

ELECTROCHEMICAL DEPOSITION OF ALLOYS BASED ON IRON GROUP METALS AND THEIR CHARACTERIZATION FOR OXYGEN EVOLUTION REACTION

V. Bachvarov¹, R. Rashkov¹, R. Bretzler², A. Zielonka²

¹Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

²Forschungsinstitut für Edelmetalle und Metallchemie, Schwäbisch Gmünd, Germany

Abstract

NiCoMoW, NiCoFeP and NiCoMoFe(P) alloys were deposited under galvanostatic conditions. Morphology and components distribution were characterized by SEM and EDX analyses. The oxygen evolution reaction (OER) on these materials was investigated by galvanostatic steady-state curves. The lowest polarization for OER showed Fe₄₀Co₂₈Mo₁₆Ni₁₄P_{2,5} and Fe₄₁Mo₃₀Co₂₀Ni₁₉ alloys. The morphology after OER is also addressed.

Key words: electrodeposition, Ni-Co-Mo-Fe alloys, OER

1. INTRODUCTION

Oxygen evolution reaction (OER) is the basic reaction in different industrial processes as hydrogen production, electrowinning of metals, cathodic protection and etc. The nickel and its alloys are widely used as anodic materials in alkaline media due to the main requirement for OER to carry out with low overvoltage.

The transition metal oxides, especially cobalt and mixed cobalt-nickel oxides are extensively studied, because of their promising properties as electrocatalysts for oxygen evolution, (Tarasevich et al., 1981, Singh et al., 1991, Rashkova et al., 2002, 2007).

Various aspects of the OER at passive oxide covered polycrystalline Ni, Co and Fe (Michael et al., 2008) electrodes in aqueous alkaline solution have been studied using electrochemical techniques. The authors have found that the central metal ion of the electrocatalytically active surface complexes exist in the Ni(III), Co(IV) and Fe(VI) valance states for oxidized Ni, Co and Fe anodes respectively. To improve the electrocatalytic activity of the electrode material, the transition metals are added to nickel as mechanical alloys (Dominguez-Crespo et al., 2006), composite (Kubisztal et al., 2008) or deposit on Ni substrate (Brossard et al., 1993, Castro et al., 2000). It was revealed that iron increased the electrocatalytic activity for OER in nanocrystalline Ni-Co-Mo-Fe mechanical alloys. Nickel and molybdenum rich alloys were showed particularly high activity towards the OER in comparison with their nanocrystalline counterparts (Dominguez-Crespo et al., 2006).

The electrodeposition of the iron-group metals, their binary and ternary alloys is published in (Keith et al., 1998, Myung et al., 2001, Zech et al., 1999, Arul Raj et al., 1992, Zhuang et al., 2000). The anomalous behavior of these alloys was studied in (Zech et al., 1999, Zhuang et al., 2000). The results revealed that Ni was inhibited by the presence of Fe²⁺ and Co²⁺ ions, while Fe deposition rate was enhanced by the presence of Co²⁺ and Ni²⁺ ions. The ion of the less noble metal has a stronger influence on the deposition behavior of the partner ion.

The aim of this work is to produce multiple component systems based on iron-group metals by electrodeposition and to compare their electrocatalytic behavior for OER.

2. EXPERIMENTAL

The samples were prepared by electrodeposition under galvanostatic conditions in thermostatic glass cell with or without magnetic stirring. The electrolyte compositions are given in Table 1. The conditions are respectively for electrolyte I - 3 A/dm², t = 30°C, 0 mni⁻¹ and 100 mni⁻¹, pH-5.5; electrolyte II - 3 A/dm², t = 30°C, 0 mni⁻¹, pH-5.5; electrolyte III - 2 A/dm², t = 30°C, 100 mni⁻¹, pH-5.5; electrolyte IV - 10 A/dm², t = 50°C, 0 mni⁻¹, pH-3; electrolyte V - 9 A/dm², t = 50°C, 250 mni⁻¹, pH-10. Nickel electrodes (for electrolyte II and III) and Ti-Pt mash (for electrolyte I, IV and V) were used as anodes. Copper plates with geometric area of 2 cm² were used as substrates for cathodic layers.

