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KOMPOZYTY
COMPOSITES

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OXYGEN EVOLUTION REACTION ON ELECTROLYTIC NICKEL-BASED COMPOSITE COATINGS IN AN ALKALINE SOLUTION

Ni+W+Si and Ni+W+Mo+Si composite coatings were obtained by electrodeposition of crystalline nickel from an electrolyte containing suspension of suitable metallic and non-metallic components (W, Mo and Si). These coatings were obtained under galvanostatic conditions, at the current density of $j_{dep.}$ = 0.100 A cm^{-2} and at the temperature of 338 K. For comparison the Ni coating was also obtained and investigated in the same manner. Obtained coatings were modified in the air atmosphere by thermal treatment at the temperature of 973 K during 1 hour. Thermal treatment of obtained coatings changes their phase composition. X-ray diffraction pattern showed that the Ni+W+Si coating is composed of three phase structures, i.e., nickel, tungsten and silicon. The phase composition for the Ni+W+Si coating after thermal treatment in the air is markedly different. The main peaks corresponding to the W coexist with the new ones corresponding to new phases: $NiWO_4$ and two forms of SiO_2. X-ray diffraction pattern showed that the Ni+W+Mo+Si coating is composed of four phase structures, i.e., nickel, tungsten, molybdenum and silicon. The phase composition for the Ni+W+Mo+Si coating after thermal treatment in the air is also markedly different. This may be concluded from the presence new peaks corresponding to new phases: $NiWO_4$, $NiMoO_4$ and SiO_2. The phase composition for the Ni coating after thermal treatment in the air is different in comparison with Ni as-deposited coating. The main peaks corresponding to the Ni coexist with the new ones corresponding to new phase: NiO, what suggests that the nickel coating was also oxidized. The electrochemical activity of thermally treated coatings was studied in the process of oxygen evolution reaction (OER) from 5 M KOH solution using electrochemical impedance spectroscopy (EIS) method. It was found that Ni+W+Mo+Si composite coating after thermal treatment in the air is characterized by enhanced electrochemical activity towards oxygen evolution as compared with Ni+W+Si and Ni coatings after thermal treatment in the air. This coating to characterize least values of the logarithm impedance module log $|Z|$, phase angle Φ, charge-transfer resistance R_{ct}, and greatest values of double-layer capacitance C_{dl}. Thus obtained coating may be useful in application as electrode material for the oxygen evolution reaction.

Keywords: composite coatings, oxygen evolution reaction (OER), electrochemical impedance spectroscopy (EIS)

PROCES WYDZIELANIA TLENU NA ELEKTROLITYCZNYCH POWŁOKACH KOMPOZYTOWYCH NA OSNOWIE NIKLOWEJ W ŚRODOWISKU ALKALICZNYM

Powłoki kompozytowe Ni+W+Si i Ni+W+Mo+Si otrzymano poprzez elektroosadzanie krystalicznego niklu z elektrolitu zawierającego zawiesinę odpowiednich metalicznych i niemetalicznych składników (W, Mo i Si). Te powłoki otrzymano w warunkach galwanostatycznych ($j_{dep.}$ = 0,100 A cm^{-2}) w temperaturze 338 K. Do celów porównawczych otrzymano również powłokę Ni, którą poddano identycznym badaniom jak pozostałe. Otrzymane powłoki zostały poddane obróbce cieplnej w atmosferze powietrza w temperaturze 973 K przez 1 godzinę. Obróbka cieplna otrzymanych powłok zmieniła ich skład fazowy. Rentgenowska analiza fazowa powłok Ni+W+Si po obróbce cieplnej w atmosferze powietrza wykazała obecność następujących faz: $NiWO_4$, dwóch odmian SiO_2 oraz występującej już wcześniej fazy W. Rentgenowska analiza fazowa powłok Ni+W+Mo+Si po obróbce cieplnej w atmosferze powietrza wykazała obecność nowych faz: $NiWO_4$, $NiMoO_4$ oraz SiO_2. Natomiast rentgenowska analiza fazowa powłok Ni po obróbce cieplnej w atmosferze powietrza wykazała obecność nowej fazy NiO oraz występującej już wcześniej fazy Ni. Charakterystykę aktywności elektrochemicznej w procesie wydzielania tlenu w środowisku alkalicznym (5 M KOH) dla powłok po obróbce cieplnej w atmosferze powietrza prowadzono metodą elektrochemicznej spektroskopii impedancyjnej. Stwierdzono, że powłoka kompozytowa Ni+W+Mo+Si po obróbce cieplnej charakteryzuje się podwyższoną aktywnością elektrochemiczną w procesie wydzielania tlenu w porównaniu do powłok Ni+W+Si i Ni po obróbce cieplnej. Powłoka kompozytowa Ni+W+Mo+Si po obróbce cieplnej charakteryzuje się najmniejszymi wartościami logarytmu modułu impedancji log $|Z|$, kąta przesunięcia fazowego Φ i oporu przeniesienia ładunku R_{ct} oraz największymi wartościami pojemności warstwy podwójnej C_{dl}. Tak otrzymana powłoka może być zastosowana jako materiał elektrodowy w procesie wydzielania tlenu.

