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NANOSTRUCTURED MAGNETIC MATERIALS BY MAGNETOELECTROLYSIS

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In this paper we report the effects of a high magnetic field up to 15.0 T on the deposition process, morphology, structure and magnetic properties of Co thin films prepared by electrodeposition. Cobalt metal films were deposited from a sulfate bath on a copper substrate with and without magnetic field. The variation of deposition current with applied field was studied. At higher fields a nonlinear increase of deposition current density was observed. Hexagonal phase cobalt with a strong preferred orientation of <100> is deposited by the application of magnetic field antiparallel to the ions motion. The orientation of the c axis of the hexagonal cobalt is distributed both parallel and perpendicular to the film plane as shown too by the hysteresis loops. It is encouraging to note that by the application of magnetic field during the electrodeposition of ferromagnetic films the morphological, crystallographic and magnetic properties may be modified and this technique may be used in technological applications.

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1. Introduction

The intersections of magnetism and electrochemistry are interesting interdisciplinary zones. Magnetoelectrolysis is the term used for the effect of an applied magnetic field on heterogeneous electrochemical processes at an electrode/solution interface. Research into the influence of a magnetic field on electrochemical reactions has been ongoing for most of the past century. However, many of the published data on the subject are characterized by apparent contradictions and lack of reproducibility. Notable reviews of magnetoelectrolysis are those by Fahidy [1], Tacker and Jansen [2] and Oliviert *et al.* [3].

Magnetic field affects the film growth, morphology, phase transformation, texture, pore filling and the magnetic properties. These effects may be explained by the Lorentz force,

$$\vec{F}_L = \vec{j} x \vec{B} \left(N / m^3 \right), \tag{1}$$

where $\vec{j}$ is the current density and $\vec{B}$ is the magnetic flux density, extended on moving ions under the influence of an electric field between the electrodes of an electrolytic cell. A magnetic parallel to the plane working electrode induces a convective flow and the mass transport towards the electrodes is enhanced. This phenomenon is well known as a magnetochydrodinamic (MHD) effect and has been examined experimentally as well as theoretically. It was established that the diffusion – limited current should vary as $c^{4/3}$ and $B^{1/3}$, where $\underline{c}$ is the bulk electrolyte concentration [3]. These effects also change the morphology and interface properties. However for nanometres-thick films is necessary to understand and control the initial stages of deposition and kinetic processes such as adsorption, discharging or electron transfer. It has been argued that all these effects are much smaller than convective effects and so they have to be investigated in higher magnetic fields. To control the

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structure and properties of these kinds of nano-deposits it is necessary to understand and control the initial stages of deposition and kinetic processes such as adsorption, discharging or electron transfer to the electrode/solution interface.

In this paper we report the effects of a magnetic field on the deposition current density, morphology, crystalline structure and magnetic properties of a cobalt film deposited on copper support by electrodeposition. We are especially interested in the deposition of cobalt on copper because Co/Cu multilayer systems show the GMR effect [4].

2. Experiment

For Co films deposition a sulfate bath of composition 25 g/l $CoSO_4 \cdot 7H_2O$, 40 g/l H_3BO_3 buffered to pH 3.0 and a current density of 12 mA/cm^2 were used. The deposition was carried out on a copper substrate using a three-electrode cell of diameter 25 mm and depth 45 mm which could be placed centrally in the bore of a cylindrical magnet. A magnetic field of 15 T was applied (1) parallel (up normal) and (2) antiparallel (down-inverse) to the Co^{2+} ions motion during electrodeposition. Figure 1 shows the scheme of the experimental setup (the experiment was done in GHMFL-Grenoble High Magnetic Field Laboratory with a resistive magnet).

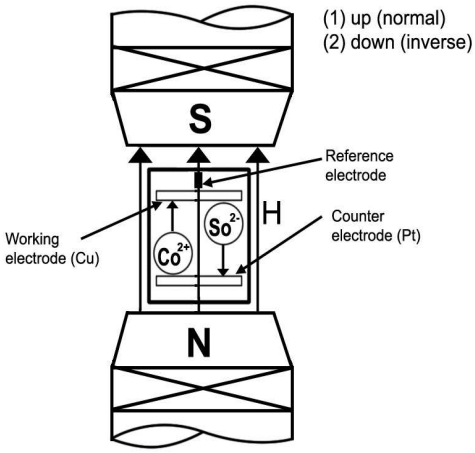

Fig. 1. Schematic illustration of cell for Co film electrodeposited in a magnetic field.

The effects of magnetic field direction and overpotential on Co deposition have been performed using potentiostatic experiments.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for the structural and morphological investigations. Hysteresis loops at room temperature and in a magnetic field up to 10 kOe were measured using a vibrating sample magnetometer (VSM) and magnetic parameters such as coercivity H_c, remanence M_r, saturation magnetization M_s and saturation field H_s of the Co films were derived from these loops.

3. Experimental results and discussion

The effect of a magnetic field up to 15 T on the deposition current density is shown in Fig. 2. Up to 0.8 T no current density with B was observed. At higher fields a B exponent between 0.39 and 0.45 could be estimated for different over-potential (–1350 and –1550 mV vs. reference electrode - silver/silver chloride), which is a little bit higher than the classical 1/3 but seems to be independent of the magnetic field direction. Two distinct regimes may be identified: the mass transport regime, characterized by the current plateau and the activation regime close to the rest potential. A third regime should be hydrogen evolution, which is identifiable on the cathode surface. No effect of the field is immediately obvious in the activation regime. However, this in itself is not

sufficient evidence to eliminate the possibility of an influence of the field on the electrode kinetics since mass transport effects may obscure kinetics effects even at relatively low overpotentials. Potentioastatic diagram on Fig. 2 indicates that in higher fields the hydrogen evolution reaction is somehow suppressed. The current density increase (Fig. 2) means the enhancement of mass transport in the field that a limiting current is not reached before hydrogen evolution sets in.