Table 1. Electrolyte compositions of electrodeposited alloys

Electrolyte compositions	I	II	III	IV	V
NiSO ₄ .7H ₂ O g/l	87	87	87	40	-
Ni ²⁺ [Ni(SO ₃ NH ₂) ₂] g/l	-	-	-	-	16
NiCl ₂ .6H ₂ O g/l	-	-	-	40	-
FeSO ₄ .7H ₂ O g/l	25	25	25	30	-
CoSO ₄ .7H ₂ O g/l	25	25	25	5	-
Co ²⁺ [Ni(SO ₃ NH ₂) ₂] g/l	-	-	-	-	16
Na ₂ WO ₄ .2H ₂ O g/l	-	-	-	-	24
Na ₂ MoO ₄ .2H ₂ O g/l	12	12	12	-	6
Na ₃ C ₆ H ₅ O ₇ .2H ₂ O g/l	100	125	125	-	72
NaH ₂ PO ₂ .H ₂ O g/l	-	25	50	4	-
H ₃ PO ₂ (50 %) ml/l	-	-	-	11	-
β-alanine g/l	-	-	-	26	-
Glycin g/l	-	-	-	26	-

Electrochemical measurements for OER were made in a conventional three-electrode cell with platinum and SCE electrodes used as a counter and as a reference, respectively in 6 M KOH.

The surface morphology of the alloys was analysed by scanning electron microscopy (SEM) using Leo 1455VP and Leo Supra 55VP equipped with energy dispersion X-ray (EDX) detectors Oxford Inca 200.

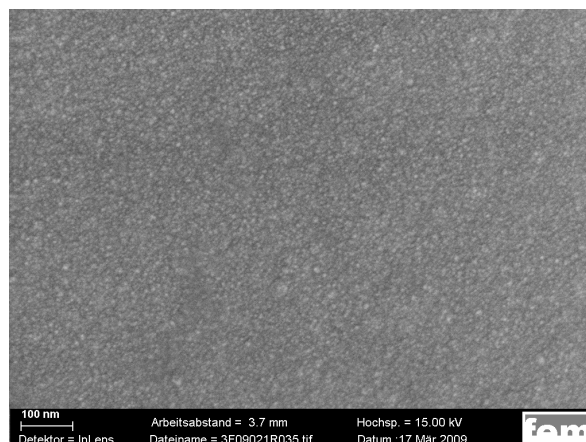
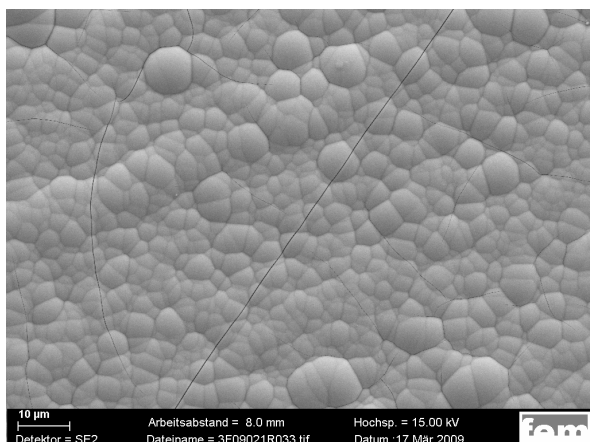
3. RESULTS AND DISCUSSION

The composition of the alloys deposited from electrolytes given in Table 1 was determined by EDS analyses. The results are performed in Table 2. From the experimental data one can see that despite of higher amount of Ni in the electrolytes the iron alloys are electrodeposited. Codeposition of iron group metals leads to a reduction of the reaction rate of the nobler component and an increase of the reaction rate of the less noble component compared to single metal deposition (Brossard et al., 1993). The amount of Fe is more enhanced in the ternary alloys than in the NiFe binary alloys suggesting a synergistic process due to combined presence of Ni and Co (Keith et al., 1998). Probably this is the reason to produce alloys with large amount of iron. On the other hand, the stirring is strongly influenced by the composition (see Table 2 electrolyte I). The stirring extremely increases the reaction rate of Ni and its amount in the alloys respectively, while in the absent of stirring the iron dominates in the alloys ($\text{Fe}_{41}\text{Mo}_{30}\text{Co}_{20}\text{Ni}_{19}$ and $\text{Ni}_{38}\text{Mo}_{36}\text{Fe}_{16}\text{Co}_{11}$ from the same electrolyte I).