Słowa kluczowe: powłoki kompozytowe, proces wydzielania tlenu, elektrochemiczna spektroskopia impedancyjna

INTRODUCTION

Electrolytic hydrogen and oxygen evolution on various electrode materials and from various electrolyte solutions are two of the most frequently studied electrode reaction. The reasons for this are both theoretical and practical, since the two gases represent major products or byproducts of several industrial electrolytic processes. Oxygen electrode reactions have an important role in electrochemical technology because they constitute basic processes in systems like water electrolysers, fuel cells, metal-air batteries, sensors, etc.

Properties of electrolytic nickel and nickel-based composite coatings are well known. Their wide application is a result of specific properties of nickel, which exhibit good corrosion resistance in aggressive solutions and also high catalytic activity for many electrochemical processes, in particular for the hydrogen and oxygen evolution reactions. It should be added that electrochemical processes depend markedly on the chemical and phase composition, geometric properties and structure of the electrode surface. In general, oxygen evolution reaction on metals normally takes place on the surface, which is firstly covered with appropriate oxides. In order to improve the utilization of these materials, various methods of their modifications could be applied [1-5]. Present study was undertaken in order to evaluate suitability of Ni+W+Si and Ni+W+Mo+Si composite coatings after thermal treatment in the air atmosphere, as electrode materials for the oxygen evolution in an alkaline solution. Additionally, composite coatings were compared with nickel coating subjected to the analogous thermal treatment.

EXPERIMENTAL

Ni+W+Si coating were obtained by electrodeposition from the following electrolyte (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 + 50 g dm^{-3} of tungsten powder (100 mesh, *Aldrich*) + 50 g dm^{-3} of silicon powder (325 mesh, *Aldrich*). Ni+W+Mo+Si coating were obtained by electrodeposition from the following electrolyte (concentrations in g dm^{-3}): $NiSO_4 \cdot \cdot 7H_2O$ - 84, H_3BO_3 - 8, CH_3COONa - 10, $C_6H_5O_7Na_3 \cdot \cdot 2H_2O$ - 30, NH_4Cl - 10 + 50 g dm^{-3} of tungsten powder (100 mesh, *Aldrich*) + 50 g dm^{-3} of molybdenum powder (100 mesh, *Aldrich*) + 50 g dm^{-3} of silicon powder (325 mesh, *Aldrich*). Distilled water and 'analytical grade' reagents were used for preparation of the electrolyte. The process was carried out at the temperature of 338 K, with intensive mechanical stirring (200 rpm). Coatings were electrodeposited under galvanostatic conditions, at the current density $j_{dep.}$ = = 0.100 A cm^{-2}. A platinum mesh served as an auxiliary electrode. The coatings were deposited on the steel plate (St3S) of the geometric surface area of 1 cm^2 and were used as working electrodes. For comparison the Ni coating was also obtained and investigated in the same manner. In order to obtain superficial oxides of the transition metals on Ni+W+Si, Ni+W+Mo+Si and Ni coatings the samples were kept at the temperature of 973 K during 1 hour in the air atmosphere.

