P.R. ŻABIŃSKI*, K. MECH*, R. KOWALIK*

Co-Mo AND Co-Mo-C ALLOYS DEPOSITED IN A MAGNETIC FIELD OF HIGH INTENSITY AND THEIR ELECTROCATALYTIC PROPERTIES

STOPY Co-Mo ORAZ Co-Mo-C OSADZANE W POLU MAGNETYCZNYM O WYSOKIM NATĘŻENIU ORAZ ICH WŁAŚCIWOŚCI ELEKTROKATALITYCZNE

The article presents results of tests on electrodeposition in a magnetic field of Co-Mo and Co-Mo-C alloys characterised by low overvoltage of hydrogen evolution. Addition of molybdenum and carbon was to lower the values of overvoltage of hydrogen evolution on cobalt. The influence of a magnetic field of high intensity (1 – 12 T) on the deposits composition, structure and morphology was determined. The deposition was conducted in a magnetic field of parallel orientation of the magnetic field forces lines in relation to the working electrode. Electrocatalytic properties of the obtained alloy coatings within the range of hydrogen evolution were tested in a concentrated solution of NaOH. The obtained alloys were analysed with the XRD method, their composition was tested with the WDXRF technique and they underwent observation applying scanning electron microscopy (SEM). The comparison of electrocatalytic properties of Co-Mo alloys with properties of Co-Mo-C ones enabled determining the influence of carbon presence in cathodic deposits on the overvoltage value of hydrogen evolution on them.

Keywords: hydrogen evolution, electrocatalytic properties, electrodeposition, Co-Mo alloys, Co-Mo-C alloys, magneto-electrochemistry

W artykule przedstawione zostały wyniki badań nad elektroosadzaniem w polu magnetycznym stopów Co-Mo oraz Co-Mo-C charakteryzujących się niskim nadnapięciem wydzielania wodoru. Dodatek molibdenu oraz węgla miała celu obniżenie wartości nadnapięcia wydzielania wodoru na kobalcie. Określony zostałwpływ pola magnetycznego o wysokim natężeniu (1 – 12 T) na skład, strukturę oraz morfologię osadów. Osadzanie prowadzone było w polu magnetycznym o równoległej orientacji linii siłpola magnetycznego względem elektrody pracującej. Właściwości elektrokatalityczne otrzymanych powłok stopowych w zakresie wydzielania wodoru badano w gorącym stężonym roztworze NaOH. Otrzymane stopy poddano analizie XRD, analizie składu z wykorzystaniem techniki WDXRF oraz obserwacjom z wykorzystaniem skaningowej mikroskopii elektronowej (SEM). Porównanie właściwości elektrokatalitycznych stopów Co-Mo z właściwościami stopów Co-Mo-C pozwoliło na określenie wpływu obecności węgla w osadach katodowych na wartość nadnapięcia wydzielania na nich wodoru.

1. Introduction

Growing prices of fuels, a continuous decrease of oil reserves and concern about natural environment encourage many science and research centres to try to find alternative, inexpensive and environment friendly energy sources. Undoubtedly, one of them is hydrogen. Many research centres in the world are working to obtain alloys that could be applied to produce electrodes for hydrogen evolution. The best electrocatalytic properties in hydrogen evolution are ascribed to platinum group metals [1], however, high prices and their limited reserves make their common application impossible.

Metals or alloys of low overvoltage of hydrogen evolution are characterised by a low coefficient of Tafel slope within the range of activation control where the process of hydrogen evolution is controlled by the speed of electrode reactions taking place. Catalytic activity of materials used in the production of electrodes for hydrogen evolution are influenced mainly by: the composition [2÷6], morphology [7÷12], structure and physicochemical properties (e.g. electronegativity of elements included in the alloy composition or energy of electrons bonds) [13÷15]. There is a lot of interest in alloys on nickel matrix due to low overvoltage of hydrogen evolution. Many works have been written presenting results of tests on the

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS METALS, LABORATORY OF PHYSICAL CHEMISTRY AND ELECTROCHEMISTRY, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND

influence of alloy additives on electrocatalytic properties of the alloys. Catalytic activity of cobalt within the range of hydrogen evolution is comparable to the activity of nickel. It enables application of alloys on cobalt matrix for hydrogen evolution, too. Alloys of Ni-Mo and Ni-Fe immersed in hot alkaline solutions with an access of air undergo selective corrosion based on preferential solubility of one of the components. Addition of elements such as oxygen or carbon can effectively prevent preferential solubility of molybdenum or iron. Addition of carbon to alloys of Co-Mo deposited in the electrolytic way also enhances their catalytic activity within the range of hydrogen evolution and corrosive properties at oxygen access in 8 M NaOH at 90°C. The improvement of electrocatalytic properties bases on limiting molybdenum solubility [16÷17].

