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Studies on electrochemical deposition and physicochemical properties of nanocrystalline Ni-Mo alloys

Agnieszka Bigos [a,*], Ewa Beltowska-Lehman [a], Marcin Kot [b]

[a] Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta St., 30-059 Krakow, Poland
[b] Faculty of Mechanical Engineering and Robotics, AGH University of Science and Technology, 30 Mickiewicza Av., 30-059 Krakow, Poland

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Nanocystalline Ni-Mo coatings were deposited from citrate-ammonia solution, in a model system with a rotating disc electrode (RDE) using low carbon steel discs as the cathode. The effect of parameters such as electrolyte solution pH (from 4 to 10), temperature (from 20 °C to 60 °C), and hydrodynamic conditions (RDE speed in the range of 0 to 640 rpm) on chemical and phase composition, microstructure, average crystallite size of coatings and current efficiency of electrodeposition was investigated. It was confirmed that, in the induced co-deposition process, molybdenum acts as a grain refinement modifier. This, apart from influencing changes in surface morphology, has a significant effect on the mechanical properties of the layers. For alloys containing less than 16 wt% of Mo (related to the crystallite size of 7 nm) loss of strengthening effect (the inverse Hall-Petch relationship) was observed, which was correlated with the decrease in coatings' resistance to wear. Hence, for electrodeposition nanocrystalline Ni-Mo alloys characterised by high microhardness, good resistance to wear and adhesion to the steel substrate, the suitable conditions for electrolysis were determined. These conditions include: electrolyte solution pH above 7, plating temperature in the range of 20 °C to 40 °C, and hydrodynamic conditions corresponding to the RDE speed of 260 to 640 rpm.

1. Introduction

Nanostructured alloys possess a variety of chemical and physical properties that are strongly affected by their nanoscale microstructure [1,2]. In general, by selecting suitable manufacturing process conditions it is possible to obtain nanocrystalline coatings that exhibit distinctive mechanical properties, such as high strength, wear and friction resistance, and enhanced hardness, not achievable for materials with a larger crystalline size. A low-temperature and relatively simple electrodeposition technique is a convenient way of producing such alloys. Appropriate selection and control of the composition of the plating bath and conditions of electrolysis enable uniform surface coverage, simultaneously allowing control over the thickness, chemical composition and microstructure of the coating. Moreover, it allows coatings containing refractory metals, such as Ni-Mo, to be obtained. These are difficult to produce by conventional thermal methods, because of the great difference in the melting points of the metals (Ni – 1455 °C, Mo – 2620 °C) and limited mutual solubility. During the electrodeposition process, the simultaneous discharge of Ni(II) and Mo(VI) ions (responsible for an alloy formation) as well as hydrogen evolution occur at the cathode. The hydrogen evolution reaction is treated as a side reaction, which leading to a reduction of the current efficiency of the electrodeposition and may causes embrittlement of the resulting alloys. These processes depend on the type of plating bath, electrodeposition variables as well as the kind of the substrate material. However, the mechanism of Ni-Mo coating deposition is complex. While numerous hypotheses have been presented in the literature [3–7], the process has still not been fully elucidated. As it was previously established, it is highly possible that in the Ni-Mo alloys formation, the intermediate, mixed oxides products (such as MoO_2Ni_4) could take part [8]. Nevertheless, it is known that molybdenum (as well as other reluctant elements, such as W and Ge), could be readily co-deposited with iron-group metals with an alloy formation. Such co-deposition is described by Brenner as “induced”, and by Landolt as “catalytic” [9,10].

Electrodeposition of the Ni-Mo alloy without the inclusion of any oxides from electrolyte solutions containing only nickel(II) and molybdate ions is impossible. In these conditions, electrocrystallisation is inhibited by the formation of a large heteropolymolybdate cluster species $[H_pNi_qMo_rO_s]_t$, which are difficult to reduce [11]. Decomposition of heteropolymolybdate species to electroactive ionic forms of nickel and molybdenum could be caused by the addition of polycarboxylates. In practice, the most promising results were obtained for citrate electrolytes, because the citric acid and citrates are useful complexing agents for many metals, which stabilise the electrolyte solution pH [12–14].

