Structure characterization of nanocrystalline Ni–W alloys obtained by electrodeposition

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ABSTRACT

Ni–W coatings of different tungsten content (2–50 wt%) were electrodeposited on a steel substrates from an aqueous complex sulfate–citrate galvanic baths, under controlled hydrodynamic conditions in a Rotating Disk Electrode (RDE) system. The optimum conditions for the electrodeposition of crack-free, homogeneous nanocrystalline Ni–W coatings were determined on the basis of the microstructure investigation results. The XRD structural characterizations of Ni–W alloy coatings obtained under different experimental conditions were complemented by SEM and TEM analysis. Results of the study revealed that the main factor influencing the microstructure formation of the Ni–W coatings is the chemical composition of an electrolyte solution. X-ray and electron diffraction patterns of all nanocrystalline Ni–W coatings revealed mainly the fcc phase structure of an α-Ni(W) solid solution with a lattice parameter increased along with tungsten content. The use of additives in the plating bath resulted in the formation of equiaxial/quasifibrous, nanocrystalline Ni–W grains of an average size of about 10 nm. The coatings were characterized by relatively high tensile residual stresses (500–1000 MPa), depending on the electrodeposition conditions. Ni–W coatings exhibited weakly pronounced fiber type ⟨110⟩ crystallographic texture, consistent with the symmetry of the plating process. Coatings of the highest tungsten content 50 wt% were found to be amorphous.

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1. Introduction

The electrodeposition of Ni-based alloys with refractory metals, such as tungsten or molybdenum, has been the subject of considerable interest during the past few years. Among such materials, Ni–W alloys exhibit distinguishing properties which provide enhanced surface performance for engineering applications [1]. In recent years much effort has been dedicated to the search for alternatives to electroplated hard chromium coatings, which must be eliminated from the manufacturing processes, e.g. in the aviation and automotive industries (according to EU directives) due to environmentally hazardous manufacture process based on hexavalent chromium [2]. The investigated Ni–W coatings could successfully offer an important alternative to hard chromium coatings due to their excellent mechanical and tribological characteristics [3,4]. Recently Tsyntsaru presented a vast overview of the research dealing with electrodeposition of tungsten alloys with iron group metals, describing the chemistry of electrolytes, co-deposition mechanisms, physicochemical properties and applications of tungsten alloys as a main alternative to sustain the hard

chromium coatings [1]. Reported results support the thesis that the amount of W in the Ni–W alloys is governed by the ratio of the partial current density for electroreduction process of W(VI) and Ni(II) species present in the plating solution. Authors also indicated the role of citrate species as an important factor to achieve the desirable morphology and structure of deposits. Following the reports it has been found that the W content in the deposit is more sensitive to pH than to the current density changes, what has been shown also in this work. Further understanding of the composition-structure relationship in the Ni–W system that could lead to precise patterning of both the structure and properties of the nanocrystalline alloy coatings was given by Detor and Schuh [5]. With increasing tungsten content a clear refinement of the nanocrystalline structure occurs. Such nanostructures have interesting practical applications and are very important from fundamental science point of view. However, nano-size structures are difficult to study e.g. X-ray analysis of the coatings obtained by electrochemical techniques is usually impeded not only due to strong grain refinement of the material but also due to high structural defect accumulation [6]. Consequently, Ni–W coating microstructure is characterized by a combination of the amorphous and nanocrystalline phases. As a result, diffraction patterns obtained from these materials are diffused and/or diffraction reflections are much

broader than for those materials obtained by conventional metal-lurgical methods.