Addition of carbon significantly lowers the energy of electrons bonds of $2p_{3/2}$ and Mo $3d_{5/2}$. It indicates a transfer of electrons from carbon atoms to atoms of a metal contained in the alloy composition. The transfer of electrons from carbon to a metal may facilitate a transfer of charges from the metal to protons, i.e. their discharging, thus enhancing hydrogen evolution. Creation of carbon-metal bonds may also influence limitation of Mo solubility [19].

The presence of an applied external magnetic field during electrolytic deposition of an alloy causes induction of additional convection in the diffusive layer at the electrode surface through the magnetohydrodynamic effect (MHD). The additional convection enhances creation of laminar flow at the electrode surface, and subsequently a decrease of the diffusive layer thickness. The effect of an additional convection occurrence may be a change of the alloy composition, structure and morphology. The differences may affect the electrocatalytic properties of such alloys.

The article presents properties of Co-Mo and Co-Mo-C alloys deposited in the magnetic field (B = 1÷12 T) of parallel orientation of the magnetic field forces lines in relation to the working electrode. Particular attention was focused on the influence of molybdenum and carbon on catalytic activity of the alloys obtained in the process of hydrogen evolution in 8 M NaOH at 90°C as well as on the influence of the applied outer magnetic field.

2. Description of the experiment

The concentrations of individual components of the electrolyte were as follows: 60 $\left[\frac{g}{l}\right]$ of hydrated cobalt sulphate (CoSO$_4$· 7H$_2$O), 3.9 $\left[\frac{g}{l}\right]$ of ammonium molybdate (NH$_4$)$_6$Mo$_7$O$_{24}$· 4H$_2$O), 7 $\left[\frac{g}{l}\right]$ of sodium chloride, 84 $\left[\frac{g}{l}\right]$ of sodium citrate (Na$_3$C$_6$H$_5$O$_7$· 5H$_2$O), 0.08 $\left[\frac{g}{l}\right]$ sodium dodecylsulphate (NaC$_{12}$H$_{25}$SO$_4$), 1 $\left[\frac{g}{l}\right]$ of saccharin (C$_7$H$_5$NO$_3$S) and in case of electrolyte for deposition of Co-Mo-C alloys 0.1 M of arginine (C$_6$H$_{14}$N$_4$O$_2$) being a source of carbon in the alloy. The electrolyte got alkalized by addition of ammonia to pH = 10.8. The alloys were deposited on copper disks of 2.83 cm^2 surface area and 0.1 mm thickness. The counter electrode was platinum of 4 cm^2 surface area. The copper disks were etched before the use in temperature of 60°C (HNO$_3$:CH$_3$COOH:H$_3$PO$_4$ – 1:1:1). The electrolyte temperature was 20°C. The electrolysis process was performed in galvanostatic conditions (i= 40 mA/cm^2) for 60 min in the presence of a magnetic field of parallel orientation of the magnetic field forces lines in relation to the cathode surface and various value of the magnetic induction vector (1 T, 3 T, 6T, 9T and 12 T). The alloys were deposited with the use of a magnet accessible at the Grenoble High Magnetic Field Laboratory that ensured homogenous and stable magnetic field. Structural tests were performed on the Rigaku MiniFlex II diffractometer. The (WDXRF) Rigaku Primini II spectrofluorimeter was used to conduct elemental analyses. Observation of surface morphology of the deposited alloys applied the SEM Hitachi SU-70 microscope. The overpotential of hydrogen evolution on the obtained alloys was determined based on the dependence:

$$\eta = E_i - E_s \tag{1}$$

where: E_i – potential of the electrode polarized by electric current flow (determined in galvanostatic measurements (t = 120 s) with the use of the Autolab PGSTAT30 potentiostat/galvanostat in 8 M NaOH in 90°C, E_s – stationary potential (read for an electrode not polarized by electric current flow after t = 240 s). The ohmic drop was corrected by the current interruption method.

