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Surface morphology and electrochemical characterization of electrodeposited Ni–Mo nanocomposites as cathodes for hydrogen evolution

R. Abdel-Karim [a,*], J. Halim [a], S. El-Raghy [a], M. Nabil [a], A. Waheed [b]

[a] Department of Metallurgy, Faculty of Engineering, Cairo University, 12613 Giza, Egypt
[b] Department of Metallurgy, Nuclear Research Center, P.O Box 13759 Ca, Anshas, Egypt

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ABSTRACT

Ni–Mo nanocomposite coatings (18–32 nm) were prepared by electrodeposition of nickel from a nickel salt bath containing suspended Mo nanoparticles. All the coatings have been deposited under galvanostatic conditions using current densities in the range 5–80 mA/cm^2. According to structural investigation carried out by X-ray diffraction, the obtained coatings consisted of crystalline Mo phase incorporated into Ni matrix. The molybdenum content diminished with increasing the deposition current density and ranged between ~6 and ~17% Mo. The crystallite size and the surface roughness increased by raising the current density. A remarkable deterioration in the corrosion resistance of Ni–Mo composites was observed with the increase of Mo content due to crystallite size-refining and surface roughness effect. Electrocatalytic effect for hydrogen production was improved mainly as a result of increasing the surface roughness and thus providing more accessible surface area.

1. Introduction

Broad application of nickel-based composite coatings in electrochemistry is due to the highly catalytic activity in electrocatalytic hydrogen evolution (HER) and electrocatalytic oxygen evolution (OER) as well as good corrosion resistance of nickel in aggressive environments [1]. In order to improve the properties of these materials, and enhance their catalytic activity, various modifications could be applied, such as alloying with other elements, incorporating composite components. All these modifications aimed at obtaining the electrodes with very developed, rough or porous electrode surface. Many types of particles were used to improve mechanical, physicochemical or electrocatalytic properties of composite coatings, like carbides, silicides, nitrides, and oxides [2–4].

Recent research in electrodeposition suggested a technique involving codeposition of metallic particles to form electrodeposited metal matrix/metal particle composites [2]. Among these composites are those containing metals like Al, Ti, V, Mo, which could not be directly deposited from aqueous solutions. Incorporating such powdered components to the metal matrix leads to obtain a new kind of composite material which could be applied as electrode materials [5–9]. Ni based binary composite coatings like Ni–Mo, Ni–Zn, Ni–Co, Ni–W, Ni–Fe and Ni–Cr were tried for hydrogen electrodes; out of these electrodes, Ni–Mo was found to be best and most stable electrode with an overpotential of 0.18 V in 6 M KOH solutions [10].

Also according to Kubisztal et al. [11] electrolytic Ni–Mo and Ni–Mo–Si coatings were prepared by codeposition of nickel with silicon and molybdenum powders from a nickel bath in which Mo and Si particles were suspended by stirring. Composite coatings are characterized by very porous surface in comparison with nickel coating after the same thermal treatment.

Ni–Mo composite coatings, obtained by electrodeposition of Ni with Mo particles on a steel substrate from the nickel bath containing suspended Mo powder, showed pronounced improvement in the electrochemical performance for HER in an alkaline environment compared to nickel electrode [2,12]. The molybdenum content and the thickness of the Ni–Mo composite coatings change between 28–46 wt%, and 100–130 μm, respectively depending on the deposition current density. Ni–Mo electrodeposits were characterized by larger surface than the Ni electrodeposits. According to Jovic et al. [13], improved performances are to be expected if a composite compact layer of Ni and some Mo oxides could be prepared by the simultaneous electrodeposition of Ni and MoO_3 from an electrolyte solution in which MoO_3 particles are suspended. It seems a unique way for solving the problem of porosity of electroplated Ni–Mo coatings and low mechanical stability of thermally prepared Ni–Mo catalysts.

Nanocomposite coatings have been of a great interest to many researches and many investigations have been done on them for various applications. However, published articles on corrosion stability of these composites are limited.

* Corresponding author. Fax: +20 02 35723486; mobile +2 01006690945.
E-mail address: randaabdelkarim@gmail.com (R. Abdel-Karim).

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Table 1
Composition of solution and working conditions for electroplating of Ni–Mo composites.

Composition	$NiSO_4{\cdot}6H_2O$ (mol/l)	0.2				
	$Na_3C_6H_5O_7{\cdot}2H_2O$ (mol/l)	0.3				
	Mo powder (g/l)	1.92				
	Ammonia solution	Excess				
Conditions	pH	9.5				
	Current density (mA/cm^2)	5	10	20	40	80
	Quantity of charge (C/cm^2)	50				
	Time (min)	167	83	42	21	11
	Speed (rpm)	350 ± 5				
	Temperature (°C)	25 ± 1				

The purpose of this work was to study the effect of changing the plating current density on the morphology and structure of Ni–Mo electrodeposited composites, using alkaline bath. In addition, the mechanical as well as the electrochemical properties of the composites were investigated as a function of current density.

