Electrodeposition of NiW, NiWMo and NiMo Alloy Thin Films and

NiW Nanowires

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Tetiana Bairachna

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ABSTRACT

Tungsten and molybdenum alloys with iron-group metals, particularly NiW and NiMo alloys, are well known to possess outstanding functional properties such as thermal, wear and corrosion resistance, high microhardness, and excellent catalytic activity towards hydrogen evolution. They have been electrodeposited as thin films, and rarely as nanowires, despite the potentially superior properties and applications that nanowires can offer. The research presented is the first demonstration of NiW nanowires.

The electrolytes for deposition of NiW, NiWMo and NiMo alloy thin films and NiW nanowires were developed. One challenge in depositing these alloys is in reaching a high amount of W or Mo. Both W and Mo cannot be electrodeposited from aqueous electrolytes, but require Ni ions to induce their reduction, while at the same time depositing Ni. This research shows that it was possible to deposit NiW alloys with W content in the range of 40 to 60 wt % using direct current of 2-50 mA/cm$^2$, current efficiency being 7-62 %. NiWMo alloys with Mo content in the range of 48 to 70 wt % pushed the combined Mo+W content to the high range of 60 to 79 wt %. Replacement of W for Mo in the electrolyte for NiW alloy resulted in NiMo alloy deposition with 69 to 82 wt % of Mo in the deposit. The trade-off for comparatively high refractory metal content is a very low current efficiency for NiWMo and NiMo alloys between 0.5-2 %, and needs to be significantly improved in the future. Deposition of NiWMo and NiMo alloys required higher values of current densities (200-300 mA/cm$^2$) than for NiW (2-50 mA/cm$^2$).
The NiW nanowires with diameters from 40 nm to 250 nm and length of 6 µm had W contents from 33 wt % to 54 wt %. The nanowires were deposited into polycarbonate templates and released by dissolution of the membrane in dichloromethane. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) showed that the NiW nanowires had a bumpy morphology even when deposited under direct current. The dimension of bumps and W content depended on both the membrane pore diameter and deposition conditions.

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1.0 Introduction

According to the report *Clean Energy Trends 2010* by Clean Edge, a private research firm, approximately $100 billion of the $787 billion US stimulus package is allocated to build clean-energy investments and activities. Alternative fuels made in a clean way are of interest. One possible source of an environmentally friendly fuel is electrochemical hydrogen, from the decomposition of water. Tungsten and molybdenum alloys with iron-group metals, particularly NiW and NiMo alloys, are well known to possess outstanding functional properties such as thermal, wear, and corrosion resistance, high microhardness, and also excellent catalytic activity towards hydrogen evolution. These alloys decrease the overpotential of the hydrogen evolution reaction, and therefore lower cost connected with this gas production process.

Unique to the electrodeposition of these coatings is that the mechanism exhibits coupled kinetics, referred to as induced codeposition first introduced by Brenner\(^1\) The essence of induced codeposition is that tungsten and molybdenum cannot be reduced completely to a zero valence state in aqueous electrolytes, but it is possible to codeposit it as an alloy with iron, cobalt or nickel. A mechanism reported by Podlaha and Landolt\(^2\) in a system of NiMo suggests that the iron-group metal ion catalyzes the reduction of the inducing element via the formation of an adsorbed oxide intermediate at the electrode surface.

Papers dealing with the electrodeposition of tungsten and molybdenum alloys with iron-group metals have been published as early as in 1930s, with a parametric focus.\(^3\)-\(^5\) These studies continued until about the 1970s and the most significant contributions into understanding the operating conditions for electrodeposition of
tungsten and molybdenum reduction, among others, were made by such scientists as Holt and Vaaler, Fukushima, Brenner, Frantzevich-Zabludovskaya and Zayats, Vas'ko. The next wave of interest in tungsten and molybdenum alloys started in 1990s when investigators from all over the world began exploring the systems under consideration: Podlaha and Landolt (USA, Switzerland), Younes, Gileadi and Eliaz (Israel, USA), Dikusar and Tsyntsaru (Moldova), Cesiulis (Lithuania), Donten and Stojek (Poland), Anatassov, Gencheva and Bratoeva (Bulgaria), Mizushima and Hansen (Denmark), Obradović, Stevanović and Despić (Yugoslavia), Kublanovskii and Yapontseva (Ukraine), Kudriavtsev and Pavlov (Russia), Auerswald and Fecht (Switzerland, Germany).

As a result researchers have studied the influence of modes (direct current/pulse current), temperature, hydrodynamic conditions, electrolyte composition as it influences deposit composition, morphology, crystalline structure and properties of electrodeposited alloy coatings, proposed various schemes of the process kinetics, and suggested new applications for industry. Nevertheless the literature cited does not mention nanowires, or the combined ternary NiWMo with high refractory metal content.

Thus, the goal of the given project was to develop electrolytes and conditions for electrochemical deposition of NiW, NiWMo, and NiMo alloys and mechanically robust NiW nanowires since nanoscale structures may exhibit properties not found on the micro- and macro level for the materials of the same chemical composition.
2.0 Critical Literature Review

The main focus of the given study consisted of electrodeposition of NiW, NiWMo, and NiMo alloy thin films with high content of refractory metals and further fabrication of NiW nanowires. The electrolytes for NiWMo and NiMo alloy plating were developed on the basis of that for the NiW system.

2.1 NiW and NiMo alloys electrodeposition: kinetics, modes, and properties

Brenner\(^1\) was the first who systematized knowledge available at that moment about electrodeposition of alloys in general, including NiW alloys. The review consists of comprehensive analysis of operating conditions, electrolyte composition as well as pH value influence on W content in the coating and current efficiency of the process. To summarize the content of the chapter devoting to W alloys there are both acidic and alkaline baths for NiW deposition. Alkaline solutions operate at pH ranging from 7 to 10 while for acidic electrolytes it is reported to be 2 to 5. The role of pH in acidic baths onto alloy composition is rather small; variations in current densities and temperature also have little effect according to the author. In the case of alkaline solutions it is recommended to carry out the deposition with temperature above room temperature (50-90 °C) as its increase raises current efficiency. Alloys deposited at lower temperatures are mechanically weak and of poor quality. Current densities vary significantly – 1 to 20 A/dm\(^2\), higher densities are recommended to make thicker coatings. Current efficiencies reported for NiW are up to 90 %. It is found that the percentage of tungsten in the deposit is higher than the metal percentage of tungsten in the bath. Hardness of NiW changes with W content and varies from 350 to 700 HV.
A unique feature of NiW and NiMo electrodeposition is that their deposition behavior is similar. Both W and Mo cannot be electrodeposited from aqueous electrolytes without an inducing metal, such as Ni. This behavior is referred to as induced codeposition. Several theoretical approaches have been discussed to describe this phenomenon. For example, Fukushima et al.\textsuperscript{22} worked on electrodeposition of Mo alloys and proposed a mechanism when depositing alloys with Mo or W. According to them the role of the iron group metal in this coupled mechanism consists of the ability of holding high amounts of atomic hydrogen at the electrode surface to explain the reason for Mo to be deposited from aqueous solutions. The mechanism assumes that partly-reduced refractory metals form a film of oxide and are further reduced completely by atomic hydrogen:

\[
\begin{align*}
\text{MoO}_4^{2-} + (6-n)\text{e}^- &\rightarrow \text{Mo}^{n+} \text{oxide (hydroxide)} \\
\text{Me}^{2+} + 2\text{e}^- &\rightarrow \text{Me} \\
\text{H}^+ + \text{e(Me)} &\rightarrow \text{H(Me)} \\
\text{Mo}^{n+} \text{oxide (hydroxide)} + n\text{H(Me)} &\rightarrow \text{Mo(Me)}
\end{align*}
\]

where \( n \) - valence of Mo, \( \text{Me} \) - inducing metal of iron group, \( \text{H(Me)} \) – atomic hydrogen on the surface of a metal, \( \text{Mo(Me)} \) – molybdenum deposited on the surface of an iron group metal.

Experiments by Podlaha and Landolt\textsuperscript{2} showed that the amount of Mo in the deposit was not correlated by the amount of hydrogen evolved in the side reaction. High Mo content could be deposited from aqueous electrolytes with both high and low current efficiency, thus suggesting that hydrogen is not a governing component for induced codeposition. They suggested the following mechanism that was used to predict the
electrodeposition of NiMo, CoMo, and FeMo. Mo deposits from an intermediate compound of mixed-metals containing the iron group metal and complexing agent, in this case citric acid or sodium citrate:

\[
\text{NiCit}^- + \text{MoO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- \rightarrow [\text{NiCitMoO}_2]_{\text{ad}}^- + 4\text{OH}^-
\]

\[
[\text{NiCitMoO}_2]_{\text{ad}}^- + 2\text{H}_2\text{O} + 4e^- \rightarrow \text{Mo}_{\text{solid}} + \text{NiCit}^-
\]

\[
\text{NiCit}^- + 2e^- \rightarrow \text{Ni}_{\text{solid}} + \text{Cit}^{2-}
\]

Therefore molybdenum reduces from an adsorbed intermediate, treating the nickel ion as a catalyst.

Nenastina et al.\(^{23}\) came up with the similar scheme for NiW alloy codeposition having taken into consideration previous schemes:

\[
[\text{NiCitWO}_4]^3- \leftrightarrow [\text{NiCitWO}_4]_{\text{ads}}^3-
\]

\[
[\text{NiCitWO}_4]_{\text{ads}}^3- + 2e^- + 2\text{H}_2\text{O} \leftrightarrow [\text{NiCitWO}_2]^+ + 4\text{OH}^-
\]

\[
[\text{NiCitWO}_2]^+ + 2e^- \leftrightarrow \text{Ni|WO}_2 + 3\text{Cit}^{3-}
\]

\[
\text{Ni|H}_2\text{O} + e^- \leftrightarrow \text{Ni|H}_{\text{ads}} + \text{OH}^-
\]

\[
\text{Ni|WO}_2 + 4\text{H}_{\text{ads}} \leftrightarrow \text{Ni} + \text{W} + 2\text{H}_2\text{O}
\]

They studied NiW (and CoW) electrodeposition from citric baths containing boric acid as a buffer agent, namely the relationship between electrolyte composition, pH value, mode of electrolysis (direct/pulse current), temperature and composition/properties of coatings obtained (corrosion resistance, catalytic activity in hydrogen evolution reaction, microhardness, magnetic properties such as coercive force, saturation magnetization, residual magnetization). Ni-W alloy deposits were obtained with W content 5-55 wt %, having microhardness about 400-700 HV and coercive force up to 35 Oe. A current
density rise in the range 1-5 A/dm$^2$ was found to increase W content in the alloy. A maximum portion of W has been achieved at pH 6.5-7.3.

