. For the systematic investigation of the magnetic field effects the electrode arrays were fixed in a holder with well defined distances between the working electrodes (i.e. the micro disks), the counter electrode (a Pt sheet of 100mm^2) and the reference electrode (a saturated calomel electrode, SCE). In addition a stirring paddle could be put in the holder to work under conditions of forced convection.

A water-cooled electromagnet (VEB Polytechnik, Phylatex, Chemnitz, Germany) was used to apply magnetic fields up to 0.8 T.

2. Influence of an alternating magnetic field on the current efficiency during anodic dissolution of copper. To study the time dependence of the magnetic field effect the copper samples were polarized at 500 mV vs. SCE
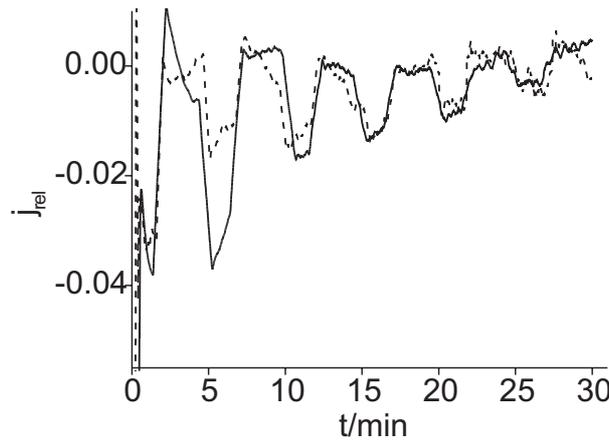
Fig. 1. Relative changes of the current density during the potentiostatic dissolution of copper under the presence of a parallel magnetic field (0.6 T). The solid and the dashed line are for two different orientations of the B field which are further explained in Fig. 2.

while magnetic field was periodically switched on and off (period 2/3 min). As a quantitative measure the relative change of the current density was calculated according to Eq. (3).

$$j_{\text{rel}} = \big(j(B) - j(B=0)\big)/j(B=0), \qquad (3)$$

where $j(B)$ and $j(B=0)$ are the (time dependend) current densities with and without the magnetic field applied, respectively.

Interestingly we found an inhibition of the current density when the current lines and the B field were aligned parallel in quiet and mechanically stirred solution. The inhibiting effect decreased with increasing etch time, i.e. increasing depth of the holes (Fig. 1).

According to Eq. (1) the Lorentz force is zero for a parallel arrangement of B and j. Therefore, only the gradient force density, Eq. (2), remains as a source of momentum transfer to the fluid. The direction of this force is the same as the concentration gradient; it does not depend on the direction of the magnetic field. The experimental data shown in Fig. 1 are in perfect agreement with the theory. For the dashed line the B field points into the structure and for the solid line out
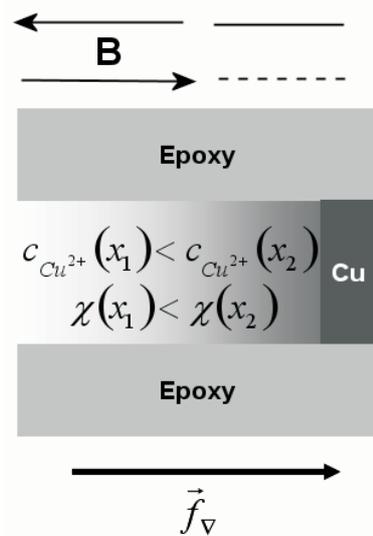
Fig. 2. Schematic representation of the influence of a magnetic field parallel to the current lines during the anodic dissolution of copper in a microstructure.
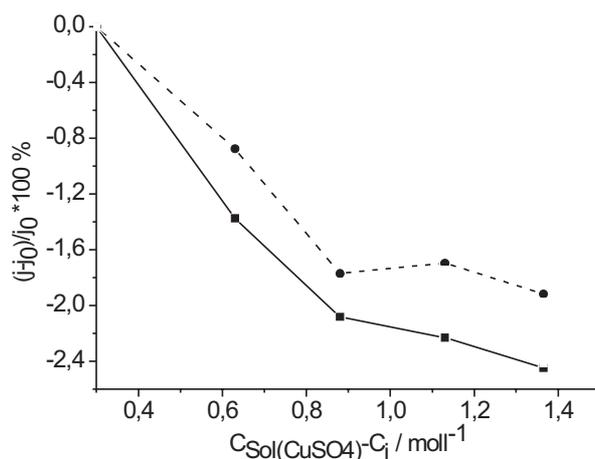
Fig. 3. Relative changes of the current density during the potentiostatic dissolution of copper under the presence of a parallel magnetic field (0.6 T) in unstirred solution. The solid ($t = 5$ min.) and the dashed line ($t = 10$ min.) show the decrease of the magnetic field effect with increasing etch time.

