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EFFECT OF HYDRODYNAMIC CONDITIONS ON CERAMIC PARTICLES DISTRIBUTION IN ELECTRODEPOSITED Ni-Mo/Al$_2$O$_3$ NANOCOMPOSITES

The electrodeposition of the nanocrystalline Ni-Mo matrix composite containing nano-sized oxide Al$_2$O$_3$ has been investigated with the aim of preparing hard protective coatings. The Ni-Mo/Al$_2$O$_3$ composites were deposited on ferritic steel substrates in a system with a rotating disk electrode (RDE) from aqueous sulfate-citrate electrolyte solutions containing ultrafine ceramic particles in the suspension. The conditions for the electrodeposition of Ni-Mo/Al$_2$O$_3$ nanocomposite coatings have been developed. The effect of the most important plating parameters namely density, hydrodynamic condition and the Al$_2$O$_3$ concentration in the bath on the content and distribution of the co-deposited ceramic particles in the Ni-Mo matrix was considered. The structural properties, i.e. morphology, phase composition, crystallite dimension of the obtained coatings have been determined. It has been found that the content of the incorporated particles in the deposit rises with increasing applied current density, Al$_2$O$_3$ concentration and stirring rate (in a relatively high cathode rotation range). The rotation speed has also resulted in an increase of the molybdenum content in the Ni-Mo matrix as well as the homogeneity of the ceramic phase distribution in the whole composite volume. At the same time, a significant change in the surface morphology of the electrodeposits and a reduction of the average matrix grain size from about 40 to 10 nm has been observed.

Keywords: electrodeposition, Ni-Mo matrix nanocomposite, Al$_2$O$_3$ nanoparticles

WPŁYW WARUNKÓW HYDRODYNAMICZNYCH NA ROZKŁAD FAZY CERAMICZNEJ W ELEKTROOSADZANYCH NANOKOMPOZYTACH Ni-Mo/Al$_2$O$_3$

Badano proces elektroosadzania powłok kompozytowych zawierających nanokrystaliczną osnowę Ni-Mo oraz fazę ceramiczną Al$_2$O$_3$ o rozmiarach nanometrycznych w celu wytworzenia twardych powłok ochronnych. Kompozyty Ni-Mo/Al$_2$O$_3$ osadzano na podłożu ze stali ferrytycznej, w układzie z wirującą elektrodą dyskową (WED), z wodnych siarczanowo--cytrynianowych roztworów elektrolitów zwierających ceramiczną fazę dyspersyjną w postaci zawiesiny. Opracowano warunki elektroosadzania nanokompozytowych powłok Ni-Mo/Al$_2$O$_3$. Określono wpływ najważniejszych parametrów elektroosadzania, jak gęstość prądu, warunki hydrodynamiczne, stężenie Al$_2$O$_3$ w kąpieli na zawartość i jednorodność rozkładu ceramicznych cząstek w osnowie Ni-Mo. Zbadano również parametry strukturalne wytworzonych powłok, jak morfologia, skład fazowy, rozmiar krystalitów. Stwierdzono, że zawartość cząstek ceramicznych wbudowanych w osnowę rośnie ze wzrostem gęstości prądu, zawartości proszku w kąpieli oraz szybkości mieszania (w relatywnie wysokich zakresach prędkości wirowania katody). Wzrost szybkości mieszania również spowodował zwiększenie zawartości molibdenu w osnowie Ni-Mo oraz poprawę jednorodności rozkładu fazy ceramicznej w objętości kompozytu. Jednocześnie zaobserwowano znaczną zmianę w morfologii powłok oraz obniżenie średniego rozmiaru krystalitów od około 40 do 10 nm.