Eliaz and Gileadi$^{24}$ made a review of up-to-date information on Mo and W alloys with transition metals. The citrate concentration increase was reported to decrease overall current efficiency. Adding nickel sulfamate or saccharin appeared to elevate current efficiency as well. Citrate baths provided higher W content in comparison with those containing tartrate or malate. The effect of temperature was proved to depend on solution composition. Increasing the current density led to higher W portion for most electrolytes. Formation of different phases as a result of deposition has been reported: solid solution of W in Ni, amorphous phase, orthorhombic phase, body-centered tetragonal phase. These authors suggest the next mechanism of NiW alloy formation:

\[
[(\text{Ni})(\text{Cit})]^{-} + [(\text{HWO}_4)(\text{Cit})]^{4-} \rightarrow [(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + \text{Cit}^{3-} \\
[(\text{Ni})(\text{HWO}_4)(\text{Cit})]^{2-} + 8e^{-} + 3\text{H}_2\text{O} \rightarrow \text{NiW} + 7(\text{OH})^{-} + \text{Cit}^{3-}
\]

Due to the high hardness and increase of strength found in NiW alloys, Cesiulis and Podlaha-Murphy$^{25}$ examined conditions to electrodeposit them into deep recesses for microelectromechanical systems (MEMS) applications. They found that in the presence of CO$_3^{2-}$ the alloy composition is less dependent on current density and pH value, and was also critically dependent on pulsing to help maintain the surface pH. W content in the films was 9-15 wt %.

Huang$^{26}$ has shown that addition of diammonium citrate into the electrolyte increases both W content and internal stresses in the film obtained. The W deposit concentration varied in the range of 1-5 % and internal stress changed from 16 to 108 MPa. Also the author established that the relationship between the final coating
microhardness (200-700 HV) and current density value depended on electrolyte composition.

Sriraman et al.\textsuperscript{27} examined the hardness and sliding wear resistance of electrodeposited nanocrystalline NiW alloys. They found that crystallite size reduced to 15 nm with an increase in current density due to an increase in the W content with current density. Conversely efficiency of the process was shown to decrease with current. Very small grain size results in a microstructure consisting of two phases: the crystalline material and the amorphous grain boundary volume. NiW alloys with 9.33 at % W plated at 75 °C exhibited the maximum hardness of 638 HV. Specific wear rate reduced as the crystallite size reduced due to increase in hardness and it attained a minimum value when the crystallite size was 20 nm. The specific wear rate increased with a further reduction in the crystallite size to 13 nm. Coatings with 6–8 at % W exhibited superior wear resistance.

Ruan et al.\textsuperscript{28} electrodeposited nanocrystalline NiW alloy with grain size 5-22 nm and W content 13-22.5 at %. They investigated grain “colonies” that were orders of magnitude larger than the nanoscale grain size, and which influence crack propagation and electrochemical corrosion. The authors pointed out that the physical and chemical properties of these mesostructures were affected by and might thus be manipulated through the deposition conditions.

Similar investigation has been done by Sulitanu et al.\textsuperscript{29} studying structure-properties relationship in this system. Their NiW coatings contained up to 18 at % of W. Perpendicular magnetic anisotropy was found in films with W content of 13 wt %. Deposits of this composition consisted of columnar nanocrystallites of 12.5 nm size in
diameter embedded in an amorphous NiW matrix. Electrodeposited NiW films with W portion 13 wt % might be applicable for magnetic media in perpendicular magnetic recording since the coatings possess large energy perpendicular magnetic anisotropy constant of 120 kJ/m$^3$, high perpendicular coercivity of 120 kA/m and sufficiently high saturation magnetization of 420 kA/m.

Schuh et al.$^{30}$ studied the effect of solid solution W additions on the mechanical properties of nanocrystalline Ni. Their electrochemical deposits contained 11-14 at % of W and had grain size 4-7 nm according to TEM observations. Hardness of these films was estimated to be 6.5-7.8 GPa. Range of current densities used in this experiment was 0.05-0.2 A/cm$^2$. Deposits texture changed with current density during plating. Impurity level was low of 1350 and 780 atomic ppm for H and O respectively.

Atanassov et al.$^{31}$ have deposited NiW alloy from sulfamate electrolyte. Their results proved that NiW alloy microhardness was up to 970 kg/mm$^2$. Higher cathodic current density provided deposition of more W into coating but lowered current efficiency. Without agitation films with the highest W content up to 40 wt % were obtained at pH 7. Higher temperature, pH and current density increases film microhardness due to higher W portion in the NiW alloy.

