VILNIUS UNIVERSITY

Justina Sinkevičiūtė

Corrosion Study of Electrodeposited W and Mo Alloys with Iron Group Metals

Summary of doctoral dissertation

Physical sciences, chemistry (03 P)

Vilnius, 2009

The work was carried out in Vilnius University in the period of 2005 – 2009.

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VILNIAUS UNIVERSITETAS

Justina Sinkevičiūtė

Elektrochemiškai nusodintų W ir Mo lydinių su geležies grupės metalais korozijos tyrimas

Daktaro disertacijos santrauka
Fiziniai mokslai, chemija (03 P)

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Su disertacija galima susipažinti Vilniaus universiteto ir Chemijos instituto bibliotekose.

1. Introduction

In the meantime the great attention is focused on the electrodeposition of tungsten and molybdenum alloys for some reasons:

1) the properties of cast alloys are close to the properties of chromium. Therefore, the efforts are made to exchange environmentally dangerous electrodeposition of chromium by the electrodeposition of tungsten and molybdenum alloys.
2) The introduction of sufficient amount of W or Mo into matrix of iron group metal increases the melting point of resulting alloys. The highest melting point up to 2500 °C could be achieved in electrodeposited Fe-W alloys. Therefore, these alloys have a potential to be applied into devices exploited at high temperatures.
3) One of the components of these alloys possesses magnetic properties, and it becomes possible to modify magnetic properties by the changes in content of alloys.
4) The electrodeposition of pure tungsten and molybdenum coatings from tungstate solutions is hindered by the formation of an oxide layer on the cathode during electrodeposition. That oxide cannot be reduced to metallic tungsten directly because of the very low over-voltage for hydrogen evolution on tungsten. Hence, a further reduction to metallic tungsten does not proceed, and the entire current is consumed for hydrogen evolution. On the contrary, tungsten and molybdenum ions do co-deposit with iron group metals so that alloys containing a high content of refractory elements are obtained. This phenomenon is called by Brenner “induced co-deposition”. The mechanism of co-deposition still is not fully clear, and researches in this area are of importance. Moreover, the induced co-deposition with other metals having very high negative reduction potential such as Sm, Nb are determined.
5) The grain size of electrodeposited pure iron group metals are in the range 200-400 nm, whreas the grain size of W or Mo alloys can be reduced up to 3-4 nm.

In older literature such alloys has been called “amorphous”, bet in modern time they are called **“nanocrystalline”** or **“nanostructurized”** alloys. Nanocrystalline alloys are attractive for the implementation into electroforming of micro-electro-mechanical systems (MEMS), nanostructures such as nanowires, nanotubes. In this case the electrodepositing metal or alloys can fill properly entire template. In addition, the increased mechanical hardness or lower thermal expansion is typical features of nanocrystalline materials compared with crystalline.

However, the sufficient percentage of mass in nanocrystalline materials concentrates in grains, and that can influent on the rates of electrochemical reactions whose depend on the state of surface, such as evolution of hydrogen. Consequently, it could cause the changes in the corrosion rates. The variations of the corrosion rates with their fabrication method are well known and the differences in corrosion rates in some cases could reach a factor of 10. Therefore, corrosion study became an integrated part of modern chemical engineering.

Frequently, in electrochemical literature the data obtained using cast metal are used to describe electrodeposited metal. However, the structure of these two type of materials are differs, because the structure of cast metal (alloy) is equilibrated, and the structure of electrodeposited metal is irreversible. This difference in states could cause the difference in corrosion behavior of metal.

This work is focused on the determining of corrosion and tribocorrosion properties of W and Mo alloys with Fe, Ni and Co. Also, the peculiarities of corrosion behavior of pure iron group metals are discussed.

The main aims of work were following:

1. To compare the parameters of corrosion in Na_2SO_4 and H_2SO_4 of cast Fe, Ni and Co and electrodeposited films of these metals.
2. To compare the parameters of corrosion in Na_2SO_4 and H_2SO_4 of electrodeposited films of W and Mo alloys with Ni, Fe and Co.
3. To determine the correlation of corrosion parameters and thickness of electrodeposited Ni-Mo films;

4. To explore the tribocorrosion behaviour of self-passivated films of W and Mo alloys with Ni, Fe and Co.

Statements for defence:

1. The difference in corrosion properties between cast iron-group metal and electrodeposited corresponding metal in acidic media decreases in sequence Ni<Co<Fe, whereas in neutral media the sequence is a following: Co<Ni<Fe, i.e. in all cases the corrosion resistance of electrodeposited Fe is worse than that for cast Fe.
2. The corrosion current of electrodeposited nanocrystalline W alloys (>20 at.% of W) in acidic media decreases in sequence CoW>FeW≈Ni-W, whereas in neutral media the sequence is a following: CoW >FeW>NiW.
3. The corrosion current of Ni in solutions where complexes could be formed (citrate, citrate-ammonia), at 70° can reach 2 mA/cm^2.
4. The tribocorrosion resistance of electrodeposited and further self-passivated W and Mo alloys (Fe-26 at.% W, Co- 28 at.% W; Co- 4,5 at.% P-20 at.% W; Co-25 at.% Mo) decreases in sequence FeW>CoPW>CoW>CoMo.