3. Results and discussion

The value of the induction vector of the applied field oriented parallel towards the surface of the working electrode was 1 – 12 T. The applied magnetic field was to induce additional convection in the diffusive layer at the electrode surface through magnetohydrodynamic effect (MHD). Additional convection enhances creation of the laminar flow at the electrode surface, and subsequently a decrease of the diffusive layer thickness. The effect is caused by the Lorentz force affecting an ion moving perpendicularly to the direction of the magnetic field action. An increased convection may influence morphology and structure of the obtained alloys. All the factors significantly influence electrocatalytic properties of coatings.
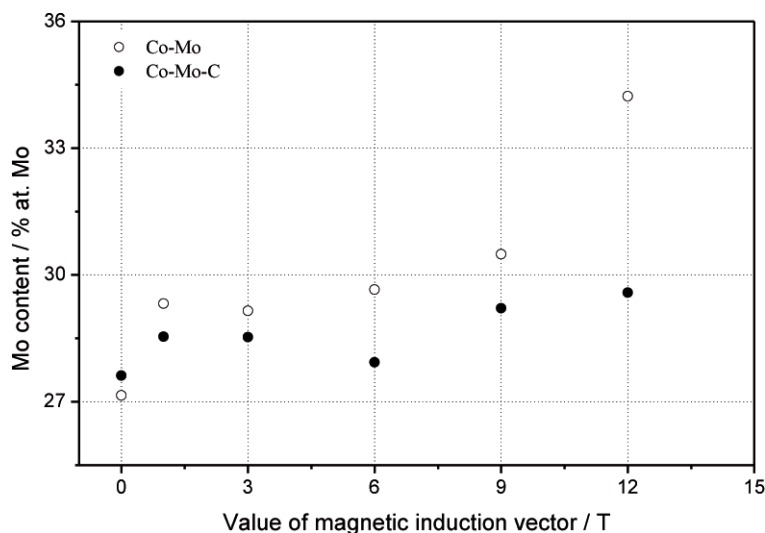
Fig. 1. Content of Mo in the obtained alloys in relation to the applied value of the magnetic induction vector

After the deposition process the obtained alloys were analysed with the WDXRF technique. The results of composition of Co-Mo and Co-Mo-C alloys deposited at different values of the magnetic induction vector are to be found in Fig. 1.

Without the presence of the outer magnetic field the alloys contained 27.2 and 27.6 at % of molybdenum for Co-Mo and Co-Mo-C alloys, respectively. Application of the magnetic field caused an increase of molybdenum content both for two-component and three-component alloys. Co-Mo alloys deposited in a parallel field featured a high content of Mo from 27.1 to 34.2% at, and the highest value of Mo was achieved for an alloy deposited in the magnetic field of 12 T intensity. Alloys of Co-Mo-C deposited in a parallel magnetic field featured the content of Mo from 27.6 to 29.6% at. Due to the lack of possibility to conduct long experiments in a high magnetic field in order to obtain proper mass of cathodic deposits essential for a carbon content analysis, such an analysis was not performed for Co-Mo-C alloys. It was observed that alloys with carbon deposited in a magnetic field demonstrate a lower content of molybdenum as compared to alloys without carbon content. It is a reverse phenomenon than in case of deposition without a magnetic field. A lowered content of Mo in Co-Mo-C alloys in relation to Co-Mo alloys is possibly a consequence of a convection induced by the magnetic field (MHD effect) and, as it seems, an increase of carbon content at the cost of decreased content of molybdenum. It may indicate a high influence of a magnetic field on the process of co-deposition of the elements. An indirect evidence might by the observed increase of the difference in molybdenum content with the increase of the magnetic field intensity. In case of Co-Mo-C alloys there was observed a slight increase: by 0.46% at for 0 T [18], whereas there was a decrease of molybdenum content in comparison to Co-Mo alloys for alloys deposited at 1 T by 0.78% at of Mo, 3 T by 0.62% at of Mo, 9 T by 1.28% at of Mo and 12 T by 4.65% at of Mo.

