

## Electrochemical deposition of alloys based on Ni-Fe-Co, containing W,P, and their characterization for hydrogen evolution reaction

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Alloys with different composition were produced by electrodeposition dependence of electrolysis conditions. Alloys, rich in Fe and Co or rich in Ni, were obtained due to anomalous electrodeposition of Co and Fe. The morphology and component distribution were characterized by SEM and EDX analyses. The hydrogen evolution reaction (HER) on these materials was investigated by galvanostatic steady-state curves in 6 M KOH. The catalytic activity is improved when the alloys contain more Fe and Co than Ni and W, and especially in the presence of P, even in small amounts (3 to 3.5%). This significantly reduces polarization for HER. This fact may be directly connected to the increase of the real surface of the alloys.

**Keywords:** electrodeposition, Ni-Fe-Co alloys, hydrogen evolution reaction, polarization curves

### Introduction

One of the most common electrode materials is based on nickel and its alloys because of their good catalytic activity for hydrogen evolution reaction (HER). These electrodes play an important role in various electrochemical processes. In order to improve the properties of these materials and increase their electrocatalytic activity, various methods are applied such as alloying with other elements, incorporation of composite components and other changes aiming to obtain electrodes with well-developed, rough or porous surface. Codeposition of nickel with transition metals, binary [1–3] and ternary alloys [4–7], which have better catalytic activity, compared with the pure metal, is one of the most popular methods.

Lupi et al. [3] studied the electrocatalytic performance of Ni-Co alloy for HER, ranging the composition from 0 to 100%. The hydrogen overpotentials appear to be lower in the case of Co concentration, ranging between 41 and 64 wt. %, where the synergism between the catalytic properties of the Ni (low hydrogen over-potential) and Co (high hydrogen adsorption) is best pronounced and which allowed obtaining of a larger value of the exchange current density.

Electrodeposited iron is more active for the hydrogen than the pure nickel, but Ni-Fe [5] alloys show further high activity for the hydrogen evolution. The carbon addition to iron or nickel

through the complexing agent (for example lysine), into the electrolyte, remarkably enhances the activity for hydrogen evolution and changes the mechanism of hydrogen evolution. Ternary Ni-Fe-C alloys show the highest activity for hydrogen evolution compared with pure Ni and Ni-Fe alloy. The Ni-P alloys also possess good catalytic activity toward HER [8–9]. The activity of these electrodes depended on the method of preparation and P content [8]. The activity was higher for the materials, deposited at lower temperatures and for those, containing smaller amounts of P. It was found that the crystal size is correlated with the catalytic activity of the hydrogen evolution in alkaline media. The activity increased when crystal size decreased [9]. It is proposed that the increased catalytic activity is caused by an increased amount of amorphous phase surrounding the Ni crystals. This phase is able to absorb large amount of hydrogen.

The electrodeposition of the iron-group metals, their binary and ternary alloys were published [4, 10–14]. Also, the anomalous behavior of these alloys was studied [13]. The results revealed that Ni was inhibited by the presence of Fe<sup>2+</sup> and Co<sup>2+</sup> ions [14], while Fe deposition rate was enhanced by the presence of Co<sup>2+</sup> and Ni<sup>2+</sup> ions.

The aim of this work is to produce multiple component systems, based on the iron-group metals (including phosphorus) via electrodeposition, and to compare their electrocatalytic behavior for HER

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## EXPERIMENTAL

The samples were prepared by electrodeposition under galvanostatic conditions in thermostatic glass cell with and without magnetic stirring. The electrolyte compositions are given in Table 1.