It is well known that alloys containing refractory metal (W, Mo) are difficult to prepare using conventional thermal methods due to the large differences in their melting points (Ni–1455 °C, W–3422 °C) and limited mutual solubility. Hence, electrochemical deposition (a cheap, simple and low temperature technique) can be proposed as an alternative technique. However, mainly due to the high residual stress level, which causes the serious problem of crack occurrence in the Ni–W deposits, is the main reason that coatings which are compact and adhere well to the substrate are still electrodeposited with technical difficulties [7,8]. In this work the optimum conditions for electrodeposition of crack-free, homo-geneous nanocrystalline Ni–W coatings have been determined on the basis of the microstructure investigation results by means of X-ray diffraction (XRD), as well as scanning (SEM) and transmis-sion electron microscopy (TEM).

2. Materials and methods

For characterization purposes, on a ferritic steel substrates, Ni–W alloy coatings of about 10–20 μm thickness were electrodeposited galvanostatically in the range of current density: 0.5–20 Adm^{-2}. Two different galvanic baths with and without 0.1 M NaCl and 0.5 M NH$_4$Cl additives were used. The influence of the mixing ratio of the Na$_2$WO$_4$ and NiSO$_4$ in the electrolytic complex sulfate–citrate plating bath (pH 8) on the microstructure, chemical composition and quality of the alloy coat-ings was investigated with respect to the applied current density (j). The sodium citrate concentration of 0.5 M Na$_3$C$_6$H$_5$O$_7$ remained constant for each plating bath. The electrolysis was carried out at 60 °C in a system with a Rotating Disk Electrode (340 rpm) supplied by a PAR 273A potentiostat [9,10]. The obtained coatings were characterized by X-ray diffraction analysis (phase composition, crystallite size, residual stresses and texture measurements) performed on a Bruker D8 Discover diffractometer equipped with multi-capillary primary optics with an open Euler goniometer (Co Kα filtered radiation). The diffracted beam was detected using a po-sition sensitive linear detector. Crystallite size and lattice strain of the coatings were evaluated using Rietveld algorithms in MAUD software [11]. Macro-residual stresses were estimated on the basis of a recent approach in the field (self-consis-tent modeling) [12] by a standard sin$^2\Psi$ method in a psi-geometry, which means that the sample was tilted around an axis parallel to the plane of the diffractometer. The crystallographic texture was analyzed using the orientation distribution func-tion (ODF) calculated by the discrete ADC (Arbitrary Defined Cells) method from the incomplete pole figures [13–15]. Structural characterization of the Ni–W coat-ings obtained under different experimental conditions was complemented by SEM (FEI XL-30 E-SEM) and TEM (Philips CM 20) microstructural studies. Chemical com-position of the coatings was determined via an energy dispersive spectroscopy (EDS) analysis in SEM equipped with an EDAX Genesis 4000 spectrometer. Thin foils for TEM observations were prepared using a conventional Ar$^+$ ion milling technique (Technoorg Gentle Ion Mill).

3. Results and discussion

Ni–W coatings were galvanostatically electrodeposited from a sulfate–citrate plating bath in order to investigate the effect of the cathodic current density (j) on their phase composition and microstructure. Depending on electrolysis current efficiency the obtained coatings were characterized by a different thickness. It can be seen in Fig. 1, that varying the current density (electrolysis current efficiency) yielded a change in the microstructure of Ni–W coatings from amorphous, formed at current densities j < 3 Adm^{-2} (corresponding to the highest tungsten content of about 50 wt%), to nanocrystalline (for samples obtained at j > 3 Adm^{-2}). X-ray dif-fraction analysis revealed that the nanocrystalline Ni–W alloy coatings exhibited the fcc phase structure of an α-Ni(W) solid solu-tion with a lattice parameter increasing together with tungsten content. The dependence of lattice parameter a_{Ni-W} on the atomic fraction X$_W$ of tungsten in a Ni–W solid solution can be obtained from the average closest atomic distance in the lattice using the following equation: $a_{Ni-W} = 2\sqrt{2}[r_{Ni} + (r_W - r_{Ni})X_W]$ [16,17]. The equation, known as Vegard's law, describes the linear lattice parameter expansion with increasing atomic fraction of tungsten X$_W$ in the Ni substitutional solid solution due to the difference
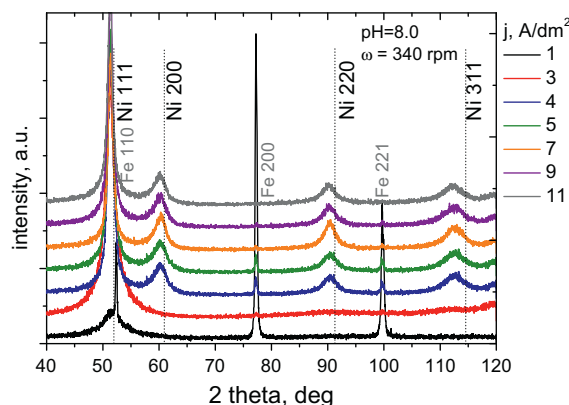