Chemical composition of the coatings was determined by EDS method and phase composition investigations were conducted by X-ray diffraction method. Investigations of electrolytic oxygen evolution on the thermally treated coatings were conducted in a three-electrode cell, using electrochemical impedance spectroscopy (EIS) method. These measurements were carried out in 5 M KOH solution, at the temperature of 293 K, using Autolab® electrochemical system. The auxiliary electrode was a platinum mesh and the reference electrode was of the type Hg/HgO/5 M KOH. In the EIS measurements the amplitude of *ac* signal was equal 0.005 V. A frequency range from 10 kHz to 0.1 Hz was covered with 10 points per decade. The real and imaginary components of the complex plane plots were analysed using a modified version of a complex non-linear least-squares fitting program (CNLS) [3, 4] from which the experimental parameters of an electrical equivalent circuit were determined.

RESULTS AND DISCUSSION

The Ni+W+Si composite coating contains about 39 wt. % of nickel, 41 wt. % of tungsten and 20 wt. % of silicon. X-ray diffraction pattern showed that the deposited coating is composed of three phase structures, i.e., nickel, tungsten and silicon. It means that in the process of nickel electrodeposition, tungsten and silicon powders grains have been built into a crystalline nickel matrix (Fig. 1a). The phase composition for the Ni+W+Si coating after thermal treatment in the air is markedly different. The main peaks corresponding to the W coexist with the new ones corresponding to new phases: $NiWO_4$ and two forms of SiO_2 (Fig. 1b). It was ascertained that the thermal treatments of Ni+W+Si coating leads to production of new kind of composite material.

The Ni+W+Mo+Si composite coating contains about 34 wt. % of nickel, 29 wt. % of tungsten, 23 wt. % of molybdenum and 14 wt. % of silicon. X-ray diffraction pattern showed that the deposited coating is composed of four phase structures, i.e., nickel, tungsten, molybdenum and silicon. It means that in the process of nickel electrodeposition, tungsten, molybdenum and silicon powders grains have been built into a crystalline nickel matrix (Fig. 2a). The phase composition for the Ni+W+ +Mo+Si coating after thermal treatment in the air is markedly different. This may be concluded from the presence new peaks corresponding to new phases: $NiWO_4$, $NiMoO_4$ and SiO_2 (Fig. 2b). It was ascertained

that the thermal treatments of Ni+W+Mo+Si coating leads to production of new kind of composite material.

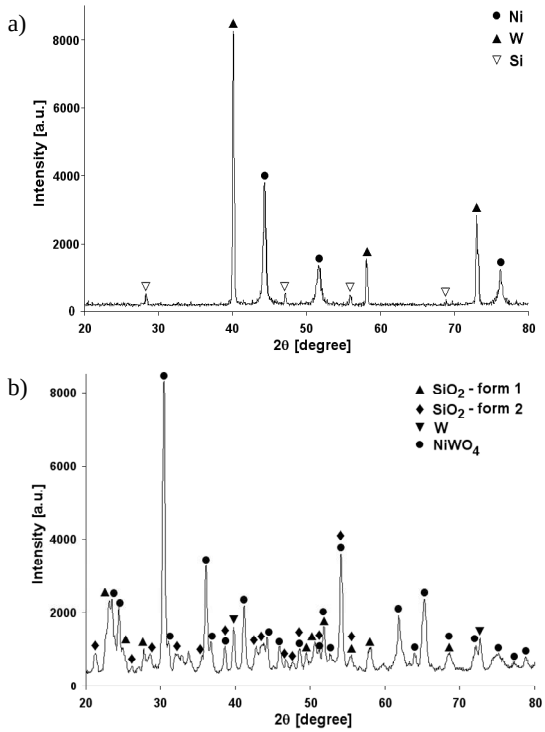

Fig. 1. X-ray diffraction patterns of Ni+W+Si composite coating: a) as--deposited, b) after thermal treatment in the air

