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MICROSTRUCTURAL AND MICROCHEMICAL CHARACTERISATION OF THE NICKEL-BASED THIN FILMS PREPARED BY ELECTRODEPOSITION

MIKROSTRUKTURALNA I MIKROCHEMICZNA CHARAKTERYSTYKA CIENKICH WARSTW NA OSNOWIE NIKLU OTRZYMANÝCH METODĄ ELEKTROCHEMICZNĄ

Ni-based alloys containing refractory metal (molybdenum or tungsten) characterized by high hardness, high wear, thermal and corrosion resistance are widely used for many industrial applications as they offer an important alternative to toxic, hard chromium coatings. In the present work the formation of the amorphous Ni-W films by electrochemical deposition from aqueous baths at room temperature has been reported. The Ni-W alloys have been electrodeposited from sulphate-citrate electrolyte, under potentiostatic or potentiodynamic regimes. To ensure a steady and controlled hydrodynamic condition, a rotating disk electrode (RDE) system was used. It was observed that alloys electrodeposited at different cathode potentials vary in chemical composition and thickness. Such effect results mainly from kinetics of nickel and tungsten induced codeposition as well as on the decrease of the electrodeposition current efficiency as the cathode potential becomes more negative. Concentrations of elements in the electrodeposits were determined using energy-dispersive X-ray spectroscopy (EDS) in a scanning electron microscopy (SEM) with a thermally assisted Schottky field emission gun (FEG). Monte Carlo calculations for characteristic X-ray intensities emitted from coatings of given thicknesses and chemical compositions were used to evaluate the most adequate electron beam energy for X-ray emission. The results obtained are compared to chemical analyses carried out by the atomic absorption spectroscopy (AAS) technique.

Keywords: Ni-W thin films, electrodeposition, microstructure characterization, EDS, Monte Carlo simulations

Stopy na osnowie niklu zawierające trudnotopliwy metal (molibden lub wolfram) charakteryzujące się dużą twardością, odpornością na ścieranie oraz na korozję, znajdują szerokie zastosowanie w wielu dziedzinach przemysłu, gdyż mogą zastąpić toksyczne, twarde powłoki chromowe. Prezentowana praca dotyczy wytwarzania metodą elektrochemiczną z wodnych roztworów, w temperaturze pokojowej, amorficznych warstw Ni-W. Stopy tego rodzaju elektroosadzano z elektrolitu siarczanowo-cytrynianowego, w warunkach potencjostatycznych lub potencjodynamicznych. W celu zapewnienia stałych i kontrolowanych warunków hydrodynamicznych zastosowano układ z wirującą elektrodą dyskową (WED). Ustalono, że warstwy elektroosadzane przy różnych wartościach potencjału katody charakteryzowały się różną grubością i zmiennym składem chemicznym. Efekt ten związany jest głównie z kinetyką indukowanego współosadzania wolframu z niklem oraz z wydajnością prądową procesu elektrosadzania w miarę przesuwania potencjału katody w kierunku wartości bardziej ujemnych. Skład chemiczny otrzymanych powłok galwanicznych określono metodą spektroskopii promieniowania rentgenowskiego (EDS) przy użyciu skaningowego mikroskopu elektronowego (SEM) ze źródłem elektronów typu Schottky z emisją polową (FEG). Na podstawie obliczeń Monte Carlo dla charakterystycznych intensywności promieniowania rentgenowskiego emitowanego z warstw Ni-W o zadanym składzie chemicznym i grubości, szacowano właściwą energię wiązki elektronowej do badań EDS. Wyznaczony skład chemiczny powłok Ni-W porównano z analizą przeprowadzoną metodą atomowej spektroskopii absorpcyjnej (AAS).

1. Introduction

Ni-based tungsten alloys are known for their excellent mechanical and tribological characteristics. Compared to pure Ni, they exhibit enhanced properties such as hardness, corrosion and abrasion resistance, useful for practical applications e.g. in the automotive and avia-

tion industries (wheel bearings, magnetic heads, catalysts etc.) [1]. They show particular promise as an engineering, functional material for substitution of hard chromium coatings, as chromates are known to be highly toxic and carcinogenic [2, 3]. The Ni-W alloys could also be a candidate for use as a barrier layer in copper metallization for ultra-large-scale integration (ULSI) for inte-

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grated circuit or MEMS applications [4 - 6]. However, these alloys are very difficult to obtain by conventional thermal methods due to the large differences in their melting points (Ni – 1455 °C, W – 3410 °C) as well as their limited mutual solubility. Hence, electrochemical deposition is proposed as an alternative technique.