2.2 NiW and NiMo alloys electrodeposition: electrolytes

Below there are tables summarizing all the varieties of electrolytes used for NiW and NiMo alloys electrodeposition. The vast majority of those solutions were prepared on the basis of nickel sulfate, sodium tungstate/molybdate, and citric acid or its derivative trisodium citrate as a complexing agent.
<table>
<thead>
<tr>
<th>#</th>
<th>Na$_2$WO$_4$</th>
<th>NiSO$_4$</th>
<th>Organic acid/salt</th>
<th>Others</th>
<th>$j$, mA/cm$^2$</th>
<th>pH</th>
<th>$T$, $^\circ$C</th>
<th>W, wt%</th>
<th>CE, %</th>
<th>Source</th>
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<tr>
<td>1</td>
<td>0.27-0.54</td>
<td>0.42</td>
<td>Roshelle salt 1.4</td>
<td>NH$_3$Cl 0.94</td>
<td>20</td>
<td>9.0</td>
<td>95</td>
<td>10-20</td>
<td>85-93</td>
<td>A. Brenner, P.S. Burkhead, and E. Seegmiller, J. Res. Natl. Bur. Standards 39, 351 (1947)</td>
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<td></td>
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<td>Sodium citrate 0.6</td>
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<td></td>
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<td>Hydroxyacetic acid 2.6</td>
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<td>2</td>
<td>0.15</td>
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<td>Cit 0.34</td>
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<td>70-150</td>
<td>8.0</td>
<td>70</td>
<td>35</td>
<td>45</td>
<td>L.E. Vaaler and M.L. Holt, Trans. Electrochem. Soc. 90, 43 (1946)</td>
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<td>3</td>
<td>0.40</td>
<td>0.01-0.10</td>
<td>Na$_3$Cit 0.25-0.60</td>
<td>Ni sulfamate 0.062-0.124</td>
<td>5-15</td>
<td>8.0</td>
<td>RT-70</td>
<td>25-90</td>
<td>8-21</td>
<td>N. Eliaz, T.M. Sridhar, and E. Gileadi, Electrochim. Acta 50, 2893 (2005); T.M. Sridhar, N. Eliaz, and E. Gileadi, Electrochem. Solid-State Lett. 8, C58 (2005)</td>
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<td></td>
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<td>Saccharin 0.0146</td>
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<td></td>
<td>NaCl 0.002-0.005</td>
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<td></td>
<td>Na$_2$SO$_4$ 0.176</td>
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<td>4</td>
<td>0.01-0.5</td>
<td>0.01-0.20</td>
<td>Na$_3$Cit 0.10-1.0</td>
<td>NH$_4$ON for pH</td>
<td>15</td>
<td>6.0-12.0</td>
<td>10-62</td>
<td>5-74</td>
<td>05-98</td>
<td>O. Younes, I. Zhu, Y. Rosenberg, Y. Schacham-Diamand, and E. Gileadi, Langmuir 17, 8270 (2001)</td>
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<td>#</td>
<td>Na$_2$W$_0$$_4$</td>
<td>NiSO$_4$</td>
<td>Organic acid/salt</td>
<td>Others</td>
<td>$j$, mA/cm$^2$</td>
<td>pH</td>
<td>T, °C</td>
<td>W, wt%</td>
<td>CE, %</td>
<td>Source</td>
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<td>5</td>
<td>0.003-0.006</td>
<td>0.38</td>
<td>–</td>
<td>NH$_3$Cl 0.93</td>
<td>5-30</td>
<td>n/a</td>
<td>30-70</td>
<td>12-20</td>
<td>43-90</td>
<td>M. Krishnan, C. J. Kennedy, S. Jayakrishnan, S. Sriveeraghavan et al, Metal Finish. 93, 33 (1995)</td>
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<td>6</td>
<td>0.14</td>
<td>0.06</td>
<td>Na$_3$Cit 0.3-0.5</td>
<td>NH$_3$Cl 0.5 NaBr 0.15</td>
<td>05.-2.0</td>
<td>8.5</td>
<td>60-90</td>
<td>17-25 at%</td>
<td>40-51</td>
<td>T. Yamasaki, R. Tomohira, Y. Ogino, P. Schoßmacher, and K. Ehrlich, Plat. Surf. Finish. 87 (5), 148 (2000)</td>
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<td>7</td>
<td>30 g/l</td>
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<td>Na$_3$Cit 90 g/l</td>
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<td>5-100</td>
<td>4.0-8.0</td>
<td>30-70</td>
<td>19-81</td>
<td>4-85</td>
<td>N. Atanassov, K. Gencheva, and M. Bratoeva, Plat. Surf. Finish., 84 (2), 67 (1997)</td>
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<td>8</td>
<td>78 g/l</td>
<td>n/a</td>
<td>Na$_3$Cit 59 g/l</td>
<td>H$_3$PO$_4$ 85 % 7.69 g/l H$_3$BO$_3$ 10.25 g/l Rokafenol N-10100ml/l Butindiol 1,4 50 mg/l</td>
<td>70</td>
<td>5.0-10.0</td>
<td>65</td>
<td>17-35</td>
<td>15</td>
<td>M. Donten, H. Cesiulis, Z. Stojek, Electrochim. Acta, 45, 3389 (2000) 3389</td>
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<td>9</td>
<td>0.4</td>
<td>0.2</td>
<td>Na$_3$Cit 0.5</td>
<td>Na$_2$CO$_3$ 0.5 NH$_4$OH 1.2</td>
<td>10-60</td>
<td>8.5-9.0</td>
<td>70</td>
<td>9-19</td>
<td>22-75</td>
<td>H. Cesiulis and E.J. Podlaha-Murphy, Materials Science (Medžiagotyra), 9 (4), 329 (2003)</td>
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<td>Components, concentrations (M)</td>
<td>$j, mA/cm^2$</td>
<td>pH</td>
<td>$T, ^\circ C$</td>
<td>W, wt%</td>
<td>CE, %</td>
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<td>$Na_2W_0_4$ 0.3 $NiSO_4$ 0.1 Organic acid/salt Na$_3$Cit 0.28 Others $H_2SO_4, NH_4SO_4$</td>
<td>40</td>
<td>3.0-8.5</td>
<td>60</td>
<td>5-25</td>
<td>n/a</td>
<td>R. Juškėnas, I. Valsiūnas, V. Pakštas, and A. Selskis, Appl. Surf. Science, 253, 1435 (2006)</td>
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<td>11</td>
<td>0.2 0/075 Cit 0.314 Others NH$_4$OH for pH</td>
<td>35-100</td>
<td>8.15</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>M.D. Obradović, R.M. Stevanović, and A.R. Despić, J. Electroan. Chem., 552, 185 (2003)</td>
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<td>12</td>
<td>0.2 0.075-0.110 Cit 0.3 Others NH$_4$OH for pH</td>
<td>50, 100</td>
<td>8.15</td>
<td>25-55</td>
<td>0.3-19</td>
<td>n/a</td>
<td>V.V. Bondar, V.V. Grinina, V.N. Pavlov, Electroosazhdenie dvoinyh splavov, Itogi Nauki i Tehniki, Moskow (1970) [in Russian]</td>
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<td>13</td>
<td>0.06 0.93 Na$_3$Cit 0.68 Others NiCl$_2$ 0.088 $H_3BO_3$ 0.5 KCl 0.27</td>
<td>50, 100</td>
<td>8.15</td>
<td>25-55</td>
<td>0.3-19</td>
<td>n/a</td>
<td>M.D. Obradović, J. Stevanović, A.R. Despić, R. Stevanović, and J. Stoch, J. Serb. Chem. Soc. 66 (11-12), 899 (2001)</td>
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<td>14</td>
<td>81.5 g/l 2.8 g/l NH$_4$Cit 59 g/l Others $H_3PO_4$ 85 % $7.69 g/l H_3BO_3$ 10.25 g/l 2-buten-2,4-diol 1.4 50 mg/l, NH$_4$OH</td>
<td>70</td>
<td>8.5</td>
<td>65</td>
<td>23-38 at%</td>
<td>n/a</td>
<td>M. Donten, J. Solid state Electrochem. 3, 87 (1999); G.A. Croopnik, D.M. Scruggs (1985) US Pat 4529668</td>
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<td>Components, concentrations (M)</td>
<td>$j$, mA/cm$^2$</td>
<td>pH</td>
<td>$T$, °C</td>
<td>$W$, wt%</td>
<td>CE, %</td>
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<td>15</td>
<td>$\text{Na}_2\text{W}0_4$ 0.15, $\text{NiSO}_4$ 0.06, $\text{Na}_3\text{Cit}$ 0.30, NH$_4$Cl 0.5, H$_3$BO$_3$ 1.0, NaBr 0.15, Na saccharin 0.08, Na laurel sulfate 0.0867</td>
<td>50, 100, 150, 200</td>
<td>8.5</td>
<td>75-85</td>
<td>0.72-16 at%</td>
<td>31-36</td>
<td>K.R. Sriraman, S. Ganesh Sundara Raman, and S.K. Seshadri, Material Sci. Eng. A 418, 303 (2006)</td>
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<td>16</td>
<td>$\text{Na}_3\text{Cit}$ 0.50, H$_2$SO$_4$ or NaOH</td>
<td>5-15</td>
<td>8.0</td>
<td>RT-70</td>
<td>20-31 at%</td>
<td>8-21</td>
<td>T.M. Sridhar, N. Eliaz, and E. Gileadi, Electrochem. Solid-State Lett. 8 (3), C58 (2005)</td>
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<td>17</td>
<td>Na$_3$Cit 147.1 g/l, NH$_4$Cl 26.7 g/l</td>
<td>200</td>
<td>n/a</td>
<td>80</td>
<td>13-22 at%</td>
<td>n/a</td>
<td>S. Ruan and C. A. Schuh, Scripta Materialia, 59, 1218 (2008)</td>
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<td>18</td>
<td>5(NH$_4$)$_2$$\cdot$12WO$_3$$\cdot$5H$_2$O+Ni(NH$_2$SO$_3$)$_2$$\cdot$4H$_2$O 0.3, Na$_3$Cit 0.3, NaOH for pH</td>
<td>100</td>
<td>6.5</td>
<td>50</td>
<td>0-55</td>
<td>0-80</td>
<td>S. Oue, H. Nakano, S. Kobayashi, and H. Fukushima, J. Electrochem. Soc. 156 (1), D17 (2009)</td>
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<td>19</td>
<td>NH$_4$ Oxalate</td>
<td>30-45</td>
<td>8.0-9.0</td>
<td>35-50</td>
<td>n/a</td>
<td>n/a</td>
<td>D.L. Leichkis, V.V. Kusch, E.P. Ignatenko (1992) Russia Pat № 4778942/26 [in Russian]</td>
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<td>20</td>
<td>Na$_2$WO$_4$ 30 g/l, NiSO$_4$ 0.01-600 g/l, Organic acid/salt –</td>
<td>H$_2$O$_2$ (30%) 21 ml/l, H$_3$BO$_3$ 50 g/l, H$_2$SO$_4$ for pH</td>
<td>100</td>
<td>1.9-2.3</td>
<td>50</td>
<td>n/a</td>
<td>n/a</td>
<td>A. T. Vas'ko, D.P. Zosimovich, J. Prikladnoi Khimii, 35 (6), 1302 (1962)</td>
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<td>21</td>
<td>0.05-0.25, 0.05-0.25, Cit 0.3</td>
<td>H$_3$BO$_3$ 0.3-0.5, NaOH, H$_2$SO$_4$ for pH</td>
<td>5-50 (DC)</td>
<td>5.5-7.3</td>
<td>50-60</td>
<td>5-55</td>
<td>40-98</td>
<td>T. Bairachna, M. Ved. M. Sakhnenko, Sviridov's Readings, 4, 222 (2008) [in Russian]</td>
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<td>22</td>
<td>0.14, 0.06, 0.10, 0.14, Cit 0.5</td>
<td>NH$_4$Cl 0.50, NaBr 0.15</td>
<td>10</td>
<td>8.5</td>
<td>75</td>
<td>7-12 at%</td>
<td>n/a</td>
<td>M. Klimenkov, A.S.M.A. Haseeb, and K. Bade, Thin Solid Films (2009)</td>
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<td>23</td>
<td>0.2, 0.1, Cit 0.3, Glycine 0.3 and/or 0.3triethanolamin</td>
<td>H$_3$BO$_3$ 0.44</td>
<td>10-150</td>
<td>7.5-8.0</td>
<td>70</td>
<td>6-17 at%</td>
<td>37-85</td>
<td>I. Mizushima, P.T. Tang, H. N. Hansen, M.A.J. Somers, Electrochim. Acta, 51, 6128 (2006)</td>
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<td>24</td>
<td>32 g/l, 16 g/l, Cit 40 g/l</td>
<td>NH$_4$OH 2-Butyne-1,4diol 0.2 g/l</td>
<td>65</td>
<td>6.5</td>
<td>65</td>
<td>40-45</td>
<td>n/a</td>
<td>Y. Wu, D.Y. Chang, D.S. Kim, S.C. Kwon, Surf. Coat. Techn., 162, 269 (2003)</td>
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<td>Components, concentrations (M)</td>
<td>j, mA/cm²</td>
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<td>T, °C</td>
<td>Mo, wt%</td>
<td>CE, %</td>
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<td>Na₂Mo₄ 0-15 g/l NiSO₄ 40 g/l Organic acid/salt 2-butyne-1,4-diol 50 mg/l Rokafenol N-10 100 µl/l</td>
<td>30</td>
<td>8.5</td>
<td>20</td>
<td>0-35 at%</td>
<td>0-33</td>
<td>M. Donten, H. Cesiulis, and Z. Stojek, Electrochim. Acta 50, 1405 (2005)</td>
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<td>0.003-0.024 g/l 0.2 Na₃Cit 0.3</td>
<td>-1.35...1.45 V vs SCE</td>
<td>8.0</td>
<td>RT</td>
<td>5-42</td>
<td>low</td>
<td>E. Beltowska-Lehman, Phys. Stat. Sol. 5 (11), 3514 (2008)</td>
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<td>0.01-0.1 g/l 0.01-0.1 Na₃Cit 0.02</td>
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<td>30</td>
<td>4.0</td>
<td>25</td>
<td>32 at%</td>
<td>n/a</td>
<td>L.S. Sanches, S.H. Domingues, A. Carubelli, L.H. Maskaro, J. Braz. Chem. Soc. 14 (5), 556 (2003)</td>
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<td>4</td>
<td>For NiMoFe: 5-15 g/l 50 g/l Na₃Cit 10 g/l</td>
<td>K₄P₂O₇ 250 g/l FeSO₄ 20 g/l NH₄OH for pH</td>
<td>60</td>
<td>8.5</td>
<td>30</td>
<td>Mo-25 Fe-7 wt%</td>
<td>n/a</td>
<td>L. Huang, F.Z. Yang, S.G. Sun, S.K. Xu, S.M. Zhou, Chin. J. Chem. 21, 382 (2003)</td>
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For NiW alloy electrodeposition, in some cases researchers utilized oxalate instead of citrate and added organic components (glycine, triethanoloamine, etc.) in order to achieve better quality of the deposit or higher value of current efficiency. Current densities applied to deposit NiW alloys were in the range of 5 to 200 mA/cm² and up to 300 mA/cm² when using pulse current. The pH of the solution for different electrolytes varied between 1.9 and 10. Deposition was conducted at both room temperature and high temperatures up to 85 °C. Under those conditions it was possible to deposit NiW thin films with W content 5 to 55 wt %, current efficiency being 8 to 96 % depending on the conditions of the process and composition of the NiW coating.

Majority of the electrolytes for NiMo alloy electrodeposition contain the same main components as solutions for NiW thin films, namely sodium molybdate and nickel sulfate as sources of Mo and Ni and trisodium citrate as a complexing agent. Almost in all studies ammonia was added as well. Reported current densities applied to deposit NiMo alloy are higher than those for NiW alloy, starting from 30 mA/cm². Deposition was usually carried out under room temperature and at pH values 8.0 to 10.5. For the most of NiMo deposits Mo content did not exceed 42 at % which was about 55 wt %. Faradaic efficiency for electrodeposited NiMo films was found to be extremely low.

To the best of our knowledge, studies on electrochemical deposition of the ternary NiWMo alloy thin films have not been reported yet. There are very few publications on NiWMo catalyst applications, but those materials were not prepared by electrodeposition and had low content of refractory metals in them. For instance, ultradispersed NiWMo catalyst was made from emulsified metallic aqueous solutions. Wang et al. developed NiWMoB films of 50-100 nm with superior thermal stability by electroless deposition.
2.3 Nanowires containing iron-group metals and refractory metals

There are very few publications found on the fabrication of nanostructures containing Fe, Co, or Ni and W or Mo, and most of those materials were not made by electrodeposition. For example, single W nanowires prepared by selective etching of NiAlW alloy were suggested to be used as pH sensitive electrodes.\textsuperscript{34} Zhang et al.\textsuperscript{35} reported on electroless deposition of NiWP nanowire arrays as materials for ultra-high-density magnetic recording.

Podlaha et al.\textsuperscript{36,37} reported about electrodeposition of FeCoNiCu nanowires and nanotubes for giant magnetoresistance. Nanowires were deposited into the template with the stated pore size of 10 and 50 nm and 60 µm length. Current density value applied was up to 100 mA/cm\textsuperscript{2}. Nanotubes were deposited into 20 nm pores with 60 µm length. Electrolyte temperature had a pronounced effect on whether nanowires or nanotubes were electrodeposited under pulsed potential conditions.

In another paper Podlaha et al.\textsuperscript{38} reported on fabrication of CuNiW thin films, nanostructured multilayers and nanowires. Electrolyte used in this study contained sodium trisodium citrate 0.6 M, sodium tungstate 0.2 M, nickel sulfate 0.3 M, and variable concentration of copper sulfate (0.03 M, 0.01 M, and 0.003 M) at pH of 8 adjusted by ammonium hydroxide at temperature 70 °C. Nanowires were electrodeposited into membranes with pore diameter of 200 nm and 60 µm length. The W content achieved in CuNiW nanowires was 31 wt %. Current densities applied were up to 35-38 mA/cm\textsuperscript{2}. Current efficiency varied from 20 to 100 %.

The publications dedicated to the nanowires of either NiW or NiMo composition were not found in the scientific literature so far.
3.0 Experimental

The experimental part of the study consists of the electrodeposition of NiW, NiWMo, and NiMo alloys; the determination of thickness and compositions of the deposits; fabrication of NiW nanowires; investigation of NiW nanowires morphology; and examination of NiW nanowires’ mechanical robustness.