2. EXPERIMENTAL

2.1. Reagents, solutions, electrodes

Analytical grade chemicals and distilled water were used to prepare solutions. Solutions were prepared by dissolution of components in stirred warm distilled water. The values of pH was controlled by pH –meter, and desired pH was achieved by adding H_2SO_4 or NaOH.

Electrodeposition and corrosion investigation has been carried out using regular 3-electrodes cell. Working electrodes were made of corresponding metal wire (Alfa Aesar, purity no less 99.9%). The diameter of working area was 1 to 2 mm. The rest part was isolated by thermal plastics. The electrode Ag/agCl electrode in saturated KCl solution was served as reference electrode, and Pt was served as counter electrode. All values of potentials had been recalculated into hydrogen electrode scale.

Prior the measurements the electrode was polishing mechanically, rinsed and treated for 30 sec in concentrated H_2SO_4, then rinsed again. All measurements are performed at 20°C, unless the other temperatures are indicated.

2.2. Electrodeposition. Electrochemical measurements

The electrodes made of corresponding metals wires served as substrate for electrodeposition. Immediately before plating the substrates were degreased and activated with dilute sulfuric acid and a seed-layer of Ni was electroplated within 1 min. from Wood's type solution containing $NiCl_2 \cdot 6H_2O$ 240 g/l + HCl 80 g/l at 30 mA/cm^2 . Then, the W-containing alloys were electro-deposited from the corresponding solutions. The duration of electrodeposition was predetermined in such way that the thickness of resulting coating would be no less than 10μm.

Electrochemical measurements were carried out by means of AUTOLAB302, software GPES was used for voltammetric measurements or electrodeposition control, software FRA for recording and analysis of electrochemical impedance spectra.

Surface morphology was examined by means of scanning electron microscope (SEM) JEOL, the content of alloys was controlled by EDS method.

2.3. Tribocorrosion measurements

This method was applied to study influence of friction on the corrosion of alloys.

The layout of used tribometer FALEX is shown in Fig. 1.

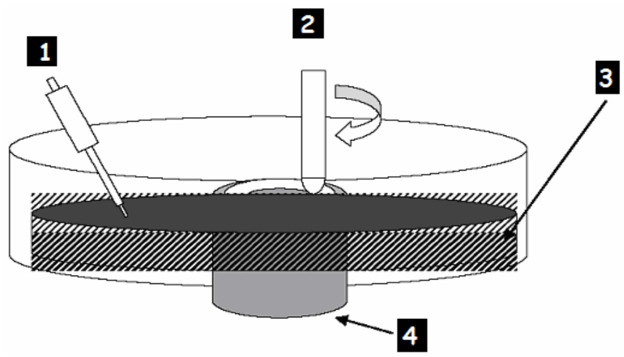


Fig. 2.1. Electrochemical cell used for tribocorrosion tests. 1- referente elektrode, 2-pin; 3-counter elektrode; 4- support of working elektrode.

The prepared samples were installed in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disk tribometer, with the working surface of the specimen facing upwards, see Fig. 2.1. The tribocorrosion properties have been studied in the following conditions: solution—1M Na_2SO_4; normal force 5 N; rotation speed 120 rpm. The counterbody (pin) was an alumina cylinder (7mm in diameter), mounted vertically on a rotating head, above the specimen. The lower spherical end (radius = 100mm) of the pin was then applied against the composite surface (disk) with an adjustable normal force. When rotation was applied, the end of the pin draws a circular wear track (16mm in diameter) on the working composite surface. The electrochemical measurements were performed at the following sequence:

No.	**Measured parameter**	**Time**	**Tribometer mode**
1	Potential	10 min	OFF
2	Electrochemical impedance		OFF
3	Potential	10 min	ON
4	Electrochemical impedance		ON
5	Potential	60 min	ON
6	Potential	60 min	ON

3. RESULTS AND DISCUSSIONS

3.1. Preparation of metals and alloys for corrosion tests

3.1.1. Electrodeposition of pure iron-group metals

Pure iron-group metals (Ni, Co and Fe) were electrodeposited from the same solutions as were used for the electrodeposition of nanostructure W and Mo alloys. The substrate was wire of corresponding metal. The thickness was no less than 10 μm. Electrodeposition conditions are presented in Table 3.1.