Rys. 1. Dyfraktogram rentgenowski powłoki kompozytowej Ni+W+Si: a) po elektroosadzeniu, b) po obróbce cieplnej w atmosferze powietrza

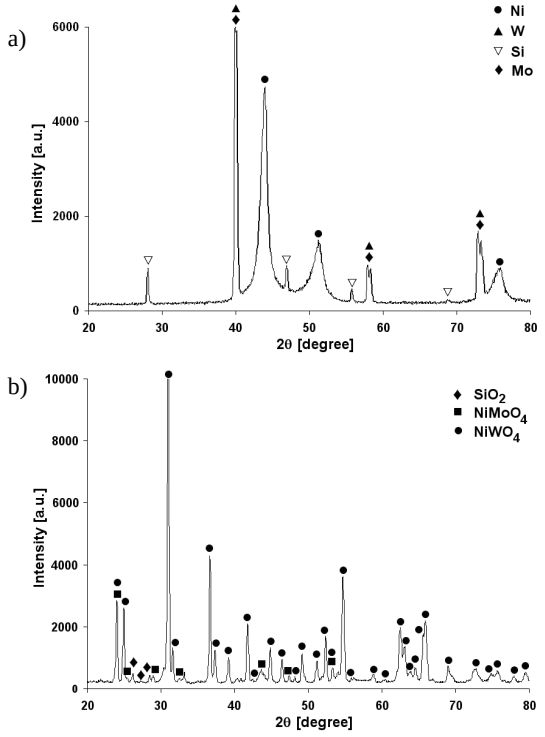

Fig. 2. X-ray diffraction patterns of Ni+W+Mo+Si composite coating: a) as-deposited, b) after thermal treatment in the air

Rys. 2. Dyfraktogram rentgenowski powłoki kompozytowej Ni+W+Mo+ +Si: a) po elektroosadzeniu, b) po obróbce cieplnej w atmosferze powietrza

The process of powders embedding in the Ni matrix is probably based on the ability to adsorb Ni^{2+} ions on a surface of powders, which was shown earlier [6]. Such a form of nickel ions, partially devoid of its hydration envelope can be more electrochemically active than hydrated Ni^{2+} ions. A suspension of this type moves towards the cathode and by applying considerable current densities, more adsorbed Ni^{2+} ions than the ones hydrated in the bath are submitted to the charge-transfer reaction. The composite structure is obtained in this way.

The phase composition for the Ni coating after thermal treatment in the air is also different in comparison with Ni as-deposited coating. The main peaks corresponding to the Ni coexist with the new ones corresponding to new phase: NiO (Fig. 3a, b), what suggests that the nickel coating was also oxidized.

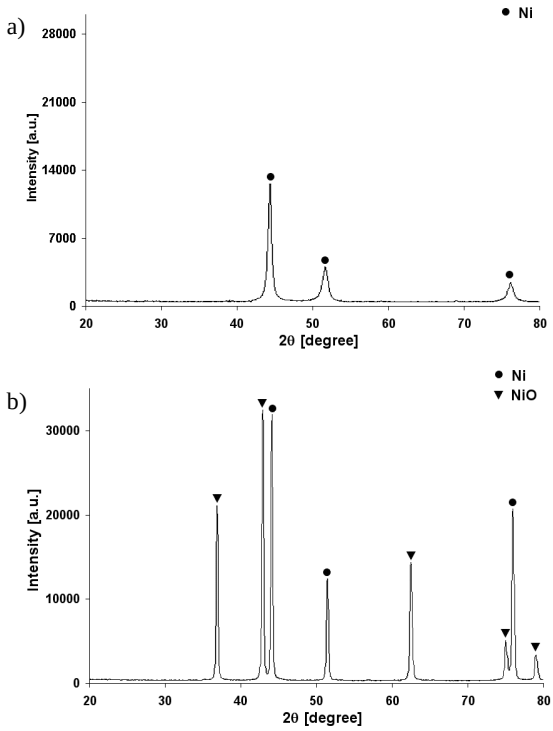

Fig. 3. X-ray diffraction patterns of Ni coating: a) as-deposited, b) after thermal treatment in the air