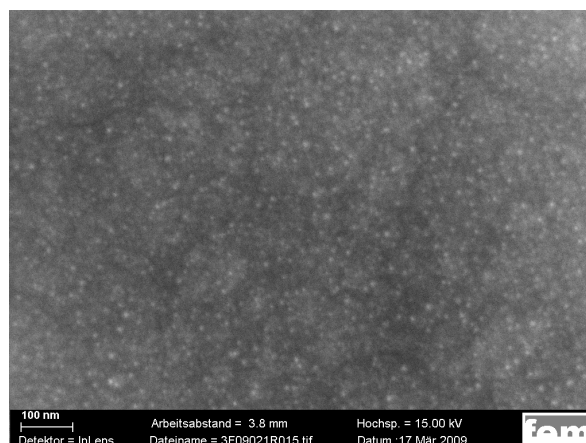
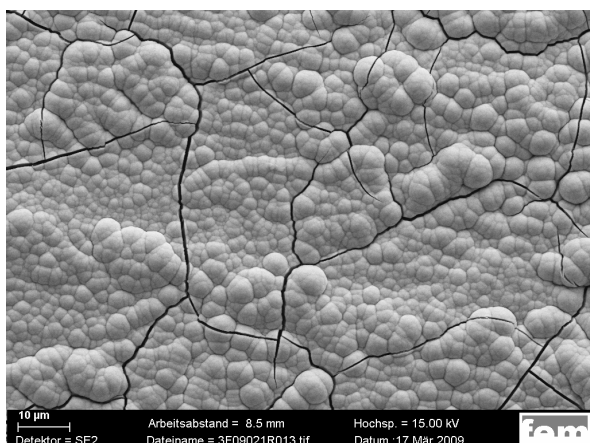
Table 2. Element compositions in the alloys

Compositions	Ni wt%	Fe wt%	Co wt%	Mo wt%	W wt%	P wt%
$\text{Ni}_{38}\text{Mo}_{36}\text{Fe}_{16}\text{Co}_{11}$ electrolyte I, 0 min⁻¹	38	16	11	36	-	-
$\text{Fe}_{41}\text{Mo}_{30}\text{Co}_{20}\text{Ni}_{19}$ electrolyte I, 100 min⁻¹	9	41	20	30	-	-
$\text{Ni}_{44}\text{Co}_{20}\text{Fe}_{19}\text{Mo}_{13}\text{P}_4$ electrolyte II, 0 min⁻¹	44	19	20	13	-	4
$\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2,5}$ electrolyte III, 0 min⁻¹	14	40	28	16	-	2,4
$\text{Ni}_{54}\text{Fe}_{26}\text{Co}_{10}\text{P}_{10}$ electrolyte IV, 0 min⁻¹	54	26	10	-	-	10
$\text{Co}_{76}\text{Ni}_{11}\text{Mo}_{8,5}\text{W}_4$ electrolyte V, 250 min⁻¹	11,6	-	76,1	8,54	3,78	-

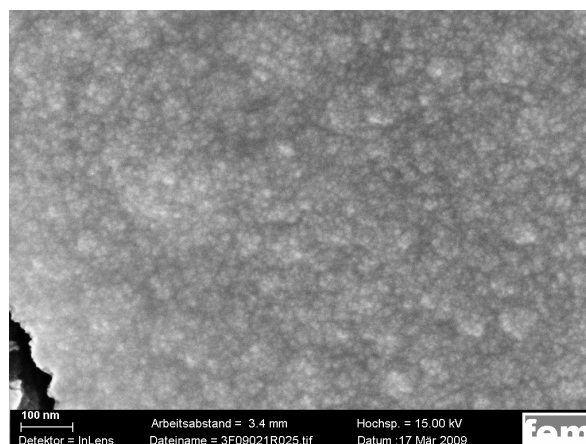
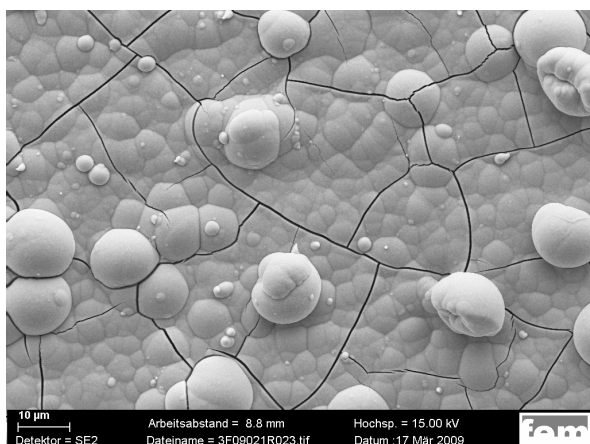
Figure 1 shows the morphology of investigated alloys at lower (on the left) and at higher magnification (on the right column), respectively. It can be seen, that the alloys containing Fe possess similar globular structure (Fig. 1a-c). The cracks must be related to the complex composition since the least cracks are observed in NiFeCoP alloy (Fig. 1a). The surface structure of CoNiMoW deposit (Fig. 1d) looks uniformly and smoothly at lower magnification. However, at higher magnification, grains with size distributions between 30-50 nm are observed. NiFeCoP alloys (Fig. 1a) reveal the finest structure. It is known that a presence of phosphorous in the iron-group alloys more than 9 wt% leads to formation of amorphous deposits. In the present NiFeCoP alloy, the amount of P is determined to be 10 wt%, which explain the formation of amorphous deposit.