**Table 1**

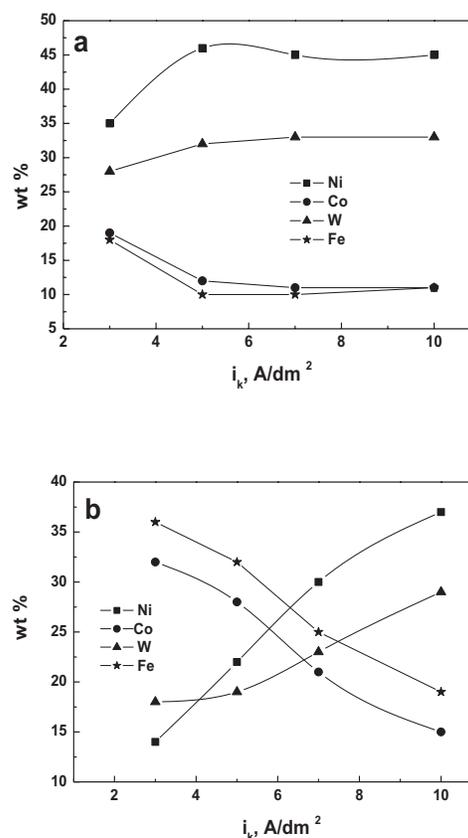
Electrolyte compositions g dm <sup>-3</sup>	Electrolyte I	Electrolyte II
NiSO <sub>4</sub> ·7H <sub>2</sub> O	75	75
NiCl <sub>2</sub> ·6 H <sub>2</sub> O	12.5	12.5
Fe SO <sub>4</sub> ·7H <sub>2</sub> O	25	25
CoSO <sub>4</sub> ·7H <sub>2</sub> O	25	25
Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	30	30
Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O	125	125
NaH <sub>2</sub> PO <sub>2</sub> ·H <sub>2</sub> O	–	25

The electrolysis conditions for electrolyte I and II are – 3, 5, 7 and 10 A/dm<sup>2</sup>, t = 50°C, stirring - 0 min<sup>-1</sup> and 100 min<sup>-1</sup>, pH-5.5. Copper plates with geometric area of 2 cm<sup>2</sup> were used as substrates for cathodic deposits, and Pt-Ti mash for an anode. Electrochemical measurements for HER were made in a conventional three-electrode cell with platinum as a counter electrode and SCE as a reference 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. The element content in the deposit bulk was determined by X-ray fluorescence analysis (Fischerscope X-RAY HDAL).

## RESULTS AND DISCUSSION

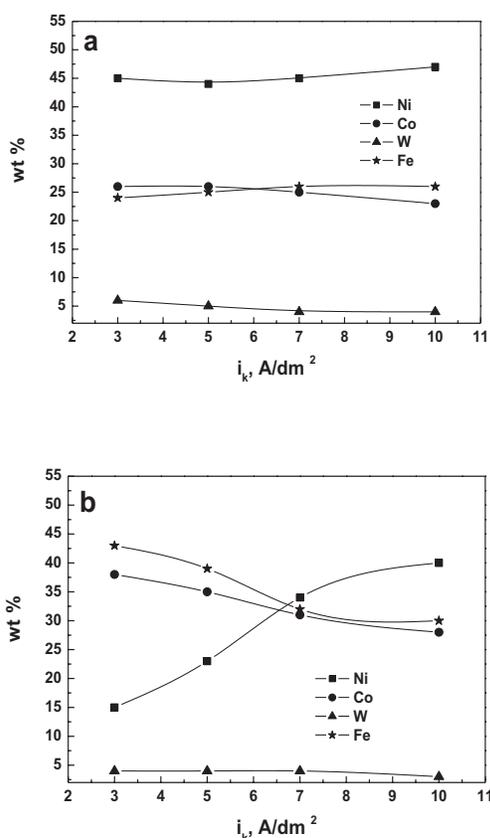
Alloys with different composition were produced by electrodeposition dependence of the electrolysis conditions. Alloys, rich in Fe and Co or rich in Ni, were obtained due to anomalous electrodeposition of Co and Fe. The alloys with different component composition of the electrolytes, given in Table 1, were electrodeposited. The component composition of the alloy was determined by X-ray fluorescence analysis (Fischerscope X-RAY HDAL). The results (Fig.1a) showed that in the absence of stirring and NaH<sub>2</sub>PO<sub>2</sub>, nickel and tungsten are predominant in the obtained alloys. The amount of W increases slightly (from 28 to 33 wt.%) with the current density increase. The content of nickel increases, while the amounts of the included Co and Fe decrease with the increasing current density (to 5A/dm<sup>2</sup>), and then remains almost unchanged for all three elements.