Rys. 3. Dyfraktogram rentgenowski powłoki Ni: a) po elektroosadzeniu, b) po obróbce cieplnej w atmosferze powietrza

In order to characterization of electrode-electrolyte processes the electrochemical impedance spectroscopy technique was applied. Measured impedance spectra in the complex plane $Z''= f(Z')$ was shown in Figure 4. It should be noticed that all electrodes are characterized by straight line at high frequencies followed by one distorted semicircle at low frequencies. The impedance of the electrodes consisting of deep cylindrical pores may be expressed as $Z(\omega) = R_s + (R_{\omega,p}/\Lambda^{1/2})[\coth(\Lambda^{1/2})]$ where $\Lambda = [1/A_p + (j\omega)^{\phi}B_p]$, $A_p = aR_{ct}$, $B_p = T/a$, $a = r/2\rho l^2$, $R_{\Omega,p} = \rho l/n\pi r^2$ (n is the number of pores per cm^2, r is the pore radius, l is the pore length, ρ is the electrolyte resistance along the pore axis) what corre-

sponds to a straight line at high frequency part and to a semicircle at low frequency part of a Nyquist plot [4, 7]. Capacitance in this model was replaced by constant phase element CPE with an impedance given by relation $Z_{CPE}(\omega) = 1/T(j\omega)^{\phi}$. Thus, to explain impedance spectra obtained for Ni+W+Si, Ni+W+Mo+Si and Ni coatings, porous model of the electrode was used. As a result of approximation of the experimental data (using CNLS fit) five parameters were obtained i.e. R_s, A_p, B_p, ϕ and $R_{\Omega,p}$.

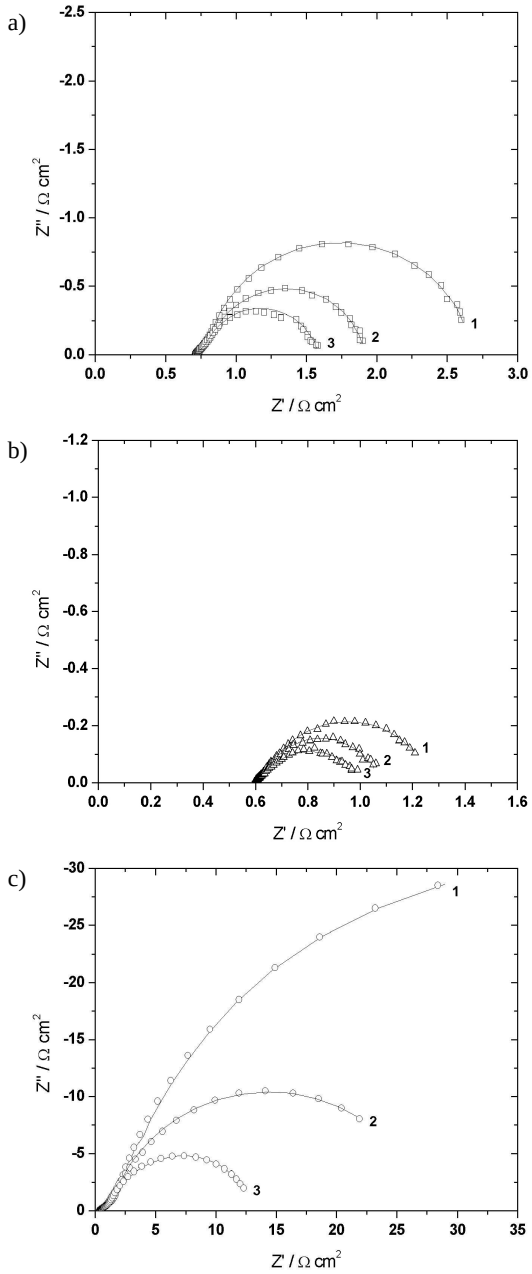

Fig. 4. Dependences of $Z'' = f(Z')$ for the: a) Ni+W+Si, b) Ni+W+Mo+Si and c) Ni coatings after thermal treatment in air, at ΔE = 0.270 V (1), ΔE = 0.290 V (2) and ΔE = 0.310 V (3), (□, △, ○ - experimental points, — - approximation line)