Electrodeposition, as a cheap and simple method, is a superior technique for manufacturing Ni-based coatings. It is well-known that tungsten cannot be electrodeposited from aqueous electrolytes, however it can be easily deposited with iron group metals such as nickel to form an alloy [7]. This phenomenon is classified as induced co-deposition [8]. Among many galvanic baths proposed for the Ni-W alloys electroplating (such as sulfamate, ammoniacal, glycine etc.) citrate electrolytes seem to be the most promising [9 - 14]. The content of tungsten in the electrodeposited coatings has a major effect on mechanical and chemical properties. Moreover, the change in chemical composition and thickness of Ni-W coatings electrodeposited at different cathode potentials was observed. Hence, the aim of the present work was to determine the elemental concentrations in Ni-W films of different thicknesses by energy-dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM). Monte Carlo simulation for characteristic X-ray intensities emitted from coatings of given thicknesses and chemical compositions were used to evaluate the most adequate electron beam energy. The results obtained were compared to the atomic absorption spectroscopy (AAS).

2. Experimental

The Ni-W coatings have been electrodeposited from sulphate-citrate electrolytes (0.3 M Na_2WO_4 , 0.1 M NiSO_4 , 0.4 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) of the W(VI)/Ni(II) concentration ratio equals 3, under potentiostatic and potentiodynamic (2 mV/s) regimes, at room temperature. The pH was adjusted to 8 by adding sulphuric acid. The electrolysis was carried out in 0.75 dm³ cell in a system with a rotating disc electrode (RDE) to ensure steady and controlled hydrodynamic condition. Cathode potentials were referred to the saturated calomel electrode (SCE) and were corrected for ohmic drop by the current interrupt method (CI). Measurements were carried out in the potential range from -0.6 V/SCE to -1.5 V/SCE. The cathode was a low-carbon steel disc of 0.028 dm², rotating at 25 rad s⁻¹, supplied by potentiostat PAR 273A, while a platinum sheet (0.05 dm²) was used as anode. The Ni-W deposit thicknesses were estimated based on the SEM cross-section observation, whereas their chemical composition was determined by atomic absorption spectroscopy (AAS) technique using spectrometer UNI-

CAM SP-90. Characteristic X-ray intensities simulation for coatings of given thicknesses and chemical composition were determined by Monte Carlo calculations (Electron Flight Simulator Version 3.1-E) to optimize the energy of the electron beam for energy-dispersive X-ray spectroscopy (EDS) analyses. Concentrations of elements in the electrodeposits were determined by EDS in a SEM with Schottky field emission gun (FEG) FEI NOVA NANOSEM 200. The structure of deposits was studied by X-ray diffraction technique using Co-K α radiation (Philips PW 1710) and the surface morphology was investigated by the FEI XL30 ESEM. Mass of deposits was determined by the analytical balance KERN ALT 220 – 5DAM.

3. Results and discussion

3.1. Electrochemical characterization

Figure 1 shows global potentiodynamic polarization curves for the Ni separate electrodeposition and for the Ni-W co-deposition recorded under the same operating conditions. It is apparent that (in considered conditions) the formation of Ni-W alloy is energetically favoured. As seen over the whole polarisation range, the Ni-W deposition occurs at less negative cathode potentials compared to the Ni(II) separate discharge – a catalytic effect of co-deposition with tungsten was observed.

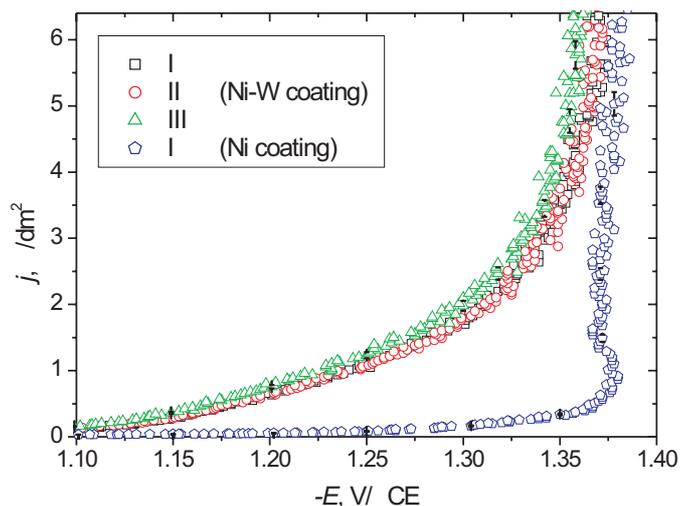


Fig. 1. Global polarization curves recorded under potentiodynamic conditions (2 mV/s) at 25 rad s⁻¹ in solutions of pH 8: 0.1 M NiSO_4 , 0.3 M Na_2WO_4 , 0.4 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and 0.1 M NiSO_4 , 0.4 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$

