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INFLUENCE OF SUPERIMPOSED EXTERNAL MAGNETIC FIELD ONTO ELECTRODEPOSITION OF Co-P ALLOYS FOR HYDROGEN EVOLUTION

WPŁYW ZEWNĘTRZNEGO POLA MAGNETYCZNEGO NA KATODOWE OSADZANIE STOPÓW Co-P DO WYDZIELANIA WODORU

The electrocatalytic activity towards the hydrogen evolution reaction is most likely related to the active surface area of the coatings (accounting for the porosity of the coatings and the presence of some nodules at the coatings surface). It is known that magnetic field (B) influence the electrodeposition process of metals. The magnetic force generates an additional convection, which can affect the morphology of the deposit.

The work aims to obtain Co-P and Co-P-C alloys with high cathodic activity for hydrogen evolution in 8 M NaOH at 90°C by electrodeposition. External magnetic field generated by permanent magnet was used in order to modify composition and morphology of alloy. The changes in morphology and composition of alloys was searched in order to determine influence of magnetic field on alloys‘ electrodeposition.

Aktywność katalityczna stopów w procesie wydzielania wodoru jest najczęściej związana z jego aktywną powierzchnią (biorąc pod uwagę porowatość i rozwinięcie powierzchni stopów). Pole magnetyczne wpływa na proces osadzania katodowego metali. Przyłożone pole magnetyczne powoduje wygenerowanie dodatkowej konwekcji, które może wpłynąć na morfologię osadzanych stopów.

Celem pracy jest otrzymanie na drodze elektroosadzania stopów Co-P oraz Co-P-C charakteryzujących się wysoką aktywnością w procesie wydzielania wodoru w 8 M NaOH w temperaturze 90°C. Zewnętrzne pole magnetyczne generowane w czasie osadzania stopu przez magnes stały zostało użyte celem modyfikacji składu i morfologii osadów katodowych. Prześledzono zmiany składu i morfologii stopów aby określić wpływ przyłożonego pola magnetycznego na proces katodowego osadzania stopów.

1. Introduction

The electrodeposition is strongly affected by the addition of nivellant agents or brighteners in the electrolytic bath. Many electroactive species can be used to modify the characteristics of the deposits; some, such as saccharin or thiourea for example, are known to be able to change the morphology and the physical properties of electrodeposited metals. Saccharin is considered to strongly decrease the constraints of metals of iron group. However, the presence of organic compounds in the baths gives alloys which properties with respect to the corrosion resistance are degraded considerably [1]. In the 1970s Aogaki deduced his law for the current enhancement in the mass-transport limited regime, which is due to the action of the Lorentz force in conditions of uniform flow [2]. Number of research groups [3-5] have explored the consequences of the magnetohydrodynamic (MHD) effect on the diffusion layer thicknes. Other magnetic effects that are attributed to the action of the Lorentz force on some scale include the enhancement or inhibition of corrosion [6], the rest-potential shift for ferromagnetic electrodes explained by the change of mass-transport-limited exchange current at a corroding electrode [7]. White has shown that intense Lorentz forces in the vicinity of microelectrodes can create vortices [8]. It is known now that the application of a magnetic field on the electrolytic cell affects the electrodeposition of metals [9-11]. The magnetic forces generated by the passage of the current and the superimposed magnetic field create additional convection which affect the morphology of the deposits. Thus, by using a magnetic field may result in obtaining alloys having better catalytic properties for hydrogen evolution (fuel cell) or new

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materials with the physical properties allowing to use them for new applications. In theory, the size of grain of the deposits is a function of speeds of nucleation and growth of the nucleus; the more numerous nucleuses are, the lower size of grain is. A magnetic field applied parallel to the surface of the electrode generates a convection (magnetohydrodynamic effect MHD) of the electrolyte; it results in a laminar flow on the surface of the electrode which reduces the diffusion layer and increases the concentrations gradients [12-14]. This results in change of the size of the grains and thus can also influence the texture and formation of various phases of the deposits.

In principle, the grain size is a function of the nucleation rate and the growth of the nuclei: the more the nuclei the smaller is the resulting grain size. It is known that the nucleation rate increases with decreasing nucleation work. Magnetic field applied parallel to the electrode generates an additional convection in the electrolyte caused by the Lorentz force, which acts on the ions. A laminar flow of ions in the electrolyte close to the electrode surface takes place. The magneto hydrodynamic effect (MHD) reduces the thickness of the diffusion layer and leads to an increasing concentration gradient, which should have an effect on the grain size. Superimposed B can influence the texture and the phase formation of electrodeposits. This can be explained by two different effects: Firstly, the layer growth can be influenced directly by B, if B induces a grain growth in the direction of the easiest magnetization. Secondly, the whole electrodeposition process is influenced by the additional convection.

The hydrogen generation properties of electrodeposited Ni-P catalysts on Ni in 1 M KOH solution was reported [15], and found that electroplating conditions affected the concentration of P in the Ni-P layer, resulting in the variations of catalytic activities. Also the effects of cathodic current density and electroplating time on the microstructures of electrodeposited Co-P catalysts and their hydrogen generation properties in alkaline $NaBH_4$ solution were reported [16]. The catalytic activity of the electrodeposited Co-P catalyst for hydrolysis of $NaBH_4$ was found to be a function of both cathodic current density and plating time. The Co-13 at.% P catalyst electroplated on Cu at a cathodic current density of 0.01 A/cm^2 for 18 min showed the best hydrogen generation rate of 954 ml/min g^{-1} catalyst in 1 wt.% NaOH + 10 wt.% $NaBH_4$ solution at 30,8 °C.