Table 3.1. *The conditions for pure iron-group metals electrodeposition.*

Components or parameter	**Concentration**
$MeSO_4$ (Me= Co, Ni or Fe)	0.2 M
Na_3Cit	0.33 M
Citric acid	0.17 M
NH_3	1,2 M
pH	8
temperature	70°C
current density	25 mA/cm^2

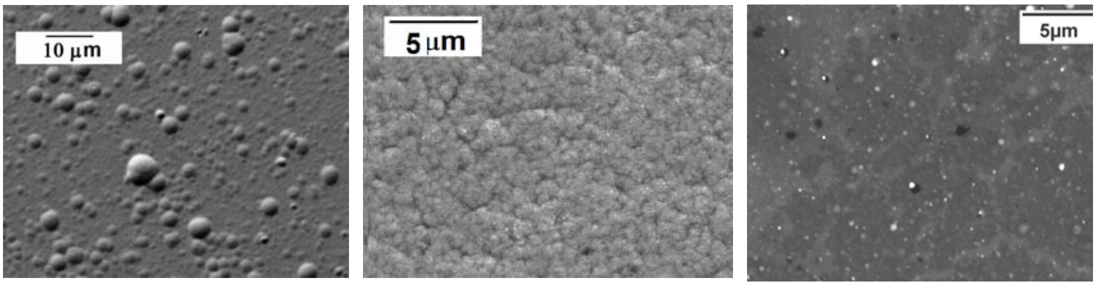
3.1.2. Electrodeposition of nanocrystalline W and Mo alloys with iron-group metals

W and Mo alloys with iron-group metals become nanocrystalline when content of W (or Mo) exceeds 20 at. %. The electrodeposition conditions are presented in table 3.2.

Table 3.2. *The conditions for nanocrystalline W alloys with iron-group.*

Components or parameter	**Concentration**	**Alloy and content of W in alloys**
$MeSO_4$ (Me= Co, Ni or Fe) Na_3Cit Citric acid NH_3 Na_2WO_4	0.2 M 0.33 M 0.17 M 1,2 M 0.4 M	Ni – W (19,5 at.%W) Fe – W (25,2 at.%W) Co – W (29 at.% W)
pH temperature current density	8 70°C 25 mA/cm^2	

Obtained alloys are smooth and bright. Their SEM images are presented in Fig. 3.1.



(a) **(b)** **(c)**

Fig. 3.1. SEM images of W alloys used for corrosion tests and values of grain size: (a): Ni-20W. Grain size 9 nm; (b) Fe-25W. . Grain size 3.5 nm; (c) Co-29W. . Grain size: 4 nm.

Bright and smooth Ni-Mo alloys were electrodeposited from pyrophosphate solution with brightening agents: 160 g/l $Na_4P_2O_7$+ 40 g/l $NiSO_4$+20 g/l NH_4Cl+6 g/l Na_2MoO_4+50 mg/l 1.4 butyndiol+100 µl/l Rokafenol N-10; current density 30 mA/cm^2, pH 8.5, t=20°C.

3.2. Parameters of electrochemical corrosion and determination of corrosion current

Noticeably, the obtained voltammograms are dissymmetrical that causes some difficulties to determine j_{corr} applying the regular routine, i.e. to estimate j_{corr} by the extrapolation of the rectilinear dependences log j vs (E - E_{corr}) in "Tafel region":200

mV>│E-E_{corr}│>20 mV where the effect of one of at least two reactions of the corrosion process could be neglected. However, if the cathodic and anodic branches of voltammogram are asymmetric due to peculiarities of cathodic hydrogen evolution and anodic metal dissolution (see Fig. 3.2), this procedure not applicable reliably to estimate j_{corr}.

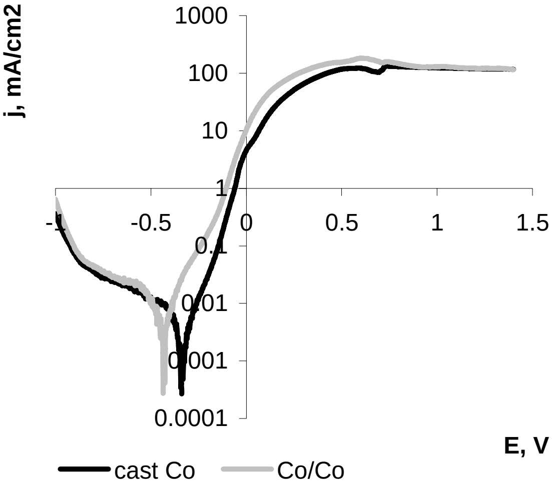


Fig. 3.2. Evans diagram for cast Co and Co electrodeposited onto Co in 1M Na_2SO_4 solution.