Rys. 4. Zależności $Z'' = f(Z')$ dla: a) Ni+W+Si, b) Ni+W+Mo+Si i c) Ni powłok po obróbce cieplnej w atmosferze powietrza, dla nadpotencjałów: ΔE = 0,270 V (1), ΔE = 0,290 V (2) i ΔE = 0,310 V (3), (□, △, ○ - punkty doświadczalne, — - linia aproksymacji)

The results of the EIS investigations were also analyzed in the form of Bode $log\ |Z| = f(log\ \omega)$ and $\Phi = f(\log\ \omega)$ diagrams, where $|Z| = ((Z')^2 + (Z'')^2)^{1/2}$ and Φ = arc tangent (Z''/Z') (Figs. 5 and 6). It was found that the Ni+W+Si and Ni+W+Mo+Si coatings are characterized by a lower value of the logarithm impedance module and phase angle compared with those for the Ni coating.

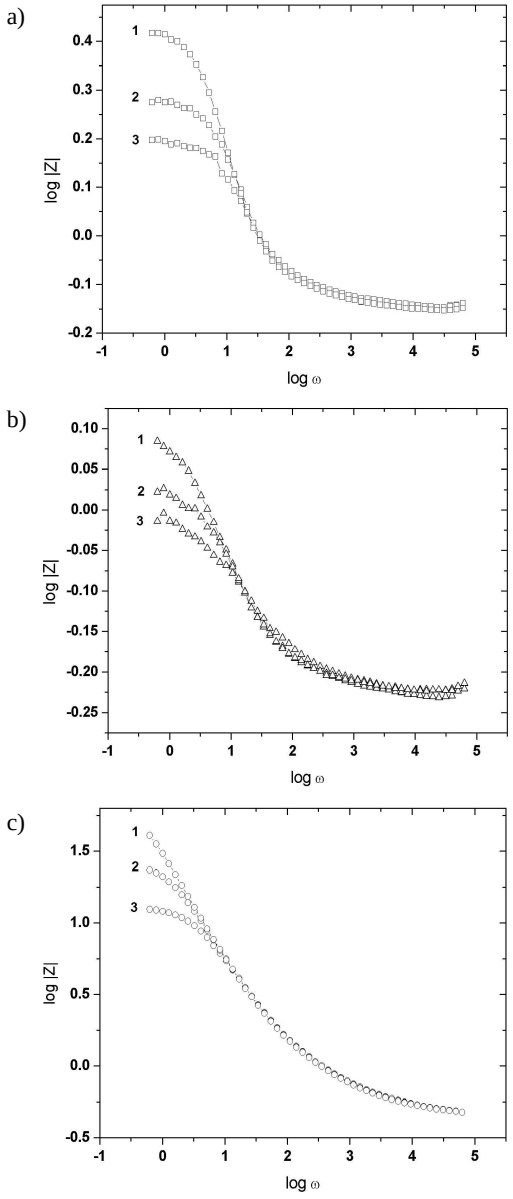

Fig. 5. Dependences of $\log |Z| = f(log\ \omega)$ for the: a) Ni+W+Si, b) Ni+W+Mo+Si and c) Ni coatings after thermal treatment in air, at the overpotentials: ΔE = 0.270 V (1), ΔE = 0.290 V (2) and ΔE = 0.310 V (3)

