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Electrolytical production of Ni + Mo + Si composite coatings with enhanced content of Si

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Abstract

Ni + Mo + Si composite coatings were prepared by co-deposition of nickel with molybdenum and silicon powders from a nickel solution in which Mo and Si particles were suspended by stirring. The layers have been deposited on a carbon steel substrate (St3S) under galvanostatic conditions. The content of Si in deposited layers was about 2–5 wt.% depending on deposition current density and the value of electric charge. For comparison Ni + Mo composite coatings were obtained under analogous current conditions. Composite coatings of enhanced Si content (15 wt.%) were deposited from an electrolyte in which 40 g/dm^3 of Si covered with electroless plated nickel was dispersed. Deposition current density was equal 0.1 A/cm^2 and the value of electric charge $Q = 500$ C/cm^2. The thickness of the coatings was about 100–300 μm depending on their kind, electric charge and the deposition current density. Surface and cross-section morphology were investigated by scanning electron microscope (SEM). All deposited coatings are characterized by great, developed surface area. No internal stresses causing their cracking were observed. Chemical composition of the layers was determined by X-ray fluorescence spectroscopy (XRF) method and quantitative X-ray analysis (QXRD). It was stated, that the content of molybdenum and silicon in Ni + Mo + Si coatings depends on deposition current density and the amount of the powder in bath. The results of structural investigation of the obtained layers by the X-ray diffraction (XRD) method show, that they consist in crystalline Mo or Mo and Si phases built into Ni matrix. Moreover, Ni + Mo + Si composite coatings were modified by thermal treatment. It has been found that the thermal treatment of Ni + Mo + Si composite coatings caused that the new phases (NiSi, Mo_2Ni_3Si and $Ni_6Mo_6C_{1.06}$) were obtained.

Keywords: Nickel; Molybdenum; Silicon; Electrolytic composite coatings; Galvanostatic deposition

1. Introduction

The nickel-based composite coatings are commonly known on account of special properties of nickel such as good corrosive resistance in aggressive environments or high catalytic activity in many electrochemical processes, especially in process of hydrogen evolution [1,2]. Among electrolytic composite layers the materials particular importance are those containing metals like Ti, Mo, W, which could not be directly codeposited in cationic form from aqueous solutions. However, it is possible to introduce these metals in a form of powders and galvanic embedding their particles into a metal matrix [3–5]. Molybdenum as component of composite coatings seems to be particularly interesting on account of its electrochemical properties. In such cathode material, Mo plays a role of an activator in hydrogen electroevolution [6].

In order to improve the utilization of these materials and to enhance their electrocatalytic activity, various modifications could be applied, such as the use of composites instead of pure elements and other modifications to obtain electrodes with very developed, rough or porous electrode surface [7].

Transition metals silicides are widely considered as a new class of high-temperature structural candidate materials because of their many unique properties. These properties include high melting point, low density, excellent high-temperature oxidation and creep resistance. They are used as new materials to work in raised temperature or in aggressive environments [8–14].

This study was undertaken in order to obtain the nickel coatings, containing additional components as molybdenum and silicon powders. Such hybride coatings should be very interesting as electrode materials for hydrogen evolution on

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account of their surface development and differentiation of chemical composition. Besides the electrolytic deposition seems to be an interesting field of the production of a substrate to synthesis of silicides by the heat treatment of the obtained composite layers [15].

The purpose of this work was to investigate the possibility of obtaining such metal–metalloid composite coatings and to investigate the influence of deposition current density and the quantity of electric charge on their surface morphology, structure and chemical composition.

2. Experimental

Electrolytic composite Ni + Mo + Si coatings were obtained from an electrolyte having the following composition (concentrations in g/dm^3): $NiSO_4 \cdot 7H_2O$, 84; H_3BO_3, 8; CH_3COONa, 10; $C_6H_5O_7Na_3 \cdot 2H_2O$, 30; NH_4Cl, 10, to which suitable amounts of Mo and Si powders were added. Reagents of analytical purity (POCh Gliwice) were used for the bath preparation.