3.1 Electrodeposition of NiW, NiWMo, and NiMo alloy thin films

NiW, NiWMo, and NiMo alloys were deposited from electrolytes of the composition provided below. The electrodeposition was performed in a standard three electrode cell. A platinum mesh was used as a counter electrode for all experiments. A saturated calomel electrode (SCE) was utilized as a reference electrode. Deposition was carried out for 30 min. All solutions were used at room temperature which was 22-23 °C. The volume of the electrolytes in which the electrodeposition was carried out was 0.5 dm³. No agitation was utilized.

NiW, NiWMo, and NiWMo thin films were deposited onto copper foil substrates. The pre-experimental preparation of the substrate consisted of etching in a sulfuric acid solution for 10-15 s in order to remove any copper oxides, followed by rinsing with water, drying with filter paper and weighing. Weighing was done before and after deposition to calculate current efficiency through Faraday’s law. The shape of the substrate was square, 2×2 cm dimension. One side of the copper substrate was covered by insulating tape and the other one was turned in the direction of the anode in order to avoid large variations in local current distribution.
All the chemicals utilized, including deionized water, to prepare the solutions for electrodeposition were purchased from Fisher Scientific, Inc. Sodium hydroxide and sulfuric acid were used to correct the pH of the solution. The pH value was controlled by a pH/mV meter AP62 (Accumet AP Series from Fisher Scientific). The electrodeposition was conducted galvanostatically using a Solartron (model SI 1287) potentiostat/function generator. Deposit thickness and composition were analyzed with a KEVEX Omicron energy dispersive X-ray fluorescence analyzer (XRF). Further thickness values obtained from the XRF were compared with the thickness of the deposit calculated through the change in mass and composition/density of the film; and the last value was used when describing the results of this work. XRF analysis of each sample was done in 5 points in order to obtain the average value for the thickness and composition of the deposit as well as standard deviation. Standard deviation values were not represented in the figures since they did not influence the trend significantly. For low applied current densities (2 to 100 mA/cm$^2$) the calculated standard deviation value for metal content was about 0.5-1 wt % and for high current densities (200-700 mA/cm$^2$) 2-3 wt %.

NiW alloy thin film was deposited from the electrolyte of composition (M): sodium tungstate dihydrate 0.15; nickel sulfate hexahydrate 0.1; trisodium citrate 0.375; boric acid 1.0; pH 7.0±0.1.

NiWMo alloy thin films were deposited from the electrolytes of composition (M):

a) when Mo:W ratio was 1:1. Sodium tungstate dihydrate 0.075; sodium molybdate dihydrate 0.075; nickel sulfate hexahydrate 0.1; trisodium citrate 0.375; boric acid 1.0; pH 7.0±0.1 if other not stated;
b) when Mo:W ratio was 3:1. Sodium tungstate dihydrate 0.0375; sodium molybdate dihydrate 0.1125; nickel sulfate hexahydrate 0.1; trisodium citrate 0.375; boric acid 1.0; pH 7.0±0.1 if other not stated;

c) when Mo:W ratio was 1:3. Sodium tungstate dihydrate 0.1125; sodium molybdate dihydrate 0.075; nickel sulfate hexahydrate 0.1; trisodium citrate 0.375; boric acid 1.0; pH 7.0±0.1 if other not stated.

NiMo alloy thin film was deposited from the electrolyte similar to that for NiW deposition but with tungstate replaced for molybdate (M): sodium molybdate dihydrate 0.15; nickel sulfate hexahydrate 0.1; trisodium citrate 0.375; boric acid 1.0; pH 7.0±0.1.

### 3.2 Fabrication and examination of NiW nanowires

NiW nanowires were electrodeposited into 25 mm circle polycarbonate templates from Whatman (stated pore diameter 50 and 100 nm) and OsmonicsInc (stated pore diameter 10 nm). Actual NiW nanowires diameter did not correspond to the stated pore diameter and varied along the length of a nanowire which was about 6 µm. More details on NiW nanowire dimensions are presented in the results of the project.

In order to provide the electric contact to the membrane a layer of gold as sputtered on the one side of the template. Sputtering during 10 min was done using Hummer sputtering setup from Anatech Inc. This Au layer served as a cathode at the beginning of the deposition. The template with the sputtered Au layer was then fixed on the stationary holder (Fig.1) exposing a circle area of 2.5 cm². For all experiments the cathodic current applied was -9.82 mA. This value was taken from the results obtained for NiW thin films to provide current density of about 25-30 mA/cm² in order to achieve the highest possible W content in NiW nanowires. The wide range of porosity of
membranes given by manufacturers makes the calculation of actual applied current density approximate.

![Diagram of the cell for the electrodeposition of NiW nanowires. Schematic is taken from M. Guan PhD dissertation, Louisiana State University, 2008](image)

**Figure 1: Schematic of the cell for the electrodeposition of NiW nanowires. Schematic is taken from M. Guan PhD dissertation, Louisiana State University, 2008**

Upon deposition, the polycarbonate membrane was dissolved in dichloromethane, thus releasing NiW nanowires into the solution. Experiments on corrosion resistance of NiW thin films in dichloromethane showed that this dissolvent does not affect the deposit but dissolves polycarbonate membrane very well.

The shape and morphology of NiW nanowires then was examined by electron microscopy, both transition (TEM) and scattering (SEM). The SEM analysis was conducted with a JEOL JSM-840A microscope, operated at 5 kV. The TEM imaging was
made by JEM-100CX operated at 80 kV. Qualitative composition analysis was obtained with an energy dispersive X-ray (EDX) detector option in the SEM.

NiW nanowires were deposited under direct current and pulse current. When pulsing, for the majority of experiments the on-time was 1 s and the off-time was 1.5 s. When varying frequency (number of cycles per unit time, 1/s or Hz) and keeping the duty cycle (portion of on-time to the cycle duration) constant, the on-time used was 10 s and 100 s, and the off-time was 15 s and 150 s, respectively. Usually deposition took from 2 h to about 6 h to fill the pores with NiW alloy completely. When there was a potential response on E-I dependence, indicating that NiW started depositing on the top of the membrane, the deposition was stopped.

In order to test NiW nanowires mechanical robustness they were treated by ultrasound during 3 h (BRANSON 1510 Ultrasonic cleaner). The initial assumption for this kind of experiment was that cavitation resulted from ultrasound would break NiW nanowires apart depending on their mechanical robustness.
4.0 Results and Discussion

4.1 Electrodeposition of NiW, NiWMo, and NiMo thin films

In this section the conditions for electrodeposition of NiW alloys with added Mo, and, with and without W, are presented. The composition of electrolytes and the recommended operating conditions, e.g., applied current density, are discussed.

4.1.1 NiW alloy deposition

Electrolytes for the electrochemical deposition of NiW alloys having tungsten deposit content from 5 to 55 wt % were adapted from Sakhnenko’s group. The component concentrations were: nickel sulfate hexahydrate NiSO₄·6H₂O – 0.1 M, sodium tungstate dihydrate Na₂WO₄·2H₂O – 0.15 M, trisodium citrate dihydrate Na₃C₆H₅O₇·2H₂O - 0.375 M, and boric acid H₃BO₃ – 1 M; pH was adjusted to 7.0 by sodium hydroxide or sulfuric acid.

Fig. 2 shows the resulting composition and current efficiency of deposits galvanostatically plated at a constant time of 30 min in unstirred, quiescent conditions. The resulting composition was relatively high in tungsten content in the NiW alloy while maintaining a reasonable value of current efficiency. Higher current density favors higher tungsten content in the deposit and at the same time diminishes both nickel weight percentage and current efficiency. The later changes in the range of 63 to 7 %, attributed to an increase in the side reaction rate of hydrogen evolution (thermodynamically possible side reaction for given conditions). This phenomenon decreases the overall current efficiency for the deposition of NiW alloys, but has the advantage of producing high W wt % deposits.
Figure 2: Dependence of W and Ni content in NiW alloy and current efficiency on applied current density

Nevertheless, the low efficiency is expected since NiW alloys are noted to catalyze electrolytic hydrogen production. The drop in current efficiency when raising the current density from 2 to 50 mA/cm² is explained by the electrolytic decomposition of water, requiring the potential to exceed -1.23 V vs normal hydrogen electrode at standard conditions (or -0.988 V vs SCE). The deposition potential does reach the value of water decomposition and the hydrogen evolution rate increases significantly, making current efficiency lower (Fig. 3). Also, analysis of partial current densities of alloy forming metals demonstrates that at current density values higher than 10 mA/cm² more current is used to reduce the refractory element, tungsten, characteristic of a kinetically controlled reaction. The partial current density of Ni reaches a limiting value at potentials greater than 1.6 V vs SCE.
Figure 3: Partial current densities for W and Ni in NiW alloy

The rate of deposition of NiW alloys increases linearly in the range of current density from 2 to 20 mA/cm² having value 1.22-2.45 µm/h, going up only to 2.8 µm/h when further increasing current (Fig. 4). Applying higher current density higher than 20 mA/cm² up to 50 mA/cm² slightly increases tungsten content in the NiW alloy (54 to 58 wt %) (Fig. 2), while decreasing current efficiency 15 to 7 %.

In the attempt of achieving higher W content in NiW alloy the value of current density was increased significantly up to 700 mA/cm². When increased higher than 50 mA/cm² current density favors Ni electroreduction instead of W, as shown in Figs. 5 and 6. Current efficiency diminishes dramatically to less than 3 %. The only positive change for these conditions is that deposition rate goes up from 2.8 to 16 µm/h which is beneficial in terms of time economy when depositing NiW alloy electrochemically (Fig. 7).
Figure 4: Dependence of deposition rate on applied current density when depositing NiW alloy in the range of applied current densities of 2-50 mA/cm².

Figure 5: Dependence of W and Ni content in NiW alloy and current efficiency on applied current density in the range of applied current densities of 10-700 mA/cm².
Figure 6: Partial current densities for W and Ni in NiW vs potential in the range of applied current densities of 10-700 mA/cm².

Figure 7: Dependence of deposition rate on applied current density when depositing NiW alloy in the range of applied current densities of 10-700 mA/cm².
A plot of the logarithm of partial current densities for Ni and W in NiW alloys shows that the dependence is not linear and therefore the whole electrodeposition process for both Ni and W is not a straightforward single kinetic reaction. For W, there is a kinetic reaction governing the rate at noble potentials, a decrease in the rate at intermediate potentials and then an increase again, that is characteristic of a kinetic control. The slopes of the kinetic regions are 1.27 and 0.74 V\(^{-1}\) (Fig. 8). The regions of low (1-1.5 V) and very high (5-7 V) potentials for Ni reduction is to be linear and have Tafel slopes of 0.42 and 0.58 V\(^{-1}\). The potential was not corrected for ohmic drop.

![Log of partial current density of Ni and W during NiW alloy deposition](image)

Figure 8: Dependence of Log of partial current density of Ni and W during NiW alloy deposition

Taking into account results obtained for the electrolyte under consideration, the conditions for NiW nanowire electrodeposition was estimated to be at a current density of 30 mA/cm\(^2\), used to guarantee high tungsten content in the deposits and keeping current efficiency as high as possible without changing its composition.
4.1.2 NiWMo alloy deposition

The electrolyte for NiWMo electrodeposition was developed on the basis of the solution for NiW alloy deposition with the addition of Mo salt. The concentration of the refractory metals Mo:W in the electrolyte was varied in the ratios of 1:1, 1:3, and 3:1.