From the other hand, it has been known that the addition of carbon to Ni-Fe alloys prevents corrosive dissolution of iron from the Ni-Fe electrode in the hot alkaline solution during the shutdown period of electrolysis and speed up the hydrogen evolution [17].

The present work aims to obtain Co-P and Co-P-C alloys by electrodeposition having high cathodic activity for hydrogen evolution in 8 M NaOH at 90°C. Particular attention was paid at the effect of phosphorous and carbon additions in enhancing the activity for hydrogen evolution in the hot alkaline solution. External magnetic field generated by permanent magnet was used in order to modify composition and morphology of alloy. The changes in morphology and composition of alloys was searched in order to determine influence of magnetic field on alloys‘ electrodeposition.

2. Experimental

The basic electrolyte used for electrodeposition was an aqueous solution consisting of 70 g/l $CoSO_4{\cdot}7H_2O$, 15 g/l $CoCl_2{\cdot}6H_2O$, 15 g/l HPO_3, 40 g/l H_3PO_4. The addition of 0.001-0.100 M arginine to the electrodeposition solution as a carbon source was attempted for preparation of Co-P-C alloys. In order to keep the same alloys‘ layer thickness electrodeposition lasted for 120, 60, 45, 30, 25, 20 minutes at cathodic current densities of 250, 500, 750, 1000, 1250, 1500 A/m^2 respectively. The pH of the electrodeposition solution was adjusted to 1.3, 1.0, 0.7, 0.4 by addition of concentrated H_2SO_4 or NaOH.

The substrate for electrodeposition was a copper metal disc of 2.8 cm^2 active surface. The disc was inserted into Teflon holder and placed in electrolytic cell. The dimensions of cells used for electrodeposition were 40 mm wide, 100 mm long and 45 mm high. Platinum metal anode of 0.1 mm thickness and copper metal cathode were placed vertically at the end of the cell, facing each other with distance of about 70 mm. The surface of the anode facing to the inside of the cell was 4 cm^2. The substrates were chemically etched in the HNO_3 : CH_3COOH : H_2PHO_3 1:1:1 mixture for 10 s at temperature 60°C. According to preliminary experiments, agitation of the deposition electrolyte did not affect definitely the composition and hydrogen evolution performance of the deposits because of violent hydrogen evolution during electrodeposition, and hence electrodeposition was carried out under a stagnant condition at 25°C. External magnetic field generated by NdFeB permanent magnet (B = 0,25 T) placed inside the Teflon holder as close as possible to the surface of alloy substrate was used in order to modify composition and morphology of alloy.

The composition of elements in the electrodes was analyzed by EDS method. Carbon was chemically analyzed by combustion infrared absorption method. For carbon analysis thick alloys were prepared on mechanically polished substrate by deposition for 24 hours. The deposits were peeled off from the substrates and used for carbon analysis.

The current efficiency for electrodeposition was estimated from the mass of the deposit and the charge passed the cell measured by means of coulometer. The structure of the electrodes was identified by X-ray diffraction using Cu Kα radiation. The grain size of the deposits was estimated from the full width at half maximum of the most intense diffraction line by Scherrer's equation [18].

The hydrogen evolution activity of the electrodes was examined in 8 M NaOH solution at 90°C by galvanostatic polarization. The galvanostatic polarization measurements was carried out starting from lowest current density. Potential of cathode was measured after 2 minutes of setting the current. A cell of acrylic resin with the specimen electrode, a platinum counter electrode and an external calomel reference electrode having a reversible potential of 1.05V for the hydrogen reaction was used. The ohmic drop was corrected using a current interruption method.

3. Results and discussion

Active cobalt-phosphorous alloy cathodes for hydrogen evolution in hot concentrated sodium hydroxide solution was prepared by electrodeposition.

According to Burchardt [15], the reaction mechanism of Ni-P alloy deposition is based on the fact that PH_3 was detected during the deposition. Since Ni and Co posses similar chemical properties, the same mechanism for Co-P alloy deposition is possible.

Table 1 shows the change in binary Co-P alloy composition with pH of electrolyte solution at six different current densities. Decreasing pH of the solution leads to an increase in phosphorous content in deposit at lower applied current densities. Increasing current density over 750 A/m^2 leads to obtaining alloys with low phosphorous content (less than 1 at %) regardless of electrolyte pH. The maximum content of phosphorous in the alloys electrodeposited at 500 A/m^2 from the electrolyte with pH 0,38 was about 12,6 at%. As shown in Table 1 the current efficiency is about 29 % at pH 1,3 and it decrease to about 1 % with the decrease in pH of electrolyte to 0,38 and with the decrease of applied current density. The decrease of cathodic current efficiency is caused by hydrogen evolution during electrodeposition process. When the electrolysis is performed at low pH the hydrogen evolution is more intense and by this way the current efficiency is lower. The alloy deposition conditions, i.e. current density 500 A/m^2 and electrolyte with pH 0,38 have been selected for ternary Co-P-C deposition because of highest phosphorous content.