The structural tests of the deposited coatings showed that all the alloys feature an amorphous structure (Figs. 2a, 2b). However, for three-component alloys of Co-Mo-C deposited in the magnetic field of intensity at 6 Tesla, there was observed occurrence of little peaks originating from the hexagonal crystalline phase against a background of a diffuse peak from the amorphous phase. It suggested a reconstruction of a crystalline structure of the alloy and finally an alloy with mixture of crystalline and amorphous phases was obtained. It is difficult to determine whether an increase of the magnetic field intensity caused the increased participation of the crystalline phase in the alloy. Apart from the diffuse peak typical for amorphous substances, all diffraction patterns show also peaks coming from planes (111), (200) and (220) of Cu background, adequately. It proves that the alloy layer was thin.
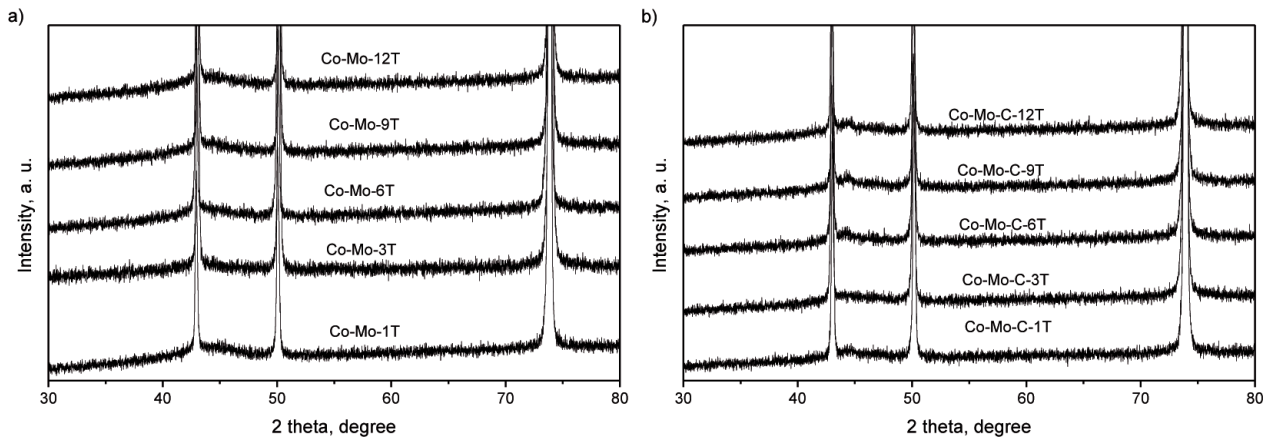
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Fig. 2. Diffraction patterns of the alloys a) Co-Mo and b) Co-Mo-C deposited in a magnetic field of different values of the induction vector

Fig. 3 presents microphotographs of the obtained coatings. There can be seen a significant influence of carbon addition on the cathodic deposits morphology. Places in which accumulation of hydrogen co-evolved during the electrolysis process took place can be clearly seen in microphotographs of Co-Mo alloys. They are not seen in microphotographs of Co-Mo-C alloys. The surface of the alloys is much smoother. Therefore, it can be deduced that the addition of carbon lowered the amount of co-evolved hydrogen and at the same time the magnetic field significantly decreased the size of evolved hydrogen bubbles and enhanced their separation from the alloy surface, similarly to the work of Koza et al. [20]. Also, there is a noticeable increase of the level of the alloy surface development with a rise of the magnetic induction value of the applied magnetic field. The microphotographs also show microcracks caused probably by inner stresses created in the material during deposition.

Overvoltage of hydrogen evolution on the obtained alloys of Co-Mo-C was determined based on measurements conducted in galvanostatic conditions in hot (90°C), concentrated (8 M) NaOH. The measurements results are presented in Fig. 4. The Tafel slope was determined within the range of activation control which is the measure of electrocatalytic properties. The speed of electrode reaction is proportional to the inclination coefficient of the line defined by the equation (2). An increase of the diffusive layer resistance at the electrode surface connected with hydrogen bubbles gathered at it is responsible for the decrease of the Tafel slope.

$$\eta = b + a \cdot \log(i) \qquad (2)$$

The change of the Tafel slope illustrates changes of the control range of hydrogen ions reduction process. If the Tafel slope is about 150 mV/dec, it is assumed that the slowest stage of the reaction is discharging of H^+ ion.

When the Tafel slope is about 35 mV/dec, the discharging process is so fast that the slowest stage is recombination of adsorbed atoms of hydrogen with creation of H_2. Thus, the Tafel lines inclination is also the source of information on the mechanism of proceeded electrode processes.