**Fig.1.** Dependence of the weight % of alloy components obtained from electrolyte I (Table 1) on the current density by X-ray fluorescence analysis: a) – without stirring; b)- stirring 100 min<sup>-1</sup>

The current density increase leads to growth of the nickel and tungsten content in the deposit (Fig.1b), while the amounts of Co and Fe decrease by stirring (100 min<sup>-1</sup>). Thus, different composition of layers is produced. For example, Fe-Co-W-Ni alloys are obtained at 3 A/ dm<sup>2</sup> while Ni-W-Fe-Co alloys at 10 A/dm<sup>2</sup>.

The content of W strongly reduces without stirring in the presence of phosphorus in the electrolyte (Fig.2a). The current density increase does not influence essentially the composition of the electrochemically obtained alloys. The nickel content increases up to 40%, while the content of Co and Fe decreases by stirring (fig.2b). The Fe-Co-Ni-W alloys are obtained at a low current density, while the Ni-Fe-Co-W alloys are prepared at high current densities. It is interesting that the amount of the main components (Ni-Fe-Co) is approximately the same (about 31–34 wt.%) in the alloy at 7 A/dm<sup>2</sup> (Fig.2b). The obtained results show that qualitatively different alloy composition



**Fig. 2.** Dependence of the weight % of alloy components obtained from electrolyte II (Table 1) on the current density in the presence of P by X-ray fluorescence analysis: a) – without stirring; b)- stirring 100 min<sup>-1</sup>

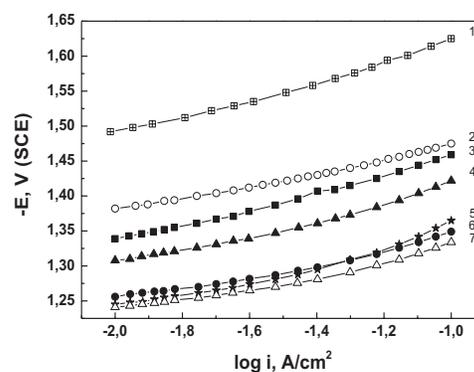
**Table 2**

Current density, A/dm <sup>2</sup>	Ni wt %	Co wt %	W wt %	Fe wt %	P wt %
3, stirring 100 min <sup>-1</sup>	15	37	5	40	3
7, stirring 100 min <sup>-1</sup>	32	30	4	31	3
10, stirring 100 min <sup>-1</sup>	37	26	5	29	3
3, without stirring	42,5	25	6	23	3,5
10, without stirring	44	23	5,5	24	3,5

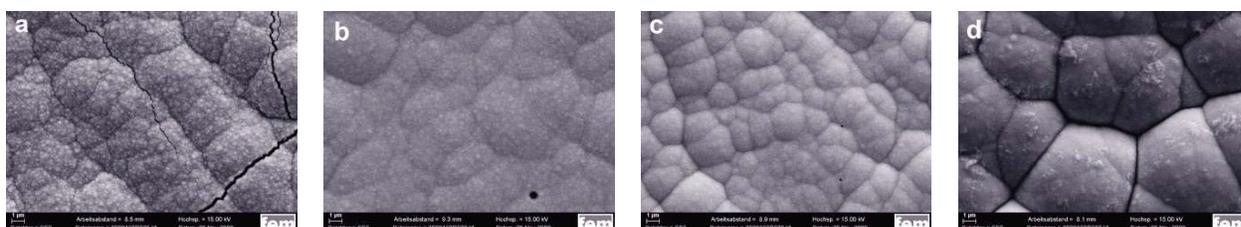
deposits can be obtained under the varying conditions of the electrolysis process.