4.1.2.1 Mo:W ratio 1:1

In the electrolyte for NiW alloy deposition the concentration of tungstate was 0.15 M. This concentration was divided between the two refractory metals: W (0.075 M) and Mo (0.075 M) in order to deposit NiWMo alloy. The remaining components of the electrolyte were the same as the NiW bath: nickel sulfate hexahydrate NiSO₄·6H₂O – 0.1 M, trisodium citrate dihydrate Na₃C₆H₅O₇·2H₂O - 0.375 M, and boric acid H₃BO₃ – 1 M. pH was kept constantly 7.0.

A broad variation of applied current was chosen from previous results obtained for rotating cylindrical electrode. In the condition of no stirring there is no reason to use current density higher than 300 mA/cm² since further increasing of current density is not useful neither in terms of W and Mo content in the deposit nor for current efficiency.

The results of the galvanostatic deposition are shown in Fig. 9. It was possible to deposit thin films of NiWMo alloy with up to 75 wt % of refractory metals in them, namely Mo 60-67 wt % and W 3-9 wt %. For all potentials, applied partial current densities for Mo are higher than for Ni and W (Fig. 10). The electrochemical equivalent of Mo is 0.597 g/(mol·eq), which is lower than 1.143 g/(mol·eq) for W and 1.095 g/(mol·eq) for Ni. That is why high molybdenum content inevitably results in lower current efficiency.
Figure 9: Dependence of W, Ni, Mo, and Mo+W content in NiWMo alloys with applied current density. Mo:W=1:1

For the investigated range of current densities it was extremely low – 1-11 %, which is understandable taking into consideration very negative potential corresponding high values of current density (Fig. 11). Tafel slopes (Fig. 12) for W, Ni, and Mo in NiWMo alloy with Mo:W ratio 1:1 are listed in Table 1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Tafel slope, V⁻¹</th>
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<tbody>
<tr>
<td>W</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.07</td>
</tr>
<tr>
<td>Mo</td>
<td>0.05</td>
</tr>
<tr>
<td>W</td>
<td>1.06</td>
</tr>
<tr>
<td>Ni</td>
<td>1.33</td>
</tr>
<tr>
<td>Mo</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Table 1: Tafel slopes for W, Ni, and Mo in NiWMo alloy. Mo:W ratio 1:1
Figure 10: Partial current densities of W, Ni, and Mo during NiWMo alloy deposition. Mo:W=1:1

Figure 11: Dependence of deposition rate, deposition potential, and current efficiency on applied current density when depositing NiWMo alloy. Mo:W=1:1
There are two regions where the dependence of Log of partial current densities for W, Ni, and Mo vs potential is linear, so there are also two values of the Tafel slopes for metals reported.

4.1.2.2 Mo:W ratio 1:3

The ratio of refractory metal salts concentration was kept 1 to 3. In one case, more W was in the electrolyte, and in the other more Mo. For the electrolyte of composition (M) NiSO$_4$·6H$_2$O 0.1, Na$_2$WO$_4$·2H$_2$O 0.1125, Na$_2$MoO$_4$·2H$_2$O 0.0375, Na$_3$C$_6$H$_5$O$_7$·2H$_2$O 0.375, H$_3$BO$_3$ 1. pH 7.0, where c(Mo)/c(W)=1/3, the tungsten content also was found to be much lower in comparison with Mo weight percentage – 7-17 wt % vs 45-58 wt % (Fig. 13).
Figure 13: Dependence of W, Ni, Mo, and Mo+W content in NiWMo alloys with applied current density. Mo:W=1:3

A summation of refractory metal contents gives a lower number than for a previously discussed case of 1 to 1 ratio of W and Mo salts in the electrolyte. It is interesting that for the electrolyte of composition under consideration the shape of dependences of partial current densities of tungsten, molybdenum, nickel and NiWMo alloy differs from that for 1:1 ratio of Mo:W solution (Fig. 14). Curves for Ni, Mo, and NiWMo have extremes (both minimums and maximums) for current density values of 200, 350, and 500 mA/cm². Yet, for Mo current density is much higher than for W or Ni.

The highest value of the current efficiency was achieved when applying low current densities 2 to 50 mA/cm², while the deposition rate goes up with current (Fig. 15). Yet, the quality and appearance of the NiWMo deposits plated under low current densities suggests formation of oxides of refractory metals.
The formation of oxides may happen due to partial reduction of $\text{WO}_4^{2-}$ and $\text{MoO}_4^{2-}$ from the solution. Indeed, the complete reduction to a metallic state requires the transfer of 6 electrons for both W and Mo, which is an energy-consuming process and might require higher than usual values of applied potentials or current densities.

Fig. 16 shows that the electrochemical stage of the process is not the only limiting reaction (the dependence is not linear). For potentials 1-3 V, Tafel slopes for metals are: 0.64 $\text{V}^{-1}$ for W, 0.46 $\text{V}^{-1}$ for Ni, and 0.60 $\text{V}^{-1}$ for Mo. Deposition of NiWMo alloy under potentials higher than 3 V leads to the nonlinear dependence of the logarithm of partial current densities of alloy-forming metals versus potential.
Figure 15: Dependence of deposition rate, deposition potential, and current efficiency on applied current density for NiWMo alloy. Mo:W=1:3

Figure 16: Dependence of Log of partial current density of W, Ni, and Mo during NiWMo alloy deposition. Mo:W=1:3
4.1.2.3 Mo:W ratio 3:1

Increasing Mo salt concentration 3 times and lowering accordingly the concentration of W salt in the electrolyte, keeping the total concentration of refractory metals in the solution constant, at 0.15 M, allows for achieving Mo content in the NiWMo alloy 65-70 wt % (Fig. 17).

Figure 17: Dependence of W, Ni, Mo, and Mo+W content in NiWMo alloy on applied current density. Mo:W=3:1

The deposits are even, solid and continuous, of a good overall quality. In comparison with the electrolyte with c(Mo)/c(W)=1/3, the 3-times lowering in W concentration in the solution leads to less W in the final deposit 1-13 wt % instead of 7-17 wt %. Nevertheless, the total W+Mo percentage in the deposit turns out to be even higher – up to 78 wt %.
The partial current density curve shape exhibits a behavior between those for electrolytes with Mo:W=1:1 and Mo:W=1:3 (Fig. 18). Overall, partial current densities for W, Mo, Ni, and Mo+W goes up with potential, similar to Mo:W=1:1, and Mo:W=1:3.

Figure 18: Partial current densities for W, Ni, and Mo during NiWMo alloy deposition. Mo:W=3:1

For the case where Mo:W=3:1, the current efficiency drops significantly when increasing current density from 10 to 50 mA/cm² (Fig. 19). Higher current density provides nearly the same Mo content as a lower value. There is a change in the deposit composition that does not coincide with the same change in the electrolyte composition. The higher Mo content occurs at the lower rate of deposition. The Tafel slopes for metals for low potentials are: 0.01 V⁻¹ for W, 0.35 V⁻¹ for Ni, and 0.35 V⁻¹ for Mo (Fig. 20).
Figure 19: Dependence of deposition rate, deposition potential, and current efficiency on applied current density when depositing NiWMo alloy. Mo:W=3:1

Figure 20: Dependence of Log of partial current density for W, Ni, and Mo in NiWMo alloy vs potential. Mo:W=3:1
Since it was established earlier that lower current densities favor both higher Mo+W content and current efficiency, the electrodeposition of NiWMo alloys was conducted under 5 mA/cm$^2$ for solutions with Mo:W ratio 1:1, 1:3, and 3:1, as well as for solution without W (represented by point Mo:W=10:1). Results of those experiments are presented in Figs. 21 and 22. Interesting, a Mo:W ratio of 3:1 (0.1125 M to 0.0375 M) in the electrolyte gives only 5 % higher content of Mo in comparison with Mo:W=1:3, namely 65 instead of 60 wt %, while solution containing 0.15 M of Na$_2$MoO$_4$ and without any tungstate in it provides deposits with up to 74 wt % of Mo.

Current efficiency seems to be significantly higher than that for current densities greater than 50 mA/cm$^2$, but it is likely that this growth is due to the formation of oxides of molybdenum instead of metallic state as suggested by the appearance of the deposited films. Those plated using current densities higher than 100 mA/cm$^2$, starting from 200 mA/cm$^2$, look smooth, compact, even and solid. Those obtained using lower current densities have significantly worse overall quality.

The deposition rate seems to be determined less by the ratio of Mo:W salts concentration or deposition potential but rather by Mo+W content in the deposit. Indeed, for Mo:W ratio 1:3 the content of refractory metals in the film is about the same as for no-W solution containing 0.15 M of sodium molybdate only, even though for Mo:W ratio 1:3 Mo along content is lower than that for Mo-containing bath (Fig. 22).
Figure 21: Dependence of W, Ni, Mo, and Mo+W content in NiWMo alloy and current efficiency on Mo:W ratio. pH 7. Current density 5 mA/cm$^2$.

Figure 22: Dependence of deposition rate and potential on Mo:W ratio. pH 7. Current density 5 mA/cm$^2$. 

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Summarizing the results described above, it is observed that the increase in Mo salt concentration in the electrolyte, while lowering W, leads to a higher Mo content in the deposit. This increase in deposit Mo wt %, however, is not in the same proportion as the change in the salt concentration, indicating a coupled reaction mechanism. For example, the growth of c(Mo) from 0.0375 M to 0.075 M, an increase by a factor of 2, allows for reaching Mo weight percentage in the deposit from 65 to 69 wt %, only a factor of 1.1 (Fig. 23). Note that dependences from Fig. 23 and 24 were for the solutions with pH 5.0.

![Figure 23: Dependence of W, Ni, and Mo content in NiWMo alloy on the ratio of refractory metals concentrations in the electrolyte. C(Na$_2$MoO$_4$·2H$_2$O) 0.0375, 0.075, and 0.1125. pH 5.0. Current density 100 mA/cm$^2$. (Point c(Mo)/c(W)=10 represents case with no W in the solution)](image)

Thus, the increase in Mo salt concentration in the solution leads to a decrease of W content in the deposit but also to the more significant growth of Mo content, so overall the combined Mo+W content also increases with Mo salt concentration. The effect has more influence for Mo:W ratio 1:3 to 1:1, than 1:1 to 3:1.
Figure 24: Dependence of deposition rate, deposition potential, and current efficiency on the ratio of refractory metals concentrations in the electrolyte. $c(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O})$ 0.0375, 0.075, and 0.1125. pH 5.0. Current density 100 mA/cm$^2$. (Point $c(\text{Mo})/c(\text{W})=10$ represents case with no W in the solution)

The pH 5 electrolyte provides slightly higher current efficiency than pH 7. The deposition potential is not influenced by $c(\text{Mo})/c(\text{W})$ significantly and becomes a bit more positive with the increase of Mo concentration, while the rate of deposition decreases almost two times with higher $c(\text{Mo})$ (Fig. 24). The addition of Mo to the solution for NiW alloy electrodeposition reduces the partial current density for W (Fig. 25), and the higher the concentration of Mo in the electrolyte the lower the W partial current density (Fig. 26). With the addition of Mo in an amount of 3 times less than W concentration, namely, 0.0375 M of sodium molybdate and 0.1125 M of sodium tungstate, leads to a lower partial current density for W. Further increasing Mo concentration in the solution to 0.1125 M along with a lowering of the tungstate concentration to 0.0375 M results in a diminished W partial current density.
Figure 25: Partial current densities for W during NiW and NiWMo alloy depositions (see Fig. 26 for dependences for W in NiWMo alloy)

Figure 26: Partial current densities of W during the deposition of NiWMo alloys with varied Mo:W ratio in the electrolyte
4.1.3 NiMo alloy deposition

In order to develop the electrolyte for NiMo, the solution for NiW thin film plating was utilized. The concentration of Na$_2$WO$_4$·2H$_2$O 0.15 M was used as a starting point, and the same conditions (electrolyte composition, current density, and pH) were applied to deposit NiMo alloy.