TABLE 1

The phosphorous content in Co-P alloy and cathodic current efficiency in dependence from pH of electrolyte and cathodic current density

pH	1,30		0,96		0,68		0,38	
cathodic current density [A/m^2]	Current efficiency [%]	P Content in alloy [%at]	Current efficiency [%]	P Content in alloy [%at]	Current efficiency [%]	P Content in alloy [%at]	Current efficiency [%]	P Content in alloy [%at]
250	21,9	0,1	14,5	3,6	5,7	3,9	1,0	5,6
500	23,9	0,2	15,9	0,9	10,4	3,1	1,4	12,6
750	25,3	0,6	15,9	1,5	11,1	1,9	1,3	9,0
1000	26,8	0,4	14,3	1,5	11,3	1,2	1,6	0,4
1250	25,7	0,4	15,5	0,0	12,7	0,5	2,1	1,2
1500	28,7	0,5	18,1	1,2	14,5	0,0	3,0	0,5

Table 2 shows the relation between arginine (carbon source) concentration in the deposition electrolyte and cobalt, phosphorous and carbon content in Co-P-C alloys. The Table shows also cathodic current efficiency as a function of arginine concentration in electrolyte. The electrolysis was carried out without presence of external magnetic field and with superimposed magnetic field in two configurations: with field in perpendicular direction towards sample surface and with field in parallel direction towards sample surface.

TABLE 2

The cobalt, phosphorous and carbon content in Co-P-C alloy and cathodic current efficiency in dependence from arginine concentration in electrolyte, i=500 A/m^2

Arginine concentr. [mol/dm^3]	Co content in alloy [%at]	P content in alloy [%at]	C content in alloy [%at]	Current efficiency [%]
Without magnetic field				
0,000	87,4	12,6	0	1,4
0,001	96,7	2,0	1,3	4,5
0,005	96,4	1,3	2,3	3,3
0,01	95,9	1,7	2,4	1,4
0,05	92,8	2,8	4,4	0,6
0,1	92,8	5,5	1,8	0,8
perpendicular magnetic field				
0,000	98,8	1,2	0	1,8
0,001	97,2	1,0	1,7	3,2
0,005	95,1	2,2	2,7	3,3
0,01	95,9	0,9	3,3	1,4
0,05	90,2	3,9	5,9	0,6
0,1	89,5	6,7	3,8	0,4
parallel magnetic field				
0,000	98,6	1,4	0	0,8
0,001	94,3	3,6	2,1	3,6
0,005	94,5	2,9	2,6	3,3
0,01	91,4	4,1	4,5	1,9
0,05	92,2	3,5	4,3	0,9
0,1	91,5	5,3	3,2	0,4

The alloy deposited from the solution without arginine does not contain carbon. The addition of arginine to the electrolyte leads to deposition of ternary Co-P-C alloys. The presence of arginine in electrolyte definitely leads to the appearing carbon in the alloy.

When the external magnetic field is not present, the presence of the carbon in the alloy results in a decrease in the phosphorous content to about 2 at%, while the cobalt content of the alloy increased to more than 96 at%. The increase in arginine concentration leads to a increase in the phosphorous content to 5,5 at % at highest arginine concentration in electrolyte. At the same time cathodic current efficiency decreases from 4,5 % to less than 1 %. The carbon content in alloy attain maximum (4,4 at%) at arginine content in electrolyte 0,05 M. Further increase of arginine concentration leads to decrease of carbon content, and hence the excess concentration of arginine in electrolyte is detrimental.

The superimposed magnetic field, independently from orientation toward cathode surface, does not influence the composition of deposited alloys. The changes in carbon, phosphorous and cobalt content in alloy, as well changes in cathodic current efficiency are analogical to those observed for alloy deposition without presence of applied external magnetic field.

The hydrogen evolution reaction (HER) on a metallic electrode M, proceeds according to the three-reaction mechanism [19]:

$$M + H^+ + e^- \leftrightarrow M - H_{ads} \text{ (Volmer reaction)} \quad (1)$$

$$M - H_{ads} + H^+ + e^- \leftrightarrow H_2 + M \text{ (Heyrovsky reaction)} \quad (2)$$

$$M - H_{ads} + M - H_{ads} \leftrightarrow H_2 + 2M \text{ (Tafel reaction)} \quad (3)$$

These reactions are usually referred to as the charge transfer (discharge) or Volmer reaction (1), the electrochemical desorption (ion-atom recombination) or Heyrovsky reaction (2), and the atom-atom recombination or Tafel reaction (3). M here represents the free metal surface (*e.g.*, Ni), and M-H$_{ads}$ the atomic hydrogen adsorbed on the metal surface. In this mechanism, Reaction 4 is followed by an electrochemical reaction (5), or a chemical desorption reaction (6) step. For metals that are good catalysts toward HER, the Tafel reaction is the rate-determining step (rds) at low overpotentials, while at higher overpotentials, the Heyrovsky reaction becomes the rds. At large overpotentials, the Volmer reaction becomes the rds due to surface coverage by adsorbed H [20]. Two properties play an important role in selecting catalytically active materials for the HER: the actual electrocatalytic effect of the material, which is directly dependent on the overpotential used to operate the electrolytic cell at significant current densities and the catalyst stability. A desired decrease in overpotential can be achieved by choosing an electrode material of high intrinsic catalytic activity for the HER and/or by increasing the active surface area of the electrode.

The changes of phosphorous content in Co-P alloys may lead to changes in electrocatalytical properties of deposited alloys. In order to search those dependence the hydrogen evolution activity of deposited alloys have been measured in 8M NaOH at 90°C by means of the galvanostatic polarization curves. The Co-P alloys have been deposited without presence of external magnetic field and with magnetic field oriented parallel and perpendicular toward surface of substrate. The deposition was carried out from electrolytes with pH from 0,38 to 1,3 and cathodic current density 250 – 1500 A/m^2.

The increase of phosphorous content in alloy leads to change in Tafel slopes of galvanostatic polarization curve of hydrogen evolution process. It means the there is influence of phosphorous content onto activity for hydrogen evolution.