The electrolysis was carried out at selected cathode potentials in the range between -1.1 V/SCE and -1.3 V/SCE

(for quantity of electricity of 50 C). Based on these experiments the steady-state polarization curves were constructed (Fig. 2. curve 1). On the other hand, the efficiency of electrodeposition process decreases systematically with more negative cathode potential, as a result of the increase of hydrogen evolution reaction rate (side process of Ni-W deposition). Thus, the coatings of different thicknesses have been obtained (Fig. 2. curve 2).

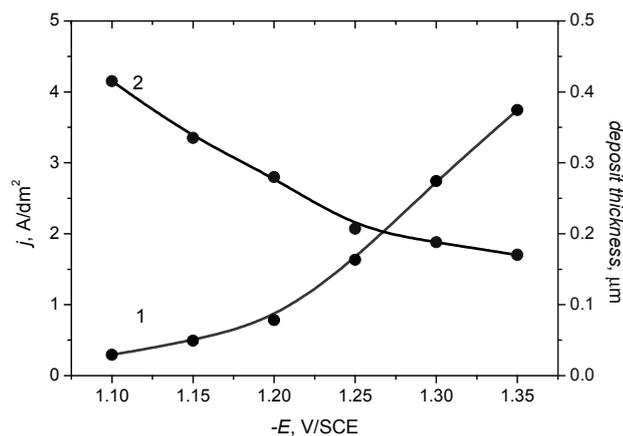


Fig. 2. Steady-state global polarization curve for Ni-W electrodeposition recorded under potentiostatic conditions at 25 rad s^{-1} in solution: 0.1 M NiSO_4 , $0.3 \text{ M Na}_2\text{WO}_4$, $0.4 \text{ M Na}_3\text{C}_6\text{H}_5\text{O}_7$ of the pH 8 (1) and coating thickness in function of cathode potential (2)

3.2. Determination of Ni-W chemical composition

The tungsten content in the alloys depends mainly on the operating conditions (cathode potential or current density, concentration of tungsten and nickel species in the plating bath, pH, temperature, hydrodynamic conditions, etc.). Generally, the chemical composition of Ni-W alloy is determined by the ratio of rates of two cathodic processes (electroreduction of Ni(II) and W(VI) species). Hydrogen evolution does not affect alloy deposition except reducing the current efficiency.

The chemical composition of Ni-W coatings was determined by AAS technique (Table I), whereas their thicknesses were estimated from SEM cross-section observations (Fig. 3a) as well as on the basis of the electrochemical calculations from current efficiency and deposit weight determined for every cathode potential. For layers of poor adhesion, cross-section observation could not be used for the thickness determination due to not well-defined interface between the coating and substrate (Fig. 3b.). The cracks visible on SEM images were observed when the tungsten content in Ni-W alloys exceeds approximately 80%wt. For lower W content, the com-

pact Ni-W coatings well adhered to steel substrate were obtained.

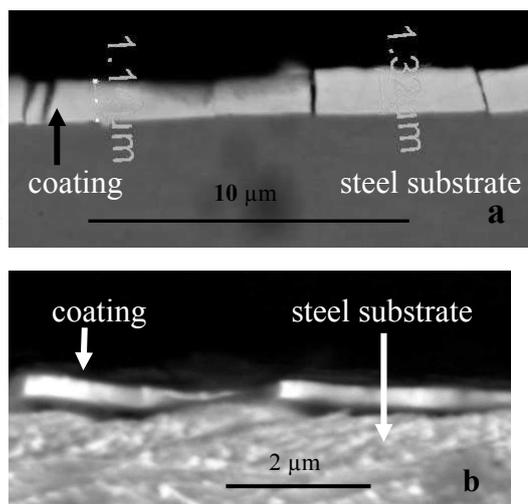


Fig. 3. SEM images (BSE) of Ni-W cross-section electrodeposited under potentiostatic conditions a) -1.2 V/SCE , 200 C ; b) -1.1 V/SCE , 50 C