2. Experimental

As illustrated in Table 1, the electroplating bath used for the electrochemical deposition of Ni–Mo composite coatings consists of the following composition: 0.2 mol/l hydrated nickel sulfate ($NiSO_4{\cdot}6H_2O$), 1.92 g/l Mo nano-powder, 0.3 mol/l sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$), and excess of ammonia solution in distilled water. The size of Mo nano-powder was in the range of 60–80 nm in diameter supplied by Skyspring Nanomaterials Inc. TX, USA. Ni–Mo composite coatings were deposited on a low-carbon low-alloy steel substrate (2 cm × 2 cm) supplied by Clas Ohlson (Sweden). Nickel plate (5 cm × 5 cm) having 99.5% Ni, supplied by Alfa Aesar, Germany was used as anode. Test specimens were prepared for electroplating by grinding, polishing (using silica suspension), ultrasonic cleaning in acetone, and then rinsing in ethanol. The substrates were degreased using a solution containing 30 g/l of sodium carbonate (Na_2CO_3) and 30 g/l of sodium triphosphate ($Na_5P_3O_{10}$). Finally, an acid pickling treatment was performed by dipping the samples in 75% HCl solution to remove any oxide traces or scales.

Nano-composite coatings were deposited at different plating current densities namely; 5, 10, 20, 40, and 80 mA/cm^2. These conditions correspond to an electric charge value of 50 C/cm^2 per electroplated area of cathode. The stirring speed was 350 ± 5 rpm. The bath temperature was maintained at 25 ± 1 °C and pH of 9.5.

Chemical composition of the Ni–Mo nano-composite coatings was determined by energy dispersive X-ray spectroscopy (EDS) method. Microstructure and phases morphology of the deposits were examined by scanning electron microscopy (ULTRA 55-Zeiss field emission). Structural investigations were conducted by XRD method using (PANalytical B'Pert PRO diffractometer) with a copper anode (Kα = 1.54059 Å) to demonstrate the phases and their crystallite size of the nano-composite coatings. The supplied current and voltage parameters to the XRD were 35 A and 45 kV, respectively. The numerical analysis was facilitated by using the PANalytical B'Pert Highscore Plus computer software. The crystallite "size D" was calculated by applying Scherrer's equation. Microhardness measurements were carried out using micro-hardness tester (Shimadzu Hardness tester HMV-2 T) with a load of 1.9 N. The roughness measurements were carried out using MITUTOYO surfest 301.

Potentiodynamic polarization measurements were conducted using a standard three-electrodes cell with the coated samples (0.2 cm^2) as a working electrode, Pt as auxiliary electrode and saturated calomel electrode as a reference electrode, all immersed in 0.5 M NaOH electrolyte. This cell was connected to Voltalab 10 (PGZ100) device working at a scanning rate of 0.5 mV/s and in the potential range from −1000 to −100 mV. Corrosion rate (mm/y), corrosion potential E_{corr} (mV), and Tafel slopes (mV/s) were calculated using Tafel extrapolation technique provided by Volta Master 4 software.

The electro catalytic behavior of nanocrystalline Ni–Mo composites, for hydrogen evolution reaction (HER), has been evaluated by the comparison of the potential of different samples recorded at constant current density $j = -150$ mA/cm^2 in linear polarization curves (I–V) [14] as well as by the comparison of Tafel slopes of cathodic region in the polarization curves (β cathodic) [15].

3. Results

3.1. Microstructure analysis

Fig. 1 illustrates the different morphologies of Ni–Mo composites being electrodeposited on steel substrates under different current densities. Ni–Mo composites are characterized by gray, mat surface. The morphology of the composite films shows rougher, more irregular and more developed morphology than that of the alloy films [16].

The deposited films are composed of a nickel matrix in which molybdenum particles being embedded. According to the SEM micrographs in Fig. 1 (at low magnifications of 1 K×), Mo islands are widely dispersed. However, the space between the islands become narrower and the electrodeposited layer became denser for the composites being deposited at a high current density. SEM micrographs of Ni–Mo composite (Fig. 1) at higher magnification (50 K×) shows that the islands rich in molybdenum are of globular structure of a rough surface and contain fine particles embedded inside them. They also show the porous nature of the deposited structure.

3.2. EDX analysis

The chemical composition of Ni–Mo composites electrodeposited under different current densities was carried out by EDX. The point analysis confirmed the formation of Mo-rich clusters embedded in the Ni-matrix.

There is a strong influence of the current density being applied during electrodeposition of Ni–Mo composites on the molybdenum content in such deposits. The relationship between the Mo content in such composites and the applied current density is illustrated in Fig. 2. It is clear that enhancing the current density from 5 to 80 mA/cm^2, caused a drop in the molybdenum content in the deposits from ∼17 to ∼6%.

3.3. XRD characterization

XRD technique was used to determine the phases presented in the electrodeposited films as well as the crystallite size of Ni–Mo electrodeposits. The characteristic XRD peaks shown in Fig. 3 were analyzed by ICDD card 2000, showing that the peaks at 2θ = 44–45°, 51–52°and 76–77° represent Ni crystalline phase and correspond to the following planes: (1 1 1), (2 0 0) and (2 2 0), respectively. The peaks recorded at 2θ = 40–41°, 58–59°, 73–74°and 87° are for Mo crystalline phase and correspond to the following planes: (1 1 0), (2 0 0), (2 1 1) and (2 2 0), respectively. This indicates that the electrodeposited film is composed of Ni–Mo composite, where the matrix is of Ni electrodeposits embedded with Mo nano particles. It is interesting to note that the Ni lines are wider indicating smaller crystallite size of the electrodeposited material compared with the Mo powder.

The size of Ni crystallites, calculated from the line broadening using Scherrer's equation, increased from 18 to 32 nm as the applied current density was raised from 5 to 80 mA/cm^2 (Fig. 4).

3.4. Roughness measurements

The roughness values (Rq) of Ni–Mo composites at different applied current densities are demonstrated in Fig. 5. It is observed that as the plating current density was raised from 5 to 80 mA/cm^2,