Fig. 5. Zależności $\log |Z| = f(log\ \omega)$ dla: a) Ni+W+Si, b) Ni+W+Mo+Si i c) Ni powłok po obróbce cieplnej w atmosferze powietrza, dla nadpotencjałów: ΔE = 0,270 V (1), ΔE = 0,290 V (2) i ΔE = = 0,310 V (3)

For all obtained coatings the diameter of low-frequency distorted semicircle (dispersion parameter ϕ = = 0.61÷0.85) decreases with increasing in overpotential

ΔE. Such behavior indicates that the value of charge transfer resistance R_{ct} decreases as well. The R_{ct} values obtained for Ni+W+Si and Ni+W+Mo+Si coatings are distinctly lower then that obtained for the Ni electrode (for suitable overpotentials) respectively (Fig. 7). Parameter T is associated with the double-layer capacitance C_{dl} by relation: $C_{dl} = \left[T/\left(R_s^{-1} + R_{ct}^{-1}\right)^{(1-\phi)}\right]^{1/\phi}$ [4, 5, 7].

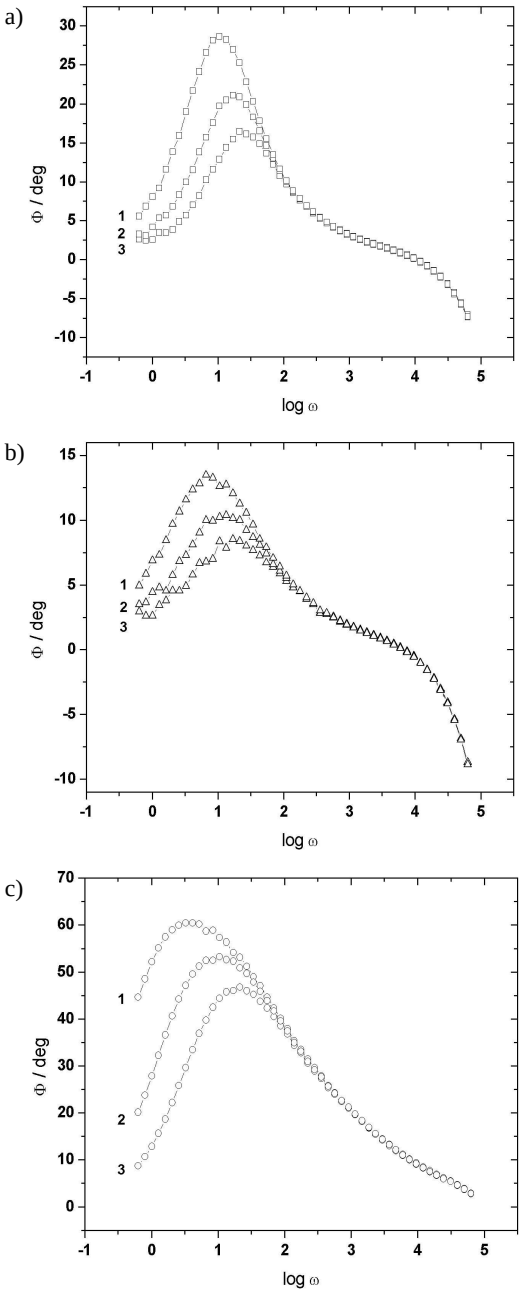

Fig. 6. Dependences of $\Phi = f(\log \omega)$ for the: a) Ni+W+Si, b) Ni+W+ +Mo+Si and c) Ni coatings after thermal treatment in air, at the overpotentials: ΔE = 0.270 V (1), ΔE = 0.290 V (2) and ΔE = = 0.310 V (3)

Rys. 6. Zależności $\Phi = f(\log \omega)$ dla: a) Ni+W+Si, b) Ni+W+Mo+Si i c) Ni powłok po obróbce cieplnej w atmosferze powietrza, dla nadpotencjałów: ΔE = 0,270 V (1), ΔE = 0,290 V (2) i ΔE = = 0,310 V (3)