The obtained data (thickness and chemical composition) were used for Monte Carlo calculations (Electron Flight Simulator Version 3.1-E) to evaluate characteristic X-ray intensities emitted from coatings and to optimize the electron beam energy for EDS investigations. Detection of characteristic X-ray intensities emitted only from the Ni-W films (and not from the substrate) is crucial for obtaining reliable chemical alloy composition by use of EDS microanalysis. Figure 4 shows an example of Monte Carlo simulations of the generated and emitted X-rays from electrodeposited Ni-W films. In the applied model, the Ni-W films numbered from 1 to 5 with growing thickness are presented as a multilayer on a steel substrate. The input data were as following: layer composition, density and thickness, accelerating voltage varying from 6 to 15 kV, element and excited line for 'X-Ray Model Excited' and 'X-Ray Model Generated', number of electron trajectories (10000 minimum to obtain proper statistics). PhiRhoZ correction was used to improve accuracy of X-ray thin films microanalysis and the beryllium detector was chosen. The X-ray model is shown as a series of green dots for generated X-rays along with a series of red dots for emitted X-rays, which have a sufficient energy to escape from the sample and reach the detector before being absorbed in the film volume. The dots represent an easily recognized X-ray excitation volume. However, the outcome of such simply simulation allowed to optimize the energy of the electron beam for energy-dispersive X-ray spectroscopy (EDS) analyses (in order to detect the signal from the film volume only).

The content of Ni and W determined by energy-dispersive spectroscopy (EDS) was compared

with the atomic absorption spectroscopy (AAS technique) (Table I). The maximum tungsten content in Ni-W

coatings was about 80.0 ± 1.6 %wt. and seemed to be homogenous in the whole volume.

TABLE 1
Chemical composition of Ni-W alloys electrodeposited at different cathode potentials, for quantity of electricity of 50 C, determined by EDS and AAS techniques. EDS analysis was performed at 15 and 11 kV* (* plus signal from the Fe background)

Cathode potential, V vs. SCE		-1.10		-1.15		-1.20		-1.25		-1.30	
Thickness, μm		0.42		0.34		0.28		0.21		0.19	
Analysis technique		EDS	AAS	EDS	AAS	EDS	AAS	EDS*	AAS	EDS*	AAS
Component %wt.	Ni	15.2 ± 0.6	16.0 ± 0.8	17.0 ± 0.7	20.8 ± 1.0	19.2 ± 0.8	22.8 ± 1.1	26.2 ± 0.5	42.0 ± 2.1	26.1 ± 0.5	49.5 ± 2.5
	W	84.8 ± 0.7	84.0 ± 4.2	83.0 ± 1.7	79.2 ± 4.0	80.8 ± 1.6	77.2 ± 3.9	58.1 ± 1.2	58.0 ± 2.9	43.2 ± 0.9	50.5 ± 2.5

As seen from data presented in Table I, a non-destructive EDS technique could be used to determine the chemical composition of Ni-W thin films of thickness above 0,2

μm . In such a thickness range a very good agreement with classic chemical analysis performed by atomic absorption spectroscopy (AAS) was achieved.

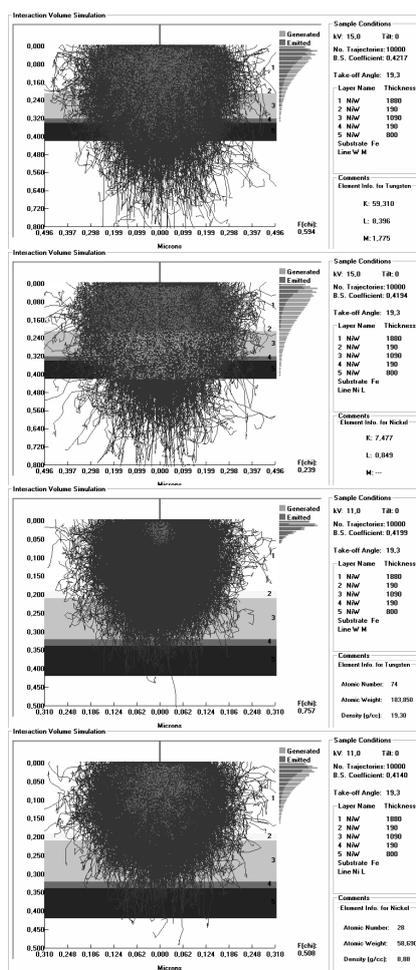


Fig. 4. Examples of an electron depth penetration in a Ni-W films simulated using of Monte Carlo methods for energy of 11 kV and 15 kV, respectively. The coatings numbered from 1 to 5 with growing thickness are presented as a multilayer on a Fe substrate