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[*] Corresponding author.
E-mail addresses: a.bigos@imim.pl (A. Bigos), e.beltowska@imim.pl (E. Beltowska-Lehman), kotmarc@imir.agh.edu.pl (M. Kot).

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Next to the appropriate selection of plating bath components, the process of Ni-Mo alloy deposition is influenced by the solution pH and electrolysis operating parameters. It was confirmed that, in induced co-deposition, molybdenum acts as a grain refinement modifier [12,13]. Hence, all the parameters influencing the growth of molybdenum concentration cause refinement of the microstructure, which has a great effect on coating properties. However, there has not been much work analysing the impact of process parameters on the chemical composition and microstructure of deposits. In complexing baths, the concentration and stability of the metal ionic forms is highly correlated with the electrolyte solution pH. In the system subject to induced co-deposition, the presence of maximum content of the refractory metal in the coating at a particular pH of the electrolyte solution is often observed. For example, Ernst et al. based on an investigation of Ni-Mo, Fe-Mo and Co-Mo deposition from citrate aqueous solutions, found that the highest molybdenum content is present at pH 9 [15]. Similar results were obtained for Ni-Mo coatings deposited from citrate-ammonia, as well as from pyrophosphate baths [16,17]. Moreover, an alkaline medium (in the pH range from 8 to 10.5) is considered the most suitable for obtaining good quality alloys with high current efficiency [12,13,18–25]. Further growth of Mo content in the coating could be brought about by increasing the plating temperature, which increases the mobility of the ions (the conductivity of the solution) and equalises their concentration in the cathode diffusion layer. However, deposition of Ni-Mo alloys is mainly conducted at ambient temperature or not higher than 40 °C, which helps control the stability of the electroplating bath [12,13,18–22,24]. The process of alloy electrodeposition also depends strongly on the agitation of the electrolyte solution, which is generally performed by use of mechanical and ultrasounds stirrers and/or different kinds of rotating cathodes. Mixing of the plating bath during Ni-Mo deposition enhances the transport of ions to the cathode and decreases the thickness of the diffusion layer [13,21–23,26]. There are not many papers explaining the influence of agitation conditions on the composition and microstructure of alloys, although this subject is gaining in importance. Tudela et al. showed that, for Ni coatings, the use of different types of stirrers or of ultrasound generators has a strong influence on the crystallographic orientation, microstructure and hardness of deposits [27]. Feng et al. studied the effect of ultasonication on Ni-Mo deposition, indicating that the concentration of molybdenum in alloys, and hence their hardness and corrosion resistance, are dependent on the application of different levels of ultrasonic power [28]. This is also an important factor in the electrodeposition of metal matrix composites, which controls the stability of the particles' suspension in the electrolyte solution and their distribution in the coating [29–32].

From the mechanical point of view, an increase of molybdenum content, which causes reduction in grain size, has significant influence on the share of grain boundaries and defects in the coating structure. This process very often leads to strengthening and increasing the hardness of the material, and to improved wear resistance, consistent with the Hall-Petch and Archard scaling, respectively. Hall-Petch hardening could continue to grains of a few nanometers in size. On the other hand, in many studies the saturation or loss of strengthening for nanometric grains is observed [12,13,22,33,34]. This effect is known as the inverse Hall-Petch relationship. In the literature there are several models proposed to explain these phenomena, such as the dislocation model, the diffusion based model, the grain boundary shearing model and the composite model [35]. Considering the application of nanomaterials, it is crucial, regardless of the mechanisms governing this process, to establish the suitable range of electrodeposition conditions in which decreased hardness and strength of the coatings is not observed. However, due to the large number of process variables it is impossible to arrive at a simple theoretical description that would allow the properties of the proposed material to be modelled. Thus, the optimisation of Ni-Mo alloy production according to the mechanism of induced co-deposition is generally based on experimental studies carried out in different operating conditions.