Słowa kluczowe: elektrochemiczne osadzanie, nanokompozyty z osnową Ni-Mo, nanocząsteczki Al$_2$O$_3$

INTRODUCTION

Particle-reinforced metal matrix composite (MMC) coatings have been commonly used in various engineering applications due to their excellent mechanical properties compared to their components [1]. MMC coatings demonstrate metallic features like electric and thermal conduction, plasticity and modifier properties (hardness, wear and corrosion resistance). One of the methods of manufacturing dispersion hardened materials is electrochemical deposition. The low-temperature electrodeposition technique is simple and allows easy control of the microstructure as well as thickness of coatings plated uniformly on substrates with complicated shapes and large surfaces. Moreover, it is an interesting approach to obtaining nanocrystalline metals and alloys as well as nanocomposite coatings in a single step without secondary treatment [2]. During the electrodeposition process, insoluble ceramic particles suspended in a plating bath are embedded in the simultaneously growing metal matrix. The codeposition mechanism is still not entirely understood despite numerous theories

presented in literature (e.g. electrophoresis, mechanical entrapment, adsorption and convective-diffusion [3]) which results mainly from many factors influencing the electrodeposition process and their interaction. Several metals such as nickel, copper, chromium, gold and zinc are generally applied to a metallic matrix. Little has been written about the applications of alloy matrixes (e.g. Ni-Cu, Zn-Co, Co-Ni, Ni-Fe) containing dispersed ceramic particles [4-7]. Particularly nickel, as a durable and tough metal, has been widely used due to its corrosion and abrasion resistance [8-11]. It is also known that Ni-based alloys containing refractory metal are characterized by enhanced tribological properties [12]. Hence, further modification of MMC mechanical properties could be expected by the introduction molybdenum into a nickel matrix. Moreover, some properties could be improved by using a metal matrix of a nanocrystalline instead microcrystalline structure, as nanomaterials exhibit unique physico-chemical characteristics. Ni-Mo based composites with embedded polyethylene (as a modifier) have been investigated with the aim to obtain a catalyst for the hydrogen evolution reaction (HER) in an alkaline environment [13]. The electrodeposition of a composite containing hard particles (oxides Al_2O_3, ZrO_2, SiO_2 or carbides SiC, WC) incorporated into a nickel matrix has been the subject of many papers [14-17], but none were related to Ni-Mo/Al_2O_3 coatings fabricated by chemical deposition. The inert Al_2O_3 ceramic particles can significantly enhance the technical parameters of Ni-Mo metallic material, including its mechanical, tribological and anti-corrosion behavior. The dimension of the dispersive phase can vary from micrometric to nanometric sizes. The typical diameter of the most often used particles are within the range of 1 and 100 µm, but recently the application of ultrafine particles has become more important. In the present study, the conditions of the electrodeposition of the Ni-Mo matrix with nanosized Al_2O_3 particles have been developed with the aim to obtain hard protective coatings. By modifying the operating parameters of electrolysis, the matrix grain size in the nanocrystalline scale has been controlled. The effect of the plating parameters in the deposition process, such as current density, hydrodynamic conditions and alumina particle content in the plating bath on the Al_2O_3 distribution and microstructure of Ni-Mo/Al_2O_3 coatings were examined.