3.3. Microstructure characterization

The tungsten content in deposited alloys affects strongly the surface topography. The decrease in cathode potential value reduces the tungsten content in the alloy, which leads to gradual transformation of fine spherical

nodules to more homogeneous deposit. The Ni-W films electrodeposited at less negative potentials are characterized by globular microstructure (Fig. 5a), which are transferred to more compact with more negative potential (Fig. 5b).

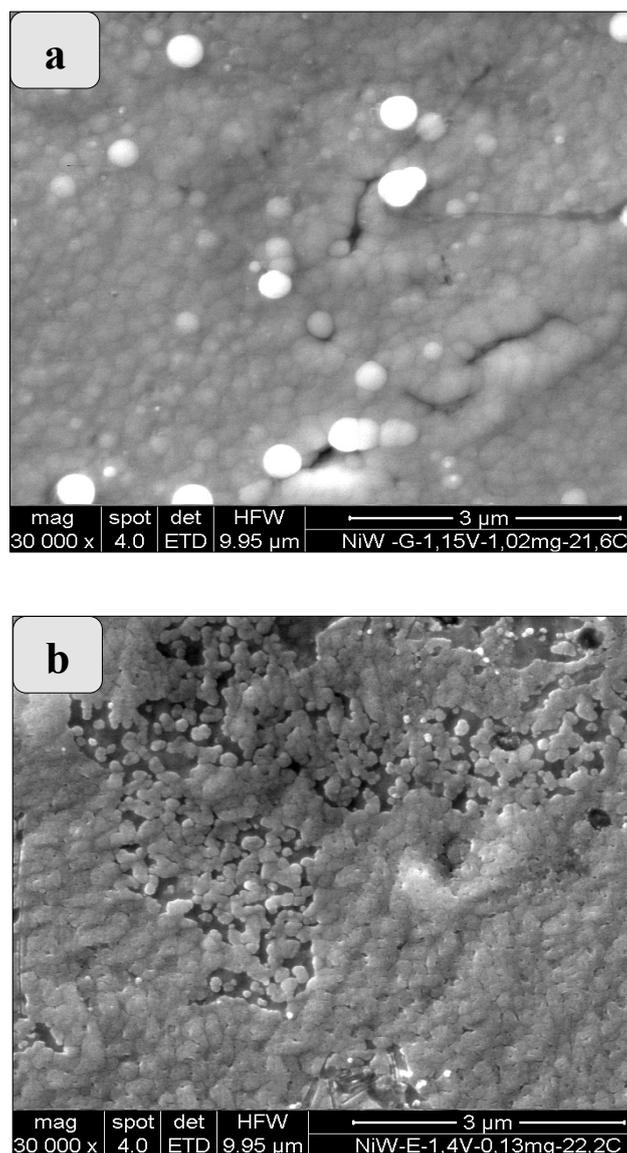


Fig. 5. SEM images of Ni-W coating surface electrodeposited under potentiostatic conditions: a) -1.1 V/SCE, 50C; b) -1.4 V/SCE, 50C

Fig. 6 shows an example of the surface morphology of thicker Ni-W coatings (300 C) deposited at -1.18 V/SCE (c) and -1.27 V/SCE (d), respectively. It can be noticed that, in the first case the deposit is cracked, whereas

the coating electrodeposited at more negative potential is smooth and compact, adherent to the steel substrate with no cracks observed.