In order to obtain Ni + Mo + Si composite coatings, two kind of Si powder were applied. In the first case the plating bath contained Si powder (325 mesh, *Aldrich*), in amount 20 g/dm^3. In the second case the silicon powder was initially nickeled by electroless method, according to generally accepted procedure [16], and next 20 or 40 g/dm^3 of such prepared Si_{Ni} powder was added to the bath. Ni + Mo composite coatings were deposited from a bath in which 10 g/dm^3 of molybdenum powder (100 mesh, *Aldrich*) was dispersed. The process of deposition was carried out at the temperature of 293 K. pH of the suspension was kept in range from 5.4 to 5.8 and the rate of stirring was 200 rpm.

The layers were deposited on a carbon steel substrate (St3S 0.3% C), which was prepared by mechanical polishing with abrasive paper, and then it was chemically treated with concentrated HCl solution and rinsed in distilled water. After etching, the steel plates were dried and weighed. Geometric surface area of the steel plates was 4 cm^2. The other side of plates was covered with chemically proof and non-conductive resin—DISTAL. The platinum grid (1 dm^2) served as anode. The distance between the electrodes was approximately 5 cm. Thickness of composite coatings was estimated basing on chemical composition and the mass increment of the coatings.

All coatings were deposited under galvanostatic conditions. Ni + Mo + Si composite layers were deposited at various deposition current densities: 100, 150, 200, 250, 300 mA/cm^2 at constant electric charge $Q = 500$ C/cm^2 or with a various electric charge: 250, 500, 750, 1000 C/cm^2 at constant current density $j = 100$ mA/cm^2. Ni + Mo coatings were obtained under analogous conditions. Ni + Mo + Si_{Ni} composite layers containing initially nickeled silicon powder were obtained at deposition current density $j = 100$ mA/cm^2 and the value of electric charge $Q = 500$ C/cm^2.

Surface morphology and cross-section of deposited coatings were determined by Hitachi S-4200(4) scanning electron microscope (SEM).

Quantitative chemical analysis of Ni + Mo coatings was carried out by X-ray fluorescence spectroscopy (XRF) using special attachment to the X-ray generator TUR-M62 with flat LiF crystal and Ni/Mo standards made with compressed and homogenized powders of nickel and molybdenum. Qualitative and quantitative composition of Ni + Mo + Si coatings was determined by X-ray diffraction (XRD) method using Philips diffractometer and Cu Kα radiation ($U = 40$ kV, $I = 20$ mA). Registration of diffraction patterns was carried out by step-scanning method. Qualitative phase identification was carried out on the base of ICDD cards. To quantitative phase analysis, both external standard and matrix methods were used. The strongest, nearest lying and not overlapping reflexes coming from three phases: Si(1 1 1), Mo(1 1 0), Ni(1 1 1) were chosen for analysis [17–19].

Moreover, the planes polar density: $p(h\,k\,l)$ was calculated on a basis of the intensities of diffraction peaks coming from nickel matrix (I) with reference to analogous peaks of polycrystalline nickel which exhibits random orientation of crystallites (I_{Ni}). The values of $p(h\,k\,l)$ were calculated according to formula (1):

$$p_{h\,k\,l} = \frac{I/I_{\mathrm{Ni}}}{\sum I/\sum I_{\mathrm{Ni}}} \tag{1}$$

Current efficiency of nickel deposition was calculated according to formula (2).

$$\eta = \frac{m_2}{m_1} \times 100\% \tag{2}$$

where $m_1 = MIt/zF$; $z = 2$; m_2 = mass of deposited nickel in Ni + Mo and Ni + Mo + Si coatings, determined by X-ray quantitative analysis (QXRD).

Ni + Mo + Si_{Ni} composite coatings were modified by thermal treatment, at the temperature of 1100 °C in argon atmosphere for 1 h.

3. Results and discussion

The content of molybdenum in Ni + Mo + Si coatings varied in the range from 17 to 33 wt.% and is smaller than in Ni + Mo coatings (28–46 wt.%) (Fig. 1). Probably, smaller content of molybdenum in Ni + Mo + Si coatings results from the presence of silicon powder in the bath which additionally builds itself into coating limiting incorporation of molybdenum into the coating. In both kinds of coatings Ni + Mo + Si and Ni + Mo the content of incorporated composite components: molybdenum and silicon diminishes with the increase in deposition current density (Fig. 1). This fact could be explained by partial desorption of nickel ions from the surface of Si and/or Mo particles resulting from the strong effect of electric field produced by the increase in cathodic current density. It leads to a drop of Mo and Si content in the deposits. Such opinion is consistent with adsorption model of electrolytic composite plating [20].