EXPERIMENTAL DETAILS

The Ni-Mo metallic and Ni-Mo/Al_2O_3 nanocomposite coatings were electrochemically deposited from aqueous electrolyte solutions containing sodium molybdate and nickel sulfate into which Al_2O_3 nanopowder in the amount of 60 and 80 g/dm^3 was added. Sodium citrate ($Na_3C_6H_5O_7$) was used as a complexing agent. The citrate concentration was equal to the sum of the ion concentration of the electrodeposited metals. The pH of the electrolyte solutions was adjusted to 8 by the addition of ammonia. The electrolysis was carried out in a 0.75 dm^3 cell at room temperature under galvanostatic regime (4÷8 A/dm^{-2}) in a system with a rotating disc electrode (RDE). The ferritic steel cathode of 0.028 dm^2 rotating at 0÷640 rpm was supplied by a potentiostat/galvanostat PAR 273A. A platinum spiral (~0.05 dm^2) was used as an anode. Figure 1 presents the experimental setup with the RDE. Prior to each experiment, the substrates were degreased, chemically polished in a solution of oxalic acid and hydrogen peroxide at 35°C and then rinsed in distilled water. Before the co-deposition process, the alumina particles were dispersed in the bath using a mechanical stirrer (500 rpm) for 24 hours, at room temperature. During the last 5 hours the suspension was extra treated by ultrasound.
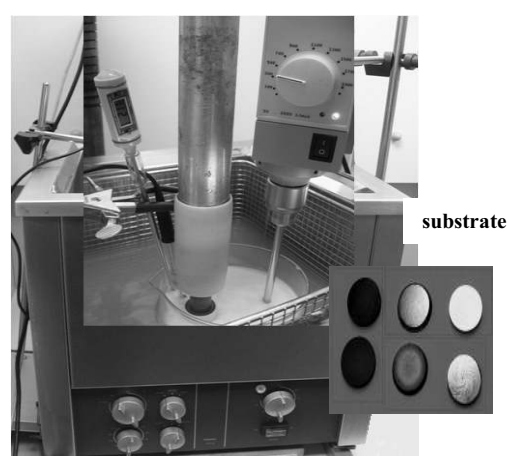

Fig. 1. Electrodeposition cell with rotating disk electrode
Rys. 1. Cela elektrolityczna z wirującą elektrodą dyskową

After electrolysis, the samples were ultrasonically cleaned in ethanol for 1 min to remove loosely adsorbed particles from the coating surface and then dried. The mass of the deposits was determined by an analytical scale, KERN ALT 220 – 5DAM, with accuracy to five points. The coating thickness (in the range of 6÷35 µm) was estimated on the basis of the deposit weight and the cross-section observations. The surface morphology of the coatings was examined by scanning electron microscopy (SEM FEI XL30). The concentrations of the elements (Ni, Mo, Al, O, Fe) in the electrodeposits were determined using energy dispersive X-ray spectroscopy (EDS) in a FEI ESEM XL30 microscope. The phase composition and crystallite size of the deposits were studied by the X-ray diffraction technique using CoK_α (diffractometer Philips PW 1710). The crystallite size was evaluated by peak broadening analysis of X-ray diffraction patterns, using the Scherrer equation:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

where d - average crystallite dimension, K - Scherrer constant (assumed as 0.9), λ - incident radiation wave-

length, β - corrected peak width at half-maximum intensity, θ - angular position.

Characterization of Al$_2$O$_3$ dispersive phase

The commercial Al$_2$O$_3$ powder produced by Sigma Aldrich has been used in the presented study. XRD and TEM techniques were used to characterize the dispersive phase parameters. The obtained results show that Al$_2$O$_3$ powder contains fine needle-shaped crystallites of a size definitely below 100 nm and an irregular fraction whose crystallite dimensions were in the range of $20 \div 50$ nm (Fig. 2). The average particle size has been estimated as about 30 nm. The diffraction pattern analysis confirmed the dominance of γ phase and to a lesser extent the presence of θ and δ phases. However, similarly to the XRD analysis, the α phase has been excluded.
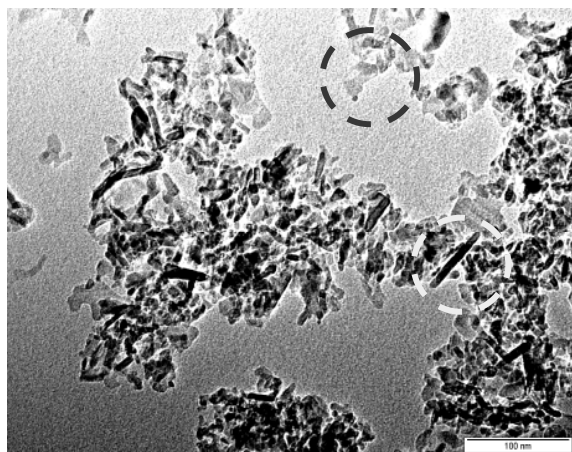