Fig. 1 shows galvanostatic polarization curves of Co-P alloys deposited at different cathodic current densities from 250 to 1500 A/m^2 from electrolyte with pH 0,38. The increase in phosphorous content in alloy leads to decrease in Tafel slope of galvanostatic polarization curve from 513 mV/dec for Co-1,2P to 240 mV/dec for alloy with 12,6at% of P. This suggests that increase of phosphorous content in alloy resulted in better activity for hydrogen evolution. However, Tafel slope of those values suggest that the process may be controlled by adsorption.

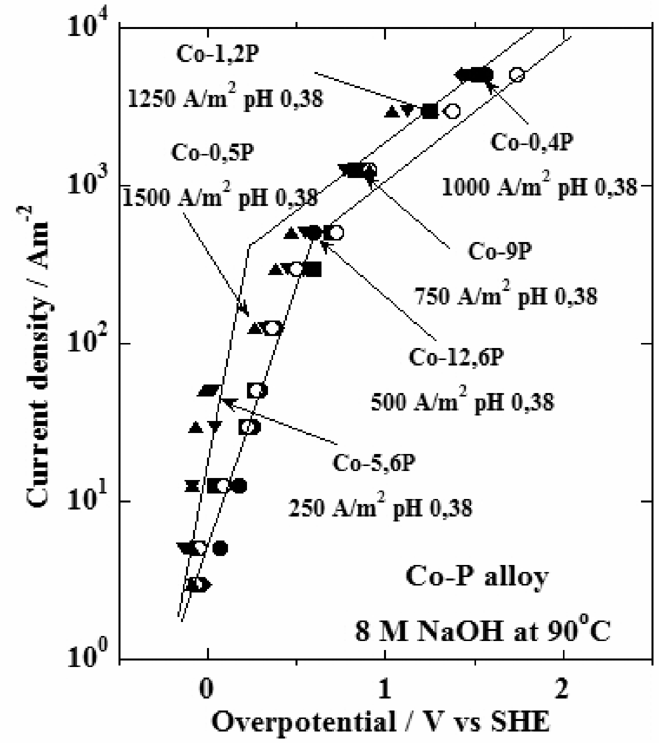

Fig. 1. Galvanostatic polarization curves of hydrogen evolution on Co-P alloys deposited at cathodic current density 250 – 1500 A/m^2 at pH = 0,38

The decrease of pH of electrolyte also affects the alloy composition (Tab. 1) and by this way leads to changes in catalytical activity of Co-P alloys for hydrogen evolution process (Fig. 2). Alloys deposited at 500 A/m^2 from electrolyte with pH 1,3 show low activity for hydrogen evolution (Tafel slope 630 mV/dec) due to low phosphorous content (0,2at%). Decrease of pH to 0,38 results in deposition of alloy with highest phosphorous content (12,6 at%) and to high activity toward hydrogen evolution (Tafel slope 240 mV/dec).

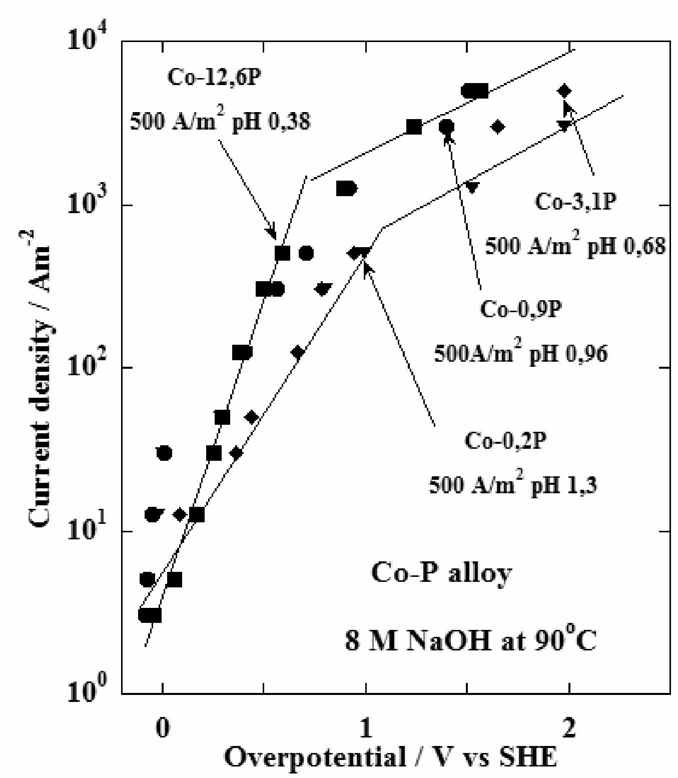

Fig. 2. Galvanostatic polarization curves of hydrogen evolution on Co-P alloys deposited from electrolyte with pH 0,38 - 1,3 at cathodic current density 500 A/m^2

