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Structure and surface studies on Ni-Mo alloys with polymers

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Materials

ABSTRACT

Purpose: The aim of this paper is the presentation of the study results provided on structure and surface of the electrodeposited Ni-Mo alloys with different polymers.
Design/methodology/approach: Composites based on Ni-Mo alloys with polytiophen, polypyrrole and polyethylene were obtained by electrochemical method. Depending on the potential and current density of electrodeposition and electropolymerization processes.
Findings: The structural analysis made by X-ray diffraction shows that, in general, the solid solution of molybdenum in nickel is forming. The unit cell parameters of solid solution are slightly changing with the increasing of molybdenum contents in the alloy. The analysis of diffraction line broadening indicates presence of the Ni-Mo solution nanocrystallites in the deposited layers. Moreover, the Auger Electron spectroscopy (AES) verifies both the presence of the solid solution of molybdenum in nickel and presence of polymers in composites. The SEM images show the general microstructure typical for the grain structure.
Research limitations/implications: Composites obtained by electrochemical method studied in this paper are unique in that the electrochemical methods can be used for processing ceramics, polymers, metals, composites and hybrid materials.
Practical implications: The codeposition of alloys with polymers or polymerisation with alloy codeposition has created new opportunities in the preparation of novel composite materials. Conductive polymers have been investigated for use as the electrode materials for a number of applications including rechargeable batteries, electrochemical sensors etc.
Originality/value: Using the electropolymerization and electrodeposition processes in preparation of the composites. The analysis of structure and surface of the electrodeposited Ni-Mo alloys with different polymers.
Keywords: Composites; Nanomaterials; X-ray phase analysis; Auger electrons

1. Introduction

The Ni-Mo alloys are widely used in the industry due to their good corrosion and heat resistance and electrochemical activity towards cathodic hydrogen evolution and anodic oxygen evolution. They are also used as protection covers for elements working in aggressive environments [1].

Auger electron spectroscopy (AES) is the surface sensitive analytical technique used mainly to determine elemental compositions of materials and in certain cases to identify the chemical states of surface atoms [2,3,4]. If a scanning primary electron is used electron images yield information related to surface topography [5].

2. Material

The Ni-Mo electrodeposited layers with polypyrrole, polytiophen and polyethylene were chosen as the material of

studies. The thickness of obtained layers were in a range of 60 – 210 μm. In case of such composites there are three ways of polymerisation and layer deposition, which are in detail described in earlier paper [6]. In short: in case of polytiophen + Ni-Mo – there is observed process of electropolymerization and Ni-Mo electrodeposition in the cathodic process. The samples electrodeposited with current densities of D_k = 25, 50, 100, 150, 200 mA/cm^2 were searching materials (Ni+Mo+Pth). In case of polypyrrole + Ni-Mo – there is observed two-step process: electropolymerization in the anodic process and Ni-Mo electrodeposition in the cathodic process. So the composite is forming when the electrodes have worked alternately as the anode and as the cathode. The samples electrodeposited with different potentials: V = +0.6/-1.2; +0.7/-1.4; +0.8/-1.6 V/cm^2 (current density: D_k = 10 mA/cm^2) and different current densities: D_k = ± 2.5, ± 5 mA/cm^2 were searching materials (Ni+Mo+PPy). In case of polyethylene + Ni-Mo – there is observed process of Ni-Mo electrodeposition with grains of polyethylene in the cathodic process. The samples electrodeposited with current densities: D_k = 10, 20, 50, 200 ma/cm^2 were searching materials (Ni+Mo+PE).

3. Experimental methods and discussion

3.1. X-ray diffraction

The X–ray diffraction patterns were measured at room temperature using Philips Diffractometer PW 1130 for all samples. The copper radiation ($\lambda_{K\alpha}$ = 1.5418 Å), graphite monochromator on the diffracted beam, the step scanning mode in a range of 30 - 110° 2Θ with the step of 0.04° 2Θ and counting time of 4 s were used.

After analysis of the X-ray diffraction patterns it was noticed that, in general, the solid solution of molybdenum in nickel is forming in most obtained samples. The fact that the obtained layers are composite types: alloy/polymer layers or alloy layers with polymer grains leads to the smaller intensity of X-ray diffraction effects. Fig. 1 shows the X-ray diffraction pattern obtained for the example sample of Ni+Mo+PTh (D_k = 150 mA/cm^2). It might be noticed that there are diffraction lines of solid solution of molybdenum in nickel and a trace of an amorphous background of polymer (polytiophene).

Moreover, the values of unit cell parameters do not depend on the type of electrochemical method. These values slightly depend on the values of potentials and current densities (3.573 – 3.610 Å). In contrast to earlier experiments carried out on the electrodeposited Ni-Mo alloys [7, 8, 9, 10] where has been shown that the values of the unit cell parameters had been strongly depended on the current densities and these values had been changed from 3.541 to 3.622 Å. Comparising the results of values of unit cell parameters obtained for composites to the values obtained for Ni-Mo electrodeposited alloys [11] it is clear to see that presence of polymers in the electrolyte influences on larger solubility of molybdenum in nickel (table 1).