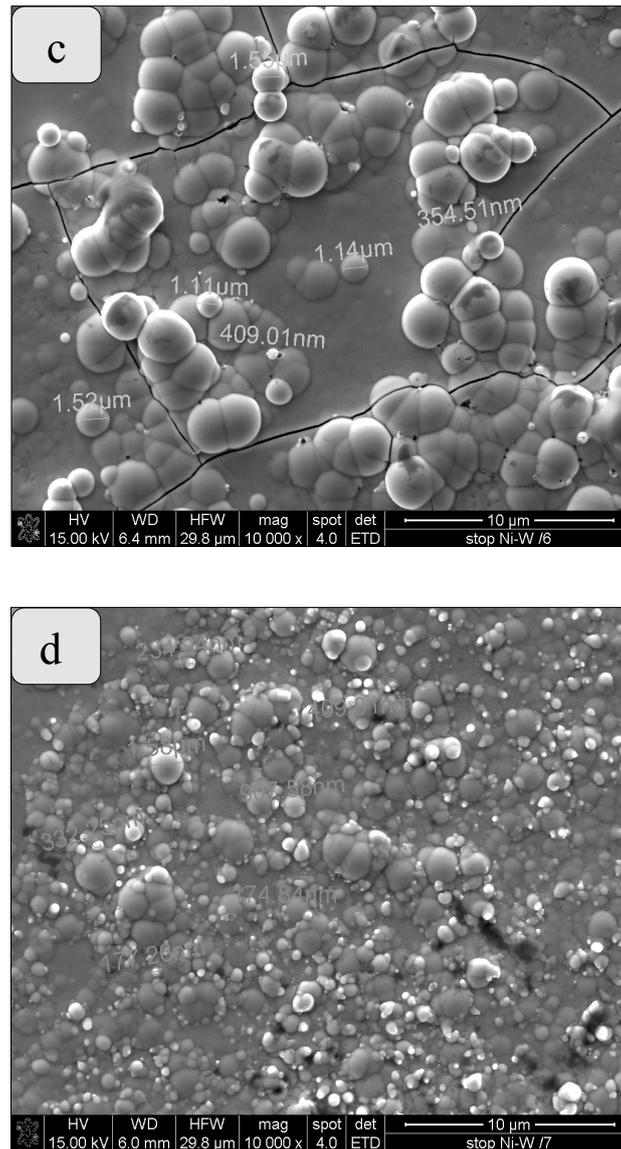


Fig. 6. SEM images of Ni-W coating:
c) -1.27 V/SCE, 300C, about 50%wt. of W

d) -1.27 V/SCE, 200C, about 80%wt. of W;

The X-ray diffraction patterns for investigated Ni-W films containing about 50.5 and 84 %wt. of tungsten are shown in Fig. 7. Both of them consist of an amorphous halo without any sharp lines, directly correlated with the absence of a crystalline phase in deposit (the Fe peaks originate from the steel substrate). The maximum of the halo at $2\theta = 50.9^\circ$ was observed. It was established that amorphous films are formed when the concentration of W in the Ni-W alloy is higher than 40%wt.

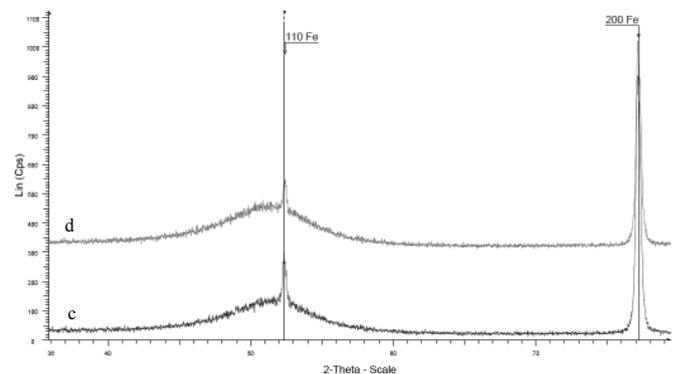


Fig. 7. X-ray diffraction pattern (CoK radiation) of sample c and d in Fig. 6

4. Conclusions

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- The designed bath allows for electrodeposition of Ni-W films of maximum tungsten content about 80%wt. The tungsten distribution seems to be homogenous in the whole volume of deposit.
 - The amorphous Ni-W films are formed when the tungsten content in the alloy is in the range of 40 – 80 wt%.
 - The obtained amorphous films which contain considerable amount of W (~80%wt.) revealed a crack pattern, characteristic for large quantity of refractory metal, whereas the coatings of lower tungsten content (electrodeposited at more negative cathode potentials) were smooth, compact, well adherent to the steel substrate with no cracks visible.
 - The efficiency of electrodeposition process decreases systematically when the cathode potential becomes more negative as a result of the increase of hydrogen evolution rate (side process), in consequence coatings of different thicknesses were obtained.
 - According to the proposed model (Monte Carlo calculations), a non-destructive EDS technique could be applied to determine the chemical composition of Ni-W films of thickness above 0,2 μm . In this thickness range a very good agreement with classic chemical analysis performed by atomic absorption spectroscopy was achieved.
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