In this case, for the j_{corr} estimation, a modified procedure proposed by Allen-Hickling could be applied successfully; it enables to estimate j_{corr} reliably from the data obtained in the relatively narrow region of potentials that are close to E_{corr}. For this purpose, the equation of polarization curves is used in the form:

$$\ln\left\{\frac{j}{1-\exp\left[-\frac{zF\left(E-E_{corr}\right)}{RT}\right]}\right\} = \ln j_{corr} + f\left(\alpha,z,T\right)\left(E-E_{corr}\right)^{\cdot}$$

Plotting of the left side term of equation (1) against (E-E_{corr}) leads to rectilinear dependences even in the region │E-E_{corr}│~ 20-50 mV. Then, the extrapolation of them to (E-E_{corr}) yields the determining the value of ln j_{corr}. The sample is presented in Fig. 3.3.

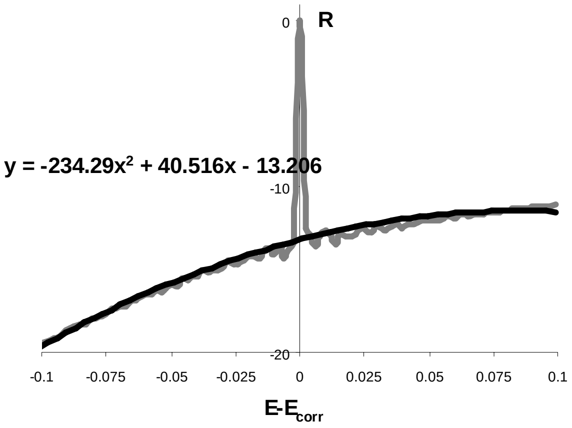
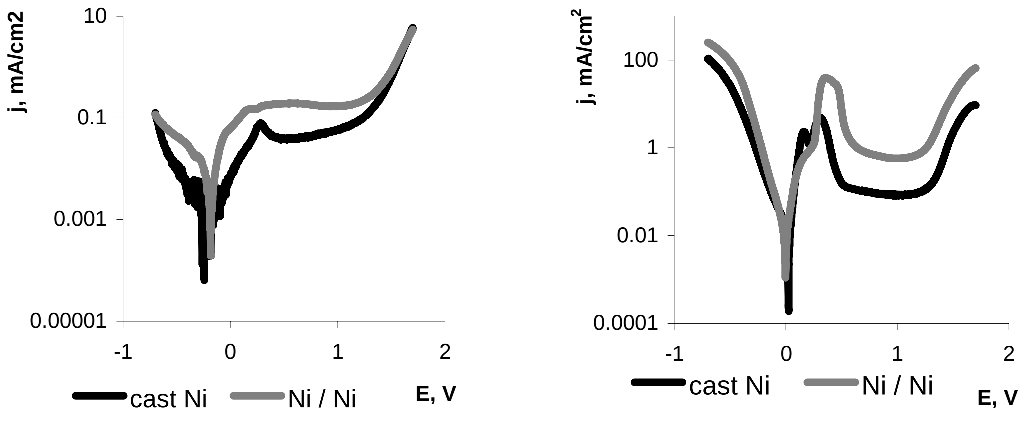


Fig. 3.3. The sample (cast Co in 1M Na_2SO_4) of determination corrosion current in Allen- Hickling coordinates.

3.3. Corrosion study of iron group metals

The corrosion behavior of cast and electrodeposited iron group metals is different. In all cases open circuit potentials (OCP) determined for cast and electrodeposited metals in 0.5M H_2SO_4 solutions are close, whereas in 1M Na_2SO_4 the difference is higher, and in the case of electrodeposited Ni the OCP is ca. 100 mV more negative than that obtained for cast Ni. The differences between cast and electrodeposited metals were obtained in Evans diagrams too – see the sample Fig. 3.4.



(A) **(B)**

*Fig. 3.4. Evans diagrams obtained for cast and electrodeposited Ni from citrate-ammonia bath in 1M Na_2SO_4 **(A)** and 0,5M H_2SO_4 **(B)** solutions.*

Differences between cast and electrodeposited metals in Evans diagram cause the variations in corrosion current (j_{corr}). The determined j_{cor}in 1M Na_2SO_4 solutions for electrodeposited iron-group metals are 1.5-4 times higher than that determined for cast metals, whereas these differences in 0,5M H_2SO_4 solutions are insufficient.