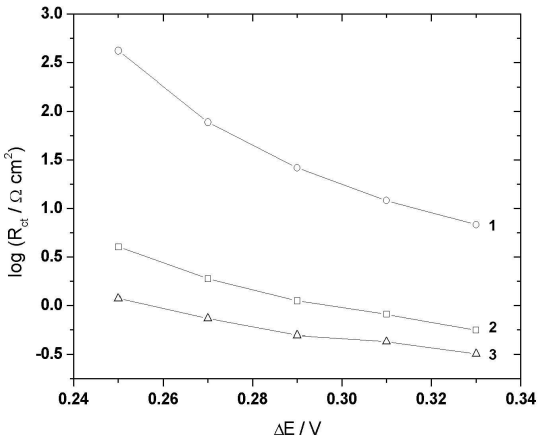

Fig. 7. Dependences of log $R_{ct} = f(\Delta E)$ for the: (1) Ni, (2) Ni+W+Si and (3) Ni+W+Mo+Si coatings after thermal treatment in air

Rys. 7. Zależności log $R_{ct} = f(\Delta E)$ dla: (1) Ni, (2) Ni+W+Si i (3) Ni+W+ +Mo+Si powłok po obróbce cieplnej w atmosferze powietrza

Figure 8 shows relation between capacitance and overpotential ΔE for all investigated coatings. The smallest values of the double-layer capacitance C_{dl} were obtained for Ni coating. Electrochemically accessible surface area is proportional to the C_{dl} values, what indicates that the presence of the W and Si particles in the Ni+W+Si coating and W, Mo and Si particles in the Ni+W+ +Mo+Si coating causes a distinct increase in electrochemically accessible area in comparison with Ni coating. It should be added that Ni+W+Mo+Si coating has the best catalytic activity towards OER of all investigated coatings. An increase in the electrochemically accessible surface area is most favorable for electrocatalysis when the whole area is accessible to reactants. However, it should be noticed that for OER the double-layer capacitance C_{dl} obtained for the Ni+W+Si and Ni+W+Mo+Si decreases with increasing in overpotential what might be due to gas bubbles, which partially block the pores.

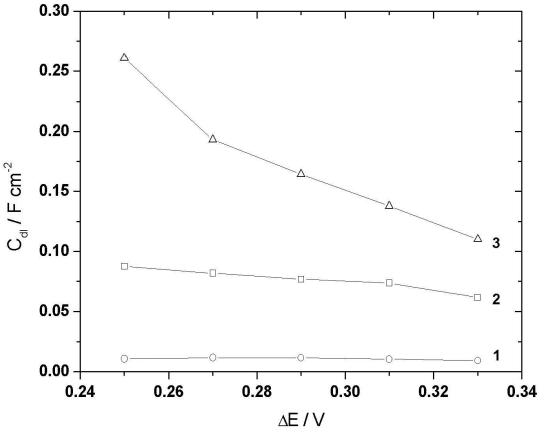

Fig. 8. Dependences of $C_{dl} = f(\Delta E)$ for the: (1) Ni, (2) Ni+W+Si and (3) Ni+W+Mo+Si coatings after thermal treatment in air

Rys. 8. Zależności $C_{dl} = f(\Delta E)$ dla: (1) Ni, (2) Ni+W+Si i (3) Ni+W+ +Mo+Si powłok po obróbce cieplnej w atmosferze powietrza

CONCLUSION

It was ascertained that the thermal treatment in the air of electrolytically deposited Ni+W+Si and Ni+W+ +Mo+Si coatings lead to the obtaining of new kinds of composite coatings containing oxides of transition metals on the surface. The apparent activity towards OER of the Ni+W+Si and Ni+W+Mo+Si composite coatings is much greater then one obtained for Ni electrode. It was ascertained that better apparent activity towards OER of the obtained composite coatings is mainly connected with an increase in the double-layer capacitance what is caused by an increase in the electrochemically active surface area. It should be added that Ni+W+Mo+Si coating has the best catalytic activity towards OER of all investigated coatings.

Acknowledgment

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