Fig. 2. TEM microstructure of Al$_2$O$_3$ powder (Sigma Aldrich)
Rys. 2. Mikrostruktura TEM proszku Al$_2$O$_3$ (Sigma Aldrich)

RESULTS AND DISCUSSION

During the electrodeposition process of metallic Ni-Mo alloys from the examined plating bath, the Mo(VI) discharge is controlled by the mass transport of the molybdenum complex species towards the cathode [12]. As a consequence of this effect, hydrodynamic conditions as well as current density markedly influence the alloy composition. The relative Mo content in the deposit diminishes when the current density increases and the cathode rotating speed decreases. The presence of ceramic particles in the bath resulted in a shift of the electrodeposition process towards more negative cathode potentials and a further decrease of the molybdenum content in the Ni-Mo matrix is observed. Figure 3 exemplifies the dependence of the current density on the molybdenum content in the metallic Ni-Mo and composite Ni-Mo/Al$_2$O$_3$ coatings. On the other hand, higher current densities favored an increase of alumina content in composites obtained under hydrodynamic conditions corresponding to the RDE speed exceeding 170 rpm. Practically, no effect of current density on the

content of the ceramic particles has been observed at a lower speed (Fig. 4). Moreover, due to the current distribution along the diameter (from the center to its edge) of the rotating disk cathode and intensive bath agitation, fluctuations in the chemical composition of the MMC coatings could be observed. Bath agitation serves two purposes, namely to keep the inert particles suspended in the plating bath and to transport the ceramic phase to the cathode surface. However, excessive agitation may lead to a lower quantity of particles in the metal matrix. Vigorous hydrodynamic forces in the electrolyte solution could remove the particles from the cathode surface before they can be entrapped in the matrix [3]. The effect of the cathode rotation speed on the distribution of the chemical composition of Ni-Mo/Al$_2$O$_3$ coatings along the disk electrode has been determined (Figs. 5 and 6). The composite coatings were electrodeposited from an electrolyte solution containing 80 g/l Al$_2$O$_3$ powder, at 5 A/dm^2, under hydrodynamic conditions corresponding to the rotation disk speed in the range of $0 \div 640$ rpm.
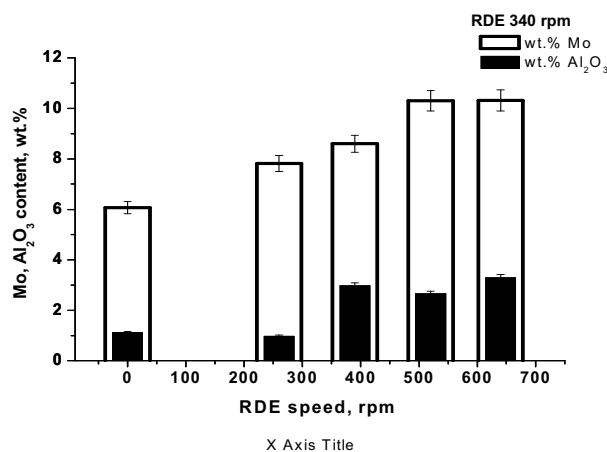

Fig. 3. Molybdenum content in metallic Ni-Mo and composite Ni-Mo/Al$_2$O$_3$ coatings as a function of current density
Rys. 3. Zawartość molibdenu w powłokach metalicznych Ni-Mo oraz kompozytowych Ni-Mo/Al$_2$O$_3$ w funkcji gęstości prądu
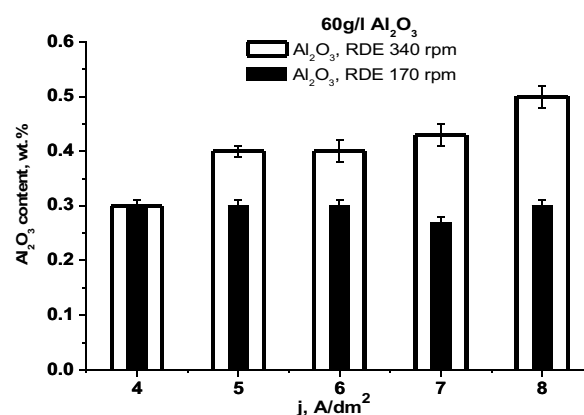