The magnetic field applied during an alloy deposition affects its electrocatalytic properties in the hydrogen evolution process. Deposition of Co-Mo alloy in a magnetic field caused a decrease of Tafel slope from 191 to about 28 mV/dec. It indicates a change of the hydrogen evolution mechanism from a mixed one to a mechanism where the discharging process is so fast that the slowest stage is recombination of adsorbed atoms of hydrogen with creation of H_2. The highest coefficient of the Tafel slope from among Co-Mo alloys is ascribed to an alloy deposited in the field of the magnetic induction vector value of 9 T and the content of 30.5% at of Mo. For three-component alloys Co-Mo-C, the influence of the magnetic field during deposition on their future electrocatalytic properties was not so clear. The Tafel slope was close regardless of the magnetic field intensity and amounted between 58,8 and 105,3 mV/dec. Only an alloy deposited at the magnetic field intensity of 1 Tesla presented improved electrocatalytic properties and the Tafel slope was 58,8 mV/dec. It is visible that the addition of carbon as an alloy component significantly lowered catalytic properties of coatings. The magnetic field of high intensity probably caused, by inducing an additional convection, deposition of large amounts of carbon which constituted a considerable part of the coating surface layers and subsequently the active part of the alloy surface decreased. For most Co-Mo surfaces, besides the one deposited at 0 T, the Tafel lines featured a significantly lower directional coefficient than Co-Mo-C alloys. However, for all alloys, besides the Co-Mo ones deposited at 0 T, the slowest stage was recombination of adsorbed atoms of hydrogen with creation of H_2 particle.