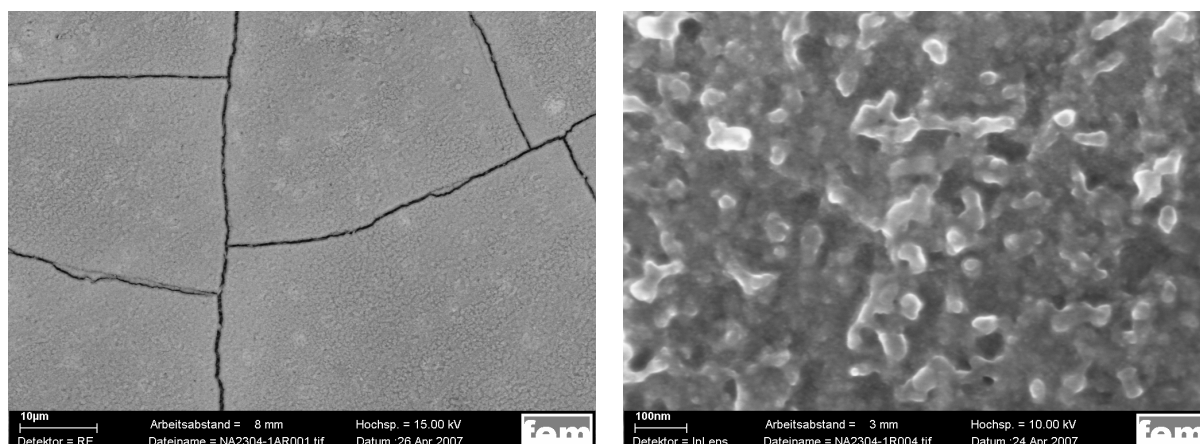
(a) $\text{Ni}_{54}\text{Fe}_{26}\text{Co}_{10}\text{P}_{10}$



(b) $\text{Ni}_{44}\text{Co}_{20}\text{Fe}_{19}\text{Mo}_{13}\text{P}_4$



(c) $\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2.5}$



(d) $\text{Co}_{76}\text{Ni}_{11}\text{Mo}_{8.5}\text{W}_4$

Fig. 1. SEM images of the obtained alloys before OER

The deposited electrodes with geometric surface 2 cm^2 were tested for OER in 6 M KOH. The experiments were carried out under galvanostatic steady state conditions. Before starting the measurements, the electrode surface was polarized for 30 min by applying a relatively high (200 mA) anodic current. Then the current was lowered to 5 mA.