Fig. 4. Alumina content in Ni-Mo/Al$_2$O$_3$ composites deposited from solution containing 60 g/l powder (at 170 and 340 rpm) as a function of current density
Rys. 4. Zawartość Al$_2$O$_3$ w kompozytach Ni-Mo/Al$_2$O$_3$ osadzanych z roztworu zawierającego 60 g/l proszku (przy 170 i 340 rpm) w funkcji gęstości prądu
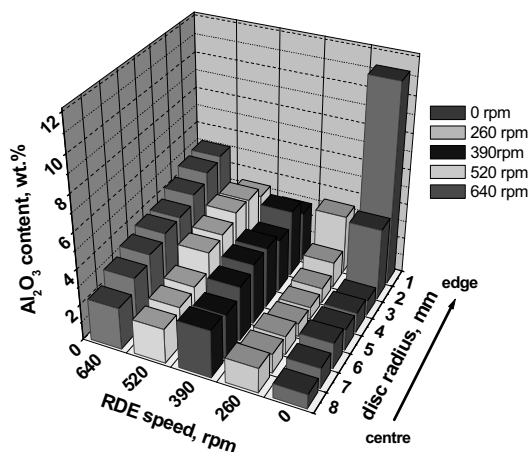
Fig. 5. Influence of rotating disk electrode (RDE) speed on Al_2O_3 content distribution along disk radius

Rys. 5. Wpływ szybkości wirującej elektrody dyskowej (WED) na rozkład zawartości Al_2O_3 wzdłuż promienia dysku
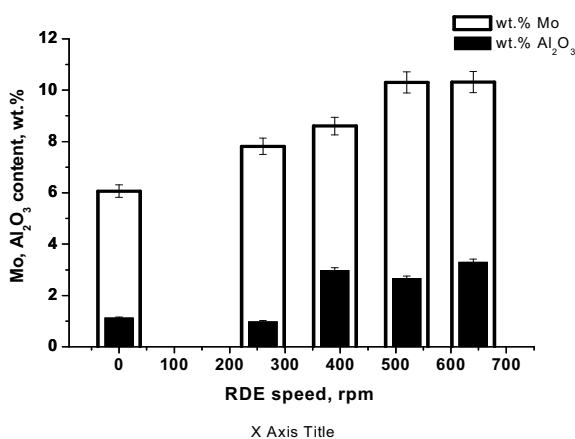

Fig. 6. Effect of disk electrode (RDE) speed on average chemical composition of Ni-Mo/Al_2O_3 composite coatings

Rys. 6. Wpływ szybkości elektrody dyskowej (WED) na średni skład chemiczny powłok kompozytowych Ni-Mo/Al_2O_3

As expected, the Al_2O_3 and Mo content in the composite coatings rises with an increasing rotation rate in the whole investigated range. The coatings obtained at the fixed applied current density of 5 A/dm^2 and at a lower rotation speed reveal a strong composition gradient along the disk radius. The effect becomes less pronounced with increasing cathode rotation speed. The electrodeposition rate (mg/dm^{2}s) practically remained unchanged in the examined range of the disk electrode rotation speed (Fig. 7). The XRD analysis reveals that the Ni-Mo matrix is composed of a nanocrystalline face-centred cubic single phase (Fig. 8). With an increase of the mass transport rate towards the cathode (increase of Mo content), the lines of the XRD patterns broadened, their intensities decrease and the (111) preferred orientation becomes less pronounced. The grain size (the size of the coherent domains) was calculated from the line broadening using Scherrer's equation. The incorporation of Al_2O_3 particles into the Ni-Mo deposit results in a reduction of the average matrix grain size