The X-ray fluorescence analysis does not allow the determination of P, included in the deposits are obtained from electrolyte II. Therefore, some of the samples were analyzed by the EDX method. The data from the analysis are presented in Table 2. The results show that independently of the electrolysis process conditions (with and without stirring and current density), the P content was approximately the same (about 3–3.5 wt %).

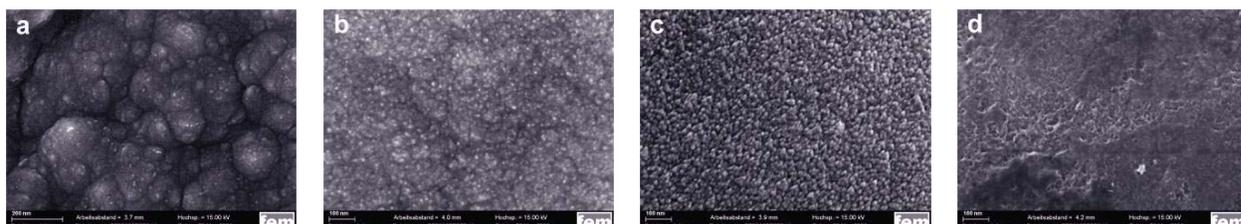
The method of polarization curves, as a criterion for the catalytic activity of the material, was used to study the HER. The deposited electrodes with a geometric surface of 2 cm<sup>2</sup> were tested for HER in 6 M KOH. The experiments were carried out under galvanostatic steady-state conditions. Before starting the measurements, the electrode surface was polarized for 30 min by applying a relatively high (100 mA/cm<sup>2</sup>) cathodic current. Then the current was lowered to 10 mA/cm<sup>2</sup>. The reproducible polarization curves are presented in Fig.3. The alloys, obtained from electrolytes I and II, with different content of basic components (Ni-Fe-Co-W), were selected. Polarization dependencies of the pure nickel and nickel-tungsten are also presented for a comparison. The Ni<sub>65</sub>W<sub>35</sub>



**Fig.3.** Polarization curves of some obtained alloys in 6 M KOH: 1-Ni; 2-Ni<sub>65</sub>W<sub>35</sub>; 3-Ni<sub>46</sub>W<sub>32</sub>Co<sub>12</sub>Fe<sub>10</sub>; 4-Fe<sub>32</sub>Co<sub>28</sub>Ni<sub>22</sub>W<sub>19</sub>; 5-Fe<sub>40</sub>Co<sub>37</sub>Ni<sub>15</sub>W<sub>5</sub>P<sub>3</sub>; 6-Ni<sub>42</sub>Co<sub>25</sub>Fe<sub>23</sub>W<sub>6</sub>P<sub>3,5</sub>; 7-Ni<sub>32</sub>Fe<sub>31</sub>Co<sub>30</sub>W<sub>4</sub>P<sub>3</sub>. alloy (Fig.3, curve-2), obtained under the conditions given in [7], shows lower hydrogen over-potential than the pure nickel. The addition of Co and Fe to NiW alloys reduces the polarization for HER. A similar dependence on the nickel-iron and nickel-cobalt alloys was established by [3,5]. The catalytic activity is improved when the alloys contain more Fe and Co (curve 4) than Ni and W (curve 3). The presence of P, even in small amounts (see Table 2), significantly reduces the hydrogen overvoltage (curves 5, 6, and 7 in Fig.3). These curves show similar catalytic characteristics, although they have radically different composition. Comparing the P containing alloys, the alloy with approximately the same content of main components (Ni<sub>32</sub>Fe<sub>31</sub>Co<sub>30</sub>W<sub>4</sub>P<sub>3</sub>) shows the lowest polarization. It is known that the high catalytic activity of nickel alloys depends not only on the



**Fig.4.** SEM images at 5 000x magnification: a)  $\text{Ni}_{46}\text{W}_{32}\text{Co}_{12}\text{Fe}_{10}$ ; b)  $\text{Fe}_{32}\text{Co}_{28}\text{Ni}_{22}\text{W}_{19}$ ; c)  $\text{Fe}_{40}\text{Co}_{37}\text{Ni}_{15}\text{W}_5\text{P}_3$ ; d)  $\text{Ni}_{32}\text{Fe}_{31}\text{Co}_{30}\text{W}_4\text{P}_3$ .