As follows from the data obtained by means of electrochemical impedance spectra (EIS), the corrosion occurs under slow discharge reaction and EIS data well-fitt the equivalent circuit containing uncompensated solution resistance and connected in parallel constant phase element and charge transfer resistance, which in our case is identified as corrosion resistance. The sample of Nyquist and Bode plots as well as their fitting to equivalent circuit is shown in Fig. 3.5, and values of the elements of equivalent circuit are presented in Table. 3.3

Table 3.3. *Values of the elements of equivalent circuit used to describe EIS data.*

Danga	**R_t, Om cm^2**	**Q, μF/cm^2**	**n**	**R_{corr}, kOm cm^2**
Cast Co	1.278	21	0.8507	0.050
Co / Co	0.995	64	0.8464	0.034

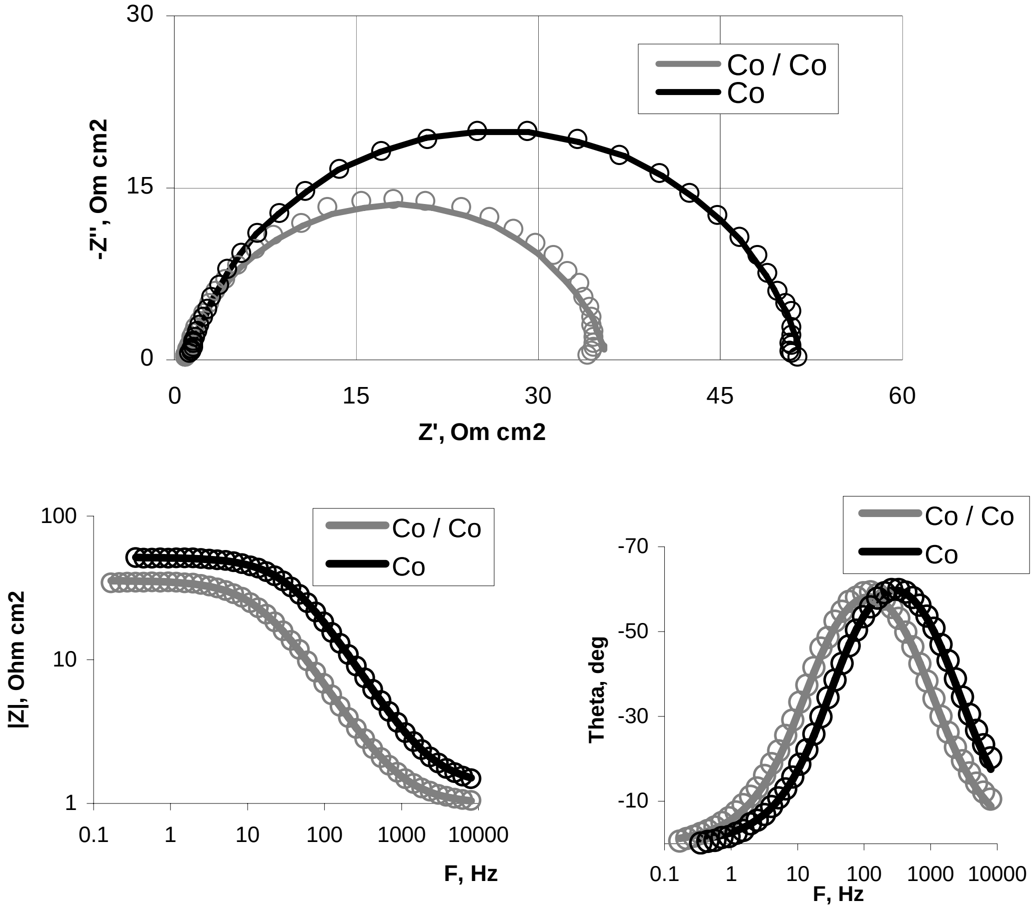


Fig. 3. Nyquist and Bode plots obtained for corrosion in 0,5M H_2SO_4 of cast and electrodeposited Co film onto Co from citrate-ammonia bath. Points – experimental data, lines – fitting results to the equivalent circuit described above.

As follows from the data obtained by means of Evans diagrams and EIS, the differences in corrosion rates between cast and electrodeposited iron-group metal in H_2SO_4 decrease in a following sequence Ni<Co<Fe, whereas in neutral media the sequence is a following: Co<Ni<Fe, i.e. in all cases the corrosion resistance of electrodeposited Fe is worse than that for cast Fe.

3.4. Corrosion study of tungsten alloys with iron group metals

The corrosion properties of electrodeposited nanostructurized W alloys with Co, Ni and Fe were compared with those obtained for each component of alloy. The values of OCP obtained in 1M Na_2SO_4 are shown in Fig. 3.6. As it can be seen the most positive value of OCP are obtained for W, and most negative values are obtained for W-contained alloys. Interestingly, the ones are close to electrodeposited Ni and Fe, whereas the values for Co-W are in between pure Co and W. Such differences in OCP probably are caused by different evolution of hydrogen in course of cathodic reaction. This statement is confirmed in Evans diagrams – see Fig. 3.7. As follows from the presented data, each alloy behaves in corrosion media in individual way, and their anodic properties cold not be predicted based on the properties of each metal.