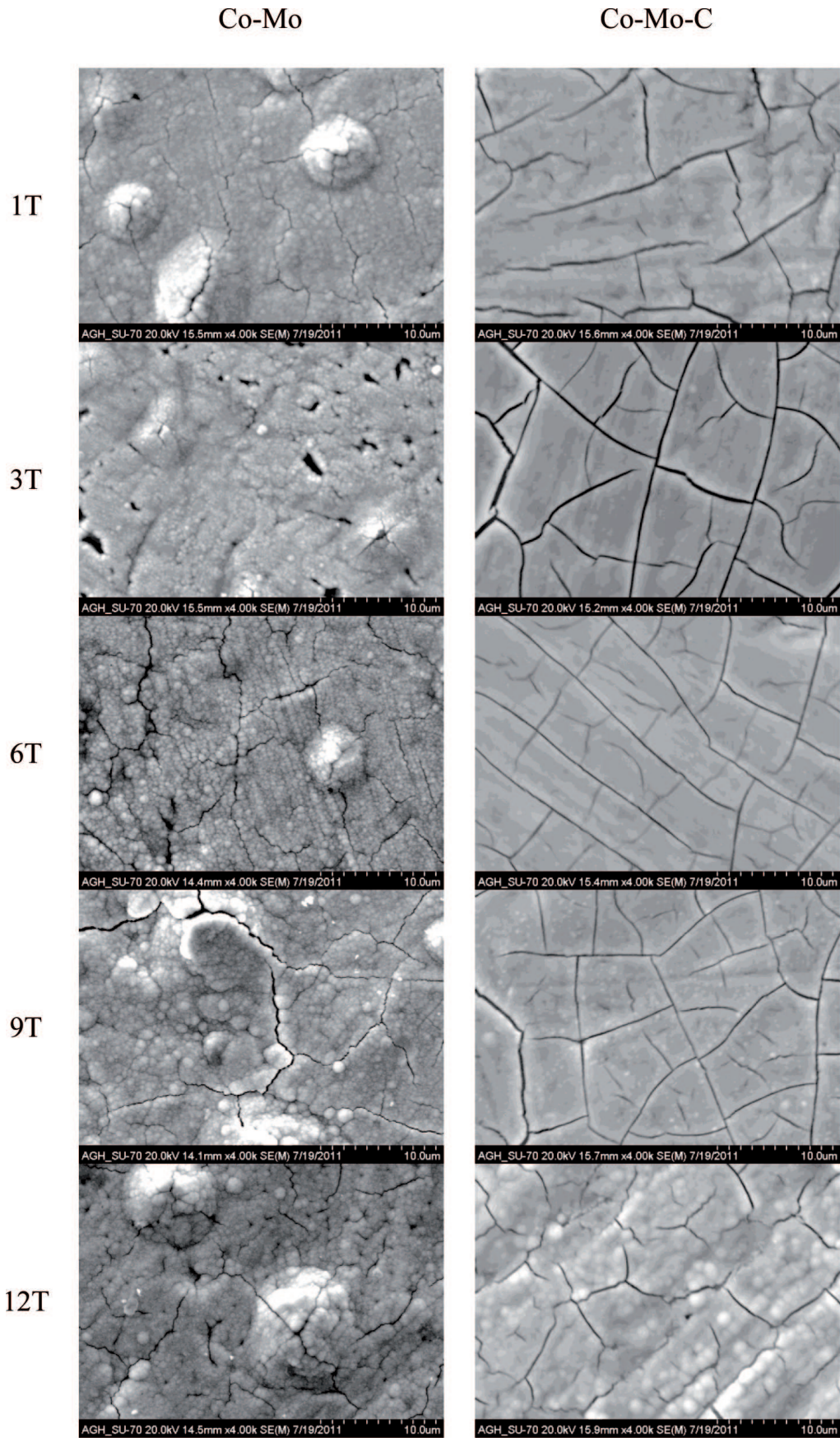
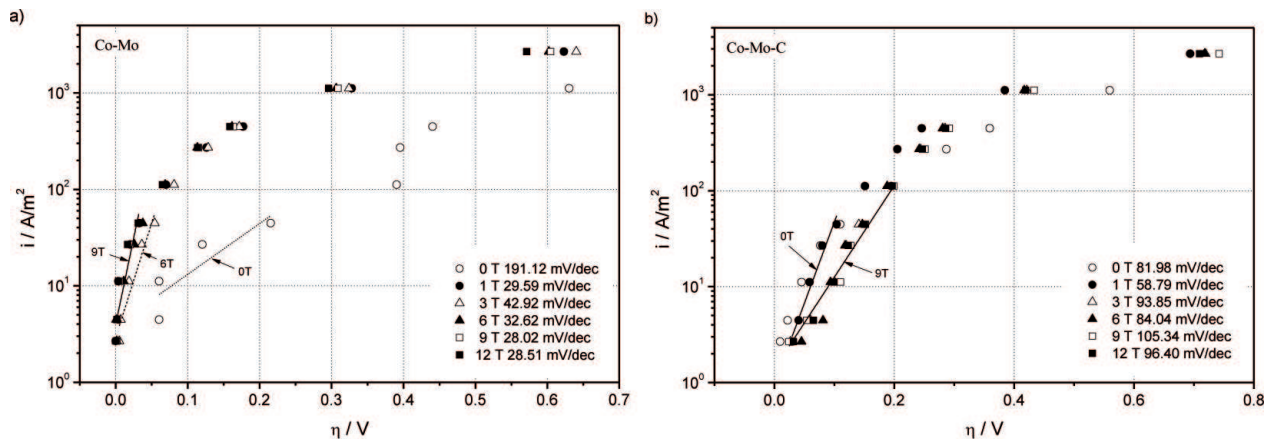Fig. 3. Microphotographs of the obtained alloys

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Fig. 4. The results of overvoltage measurements of hydrogen evolution for particular alloys

4. Summary

The Co-Mo-C alloy coatings obtained through electrolytic deposition in the magnetic field of parallel orientation of forces lines towards the working electrode are of an amorphous structure. The content of Mo in the deposited alloys ranges from 27.6% at for alloys deposited without application of an outer magnetic field to 34.2% at for alloys deposited in a magnetic field of the magnetic induction vector value of 12 T. Both for Co-Mo-C and Co-Mo alloys the lowest value of Mo was achieved at 0 T. Application of an external magnetic field enhanced co-deposition of molybdenum and subsequently the alloys deposited in the magnetic field presented an increased value of Mo in relation to alloys deposited without application of an outer magnetic field. The best electrocatalytic properties in the process of hydrogen evolution in hot, concentrated NaOH were featured by a Co-Mo alloy of the content of 30.5% at of Mo (9 T). The other alloys, beside the one deposited without a magnetic field, demonstrated slightly worse electrocatalytic properties. The observed differences in the Tafel slope confirm a high influence of the applied magnetic field and content of carbon on the mechanism of hydrogen evolution on deposited coatings.

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