Results obtained for NiMo thin films are similar to those for NiWMo alloys. The increase of current density leads to a lower content of refractory metal in the deposit (Fig. 27). The highest achievable Mo weight percentage is 77-81 wt % which is approximately the same as the total content of W and Mo in NiWMo thin films. The highest Mo content and current efficiency are reached when current density is below 50 mA/cm$^2$ (Fig. 28). For this region the potential of deposition is similar to that when depositing NiW and NiWMo alloy thin films. Current efficiency and the rate of deposition are significantly lower in comparison with those values for NiW.

Partial current density for Mo is much higher than for Ni and it goes up when applied potential is higher than 4 V with corresponding current densities higher that 200 mA/cm$^2$ (Fig. 29). A semi-log plot of partial current densities for Ni and Mo in NiMo alloys show that electrochemical discharge is not the only rate limiting reaction (Fig. 30). The Tafel slopes for low potentials are: 0.56 V$^{-1}$ for Mo and 0.44 V$^{-1}$ for Ni; the Tafel slopes for high potentials are: 0.54 V$^{-1}$ for Mo and 0.76 V$^{-1}$ for Ni.

It is interesting that addition of W to the solution changes the shape of the dependences of partial current densities as a function of potential for Mo. There is a maximum of partial current density for Mo at potential -4 V or applied cathodic current density 200 mA/cm$^2$ when Mo:W ratio is 1:3, which justifies the assumption that W
enhances the Mo deposition in NiWMo alloy, even when the concentration of W salt is 3 times higher than that for Mo (Fig. 31). At the same time, when Mo:W ratio is 1:1 or 3:1, there are no peaks near the potential value of -4 V (Fig. 32). In comparison with Mo:W ratios 1:3 or 3:1, Mo:W ratio 1:1 allows achieving higher partial current density values for Mo up to 5 mA/cm² when applying high current densities (500-700 mA/cm²) and lower when current densities 10-350 mA/cm² are used. This behavior supports the assumption about coupled mechanism of W and Mo electrochemical reduction.

4.1.3.1 The role of trisodium citrate

In an attempt to increase Mo content in the NiMo alloy and current efficiency of the process, the influence of trisodium citrate as a complexing agent was studied (Fig. 33, 34). Results suggest that the increase of citrate concentration c(Cit) from 0.375 M to 0.5 M does not change the NiMo alloy composition (for conditions used). At the same time, when c(Cit) is higher the deposition potential goes up from 2.33 V to 2.55 V vs SCE, resulting in lower current efficiency (0.77 vs 1.68 %) and rate of deposition (0.5 vs 1.11 µm/h). In the future it might be reasonable to try to deposit NiMo alloy thin films from the electrolyte under consideration but with even lower trisodium citrate concentration (<0.375 M) in order to increase current efficiency of the process. However, lowering the citrate concentration may compromise the amount of Mo found in the deposit.
Figure 27: Dependence of Ni and Mo content in NiMo alloy on current density. pH 7.0

Figure 28: Dependence of deposition rate, deposition potential, and current efficiency on applied current density when depositing NiMo alloy. pH 7.0
Figure 29: Partial current densities for Mo and Ni in NiMo alloy vs potential

Figure 30: Dependence of Log of partial current density for Mo and Ni in NiMo alloy vs potential
Figure 31: Partial current densities for Mo in NiMo and NiWMo with Mo:W=1:3 alloys vs potential

Figure 32: Partial current densities for Mo in NiWMo alloys with Mo:W=1:1 and 3:1 vs potential
Figure 33: Dependence of Mo and Ni content on trisodium citrate concentration when depositing NiMo alloy. pH 7.0. Current density 100 mA/cm²

Figure 34: Dependence of deposition rate and potential and current efficiency on trisodium citrate concentration when depositing NiMo alloy. pH 7.0. Current density 100 mA/cm²
4.1.3.2 The pH influence

Another way to influence an alloy composition is varying the pH of electrolyte. It is known that the NiW system is extremely sensitive towards the solution pH. For NiW and CoW alloy thin films the highest W content is achieved when pH is 7.0.\textsuperscript{40} In contrast, for the NiMo system it turns out that the pH of the electrolyte does not play any significant role when trying to change Mo content, but is a very important tool to control current efficiency and the rate of deposition (Fig. 35, 36). Indeed, in the range of pH from 4 to 8 Mo content remains stable – about 80 wt %, as well as deposition potential, while current efficiency and rate of deposition reach their maximum values at pH 4 to 5. In combination with the information on how current efficiency and components concentrations influence W and Mo content in NiWMo and NiMo thin films and current efficiency, pH influence gives an idea on how to achieve desirable alloy composition and current efficiency.

To achieve high Mo content in NiMo alloy and Mo+W content in NiWMo alloy it is reasonable to conduct electrodeposition at current densities below 50 mA/cm\textsuperscript{2} having pH 5.0 in order to provide high Mo content and as high as possible current efficiency. At this point it is not clear why Mo deposits easier than W from the electrolyte under consideration, resulting in higher Mo content in comparison with W content in both NiW and NiWMo system, from the same electrolyte. One factor that may influence this behavior is that the citrate ligand may complex with WO\textsubscript{4}\textsuperscript{2−} stronger than that of MoO\textsubscript{4}\textsuperscript{2−}. It is known\textsuperscript{41,42} that citrate can complex with both WO\textsubscript{4}\textsuperscript{2−} and MoO\textsubscript{4}\textsuperscript{2−}. Another possible explanation is that the boric acid not only plays a role as a buffering agent, but also may participate in the process of complex formation in an undetermined way.
Figure 35: Dependence of Mo and Ni content on pH when depositing NiMo alloy. Current density 100 mA/cm$^2$.

Figure 36: Dependence of deposition rate and potential and current efficiency on pH when depositing NiMo alloy. Current density 100 mA/cm$^2$. 
4.2 Electrochemical deposition of NiW nanowires

NiW nanowires of varied diameter and 6 µm in length were deposited from the electrolyte described earlier for NiW thin film electrodeposition. Galvanostatic deposition was carried out applying direct and pulse current of the same amplitude into nanoporous membranes.

4.2.1 Electrochemically deposited NiW nanowires: low magnification view

The analysis of low magnification TEM images of electrochemically deposited NiW nanowires alloys is shown in Fig. 37, 38. NiW nanowires from the Fig. 37 were deposited under direct current of 9.82 mA. Nanowires from Fig. 38 were fabricated using pulse current of the same amplitude of 9.82 mA, on-time and off-time being 1 s and 1.5 s. All nanowires were deposited into pores of polycarbonate membranes. Those with diameter of pores 50 nm and 100 nm were purchased from Whatman, and membranes with 10 nm pores were from OsmonicsInc. The length of both kinds of membranes was 6 µm. Upon deposition, NiW nanowires were released into the solution of dichloromethane and then investigated by electron microscopy – scanning and transmission – in order to examine their shape, morphology, and dimensions.

The resulting wires tended to stick together forming agglomerates and arrange themselves into arrays, reflecting that they are ferromagnetic. The tendency to stay together was observed for NiW nanowires deposited by both direct (Fig. 37) and pulse (Fig. 38) current, having a composition of 52.4 wt % and 50.4 wt % of tungsten, respectively, which suggests that this effect is not a result of deposition conditions but rather the composition.
Figure 37: TEM image of NiW nanowires: low magnification view. Membrane: Whatman Polycarbonate 100 nm. Direct current, I=9.82 mA. Tungsten content 52.4 wt %
Figure 38a: TEM image of NiW nanowires: low magnification view. Membrane: Whatman Polycarbonate 50 nm. Pulse current, I=9.82 mA, \( t_{\text{on}}=1 \) s, \( t_{\text{off}}=1.5 \) s. Tungsten content 50.4 wt %
Figure 38b: TEM image of NiW nanowires: low magnification view. Membrane: Whatman Polycarbonate 50 nm. Pulse current, I=9.82 mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 50.4 wt %
4.2.2 Electrodeposition of NiW nanowires using direct current

NiW nanowires deposited under direct current 9.82 mA into membranes with stated pore diameter 100 nm and with an average tungsten content of 52.4 wt % are shown on Fig. 39a and 39b. The duration of the electrodeposition process was chosen to fill the whole pore volume till the very top of the membrane with the NiW alloy. The total length of nanowires was 6 µm, and it is obvious the pore was filled completely because of “hats” on the top of nanowires which reflect the formation of the NiW layer on the top of the membrane. The TEM imaging also shows that the diameter of the pores were not constant and varied in the range of approximately 90 to 250 nm, with thinner parts towards both end of a nanowire and thicker parts in the middle. It was surprising that the morphology of NiW nanowires deposited under direct current was bumpy (Fig. 39b), which would indicate a type of modulation during electrodeposition. The origin of those bumps needed clarification – either it was a result of a pore shape, or electrodeposition mode, or combination of both. The dimensions of bumps were accordingly: width 57-60 nm, height 20-50 nm.

SEM imaging supported the observation of bumpy morphology of NiW nanowires deposited even under direct current (Fig. 40a). This is a SEM image of the same sample of NiW nanowires as shown on Fig. 39a and 39b, but under magnification 50 000 instead of 4000 and 15 000 used TEM images on Fig. 39a and 39b. SEM features allow demonstration of the bumpy morphology of electrodeposited NiW nanowires to be even more obvious in comparison with TEM pictures of the same nanowires. Definitely, even when deposited under direct current, NiW nanowires possess very bumpy structure, and that structure has continuous nature through the whole length of the nanowires.
Figure 39a: TEM image of NiW nanowires: the whole length. Membrane: Whatman Polycarbonate 100 nm. Direct current I=9.82 mA. Tungsten content 52.4 wt%
Figure 39b: TEM image of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Direct current I=9.82 mA. Tungsten content 52.4 wt%
Figure 40a: SEM images of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Direct current I=9.82 mA. Tungsten content 52.4 wt %

SEM images taken under high magnification up to 100,000 times allowed measuring the dimensions of a single NiW nanowire more precisely (Fig. 40b). It is easy to see that a NiW nanowire is not a solid smooth continuous structure but a number of well-defined segments with width of about 140-150 nm and height of 200-210 nm. At this point of the study it was easy to assume that this segmental structure would decrease the mechanical robustness of NiW nanowires, and further experiments have been conducted in order to examine the NiW nanowires mechanical robustness by means of ultrasonic treatment. The assumption consisted of the idea that NiW nanowires would break along their segments under ultrasound because of cavitation.
Figure 40b: SEM image of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Direct current $I=9.82$ mA. Tungsten content 52.4 wt %

If a NiW nanowire shown on Fig. 40b was deposited by pulse current, it would be logical to assume that the segmental structure resulted from the set of current pulses and pauses during on- and off-time. However, it is not so in the case of direct current – the current flows continually and there must not be any individual parts in a nanowire if the structure was defined only by the electrochemistry of the process. Therefore, there must be another explanation for this phenomenon. For example, if the electrodeposition process is controlled by transport limitations (which is very likely since when depositing nanowires one deals with deep recesses with extremely small diameter, creating an increase in diffusional resistance), then segments might result from the simultaneous
process of removing the products of chemical and electrochemical interaction between species in the solution and the transport of new amounts of active species to the reaction site. As a part of his procedure, hydrogen evolution might influence the deposition of a NiW nanowire. This effect is possible to explain in several ways. First, the bubbles of evolving hydrogen from a side reaction may block the pore thus making transport to the cathode surface difficult. Second, atomic hydrogen forming on the cathode may participate in a chemical reaction of tungsten reduction (assumption about what was published earlier in paper on NiW alloy codeposition mechanism) that reaction having its own rate, however, at room temperature with little driving force for this reaction, it is unlikely. Third, hydrogen evolution definitely influences the pH of the environment where deposition itself takes place, and taking into account the extremely small size of the pore, this effect may be significant, perhaps related to the formation of the described segments.