One of the main criterions for the catalytic activity of a material for OER is the polarization of this reaction at different currents. Higher polarization defines a worse catalytic activity and conversely. The reproducible polarization curves of the studied systems (Table 2) in 6 M KOH are represented in Fig. 2. Worst catalytic behaviour for OER possesses $\text{Ni}_{38}\text{Mo}_{36}\text{Fe}_{16}\text{Co}_{11}$ alloy (Sample 1). Polarization curves of alloys 3, 4, 5 remains similar, although the deposits possess different compositions. The samples 4 and 5 contain the highest amount of Ni. Mo is absent in sample 4 but it has the most wt. percent of phosphorus. Since this deposits possess the finest surface structure (see Fig. 1a at high magnification), good results for catalytic behaviour were expected. However, the results of OER polarization are similar to these of sample 3. This sample contains the highest amount of cobalt and tungsten and the surface is characterized by the largest grain size. The curves presented in Fig. 2 show that the polarization change for OER is not more than 20 mV of the deposits contain mainly Ni or Co and different wt. percents of Fe, Mo, W and P as impurities in the alloys. It should be noted that at the highest current densities the overvoltage for OER of samples 1, 3, 4 and 5 is approximately equal or lower than that of Ir - Ta mesh (see Fig.2, sample 7), which usually used as an electrode in industrial processes. The best catalytic activity towards OER shows $\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2.5}$ alloy (see Fig. 2 sample 6). The differences in polarization values of this sample and $\text{Ni}_{38}\text{Mo}_{36}\text{Fe}_{16}\text{Co}_{11}$ alloy (Sample 1) are between 80 and 100 mV. Slightly worse catalytic behavior for OER shows $\text{Fe}_{41}\text{Mo}_{30}\text{Co}_{20}\text{Ni}_{19}$ deposit, which do not contain phosphorus, but the Mo content is about 2 times higher than in sample 6. It can be concluded that the alloys in which iron predominates show better catalytic activity for OER independently of other alloy components.