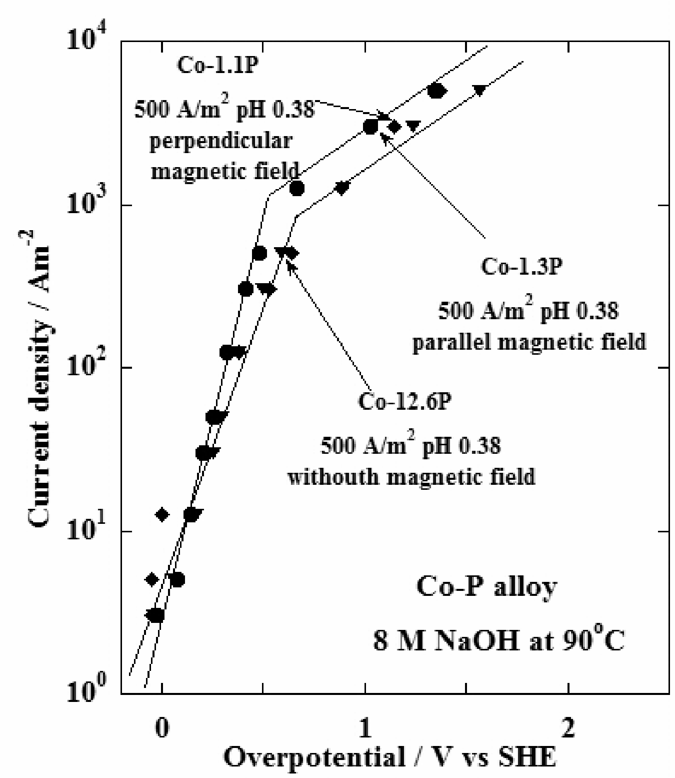

Fig. 3. Galvanostatic polarization curves of hydrogen evolution on Co-P alloys deposited from electrolyte with pH 0,38 at cathodic current density 500 A/m^2 without presence of magnetic field and with applied external magnetic field parallel and perpendicular

In order to determine the influence of applied external magnetic field on the deposition of Co-P alloys, the series of experiments has been done. The external magnetic field oriented parallel and perpendicular to the surface of cathode have been generated by permanent magnet placed as close as possible to the surface of cathode substrate. The deposition have been carried out from electrolyte which the alloy with highest content of phosphorous have been obtained.

The presence of external magnetic field during deposition results in ten time decrease of phosphorous content in alloy in comparison to alloys deposited without presence of external magnetic field. The other electrodeposition parameters remain unchanged. The galvanostatic polarization curves on the Fig. 3 show that applied external magnetic field parallel to the cathode surface leads to the deposition of alloy with lower Tafel slope of galvanostatic polarization curve. The Tafel slope is 207 mV/dec and by this way the activity for hydrogen evolution is higher. The alloys deposited with applied perpendicular magnetic field show lower activity for hydrogen evolution.

The superposition of magnetic field parallel to the substrate surface leads to the generation of magneto hydrodynamic effect (MHD). MHD effect reduces the thickness of the diffusion layer and leads to an increasing concentration gradient, which should have an effect on the grain size. The increase of number of grains leads to deposition of alloy with larger number of active centers on the surface of electrode. And hence, a desired decrease in overpotential was achieved by deposition an electrode material of high intrinsic catalytic activity for the HER and by increasing the active surface area of the electrode.

Hydrogen evolution performance is significantly higher when to carbon is introduced into alloy. Besides, the carbon content into alloy also reduces the corrosion rate of alloy [1]. Figure 4 shows galvanostatic polarization curves of Co-P-C alloys deposited from electrolyte with pH 0,38 at cathodic current density 500 A/m^2. Those electrolysis parameters lead to deposition of Co-P alloys with highest phosphorous content. Arginie concentration in electrolyte was from 0 to 0,1 M. Additionally external magnetic field has been applied with different orientation towards cathode substrate.

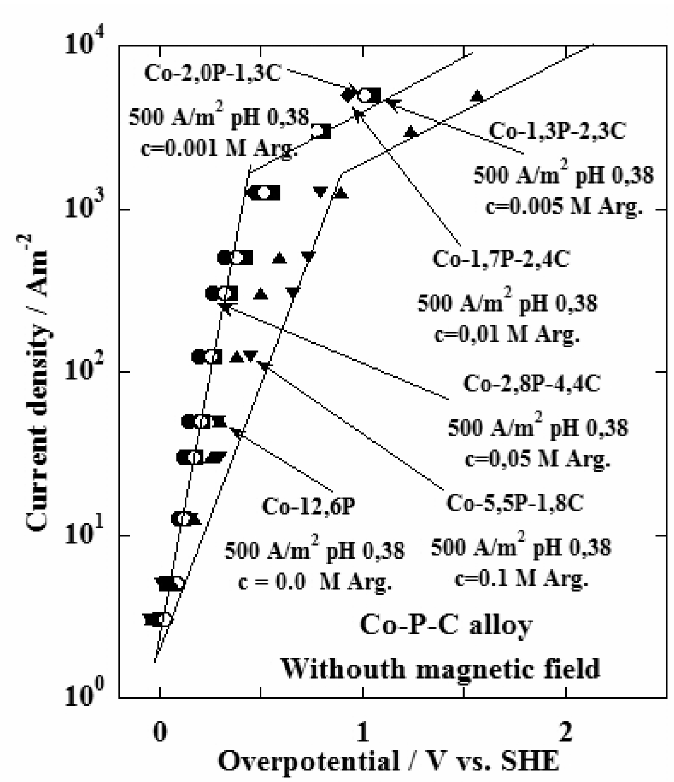

Fig. 4. Galvanostatic polarization curves of hydrogen evolution on Co-P-C alloys deposited at cathodic current density 500 A/m^2 from electrolyte with Arginine concentration from 0 to 0,1 M

The addition of carbon to binary Co-P alloys enhances the performance for hydrogen evolution. The increase in carbon content in alloy results in decrease of Tafel slope of galvanostatic polarization curves. The highest electrocatalytic properties possesses Co-2,8P-4,4C alloy deposited from electrolyte containing 0,05 M Arginine. The Tafel slope of galvanostatic polarization curve is 137 mV/dec. Excess addition of Arginine to electrolyte (over 0,05 M) lead to deposition of alloy with lower carbon content and less active for hydrogen evolution.

