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Full Length Article

Magnetic field effects on the electrodeposition of CoNiMo alloys

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ABSTRACT

In this work we have examined the influence of applying homogeneous magnetic field (MF) up to 1.2T, on Cobalt- Nickel–Molybdenum (CoNiMo) alloys electrodeposition from citric bath. The surface morphology, chemical composition and the crystallographic texture has been investigated by X-ray diffraction (XRD), X-ray composition mapping and scanning electron microscopy (SEM) images. The mass transport behaviour during the electrodeposition process has been examined through the polarization curves and electrochemical impedance methods. As expected, under MF control an enhancement in the mass transport rate was observed leading to grains refinement and homogeneous distribution of the Co, Mo and Ni atoms in the obtained CoNiMo films. These findings highlight the synergistic combination of Ni, Co and Mo by promoting the MHD convection due to the Lorentz force acting during the Ni(II) and Co(II) ions reduction.

1. Introduction

Electrochemical alloy deposition is widely used to produce new materials for specific applications (mechanics, physics or chemical applications) such as cobalt alloys due to their magnetic properties or nickel alloys due to their catalytic properties. The addition of molybdenum in their alloys leads to good soft-magnetic coating with high corrosion resistance and high catalytic efficiency during the hydrogen evolution reaction (HER) [1–12]. To substitute the hard chrome coating, Srivastava et al. [10] show that the alloying of cobalt increased the microhardness of NiMo alloy and improves its tribological properties and corrosion resistance. Using rotating cylinder Hull cell, Esteves et al. [12] show that composition strongly depends on the electrolyte composition and current density. Overall, more Ni was incorporated in the deposits when the applied current was high. Cobalt and molybdenum wt.%'s were found to be higher when lower currents were applied [12].

It is well known that during electrodeposition process, the application of uniform magnetic field (MF) with strength B, parallel to the electrode improves the deposit quality (grain size, surface homogeneity and roughness) or catalytic activity [13–23]. It was established that the observed effects are attributed to the so-called magnetohydrodynamic (MHD) effect, which introduces additional convection in the electrolytic solution [24–26]. When the electrochemical cell is subjected to an external magnetic field provided by either permanent magnets or electromagnets, the diffusion electrolytic current interacts with the magnetic field to produce Lorentz body forces, which, in turn, drive fluid motion near the electrode. Hence the MHD effect manifests itself by a decrease in thickness of the diffusion layer and an increase in the mass transport rate during the electrolysis process [24–28].

Characterization is an essential aspect of materials research and of quality control in material production. It frequently involves the determination of point-to-point variation in composition, structure and microstructure, so that a variety of imaging and analysis techniques come into play. Understanding the distribution of elements and phases in structures is critical to optimize the performance of the material. In the present work, the influence of the MF on the ternary CoNiMo alloys electrodeposition process was investigated by means of electrochemical technology and the study of microstructure and texture of the as prepared alloys. To better understand the observed modifications, voltammetric measurements are conducted for each ion reduction and compared to the global response. Electrochemical impedance spectroscopy (EIS) techniques were used to examine the mass transfer process and electrochemical reaction kinetics. The structure and texture of coatings were analyzed by scanning electron microscopy (SEM), X-ray mapping and X-ray diffraction (XRD), respectively.

2. Experimental

Experiments were performed using an electrochemical conventional three-electrode set up. The working electrode (WE) was a platinum disc of 0.196 cm^2 maintained in vertical position. A large area nickel rod ($A \approx 6\,cm^2$) is used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Prior