from about 40 nm to 10 nm in dependence of the hydrodynamic conditions under which the composites were electrodeposited (Table I).
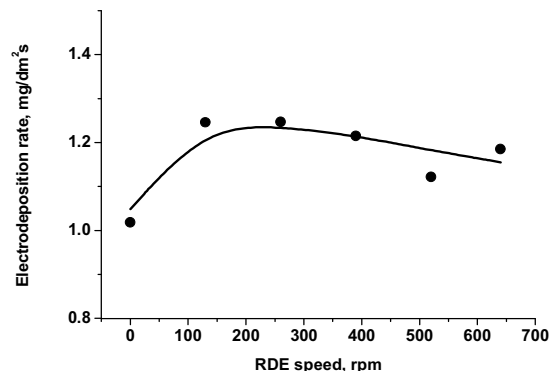

Fig. 7. Rate (mg/dm^{2}s) of Ni-Mo/Al_2O_3 composite electrodeposition from solution containing 80 g/l Al_2O_3 in relation to rotating disk electrode (RDE) speed

Rys. 7. Szybkość elektroosadzania (mg/dm^{2}s) kompozytu Ni-Mo/Al_2O_3 z elektrolitu zawierającego 80 g/l Al_2O_3 w funkcji szybkości wirowania elektrody dyskowej
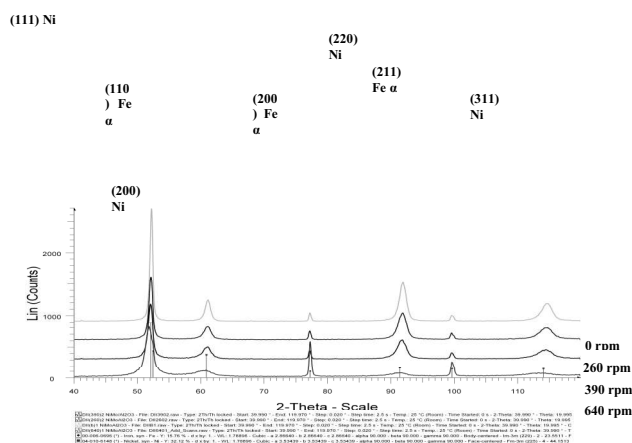

Fig. 8. XRD patterns of Ni-Mo/Al_2O_3 composite electrodeposited under different hydrodynamic conditions from solution containing 80 g/l Al_2O_3

Rys. 8. Dyfraktogramy kompozytu Ni-Mo/Al_2O_3 elektroosadzanego z roztworu zawierającego 80 g/l Al_2O_3 w różnych warunkach hydrodynamicznych

TABLE 1. **Chemical composition and crystallite size of Ni-Mo/Al_2O_3 composite coatings electrodeposited under different hydrodynamic conditions (80 g/l Al_2O_3, 5 A/dm^2)**

TABELA 1. **Skład chemiczny i rozmiar krystalitów kompozytowych powłok Ni-Mo/Al_2O_3 elektroosadzanych w różnych warunkach hydrodynamicznych (80 g/l Al_2O_3, 5 A/dm^2)**

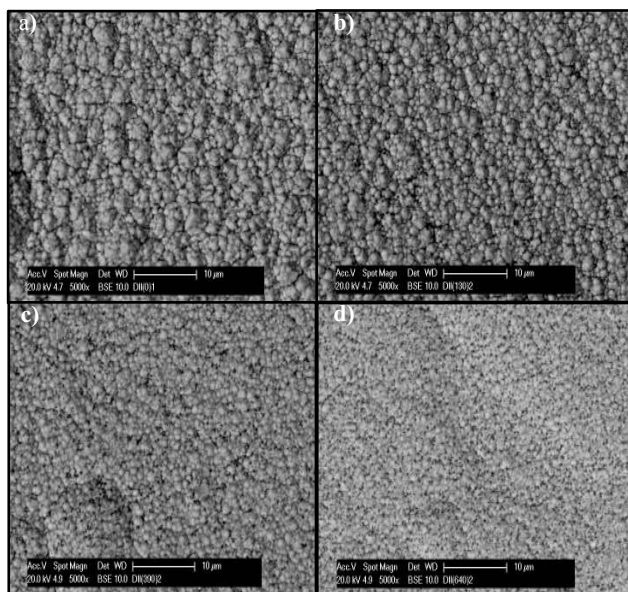| Cathode rotating rate, rpm	Crystallite size, nm	Chemical composition, wt.%		
		Ni	Mo	Al_2O_3
0	30	92.8±1.9	6.1±0.2	1.2±0.1
260	20	91.2±1.9	7.8±0.3	1.0±0.1
390	15	88.4±1.8	8.6±0.3	3.0±0.1
640	10	86.4±1.7	10.3±0.4	3.3±0.1