According to calculations, the formation of one segment lasts about 3.2 min, which is about 77 pulses of current or 77 cycles, taking into consideration that the on-time is 1 s and off-time is 1.5 s. This time may come from the interaction of all the reactions and processes discussed above. To further investigate the effect of pulse plating on the nanowires the pulse parameters were varied.

4.2.3 Electrodeposition of NiW nanowires using pulse current of constant duty cycle

TEM images of NiW nanowires deposited using pulse current are shown in Fig. 41-43. Nanowires were deposited under the same conditions (same electrolyte and applied current) but in the membranes of varied pore diameter from 10 to 100 nm. If the bumps were related to pulsing, larger pores would deposit shorter lengths of material in a
given pulse and the bumps would appear more numerous, with smaller widths. If they
don’t, then there is another factor at play.

For all NiW nanowires deposited it turns out that their morphology is bumpy. The
actual size of those bumps (average) is provided in Table 2. As listed in Table 2, indeed
the size of the bumps changes with pore diameter. On the other hand, this effect is not
defined by the pore dimensions only, since for the same pore diameter but different
deposition conditions the bumpiness differs. Also, the widths and height of bumps goes
up with the diameter. In other words, the bigger diameter of a membrane pore the bigger
width and height of the bumps. Thus, the modulation does not coincide with the pulsing
parameters and is brought about by something inherent to the electrodeposition reaction
process. Since the bumps grow with pore diameter, this effect may be related to the
lowered diffusion resistance.

The tungsten content in NiW nanowires deposited into pores with diameter 50 and
100 nm (50 to 54 wt %) is slightly lower in comparison with that of NiW thin films (55 to
57 wt %). At the same time, for NiW nanowires fabricated in membrane with 10 nm pore
size tungsten content is found to be significantly lower – 33 wt %. This might be
explained by the fact that another membrane was used for this experiment (OsmonicsInc)
but the same current applied, and that the actual current density was a lot lower. The
manufacturer provides customers with details on these membranes giving a very broad
range of possible values of porosity making calculations of actual current density not
straight forward. Also, having a small pore diameter it is reasonable to expect deviations
from the results obtained for NiW thin films because of the significant difference in the
boundary layer thickness.
Figure 41a: TEM image of NiW nanowires: the whole length. Membrane: Whatman Polycarbonate 100 nm. Pulse current $I=9.82\ mA$, $t_{on}=1\ s$, $t_{off}=1.5\ s$. Tungsten content 49.6 wt %
Figure 41b: TEM image of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Pulse current I=9.82 mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 49.6 wt %
Figure 42a: TEM images of NiW nanowires: the whole length. Membrane: Whatman Polycarbonate 50 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 50.4 wt %
Figure 42b: TEM images of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbon 50 nm. Pulse current $I=9.82 \text{ mA}$, $t_{\text{on}}=1 \text{ s}$, $t_{\text{off}}=1.5 \text{ s}$. Tungsten content 50.4 wt %
Figure 43a: TEM images of NiW nanowires: the whole length. Membrane: OsmonicsInc Polycarbonate 10 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content $33.0$ wt %
Figure 43b: TEM images of NiW nanowires: bumpy morphology. Membrane: OsmonicsInc Polycarbonate 10 nm. Pulse current I=9.82 mA, $t_{\text{on}}=1$ s, $t_{\text{off}}=1.5$ s. Tungsten content 33.0 wt %
<table>
<thead>
<tr>
<th>Deposition mode</th>
<th>Pulse current</th>
<th>Direct current</th>
</tr>
</thead>
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<tr>
<td>“Stated” membrane diameter, nm</td>
<td>10 PC, 50 PC, 100 PC</td>
<td>100 DC</td>
</tr>
<tr>
<td>Actual nanowire diameter, nm</td>
<td>35-40, 60-160, 70-245</td>
<td>90-250</td>
</tr>
<tr>
<td>Bump width, nm</td>
<td>15-16, 20-40, 91-94</td>
<td>57-60</td>
</tr>
<tr>
<td>Bump height, nm</td>
<td>6-7, 17-21, 16-29</td>
<td>23-46</td>
</tr>
<tr>
<td>Tungsten content, wt %</td>
<td>33±2.5, 50.4±0.5, 49.6±0.7</td>
<td>52.4±0.2</td>
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<tr>
<td>Deposition time, hours</td>
<td>1.7, 5.0, 5.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

**Table 2: Variation in NiW nanowire dimensions with change of membrane diameter and deposition mode**

The estimated value of the current efficiency for the NiW nanowire deposition process was close to that for NiW thin films plated under direct current – 16-19 %. The very precise calculation of current efficiency is complicated because of lower W content in NiW nanowires in comparison with NiW thin films and the approximation of applied current density due to the wide range of porosity provided by manufacturer as a characteristic for the membranes used rather than definite value. The estimation for the current efficiency of NiW nanowires deposited under pulse current was not made since there are no data for those conditions for NiW thin films.
4.2.4 Electrodeposition of NiW nanowires using pulse current of varied frequency

NiW nanowires also were deposited into a membrane with 100 nm pore diameter under pulse current of varied frequency keeping the duty cycle (the ratio of on-time to the cycle time, cycle being on-time plus off-time) value of 0.4 constant. The on-time for these series of experiments was 10 s and 100 s, and corresponding off-time was 15 s and 150 s, resulting in frequency values of 0.04 and 0.004 Hz, respectively (note, frequency is determined as a number of cycles per unit time, and a cycle consists of on-time and off-time). The applied current density amplitude was the same as for deposition of NiW nanowires described earlier in this section, namely 9.82 mA, to provide an estimated current density of about 30 mA/cm².

NiW nanowires deposited under these conditions are demonstrated on Fig. 44 and 45. Table 3 summarizes how nanowire dimensions, composition and deposition time change with frequency of pulse current. The direct current for this analysis is approximated to the case when the ratio of on-time to off-time is infinitely big. The bump width and height increase with frequency (Table 3). A lower frequency pulse current results in a smoother morphology, or in other words, the bump height goes up with frequency in the range 0.004 to 0.4 Hz. Bump widths decrease and bump heights increase when using pulse current instead of direct current. Since duty cycle for pulse current is kept constant 0.4 for all experiments, the deposition time is about the same for all frequencies used and is lower when applying direct current because of the absence of off-time. For lower frequencies of 0.004 and 0.04 Hz current efficiency seems to be a bit higher than for 0.4 Hz, so the deposition time is shorter, possibly due to diminishing the mass transfer limitations during the pause of the pulse current. Tungsten content in NiW
nanowires deposited under direct current and pulse current of varied frequency is about the same 50-54 wt %.

Figure 44a: TEM images of NiW nanowires: the whole length. Membrane: Whatman Polycarbonate 100 nm. Pulse current I=9.82 mA, t_{on}=10 s, t_{off}=15 s. Tungsten content 51.5 wt %
Figure 44b: TEM images of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Pulse current $I=9.82$ mA, $t_{on}=10$ s, $t_{off}=15$ s. Tungsten content 51.5 wt %
Figure 45a: TEM images of NiW nanowires: the whole length. Membrane: Whatman Polycarbonate 100 nm. Pulse current $I=9.82\ mA$, $t_{on}=100\ s$, $t_{off}=150\ s$. Tungsten content 54.0 wt %
Figure 45b: TEM images of NiW nanowires: bumpy morphology. Membrane: Whatman Polycarbonate 100 nm. Pulse current I=9.82 mA, t_{on}=100 s, t_{off}=150 s. Tungsten content 54.0 wt %
<table>
<thead>
<tr>
<th>On-time/Off-time, s/s</th>
<th>∞</th>
<th>100/150</th>
<th>10/15</th>
<th>1/1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current frequency, Hz</td>
<td>0 (DC)</td>
<td>0.004</td>
<td>0.04</td>
<td>0.4</td>
</tr>
<tr>
<td>Bump width, nm</td>
<td>57-60</td>
<td>73-78</td>
<td>85-89</td>
<td>91-94</td>
</tr>
<tr>
<td>Bump height, nm</td>
<td>23-46</td>
<td>6-16</td>
<td>8-20</td>
<td>16-29</td>
</tr>
<tr>
<td>Tungsten content, wt %</td>
<td>52.4±0.2</td>
<td>51.5±0.8</td>
<td>54.0±1.5</td>
<td>49.6±0.7</td>
</tr>
<tr>
<td>Deposition time, hours</td>
<td>2.3</td>
<td>5.2</td>
<td>5.1</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Table 3: Variation in NiW nanowire dimensions, composition, and deposition time with change of frequency of pulse current

This composition of NiW alloy would correspond to current density values of 10 to 20 mA/cm² in a thin film (see Fig. 2), thus there is a difference of composition due to the nano-template. The NiW nanowire morphology indeed is a result of at least a couple of factors – membrane diameter and deposition conditions, namely, direct or pulse current, and frequency of current when applying pulsing.
4.3 Mechanical robustness of NiW nanowires: ultrasonic treatment

Nanowires electrodeposited with DC and pulsed conditions not subjected to ultrasonic agitation after they are released from their template, can have a wide variety of lengths which indicate that they can break. Figures 46, 47 show that there are fewer short wire pieces as the diameter of the structure increases. NiW nanowires deposited into pores of 50 and 100 nm remain whole upon membrane dissolution, while those released from the 10 nm pores size membrane are broken. Thus, the mechanical robustness of NiW nanowires was examined by observing whether the wires break or not under a long period of ultrasonic agitation.

To further investigate NiW nanowire mechanical robustness they were exposed to ultrasonic treatment for 3 hours. The assumption was that cavitation caused by ultrasound might result in breaking nanowires.

4.3.1 Mechanical robustness of NiW nanowires from 100 nm membrane

In Fig. 46a and 47a, NiW nanowires deposited into pores of membranes with 100 nm diameter using both direct (Fig. 46a) and pulse (Fig. 47a) current are whole upon release from the template. Their length is about 6 μm. On the other hand, when treated by 3 hours of ultrasound the NiW nanowires break to some extent (Fig. 46b and 47b). The degree of NiW nanowire the breakage is illustrated on Fig. 48 and 49. Most of the nanowires from membranes with 100 nm pore diameter withstand ultrasonic treatment, only few of them break creating pieces of initial nanowires with lengths from hundreds of nanometers to microns. Leftovers of initial NiW nanowires with the length less than 500 nm were not found for these set of experiments. Results suggest that for NiW
nanowires with diameters more than 100 nm the conditions of preparation play a secondary role with their dimensions to affect mechanical robustness.