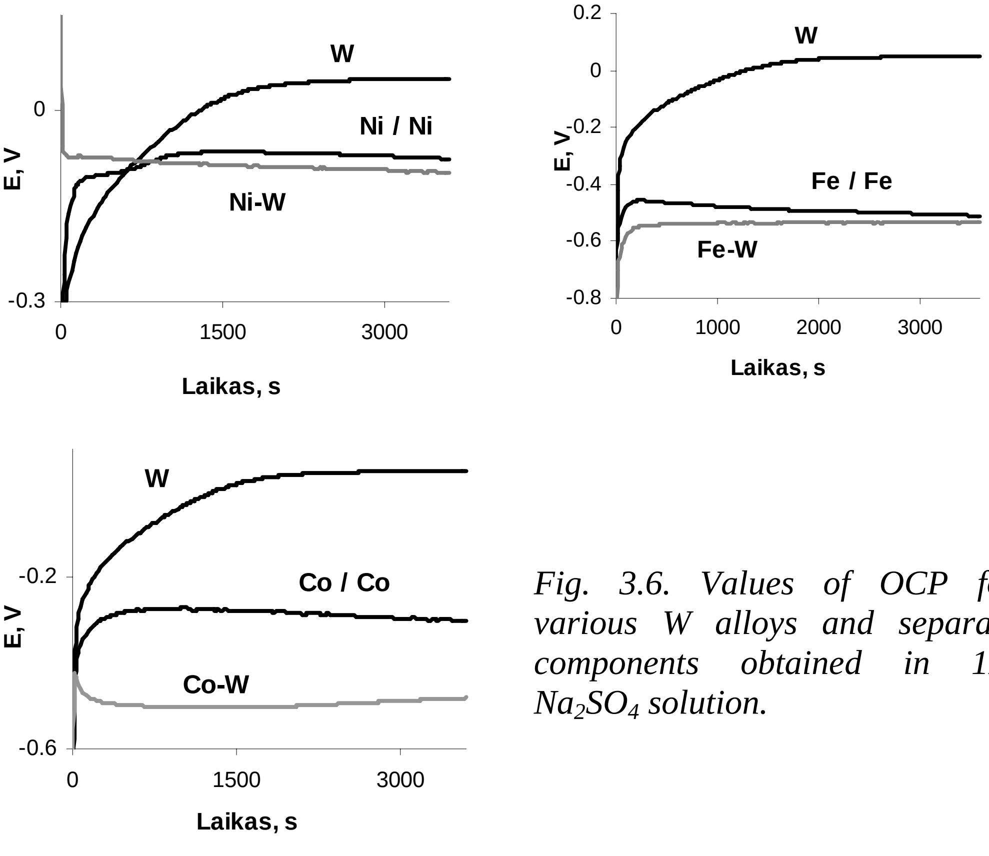


Fig. 3.6. Values of OCP for various W alloys and separate components obtained in 1M Na_2SO_4 solution.

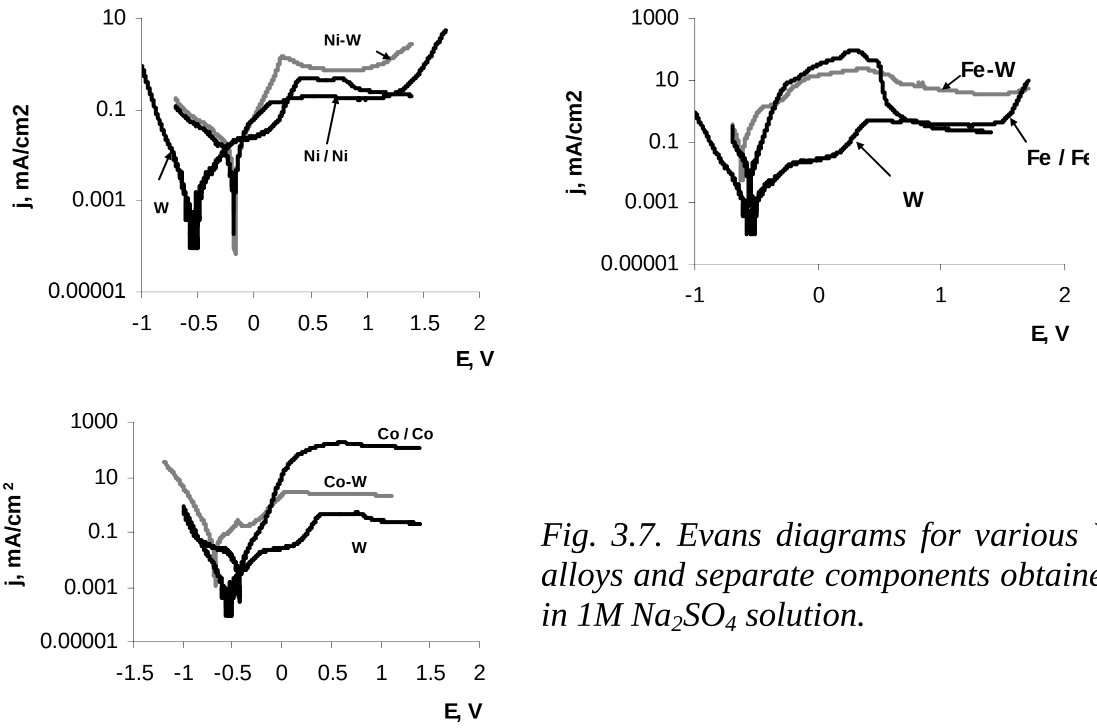


Fig. 3.7. Evans diagrams for various W alloys and separate components obtained in 1M Na_2SO_4 solution.