Fig. 9. SEM morphology of Ni-Mo/Al$_2$O$_3$ coatings deposited at: 0 (a), 130 (b), 390 (c) and 640 (d) rpm, respectively

Rys. 9. Morfologia SEM powierzchni powłok Ni-Mo/Al$_2$O$_3$ osadzanych przy następujących prędkościach: 0 (a), 130 (b), 390 (c) i 640 (d) obr/min
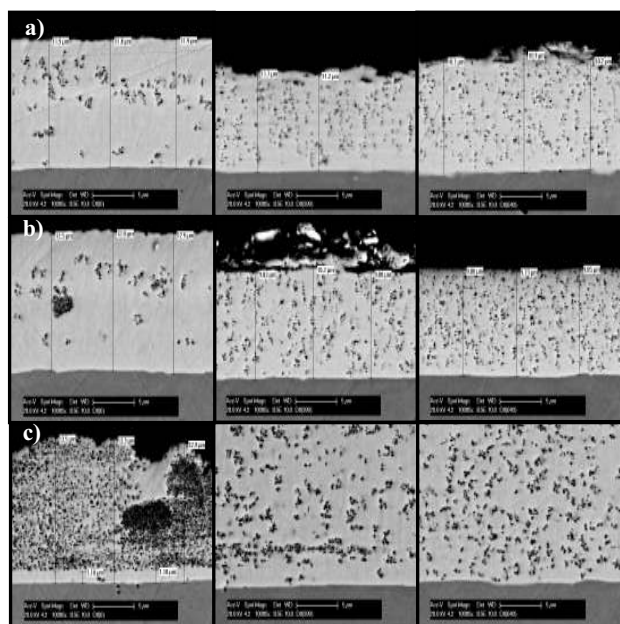

Fig. 10. SEM backscattered electron image of cross-sections of Ni-Mo/Al$_2$O$_3$ coatings electrodeposited under different hydrodynamic conditions, determined in different part of samples along radius: (a) in centre, (b) in halfway between centre and edge, (c) at edge

Rys. 10. Mikrostruktura SEM (BSE) przekroju poprzecznego powłok Ni-Mo/Al$_2$O$_3$ elektroosadzanych w różnych warunkach hydrodynamicznych, określona w różnych częściach próbek wzdłuż ich promienia: (a) w środku, (b) pomiędzy środkiem a brzegiem, (c) przy brzegu

CONCLUSION

The obtained results shown that Al$_2$O$_3$ particles can be electrodeposited with a nanocrystalline Ni-Mo matrix from a sulfate-citrate aqueous electrolyte. The cur-rent density, alumina concentration and hydrodynamic conditions are all important processing parameters that control the microstructure, the content of the incorporated ceramic phase and hence the properties of the composite. The change in the chemical composition of the coatings with an increasing bath stirring rate demonstrates the significant influence of mass transport to the cathode on the process of Ni-Mo/Al$_2$O$_3$ composite deposition. Relatively high disk rotation speeds prevent agglomeration and promote uniform incorporation of the nanoparticles during the composite electrodeposition process. From a practical point of view, it appears necessary to control the hydrodynamic conditions in order to get homogeneous and compact composite coatings.

Acknowledgment

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