The alloys with highest carbon content have been selected for testing of magnetic field influence on deposition of ternary Co-P-C alloys. Analysis of galvanostatic polarization curves in Fig. 5 suggests that magnetic field superimposed during electrodeposition of Co-P-C alloys lowers the catalytic performance for hydrogen evolution at high current densities. At low current densities the Tafel slope is the same, and there is no influence of magnetic field on the activity for hydrogen evolution. Also the orientation of external magnetic field do not play important role in changing the hydrogen evolution activity. The mechanism of hydrogen evolution on Co-P-C alloys are the same as for Co-P alloys. The Tafel slop of hydrogen evolution on Co-P-C alloys with sufficient carbon content is about 137 mV/dec.

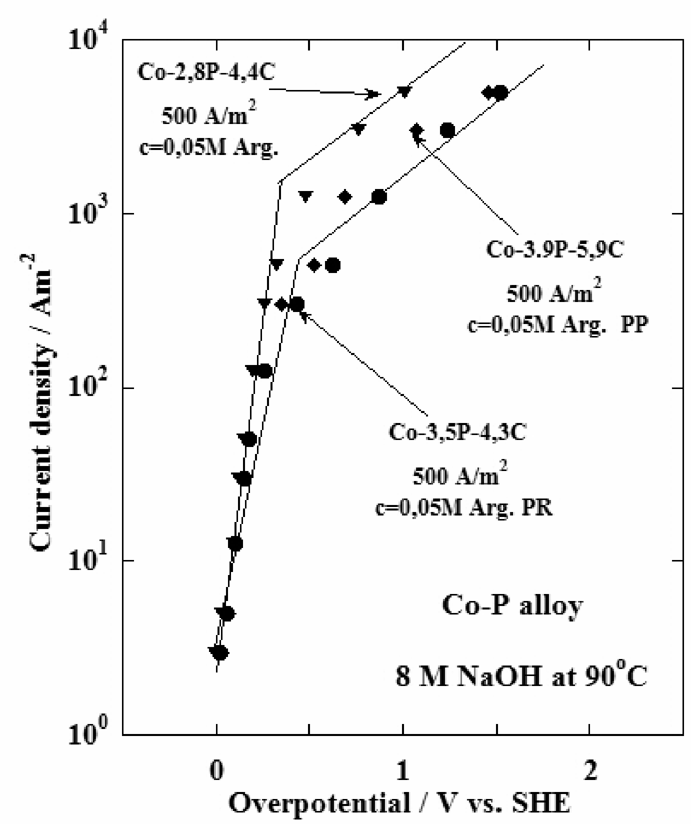

Fig. 5. Galvanostatic polarization curves of hydrogen evolution on Co-P-C alloys deposited from electrolyte with 0,05 M of Arginine at cathodic current density 500 A/m^2 without presence of magnetic field and with applied external magnetic field parallel (PR) and perpendicular (PP)

The improvement in electrocatalytical properties of Co-P-C alloys is attributed to presence of sufficient carbon content. Superimposed magnetic field do not affect the electrocatalytical properties of alloy. It only modify morphology of ternary alloys by increasing alloys‘ active surface. It is further discussed in text.

Changes in pH do not influence the Co-P deposit structure, independently from pH of electrolyte the deposit shows fcc structure (Fig. 6). The reflections at about 43.3, 50.5 and 74.2 degrees arise from the fcc copper substrate with the 110 preferred orientation. Lowering pH of electrolyte leads to deposition of alloys with higher grain size. The grain size changes from 3,9 nm for alloy deposited from electrolyte with pH 1,3 to 13,4 nm for alloy deposited from electrolyte with pH 0,38. The increase in grain size is probably related to low cathodic current efficiency during electrodeposition at low pH. Violent evolution of hydrogen during electrodeposition at low pH results in suppress of new grains nucleation and therefore the increase of grain size is preferable.

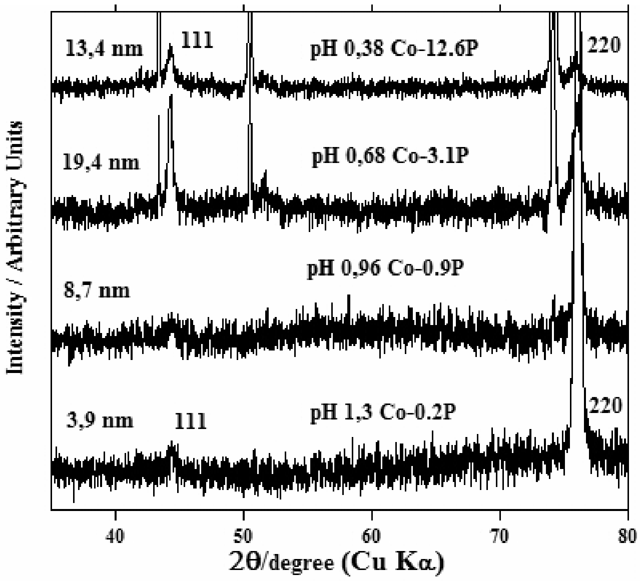

Fig. 6. XRD patterns of Co-P alloys deposited from electrolyte with pH from 0,38 to 1,3 at cathodic current density 500 A/m^2 without presence of external magnetic field

When the pH of electrolyte is maintained and the cathodic current density is changed, the structure of deposited alloy remains unchanged (Fig. 7). It means that fcc structure is observed independently from applied current density during deposition.. The cathodic current densities are similar for all samples deposited from electrolyte with pH 0,38 (Tab. 1). It suggests that overpotential for hydrogen evolution during deposition was the same and hence the size of grains is similar.