Fig. 1. Representative X-ray diffraction patterns of Ni–W alloy coatings galvano-statically deposited (at different current densities) from a plating bath containing: 0.1 M NiSO$_4$, 0.2 M Na$_2$WO$_4$, 0.5 M Na$_3$C$_6$H$_5$O$_7$, 0.5 M NH$_4$Cl, 0.1 M NaCl. Iron peaks originated from the steel substrate.

between the atomic radius of the pure elements. However, a linear correlation of Vegard's law was not strictly obeyed in investigated system. In particular, negative unconformity from of Vegard's law of Ni–W solid solution was found in the range of investigated con-centration of solute X$_W$, what may reflect the fact that in this sys-tem tungsten is present in the grain boundaries. Such a segregation over a small range of solute content may possibly hinder the growth of the grains in the Ni–W system, so that the average grain size did not excess average 10 nm. On the other hand, when the Vegard's rule is applied to alloy films deposited under nonequilib-rium conditions, it might lead to inaccuracies in the estimation of the composition. In this particular case, the results obtained using XRD pattern analysis are prone to underestimation of global W concentration. Drawing unequivocal conclusions as to the presence of, or the exact extent of grain boundary segregation in the case of nanomaterials using the investigation techniques of EDS and XRD is hindered. Mainly due to the lack of required combination of spa-tial and chemical resolution at the length scales of interest (EDS) and relatively low precision of crystal lattice constant estimation (XRD) due to the peak broadening. The average grain size of Ni–W coatings (the size of the coherent domains) calculated using Rietveld algorithms remained practically constant (∼10 nm) with respect to different galvanic conditions (Fig. 2). As can be seen from the dependence shown in Fig. 2, Ni–W coatings produced under the presented galvanic conditions consist of about 40–50 wt% of
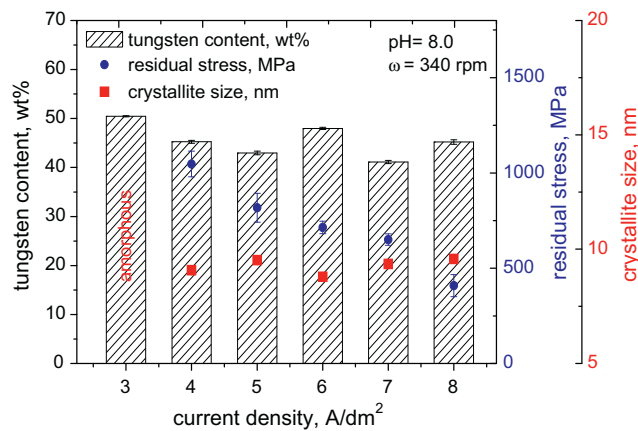

Fig. 2. Tungsten content, crystallite size and residual stresses of the Ni–W alloy coatings deposited from a galvanic bath containing: 0.1 M NiSO$_4$, 0.2 M Na$_2$WO$_4$, 0.5 M Na$_3$C$_6$H$_5$O$_7$, 0.5 M NH$_4$Cl, 0.1 M NaCl as a function of applied current density.