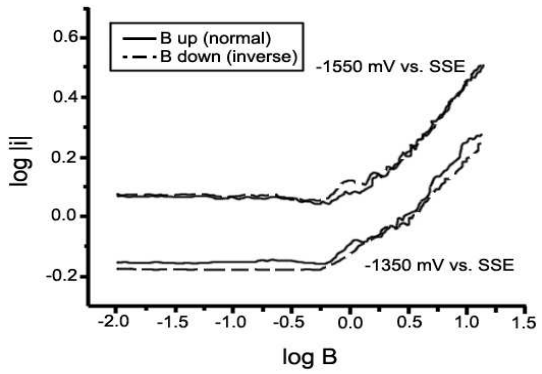

Fig. 2. Potentiostatic curves of electrodeposited cobalt films in a magnetic field.

The XRD diffractograms of the electrodeposited 300 nm thick Co films on Cu substrates are shown in Fig. 3.

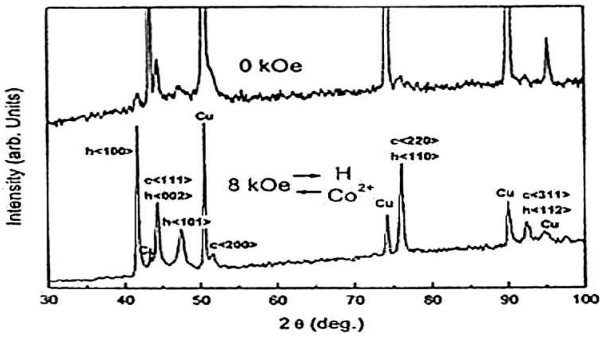

Fig. 3. XRD diffractograms of Co films.

The Co films deposited without field and with field applied parallel to the ions motion consist of cubic phase with a small volume fraction of hexagonal phase. On the other hand, the film deposited in field antiparallel to the ions motion consist of hexagonal <100>, <002> and <101> phase with a very small volume fraction of cubic phase as seen from the intensity of the <200>. This shows a strong effect of magnetic field on the structural growth of cobalt films. SEM micrographs of the same films are shown in Fig. 4.

The application of magnetic field affects the film growth and grain formation as seen in the films deposited without field and in a field applied antiparallel to the Co^{2+} ions motion. The hysteresis loops of Co films are shown in Fig. 5.

The easy axis of Co film electrodeposited without field is in the plane of film. Co film deposited in a magnetic field antiparallel to the Co^{2+} ions motion consists of mostly hexagonal phase and the C axis (easy axis of magnetization) lies parallel to the substrate plane and about 50 % of hexagonal cobalt has C-axis perpendicular to the substrate. Therefore, by the application of magnetic field during the electrodeposition a hexagonal Co-phase is formed and C-axis orientation is distributed parallel and perpendicular to the substrate plane. The Mr/Ms ratio changes from 0.05 (without field) to 0.3 (with field) measured with field direction perpendicular ($\perp$) to the substrate plane whereas the coercivity (300 Oe) remains unchanged. The Mr/Ms ratio changes from 0.68 (without field) to 0.63 (with field) measured with field direction parallel to the substrate plane and coercivity (120 Oe) remains the same.

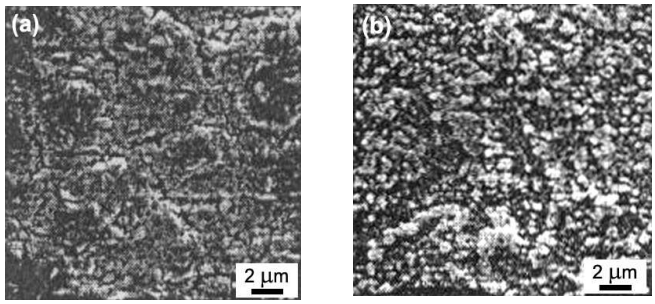

Fig. 4. SEM micrographs of Co films: (a) without magnetic field; (b) in an antiparallel magnetic field of 15 T.

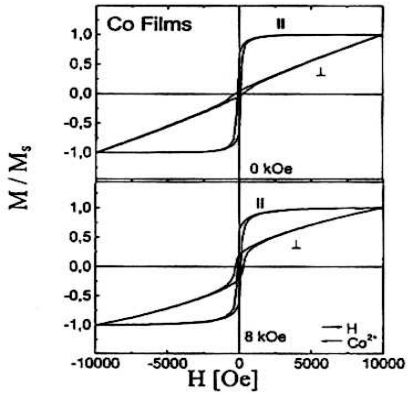

Fig. 5. Hysteresis loops of Co films with H parallel (//) and perpendicular (⊥) to the substrate plane.

4. Conclusions

By the application of magnetic field during the electrodeposition of ferromagnetic films the morphological, crystallographic and magnetic properties may be modified and this technique may be used in technological applications.

As a result of our experiments it has to be mentioned that the diffusion-limited current should vary as $i \sim B^{1/3}$, but this is only true for a special configuration (horizontal electrodes). To explain the origin of the measured effects, convective effects, other than classical, must be taken into account and existing models will be improved.

Hexagonal phase of Co with strong preferred orientation of <100> is deposited by the application of magnetic field antiparallel to the Co^{2+} ions motion.

The orientation of the C axis of the hexagonal Co is distributed both parallel and perpendicular to the film plane as shown by the hysteresis loops.

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