of the structure (Fig. 2). The sharp decreases and increases of j_{rel} mark the times when the magnetic field was switched on and off, respectively. The schematic sketch of Fig. 2 shows that the gradient force is opposite to the diffusion force and tends to hold the paramagnetic species back in the structure. The result is a decrease of the current density.

3. Concentration dependency of the magnetic field effect for copper and silver dissolution. The influence of an increase in metal ion concentration was investigated on the copper and silver dissolution respectively. If copper ion concentration of the etching media reaches the solubility of copper sulphate the reported current inhibition disappears. For silver wire dissolution 1 M nitric acid, containing the same amount of surfactant as for copper experiments, was used. In the case of silver etching the observed enhancement of mass transport disappeared near solubility border of silver nitrate as well. However, setup for silver etching
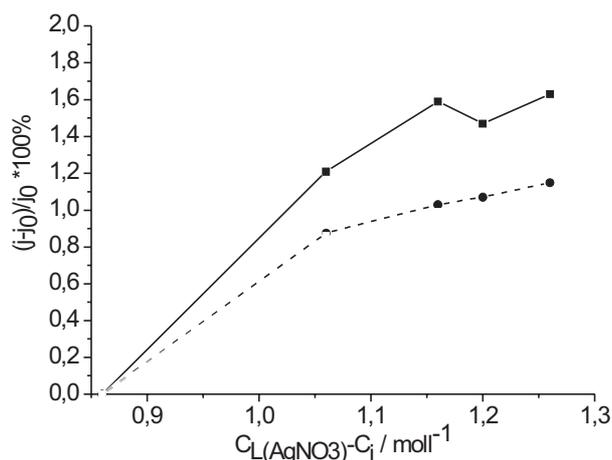
Fig. 4. Relative changes of the current density during the potentiostatic dissolution of silver under the presence of a parallel magnetic field (0.8 T, 500 rpm) in stirred solution. The solid ($t = 5$ min.) and the dashed line ($t = 10$ min.) show the decrease of the magnetic field effect with increasing etch time.

needed to apply higher flux densities ($B = 0.8\,\text{T}$, $U = 800\,\text{mV}$, $500\,\text{rpm}$) and electrolyte stirring to reach observed enhancement. The approach of metal content in the etching media makes the concentration gradient between electrode surface and the electrolyte disappearing (Fig. 2). In this consequence no magnetic gradient existed when the magnetic field was switched on (Eq. (2)). Curves for silver and copper etching show the magnetic field dependency at distinct times ($t = 5$, 10min.) over the deviation from metal salt solubility. All observed effects or copper and silver wires decreased for an increase of etching time respectively (Figs. 3, 4).

The primary gradient force, indicated in Eq. (2), is not expected to be strong enough to cause this behavior. However, experiments on defined micro structures support the assumption that paramagnetic and even diamagnetic gradient forces affected the observed current changes.

The copper measurements outlined above are supported by experimental data from galvanostatic depositon. Galvanostatic deposition of copper ($1\,\text{mol/l}\;CuSO_4$, pH 2; 120 min, $-40\,\text{mA}\cdot\text{cm}^{-2}$) was done into prior chemically etched micro wholes. The applied alternating magnetic field induced a slightly decrease of deposition potential. This potential change properly caused by a gradient effect was even found for perpendicular arrangement of current lines and the magnetic field.

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