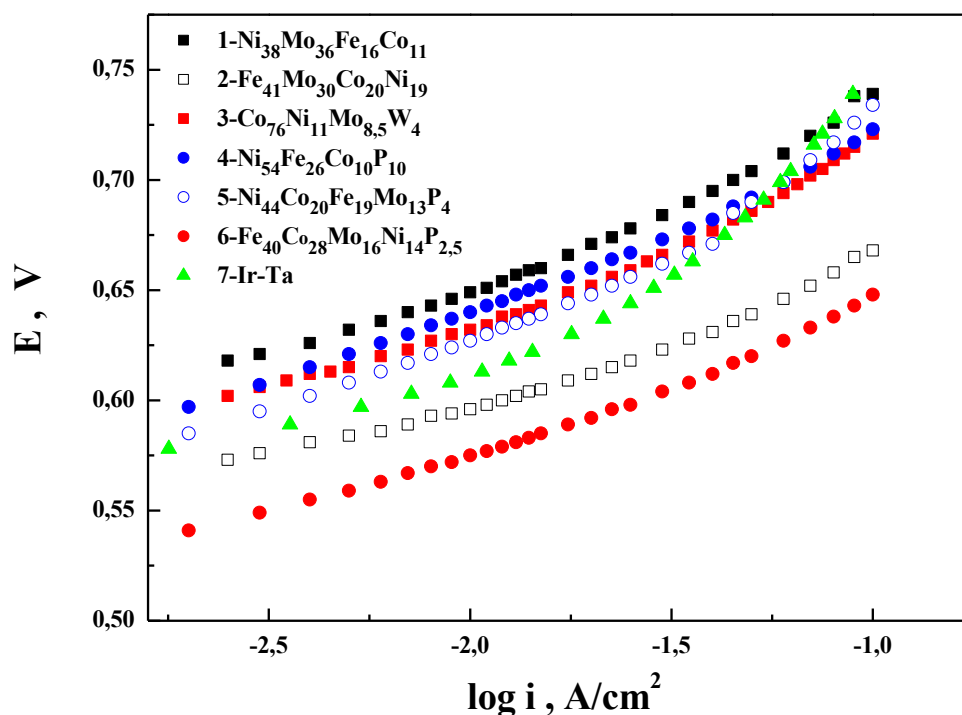
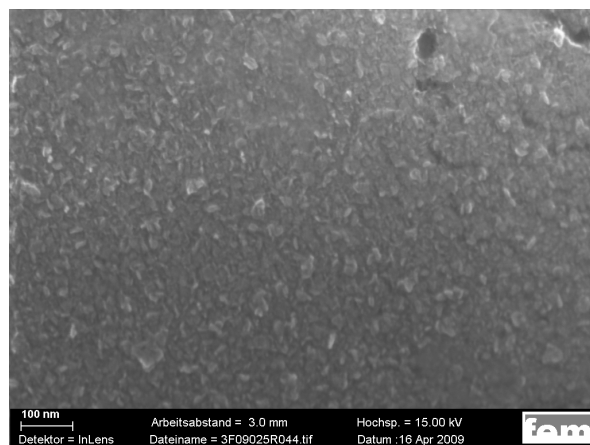
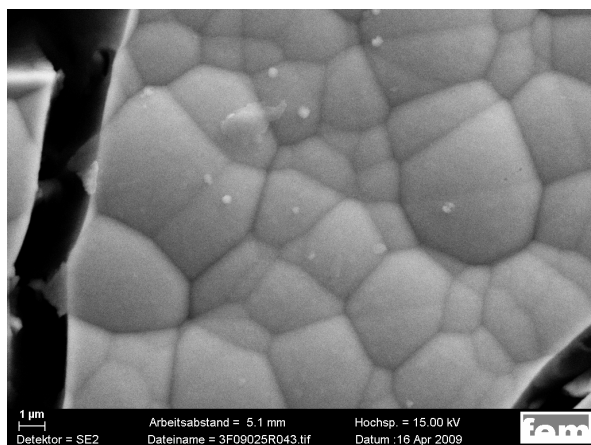
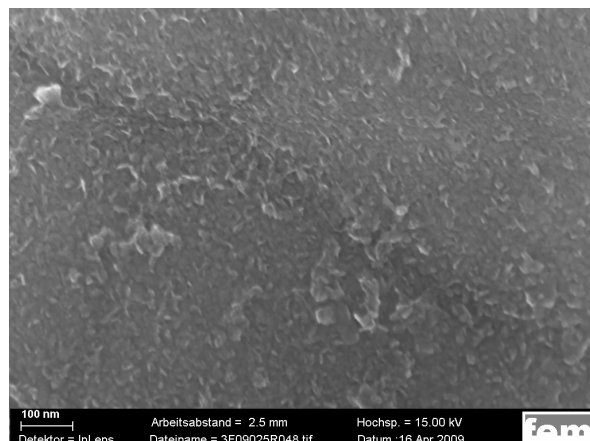
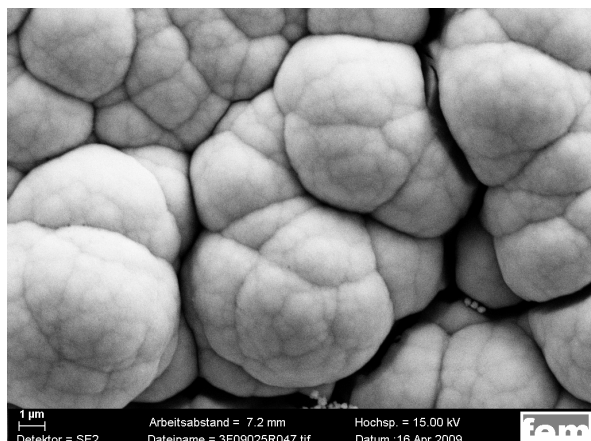


Fig. 2. Polarisation curves of the obtained alloys in 6 M KOH

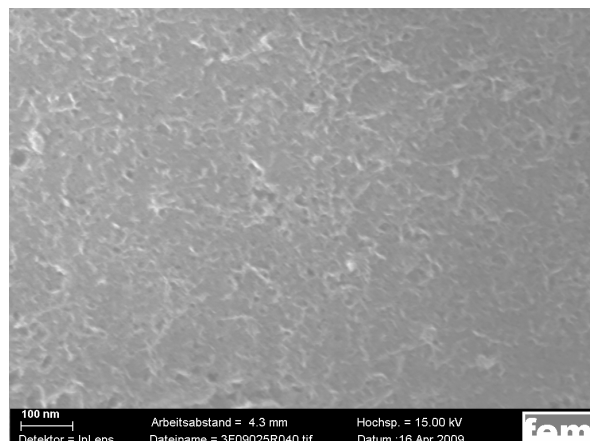
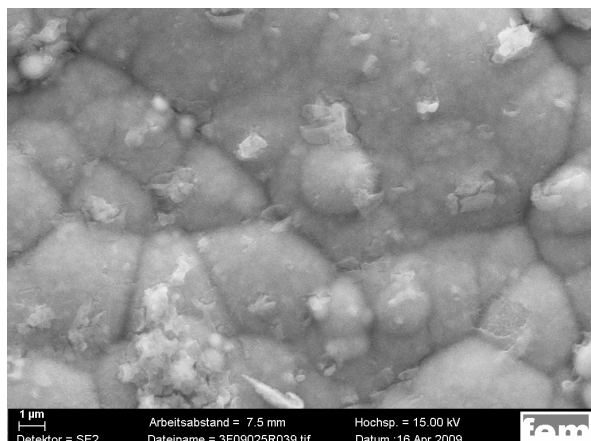
The morphology of the alloys after OER in alkaline media is shown in Fig.3. Numerous holes are observed on CoNiMoW alloy at lower magnification (Fig.3d) due to the dissolving of the deposit, which is clearer at higher magnification. EDX analysis in these areas revealed decreasing of Co and increasing of Ni. Probably, an oxide/hydroxide film on the surface of other alloys is formed during anodic treatment, which masks the morphology at higher magnification (Fig.3a-c).