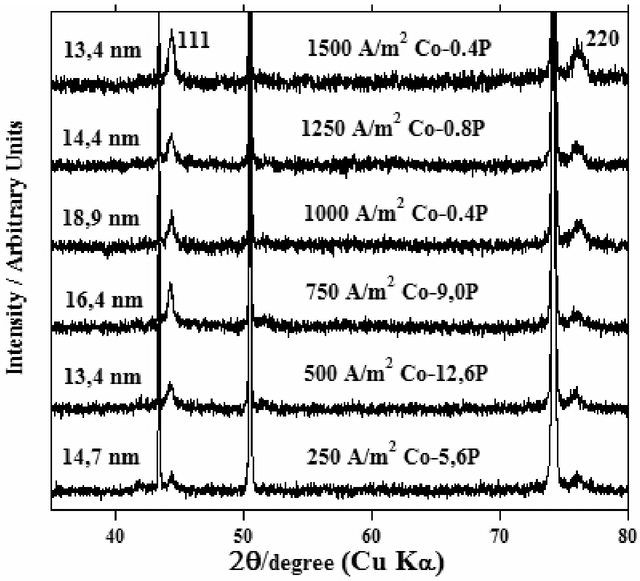

Fig. 7. XRD patterns of Co-P alloys deposited from electrolyte with pH = 0,38 at cathodic current density from 250 to1500 A/m^2 without presence of external magnetic

The presence of superimposed magnetic field during electrodeposition leads to obtaining alloys with different grain size (Fig. 8). External magnetic field parallel to the surface of copper substrate leads to decrease alloy‘s grain size to 10,5 nm in comparison to over 12 nm when the external magnetic field is absent or it is applied perpendicular to the substrate surface. The MHD effect present when the magnetic field is parallel to the cathode surface creates additional convection. It affects the morphology of the deposits. Laminar flow on the surface of the electrode reduces the diffusion layer and increases the concentration gradients. This results in reduction of the size of the grains and hence this results in the increasing of the active surface area of the electrode. The increase of active surface allows to keep high activity for hydrogen evolution even when the phosphorous content in alloy was low.

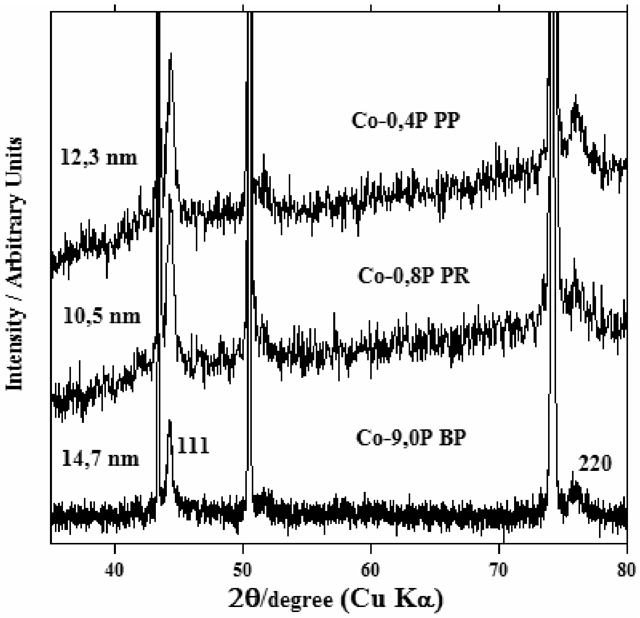

Fig. 8. XRD patterns of Co-P alloys deposited from electrolyte with pH = 0,38 at cathodic current density 500 A/m^2 without presence of external magnetic field (BP) and with parallel (PR) and perpendicular (PP) external magnetic field applied during electrodeposition

The influence of carbon present on structure of Co-P-C alloys have been searched (Fig 9). Alloys deposited from electrolyte without arginine show fcc structure. The increase of Arginine concentration to 0,005 M leads to deposition of ternary Co-P-C alloys with hexagonal structure. Further increasing of Arginine concentration in electrolyte up to 0,01 M results in deposition of alloy with relative increase of amorphous phase in deposit. From electrolyte containing 0,01 M or more Arginine the electrodeposited alloys shows amorphous structure. The amorphous structure together with sufficient carbon content in alloy guarantee high activity for hydrogen evolution by deposition the material of high intrinsic catalytic activity for the HER and by increasing the active surface area of the electrode.

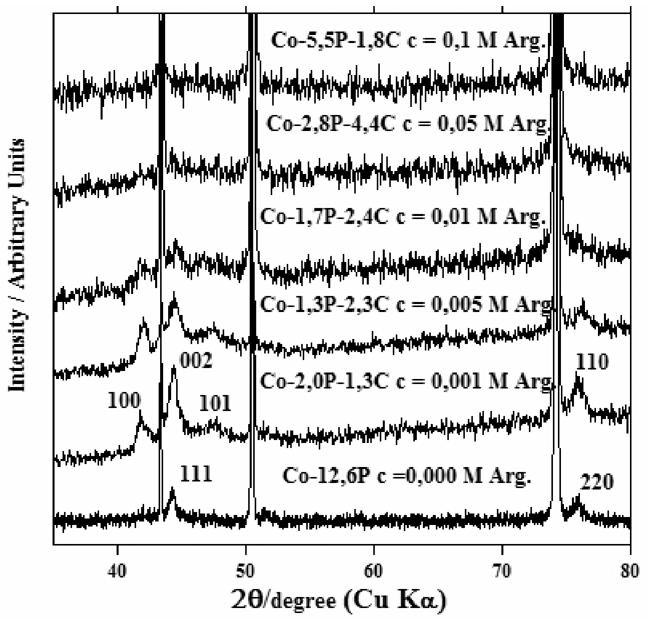

Fig. 9. XRD patterns of Co-P alloys deposited from electrolyte containing from 0 to 0,1 M of Arginine with pH = 0,38 at cathodic current density 500 A/m^2 without presence of external magnetic

By superimposing external magnetic field the modification of Co-P-C alloys structure have been searched. As can be seen from Fig.10 there is no influence of different oriented magnetic field on alloys structure. The grain size of deposit have not been estimated due to very diffused peaks.