Therefore, the first aim of the presented, preliminary work was to investigate the impact of the plating bath composition and selected operating parameters of the electrolysis process, such as electrolyte solution pH (from 4 to 10), plating temperature (from 20 °C to 60 °C), and agitation conditions (RDE speed from 130 to 640 rpm) on the chemical and the phase composition, microstructure and the current efficiency of the electrodeposition process. Afterwards, the correlation between these parameters and the mechanical and tribological properties of the Ni-Mo alloys was investigated.

2. Experimental

All of the binary Ni-Mo alloys were electrochemically deposited from aqueous solutions containing chemicals of analytical grade purity: 0.2 M $NiSO_4$, 0.003 M–0.048 M Na_2MoO_4 and 0.3 M–0.6 M $Na_3C_6H_5O_7$. No brighteners, detergents or wetting agents were used. Bath pH in the range from 4 to 10 was adjusted by the addition of sulphuric acid or ammonia. The calculations of equilibrium composition of the analysed electrolyte solution (assuming no precipitations) were carried out using the Hyperquad Simulation and Speciation program (HySS2009) [36]. Data referring to equilibrium constants adopted in the calculations were taken from [11,37,38]. Electrodeposition was conducted in a model system with a rotating disc electrode (RDE), with rotation speed from 130 to 640 rpm in the galvanostatic regime (5 A/dm^2), at temperatures from 20 °C to 60 °C. Low carbon steel (S235JR, structural, ferritic/pearlitic steel) discs (of approximate area 0.028 dm^2) were used as cathodes, which prior to electrodeposition were chemically polished in a solution of hydrogen peroxide and oxalic acid. A platinum wire (approximately equal to 0.5 dm^2) was used as an anode. The surface and cross-section morphologies of coatings were examined by scanning electron microscopy (ESEM FEI XL-30). The chemical composition was analysed by energy dispersive X-ray spectroscopy, and a mean value was calculated from a minimum of five measurements. The X-ray diffraction technique (Bruker D2 Phaser with a copper anode) was used to determine phase composition and the average crystallite size of deposits (calculated using Rietveld analysis in MAUD software). Indentation tests were carried out using the instrumented indentation method on a Micro-Combi-Tester produced by CSM Instruments. A Vickers diamond indenter was used. The maximum force applied during the tests was 50 mN with 100 mN/s loading and unloading rate. For each coating, at least seven indentations were performed. The values of microhardness and elastic modulus were calculated according to the Oliver–Pharr method [39]. The wear tests were performed on a ball-on-disc type tribometer with a constant rotation speed of 60 rpm and loads of 1 N. The adhesion of coatings to substrate was measured using the microscratch technique, with a Rockwell C spherical diamond stylus (cone apex angle 120 deg., tip radius 200 μm). Tests were carried out under increasing load from 0 to 30 N, within the distance of 5 nm.

3. Results and discussion

The electrodeposition of metallic and homogenous Ni-Mo coatings from a solution containing only nickel(II) and molybdenum(VI) ions is impossible [40,41]. The process is hindered because Ni^{2+} and MoO_4^{2-} ions form electrochemically inactive heteropolymolybdate ions $NiMo_6O_{24}H_6^{4-}$. The addition of the optimum quantity of polycarboxylates such as citrate led to decomposition of the heteropolymolybdate ions and the formation of the electroactive molybdenum $[MoO_4(Cit)H]^{4-}$, $[(MoO_4)(Cit)(H)_2]^{3-}$ [38] and then nickel $[NiCit]^{-}$ [42,43] citrate complexes ($Cit = C_6H_5O_7^{3-}$). Moreover, there is a tendency towards preferential complexation of molybdenum ions by the citrate ligand [41]. As shown in Fig. 1, the amount of molybdenum (wt%) in Ni-Mo alloys obtained under different conditions is