**Fig.5.** SEM images at 100 000x magnification: a)  $\text{Ni}_{46}\text{W}_{32}\text{Co}_{12}\text{Fe}_{10}$ ; b)  $\text{Fe}_{32}\text{Co}_{28}\text{Ni}_{22}\text{W}_{19}$ ; c)  $\text{Fe}_{40}\text{Co}_{37}\text{Ni}_{15}\text{W}_5\text{P}_3$ ; d)  $\text{Ni}_{32}\text{Fe}_{31}\text{Co}_{30}\text{W}_4\text{P}_3$ .

component composition but also on the component real surface.

The alloy morphology, corresponding to the polarization curves, is presented in Fig. 4 and 5. SEM investigations were carried out at various magnifications. A different size globular surface structure of the obtained deposits at 5 000x magnification for all alloys is observed (Fig.4). A better performance of the surface and the crystalline size is acquired at 100 000x magnification (Fig.5).

The availability of P in the alloys and probably lower content of W leads to a strong reduction in the size of crystals (Fig. 5c and d). This fact may be directly connected to the increase in the real surface of the alloys. Burchardt *et al.* [9] were found also that the differences in the electrode activities of Ni-P alloys are principally due to differences in the real surface area. Comparing figures 3 and 5, the results show that  $\text{Ni}_{32}\text{Fe}_{31}\text{Co}_{30}\text{W}_4\text{P}_3$  alloy presents the lowest polarization (Fig.3, curve 7), which owns the finest surface morphology (Fig.5d). In opposite,  $\text{Ni}_{46}\text{W}_{32}\text{Co}_{12}\text{Fe}_{10}$  alloy has the largest crystal grains (Fig.5a) and shows the highest polarization dependence (Fig.3, curve 3) for HER than the other multiple component alloys.

### CONCLUSIONS

Alloys, based on Ni-Fe-Co with the addition of W and P, were electrodeposited. It is shown that in dependence of the electrolysis process conditions rich of nickel and tungsten or iron and cobalt alloys can be obtained. The hydrogen overvoltage is reduced when the alloys contain more Fe and Co than Ni and W in the layers without phosphorus. The presence of phosphorus (3 to 3.5%) in the

alloys significantly reduces the content of tungsten in them. Polarization dependences of these alloys show better catalytic characteristics for HER than the deposits without phosphorus content. The reason for such result is probably the synergy between Ni and Co, from one hand, and the reduction of the crystal grain size, from the other hand, which determines a more developed surface.

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**ЕЛЕКТРОХИМИЧНО ОТЛОЖЕНИ СПЛАВИ НА ОСНОВА Ni-Fe-Co,  
СЪДЪРЖАЩИ W, P И ТЯХНОТО ОХАРАКТЕРИЗИРАНЕ ЗА РЕАКЦИЯТА НА  
ОТДЕЛЯНЕ НА ВОДОРОД**

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(Резюме)

Синтезирани са електрохимично различни по състав сплави в зависимост от условията на електролиза. Сплави, богати на Fe и Co или богати на Ni са получени поради аномалното отлагане на Co и Fe. Морфологията и разпределението на компонентите са охарактеризирани чрез SEM и EDX анализи. Реакцията на отделяне на водород върху тези материали е изследвана посредством галваностатични криви в 6M KOH. Каталитичната активност се подобрява, когато сплавта съдържа повече Fe и Co, отколкото Ni и W и особено в присъствието на P в сплавта, дори в малки количества (3 до 3.5%). Тази концентрация на P значително понижава поляризацията на реакцията на отделяне на водород. Този факт вероятно се дължи на увеличението на реалната повърхност на сплавта.