Effect of high magnetic field on copper and cobalt deposition

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Magnetically induced effects on electrochemical processes are of high interest from a basic point of view as well as for many applications especially in magnetoelectronics. Convective effects on mass controlled reactions induced by a magnetic field (B) parallel to the plane working electrode are well known as MHD effect and have been examined experimentally as well as theoretically (1). Until now the effect of B on kinetic processes such as adsorption, discharging or electron transfer and the initial stage of grain nucleation are an open question and conversely discussed. All these effects have been argued to be much smaller than convective effects (2). It is expected that the discharge process of paramagnetic ions with different magnetic susceptibilities is strongly affected by high B when the classical MHD effect can be excluded, *i.e.* when B is perpendicular to the electrode. To highlight and understand these effects investigations under superimposition of high B are of interest. The deposition of copper and cobalt with different paramagnetic susceptibilities forming nonmagnetic and ferromagnetic deposits were chosen for the following investigations. Recently it was demonstrated for copper deposition that the increase of limited current density $(i_{\mbox{\tiny lim}})$ depends on the orientation of B to the electrode (3). An effect was even measured, if B is in a direction perpendicular to the electrode.

The measurements were performed in the Grenoble High magnetic field laboratory with the 13T magnet and a vertical B orientation. A classical 3-electrode arrangement was used to investigate the deposition process of copper and cobalt from sulfate electrolytes with pH3 depending on the metal ion concentration, B direction, electrode position and overpotential. B was increased and decreased with a rate of 10mT/s and 50mT, respectively.

The deposition of copper dependent on the concentration and B is shown in Fig.1 for a vertical B parallel aligned to the electrode surface. The experimentally and theoretically expected dependency of the limited current density (i_{lim}) on concentration and B i_{lim} $\propto c^{3/4}B^{1/3}$ (4) could be established only for low concentration and a B up to about 1.5T. An increase of i_{lim} was not observed below 150mT due to the vertical electrode arrangement and an overlapping of the natural convection. At high copper concentration i_{lim} increases with increasing field strength not in the same order. Additional opposite effects are taking in account at higher fields (kinematic viscosity, damping forces,...)

If B is arranged perpendicular to a horizontal electrode the Lorentz force and electrokinetic effects should be negligible. For copper deposition is shown in Fig.2, that B<1T yield no remarkable arise of i_{lim} . A slightly decrease



Fig.1: Limited current density of copper deposition

dependent on $B^{1/3}c^{4/3}$, vertical B, upward, parallel to electrode

is followed by a strong increase of i_{lim} . At high fields i_{lim} is interestingly higher than in the classical electrode to B orientation (bold dashed line). During the reverse scan of B, ilim decreases uniformly. Similar results were obtained for the cobalt deposition at different potentials. An alternating increase-decrease behaviour was observed up to 1 T followed by an strong increase. Due to the lack of the Lorentz force other magnetic induced forces should act on the charged ions. Close to the surface in the electrochemical double layer a concentration gradient and therefore a gradient of volume paramagnetic and diamagnetic susceptibility exists creating a gradient of local energy density. It is expected that these gradients should cause forces and result in field effects which are higher than the Lorentz force. To explain the origin of the measured effects, other magnetically induced forces than the classical convective effects have to be taken into account and to prove by further investigations.



Fig. 2 : Limited current density dependent on B for Cu-deposition at -700mV vs. SSE , $c_{Cu2+}{=}0{,}038mol/L$

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