The broadening of the diffraction lines points out that the crystallite size of the obtained layers is in a range of 5 – 6 nanometers what is similar result to earlier studies [6-10].

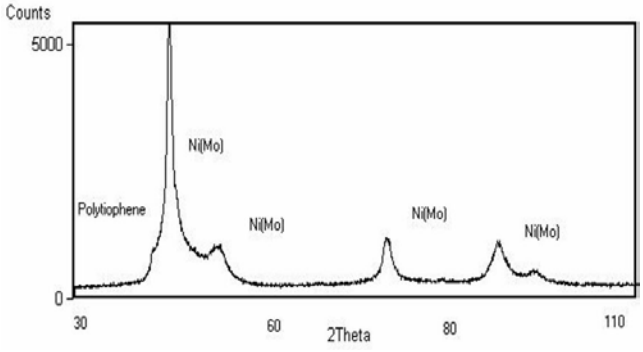

Fig. 1. The X-ray diffraction pattern obtained for the example sample of Ni+Mo+PTh (D_k = 150 mA/cm^2)

Table 1
Molybdenum content in composites (Ni-Mo alloys with polymers) in comparison to molybdenum content in Ni-Mo alloys [11]

Sample	Current density [mA/cm^2] / Potential [V/cm^2]	Unit cell parameter [Å]	Molybdenum content in solid solution Mo in Ni [%] (Vegard's low)	Molybdenum content in solid solution Mo in Ni [%] [11]
Ni+Mo+PTh	25	3.5976	17.5	11.6
	50	3.6049	20.0	12.2
	100	3.6053	20.0	13.8
	150	3.6107	23.5	13.9
	200	3.5998	17.5	14.1
Ni+Mo+PPy	± 2.5	no composite	-	2.5
	± 5	3.6003	20.0	5.9
(different potentials)	+ 10	3.6062	20.0	9.9
	+ 0.6 /- 1.2	3.5868	15.5	9.9
	+ 0.7 /- 1.4	3.6003	20.0	9.9
	+ 0.8 /- 1.6			
Ni+Mo+PE	10	3.5693	10.0	9.9
	20	3.6003	20.0	11.0
	50	3.6044	20.0	12.2
	200	3.5738	13.0	14.1

3.2. Auger electron spectroscopy

Measurements were provided in the vacuum system by the spectrometer PHI Model 660 (Scanning Auger Microprobe Systems). An electron beam energy of 3 keV with beam current of 50 nA was used for experiment.

Figures 2- 4 show the micrographs of sample surfaces obtained by SEM method. A striking feature in the SEM images is that dark and bright contrast is observed. Such changed SEM contrast is due to surface roughness. The microstructure seen in figs. 2-4 is typical of the grain structures.

Auger electron spectra were recorded according to the N(E) mode. The derivative spectra were calculated from these data (Fig. 5). The clean surfaces of the samples were obtained removing C and O atoms by means of in situ method, was additional etched by Ar^+ beam with particle energy E_j = 4 keV and density of current 0.72 μAmm^{-2}.

The results of the spectral point analysis of Ni, Mo, O and C, which was carried out in the chosen regions of the example sample of Ni+Mo+PE, are shown on the fig. 6 . Table 2 shows overall contents of main elements of samples. and table 3 summarises the intensity ratio of Ni LVV and Mo MVV. Table 2 and 3 show that the values of ratio and concentrations of samples are different and depend on the elements of polymers. From SEM and Auger studies, we may conclude that the created Ni-Mo alloys with polymers are the topological difference of the surface chemical compositions.

Table 2
Contents of elements in Ni-Mo alloys with polymers (chemical analysis with accuracy of 5 %)

Sample	Ni	Mo	C	S	N
Ni+Mo+PTh	10	67	3	9	-
Ni+Mo+PPy	18	25	13	-	7
Ni+Mo+PE	11	38	34	-	-

Table 3
Ratios of element intensities in Ni-Mo alloys with polymers

Sample	Ratios of intensities
Ni+Mo+PTh	$I_{Ni}/I_{Mo} = 6.0 \pm 0.2$
Ni+Mo+PPy	$I_{Ni}/I_{Mo} = 1.1 \pm 0.2$
Ni+Mo+PE	$I_{Ni}/I_{Mo} = 2.9 \pm 0.2$