Calculated values of corrosion parameters (E_{corr}≡OCP, j_{corr} and R_p) are presented in Table 3.5 and 3.6.

Table 3.5. *Paramneters of corrosion obtained for metals and alloys in 1M Na_2SO_4*

Metal or alloy	**E_{corr}, V**	**j_{corr}, A/cm^2**	**R_{corr}, kOhm cm^2**
Ni-W	- 0,176	$3{,}7\cdot10^{-6}$	1,124
Ni / Ni	-0,182	$2{,}5\cdot10^{-6}$	1,700
Fe-W	-0,621	$4{,}5\cdot10^{-5}$	1,018
Fe / Fe	-0,551	$9{,}9\cdot10^{-6}$	0,539
Co-W	- 0,678	$1{,}7\cdot10^{-5}$	0,536
Co / Co	-0,433	$3{,}4\cdot10^{-6}$	2,829
pure W	-0,548	$1{,}4\cdot10^{-7}$	2,663

Table 3.6. *Parameters of corrosion obtained for metals and alloys in 0.5M H_2SO_4*

Metal or alloy	**E_{corr}, V**	**j_{corr}, A/cm^2**	**R_{corr}, kOhm cm^2**
Ni-W	- 0,077	$7{,}46\cdot10^{-5}$	0,145
Ni / Ni	-0,002	$1{,}0\cdot10^{-5}$	0,439
Fe-W	- 0,216	$8{,}1\cdot10^{-5}$	0,157
Fe / Fe	-0,234	$6{,}1\cdot10^{-4}$	0,011
Co-W	- 0,103	$1{,}0\cdot10^{-4}$	0,482
Co / Co	-0,097	$1{,}7\cdot10^{-3}$	0,034
pure W	- 0,141	$2{,}8\cdot10^{-6}$	1,420