**Figure 46a:** TEM image of NiW nanowires without ultrasonic treatment. Membrane: Whatman Polycarbonate 100 nm. Direct current I=9.82 mA. Tungsten content 52.4 wt %
Figure 46b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Whatman Polycarbonate 100 nm. Direct current I=9.82 mA. Tungsten content 52.4 wt %
Figure 47a: TEM image of NiW nanowires without ultrasonic treatment. Membrane: Whatman Polycarbonate 100 nm. Pulse current \( I = 9.82 \, mA \), \( t_{on} = 1 \, s \), \( t_{off} = 1.5 \, s \). Tungsten content 49.6 wt %
Figure 47b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Whatman Polycabonate 100 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 49.6 wt %
Figure 48: Normalized quantity of NiW nanowires with the length of x after ultrasonic treatment. Membrane: Whatman Polycarbonate 100 nm. Direct current $I=9.82$ mA. Tungsten content 52.4 wt %

Figure 49: Normalized quantity of NiW nanowires with the length of x after ultrasonic treatment. Membrane: Whatman Polycarbonate 100 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 49.6 wt %
4.3.2 Mechanical robustness of NiW nanowires from 50 nm membrane

From Fig. 50a, NiW nanowires deposited under direct current into membranes with a pore diameter of 50 nm upon membrane dissolution stay whole and do not break without external treatment. Note, for these NiW nanowires the electrodeposition process was stopped earlier resulting in nanowires having lengths of less than 6 µm. Upon ultrasonification smaller pieces of NiW nanowires were found as well (Fig. 50b).

NiW nanowires deposited into pore with diameter 50 nm but under pulse current are shown on Fig. 51a (without ultrasound) and 51b (after ultrasound). Tungsten content seems to be slightly (couple wt %) higher for nanowires deposited under direct current in comparison with wires fabricated by pulse current. Also, for NiW nanowires formed from 50 nm pores W content (54.6 for DC and 50.4 for PC) is higher than that for wires from 100 nm membranes (52.4 for DC and 49.6 for PC).

Upon ultrasonification NiW nanowires deposited into pores of 50 nm using direct current break significantly. The pieces of nanowires with the length of 1-2 µm and 2-3 µm prevailed, but shorter and longer nanowires were also found (Fig. 52). In comparison with NiW nanowires from 100 nm pore membranes, wires with thinner diameter break much more, so definitely the dimensions of nanowires influence their mechanical robustness. Also, taking into consideration the shape of deposited NiW nanowires, it is possible to assume that wires from 100 nm pore membranes break mostly at the ends where their diameter is thinner and remain whole in the middle where the diameter is thicker.
Figure 50a: TEM image of NiW nanowires without ultrasonic treatment. Membrane: Whatman Polycarbonate 50 nm. Direct current $I=9.82$ mA. Tungsten content 54.6 wt %
Figure 50b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Whatman Polycarbonate 50 nm. Direct current I=9.82 mA. Tungsten content 54.6 wt %
Figure 51a: TEM image of NiW nanowires without ultrasonic treatment. Membrane: Whatman Polycarbonate 50 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 50.4 wt %
Figure 51b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Whatman Polycarbonate 50 nm. Pulse current I=9.82 mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 50.4 wt %
It was difficult to analyze the effect of ultrasonification on NiW nanowires mechanical robustness prepared by pulse current since according to the micrograph, wires were connected through the layer of NiW alloy thin film on the top of the membrane and thus they turned out to be more stable together than separately.

**4.3.2 Mechanical robustness of NiW nanowires from 10 nm membrane**

Fig. 53 and 54 show TEM pictures of NiW nanowires deposited into membranes with pore diameter 10 nm using direct (Fig. 53) and pulse (Fig. 54) current. The majority of nanowires remains whole upon releasing from the template they were fabricated in, but ultrasonic treatment influences these nanowires a lot (Fig. 55 and 56).
Figure 53a: TEM image of NiW nanowires without ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Direct current I=9.82 mA. Tungsten content 35.2 wt %
Figure 53b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Direct current I=9.82 mA. Tungsten content 35.2 wt %
Figure 54a: TEM image of NiW nanowires without ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 33.0 wt %
Figure 54b: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Osmonics Inc Polycarbonate 10 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 33.0 wt %
Figure 55: Normalized quantity of NiW nanowires with the length of x after ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Direct current I=9.82 mA. Tungsten content 35.2 wt %

For NiW nanowires of this diameter prepared by direct current, ultrasonification breaks them significantly. There are a lot of short (less than 500 nm) pieces found after the experiment which was not typical for nanowires of bigger diameter. When deposited into pores of 50 and 100 nm diameter, nanowires break in a different way: more longer pieces (more than 1 µm) were registered, not shorter ones.

Ultrasonification of NiW nanowires fabricated by pulse current in 10 nm pores also breaks them but mostly on wires of 1-2 µm in length, i.e. some of NiW nanowires break in 2 or 3 pieces when still a lot remains whole (Fig. 56). The difference between the effect of ultrasound on NiW nanowires made by different currents is shown on Fig. 57 and 58.
Figure 56: Normalized quantity of NiW nanowires with the length of x after ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Pulse current I=9.82 mA, $t_{on}$=1 s, $t_{off}$=1.5 s. Tungsten content 33.0 wt %

Obviously, both types of NiW nanowires are broken by ultrasound but those deposited under direct current seem to be more destroyed than those fabricated using pulse current. Comparison of W content for different NiW nanowires is presented in the Table 4. Pulse current provides slightly lower W content in NiW nanowires than direct current, and thinner pore diameter leads to less W in the nanowires.

<table>
<thead>
<tr>
<th>Stated pore diameter, nm</th>
<th>100</th>
<th>50</th>
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</tr>
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<tr>
<td>W content, wt %</td>
<td></td>
<td></td>
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<tr>
<td>DC</td>
<td>52.4</td>
<td>54.6</td>
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<tr>
<td>PC</td>
<td>49.6</td>
<td>50.4</td>
<td>33.0</td>
</tr>
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</table>

Table 4: Tungsten content for NiW nanowires from different membranes made by direct and pulse current
Figure 57: TEM image of NiW nanowires after ultrasonic treatment. Membrane: OsmonicsInc Polycarbonate 10 nm. Direct current I=9.82 mA. Tungsten content 35.2 wt %
Figure 58: TEM image of NiW nanowires after ultrasonic treatment. Membrane: Osmonics Inc Polycarbonate 10 nm. Pulse current $I=9.82$ mA, $t_{on}=1$ s, $t_{off}=1.5$ s. Tungsten content 33.0 wt %

Results of ultrasonic treatment experiments suggest that ultrasound does influence the NiW nanowires mechanical robustness, and the effect is defined by the diameter of nanowires and by the conditions under which they were fabricated, namely, using direct or pulse current.
5.0 Conclusions

The conclusions for NiW, NiWMo, and NiMo electrodeposition are summarized below:

1. NiW alloy thin films of good quality, with W content 42-60 wt %, from an electrolyte without ammonia at room temperature, was electrodeposited and consistent with other literature studies. A unique aspect of this work was that the partial current density of W exhibits two kinetic regions, one at low applied current densities, 2-50 mA/cm$^2$, and the other at high current densities > 100 mA/cm$^2$. The current efficiency decreased from 62 % to 7 % with W current density. Higher current density up to 700 mA/cm$^2$ led to the lower W content in NiW alloys (23 wt %), very low current efficiency (1 %), and worse quality of the deposit.

2. When depositing NiWMo alloys from the electrolyte with equal concentrations of W and Mo ions, the content of W and Mo in the deposit differs a lot: Mo 60-67 wt % and W 3-9 wt %, resulting in the total refractory metals content 63-74 wt %. When changing the ratio Mo:W to 1:3 in the electrolyte W content in NiWMo alloy was found to be much lower in comparison with Mo – 7-17 wt % vs 45-58 wt % accordingly. Summation of Mo+W content was 59-69 wt %. The ratio of Mo:W to 3:1 in the electrolyte resulted in NiWMo alloys with Mo content between 65-70 wt % and W 1-13 wt %. The total Mo+W percentage in the deposit was 65-78 wt %. Therefore, changing the concentrations of Mo and W salts in the electrolyte for NiWMo alloy deposition did not influence Mo and W content in the deposit in the same proportions. Electrodeposition of NiWMo alloys required higher current densities (200 mA/cm$^2$) to obtain a metallic film in comparison with NiW alloy.
3. When depositing NiMo alloys, the highest Mo content achieved was 77-81 wt % which was approximately the same as the total content of W and Mo in NiWMo thin films. Current densities higher than 100 mA/cm² led to lower Mo content in NiMo deposit 69-72 wt % instead of 77-81 wt %. For NiWMo and NiMo alloys it was not possible to achieve current efficiency values higher than 2 %. Current efficiency for NiWMo and NiMo alloys dropped significantly when increasing current density higher than 100 mA/cm² but applying lower current densities did not allow to completely reduce Mo into the alloy.

4. The pH of the electrolyte for NiMo alloy deposition did not influence film composition significantly but affected current efficiency: pH 4-5 provided higher current efficiency than pH 6-8. Increasing sodium citrate concentration in the electrolyte for NiMo alloy deposition did not influence Ni and Mo content in the deposit but lowered current efficiency and thus deposition rate.

NiW nanowire results are summarized below:

1. TEM and SEM imaging of NiW nanowires showed that they had a bumpy morphology even when deposited under direct current. NiW nanowire morphology was a result of at least a couple of factors – membrane diameter and deposition conditions.

2. The W content in NiW nanowires deposited into pores with diameter 50 and 100 nm (50 to 54 wt %) was slightly lower in comparison with that of NiW thin films (55 to 57 wt %). NiW nanowires fabricated in a membrane with 10 nm pore size had a W content significantly lower, 33 wt %, than pore sizes > than 100 nm diameters. Pulse current provided slightly lower W content in NiW nanowires than direct current.
3. Results of ultrasonic treatment suggest that ultrasound did influence the NiW nanowire mechanical robustness, and the effect was defined by the diameter of the nanowires and by the conditions under which they were fabricated: nanowires deposited under pulse current were more mechanically robust in comparison with those prepared by direct current, and thicker nanowires were stronger than thinner.
6.0 Recommendations

It is recommended to conduct a series of experiments to study in depth the kinetics of the process when codepositing NiWMo alloys. It is interesting that the addition of Mo to the electrolyte for NiW alloy deposition allows codeposition of higher refractory metal content, Mo+W, in comparison with W content in NiW alloy. Also, it needs to be explained why, when depositing NiWMo alloys, the Mo content in the deposit is only slightly influenced by a change in Mo and W concentrations and is significantly higher than W content.

For NiMo alloys (as well as for NiWMo) it is very important to increase the current efficiency of the process in order to consider the possibility of commercial application of the developed electrolyte.

NiW nanowires are expected to possess outstanding functional properties so magnetic and catalytic properties are to be tested in the future. NiW nanotubes are also interesting structures as well as NiMo and NiWMo nanowires and nanotubes so they are to be electrodeposited and their properties examined.
7.0 References