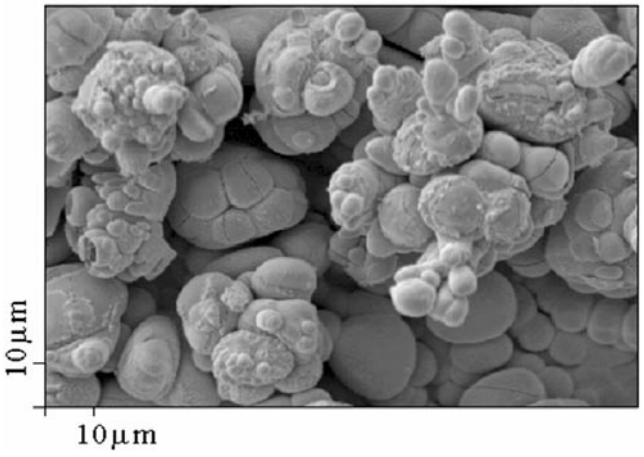

Fig. 2. SEM image of Ni+Mo+PTh

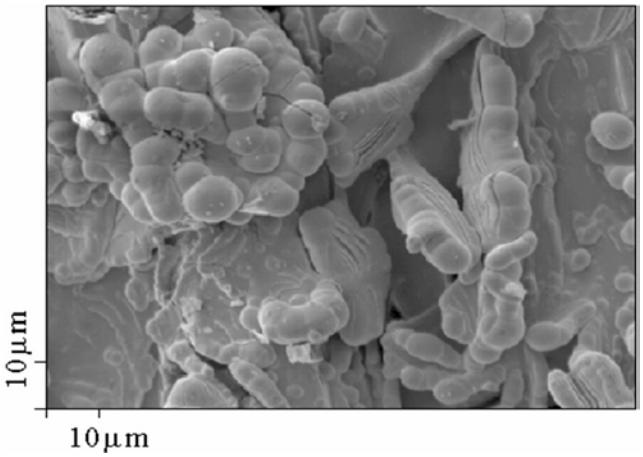

Fig. 3. SEM image of Ni+Mo+PPy

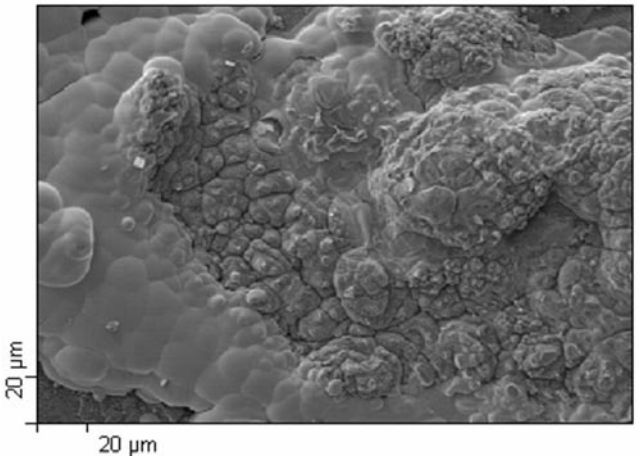

Fig. 4. SEM image of Ni+Mo+PE

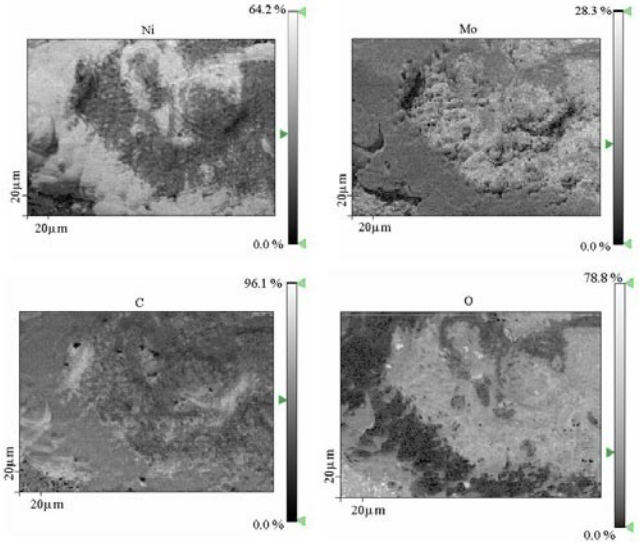

Fig. 5. Auger map of elements Ni, Mo, C, and O for Ni+Mo+PE

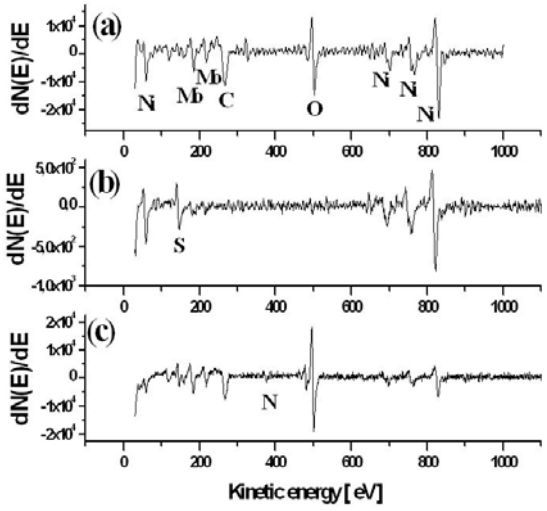

Fig. 6. Auger „point" spectra obtained for a) Ni+Mo+PE b) Ni+Mo+PTh, c) Ni+Mo+PPy

4. Conclusions

- The values of unit cell parameters slightly depend on the values of potentials, current densities and type of polymers.
- The fact that the obtained layers are composite types: alloy/polymer layers or alloy layers with polymer grains leads to the smaller intensity of X-ray diffraction effects.
- The presence of polymers in the electrolyte influences on larger solubility of molybdenum in nickel
- The Auger Electron spectroscopy (AES) verifies both the presence of the solid solution of molybdenum in nickel and presence of polymers in composites.

Acknowledgements

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