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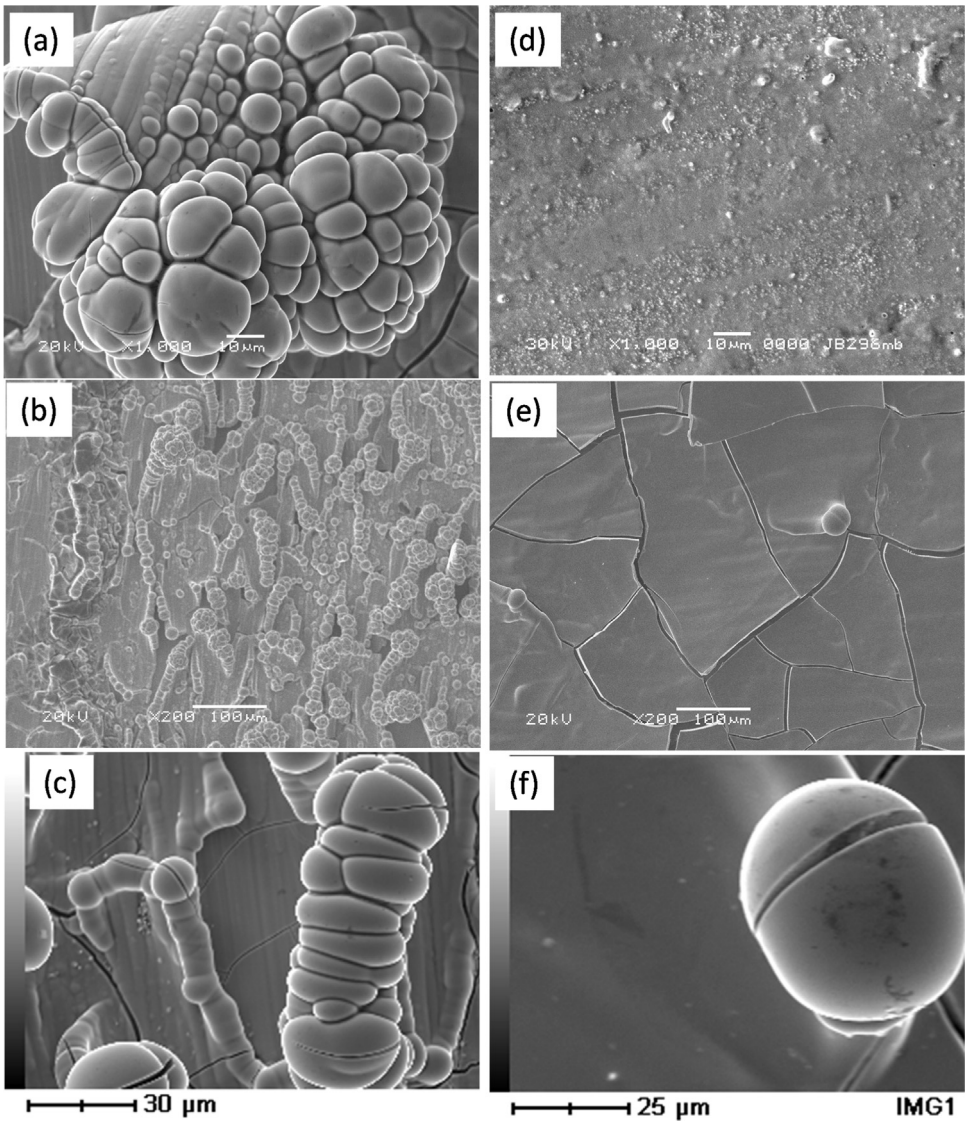

Fig. 1. SEM images for a CoNiMo alloy electrodeposited from bath deposition B5. $E_p = -1.0$ V *vs* SCE (a & d) and at $E = -1.20$ V *vs* SCE (b, c, e & f). Deposition time $\Delta t = 30$ min. (a–c) B = 0 T and (d–f) B = 0.9T.

to each experiment, the WE was mechanically polished first with emery paper (Struers P 1200 & P 4000), then to a mirror on felt with 1 μm alumina and finally rinsed with water and dried. For electrochemical study a Co-Ni-Mo pre-deposit (≈2 μm thick) was then plated at constant potential of E = −1. 20 V *vs* SCE for 2 min. For morphologic investigations a Cu cathode of 1 cm^2 was used as working electrode.

Deionised water was used throughout the experiments and the solution pH was adjusted near neutral by addition of adequate quantities of H_2SO_4 or NaOH. To avoid some salt precipitation, the bath temperature was maintained at 37.0 ± 0.5 °C with a thermostat. The chemical composition of the electroplating solution and operating conditions are summarized in Table 1.

The voltammetric experiments were performed with Radiometer (PGZ-100) Potentiostat/Galvanostat equipment controlled by VoltaMaster-4 software. The potentiodynamic polarization study was carried out at scan rate of 0.5 mV s^{-1}. The EIS measurements were carried out using Potentiostat/Galvanostat (Solartron 1286) and a frequency response analyser (Solartron 1250) monitoring by commercial Software Zplot 2.4 (Scribner Associates). The frequency range examined here lies from 65 kHz to 5 or 1 mHz and to get the EIS measurements in the linear mode, a sine wave potential amplitude of ΔE = 10 mV was used. Each experiment was performed at least in twice on various days.

Table 1
Chemical composition and pH value of baths deposition.

	B1	B2	B3	B4	B5
$Na_3C_6H_5O_4$	0.50 M	0.50 M	0.50 M	0.50 M	0.50 M
$Na_2MoO_4{,}6H_2O$	0	0.05 M	0	0	0.05 M
$CoSO_4{,}7H_2O$	0	0	0.22 M	0	0.22 M
$NiSO_4{,}6H_2O$	0	0	0	0.50 M	0.50 M
pH	6.2 ± 0.2	6.2 ± 0.2	6.2 ± 0.2	6.2 ± 0.2	6.2 ± 0.2

For the measurements with magnetic field, the cell was put into the gap of an electromagnet (Sigma-phi) coupled with a regular power supply (BOUHNIK). The magnet can generate a homogeneous MF up to 1.2T for 7 cm gap and 1.65T for 5 cm gap. The working electrode was positioned in the electrochemical cell, near the center of pole pieces.

The chemical composition and morphology of the deposits were characterized by scanning electron microscopy (SEM) using a JEOL JSM 6460LA coupled with an energy dispersive spectroscopy (EDS) JEL 1300 microprobe. To provide information about morphology