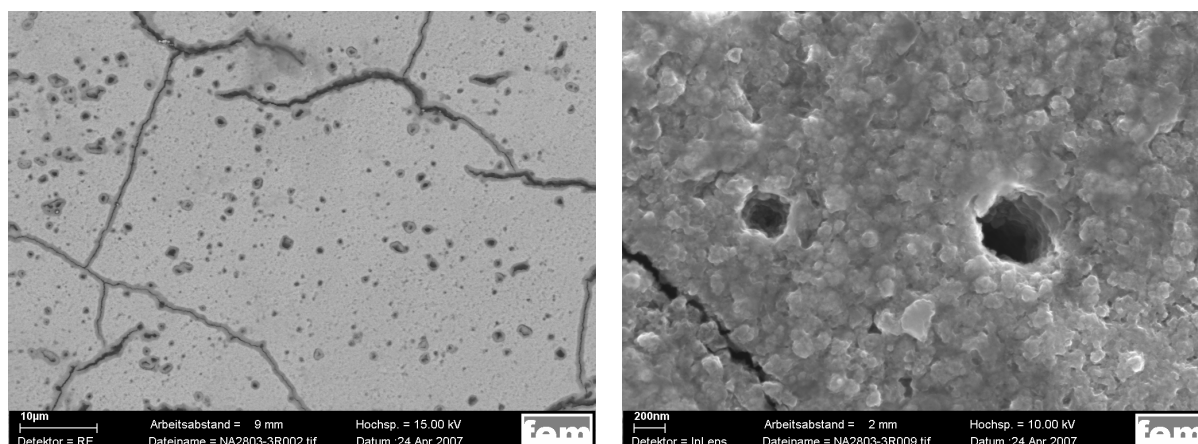
(a) $\text{Ni}_{54}\text{Fe}_{26}\text{Co}_{10}\text{P}_{10}$



(b) $\text{Ni}_{44}\text{Co}_{20}\text{Fe}_{19}\text{Mo}_{13}\text{P}_4$



(c) $\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2.5}$



(d) $\text{Co}_{76}\text{Ni}_{11}\text{Mo}_{8.5}\text{W}_4$

Fig. 3. SEM images of the obtained alloys after OER

4. CONCLUSIONS

Ni-Co-Fe-Mo-P alloys with different composition were produced by electrodeposition dependence of electrolyte conditions. Alloys rich in Fe and Co or rich in Ni were obtained due to anomalous electrodeposition of Co and Fe.

Maximum 4 wt% phosphorous could be incorporated in alloys containing Mo under performed conditions.

The catalytic behavior for OER was determined mainly of the alloy composition. In this case, the real surface might be of no importance.

The alloys containing more Ni and Co showed similar catalytic activity for OER, amount-independent of the other components.