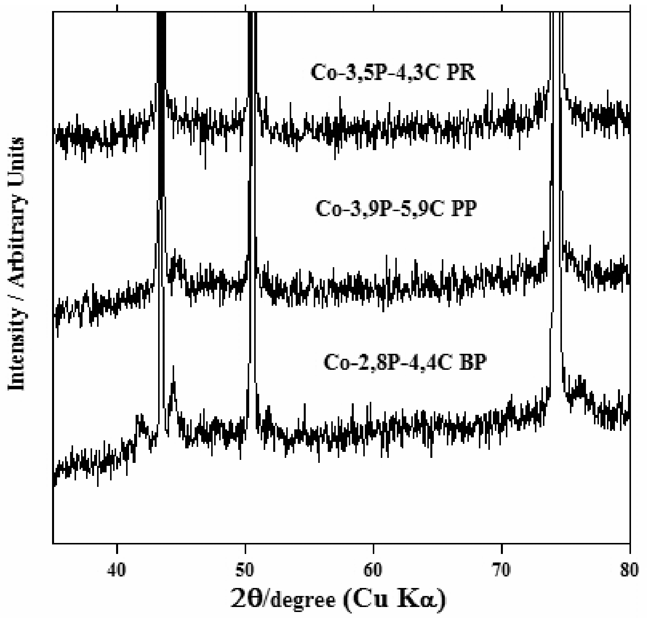

Fig. 10. XRD patterns of Co-P-C alloys deposited from electrolyte containing 0,05 M of Arginine at pH = 0,38 at cathodic current density 500 A/m^2 without presence of external magnetic field (BP) and with parallel (PR) and perpendicular (PP) external magnetic field applied during electrodeposition

4. Conclusions

Co-P and Co-P-C alloys were electrodeposited from acidic solutions containing H3PO4 as a source of P. Incorporation of P leads to a deposition of alloys with high activity for hydrogen evolution and nanocrystalline structure.

The MHD affect the morphology of the deposits. Additional convection results in the increasing the active surface area of the electrode. The increase of active surface allows to keep high activity for hydrogen evolution when the phosphorous content in alloy was low.

The addition of carbon to Co-P alloys and deposition of ternary Co-P-C alloys lead to increase of activity for hydrogen evolution. However, the excess addition of arginine to electrolyte results in lower electrocatalytical activity due to decrease of carbon content in alloy. The alloys with sufficient carbon content and amorphous structure show lowest Tafel slope of galvanostatic polarization curves . The rate determining step in this process seems to be recombination of two adsorbed hydrogen atoms.

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REFERENCES

[1] S. Meguro, T. Sasaki, H. Katagiri, H. Habazaki, A. Kawashima, T. Sakaki, K. Hashimoto, J. Electrochem. Soc. **147**, 3003 (2000) .

[2] R. Aogaki, K. Fueki, T. Mukaibo, Denki Kagaku **44**, 89 (1975).

[3] G. B. Ngo Boum, A. Alemany, Electrochemica Acta **44**, 1749 (1999).

[4] G. Hinds, F. E. Spada, J. M. D. Coey, T. R. Ni Mhiochain, M. E. G. Lyons, J. Phys Chem B **105**, 9487 (2001).

[5] P. Fricoteaux, B. Jonvel, J.-P. Chopart, J. Phys. Chem. **107**, 9459 (2003).

[6] K. Shinohara, K. Hashimoto, R. Aogaki, Chem. Lett. **8**, 778 (2002).

[7] F. M. F. Rhen, D. Fernandez, G. Hinds, J. M. D. Coey, J. Electrochem. Soc. **153**, J1 (2006).

[8] D. Mehta, H. S. White, Chemphyschem **4**, 212 (2003).

[9] T. Z. Fahidy, Progress in Surface Science **68**, 155 (2001).

[10] O. Devos, A. Olivier, J. P. Chopart, O. Aaboubi, G. Maurin, J. Electrochem. Soc. **145** 401 (1998).

[11] R. Cecchini, J. J. Mallet, W. Schwarzacher, Electrochem. Solid State Lett. **6**, C103 (2003).
[12] F. Coeuret, A. Storck, Elements de génie electrochimique, Lavoisier (1984).
[13] V. G. Levich, Physicochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, N.J. (1962).
[14] J. Newman, K. E. Thomas-Alyea, Electrochemical Systems, New York Academic Press (1970).
[15] T. Burchardt,Int.J.HydrogenEnergy27(2002)323
[16] K. W. Cho, H. S. Kwon, Catalysis Today Volume: 120, Issue: 3-4, February 28, 2007, 298-304.
[17] C. Iwakura, N. Furukawa, M. Tanaka, Electrochim. Acta **37**, 757-758 (1992).
[18] B. D. Culity, Elements of X-ray Diffraction, Addison-Wasley Publishers, Reading, Massachusetts (1978).
[19] Southampton Electrochemistry Group; Instrumental Methods in Electrochemistry, Wiley, New York, 1985.
[20] S. Trasatti, J. Electroanal. Chem. **39**, 163 (1972).

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