$\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2.5}$ alloy shows the lowest polarization for OER, which means the best catalytic behaviour. $\text{Fe}_{40}\text{Co}_{28}\text{Mo}_{16}\text{Ni}_{14}\text{P}_{2.5}$ and $\text{Fe}_{41}\text{Mo}_{30}\text{Co}_{20}\text{Ni}_{19}$ possess better catalytic activity in 6 M KOH than Ir - Ta mesh, which usually is used as an electrode in industrial processes.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Fund of Bulgaria-Ministry of Education and Science (thematic program “New power sources and energy-saving technologies”) through contract D002-163/2008 and the Project № 40 competition scheme BG 051PO- 001/07/3.3-02 for the financial support of this work. This work is partially supported by the Deutsche Forschungsgemeinschaft (DFG) within a joint research project BUL-436 112/38/04 between the Institute of Physical Chemistry of the BAS, Bulgaria and the Forschungsinstitut für Edelmetalle und Metallchemie, Germany.

REFERENCES

1. Arul Raj I, Vasu K I. Transition metal-based cathodes for hydrogen evolution in alkaline solution: electrocatalysis on nickel-based ternary electrolytic codeposits. *Journal of Applied Electrochemistry* 1992; 22: 471-7.
2. Brossard L, Messier C. Effect of cobalt deposits on nickel substrates on the oxygen evolution reaction in KOH. *Journal of Applied Electrochemistry* 1993; 23: 379-386.
3. Castro E B, Gervasi C A. Electrodeposited Ni-Co-oxide electrodes: characterization and kinetics of the oxygen evolution reaction. *International Journal of Hydrogen Energy* 2000; 25: 1163-1170.
4. Dominguez-Crespo M A, Plata-Terres M, Torres-Huerta A M, Ramirez-Rodriguez C and Arce-Estrada E M. Electrocatalytic Activity Of Nano-Crystalline Ni-Co-Mo-Fe Alloy On The Oxygen Evolution Reaction (OER). *The Electrochemical Society* 2006; 3(9): 135-148.
5. Keith Y, Sasaki and Jan B Talbot. Electrodeposition of Iron-Group Metals and Binary Alloys from Sulfate Baths. *The Electrochemical Society* 1998; 145: 981-90
6. Kubisztal J, Budniok A. Study of the oxygen evolution reaction on nickel-based composite coating in alkaline media. *International Journal of Hydrogen Energy* 2008; 33: 4488-4494.
7. Michael E, Lyons G, Michael P Brandon. The Oxygen Evolution Reaction on Passive Oxide Covered Transition Metal Electrodes in Aqueous Alkaline Solution Part 1-Nickel. *J Electrochem* 2008; 3: 1386-1424.
8. Michael E, Lyons G, Michael P Brandon. The Oxygen Evolution Reaction on Passive Oxide Covered Transition Metal Electrodes in Aqueous Alkaline Solution Part 2- Cobalt. *J Electrochem* 2008; 3: 1425-1462.
9. Michael E, Lyons G, Michael P Brandon. The Oxygen Evolution Reaction on Passive Oxide Covered Transition Metal Electrodes in Aqueous Alkaline Solution Part 3-Iron. *J Electrochem* 2008; 3: 1463-1503.
10. Myung N V and Nobe K. Electrodeposited Iron Group Thin-Film Alloys Structure-Property Relationships. *The Electrochemical Society* 2001; 148 (3): 136-144.
11. Rashkova V, Kitova S, Vitanov T. Electrocatalytic behavior of thin Co-Te-O films in oxygen evolution and reduction reactions. *Electrochim Acta* 2007; 52: 3794-3803.
12. Rashkova V, Kitova S, Konstantinov I, Vitanov T. Vacuum evaporated thin films of mixed cobalt and nickel oxides as electrocatalyst for oxygen evolution and reduction. *Electrochim Acta* 2002; 47:1555-1560.
13. Singh R, Koenig J, Poillerat G, Chartier P. Thin films of CO_3O_4 and NiCo_2O_4 prepared by the method of chemical spray pyrolysis for electrocatalysis: Part IV. The electrocatalysis of oxygen reduction. *J Electroanal Chem* 1991; 314: 241-257.
14. Tarasevich M, Efremov B (1981) in Trasatti S (ed) *Electrodes of Conductive Metallic Oxides. Part A*, Elsevier, Amsterdam
15. Zech N, Podlaha E J and Landolt D. Anomalous Codeposition of Iron Group Metals 1.Experimental Results. *The Electrochemical Society* 1999; 146 (8): 2886-2891.
16. Zhuang Y and Podlaha E J. NiCoFe Ternary Alloy Deposition 1. An Experimental Kinetic Study. *The Electrochemical Society* 2000; 147 (6): 2231-6.