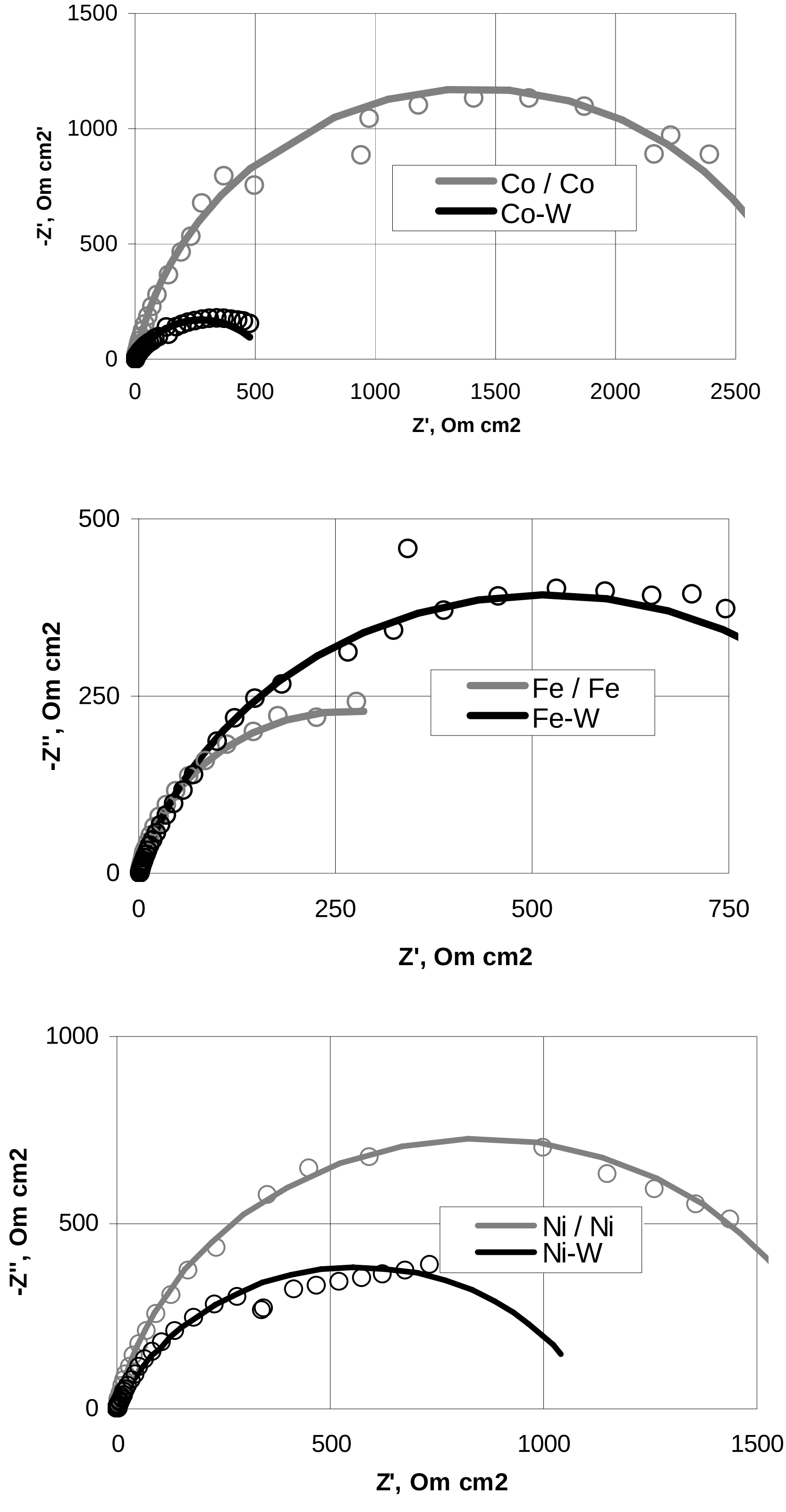


Fig. 3.8. Nyquist plots for W alloys and electrodeposited iron-group metal (indicated in graph) obtained in 1M Na_2SO_4. Points – experimental data, lines – fitting results to the equivalent circuit described above using values of elements summarized in Table 3.7.

The EIS data can be described successfully using the same equivalent circuit as defined above – see Fig. 3.8. However, the values of Q (a member of constant phase element, describing capacity of double electric layer) are quite big. To determine reasons need additional experiments.

As follows from the data obtained by voltammetric and EIS, the all W alloys show a higher corrosion current and lesser corrosion resistance than pure metals in Na_2SO_4 solution. The smallest corrosion current was determined for Ni-W, and highest – for Co-W alloy. In H_2SO_4 solution Fe-W and Co-W show lesser corrosion current than pure Fe and Co, respectively.

Summarizing all obtained data it can be stated that the corrosion resistance of electrodeposited nanocrystalline W alloys (>20 at.% of W) in acidic media decreases in sequence CoW>FeW≈Ni-W, whereas in neutral media the sequence is a following: CoW>FeW>NiW.

Table 3.7. Values of the elements of equivalent circuit used to describe EIS data presented in Fig.3.8.

Metal or alloy	**R_t, Ohm cm^2**	**Q, µF/cm^2**	**n**	**R_{corr}, kOhm cm^2**
Ni – W	1,705	344	0,7575	1,124
Ni / Ni	2,360	64	0,8987	1,700
Fe – W	1,381	437	0,8174	1,018
Fe / Fe	1,346	4596	0,9021	0,539
Co – W	1,759	908	0,7004	0,536
Co / Co	1,994	102	0,8796	2,829
W	2,077	1905	0,6698	2,663

3.5. Corrosion study of Ni in citrate and citrate –ammonia solutions

The major limiting factor for the adaptability of conventional plating baths to deep recess plating is the variance in hydrodynamic conditions. Some problems might be solved by applying pulse current deposition, because in this case the morphology of surfaces improves sufficiently. The baths composition allows to obtain Ni-W electrodeposits with reasonable properties in pulse current mode was developed in our lab. This solution contains citrates, ammonia and carbonates, and electrodeposition of

Ni-W alloys in deep recesses could be performed successfully in pulse current mode (ON 10 s, OFF 30 s) in citrate-ammonia baths at 60-70°C using Ni anodes. The process of electrodeposition and filling up of recesses lasts up to 30-48 h. It is important to obtain coatings having uniform composition through the entire length. The citrate-ammonia surrounding is aggressive for nickel *a priori*, and concentration of Ni(II) in the bath is changed due to corrosion of Ni anodes at least during pause. The increase of Ni(II) concentration causes the decreasing of W amount in alloys. Moreover, the deposition rate should decreases during pause. Therefore, the attention on the corrosion of Ni in the similar solutions should be paid.

The variation of the OCP for Ni in solutions contained only citrates in comparison with the solutions not contained complexing agents at 20 °C and 70 °C is shown in Fig. 1. The fastest changes of the OCP are obtained during immersion moment, and steady state is reached within similar periods around 30 minutes at 20 °C. Also, at 70 °C, the similar values of the OCP are settled, but within longer period, and from the range of the potentials more negative than that observed at 20 °C. The OCP in the presence of citrates are more negative than that in solutions does not containing complexing agents at higher values of pH.

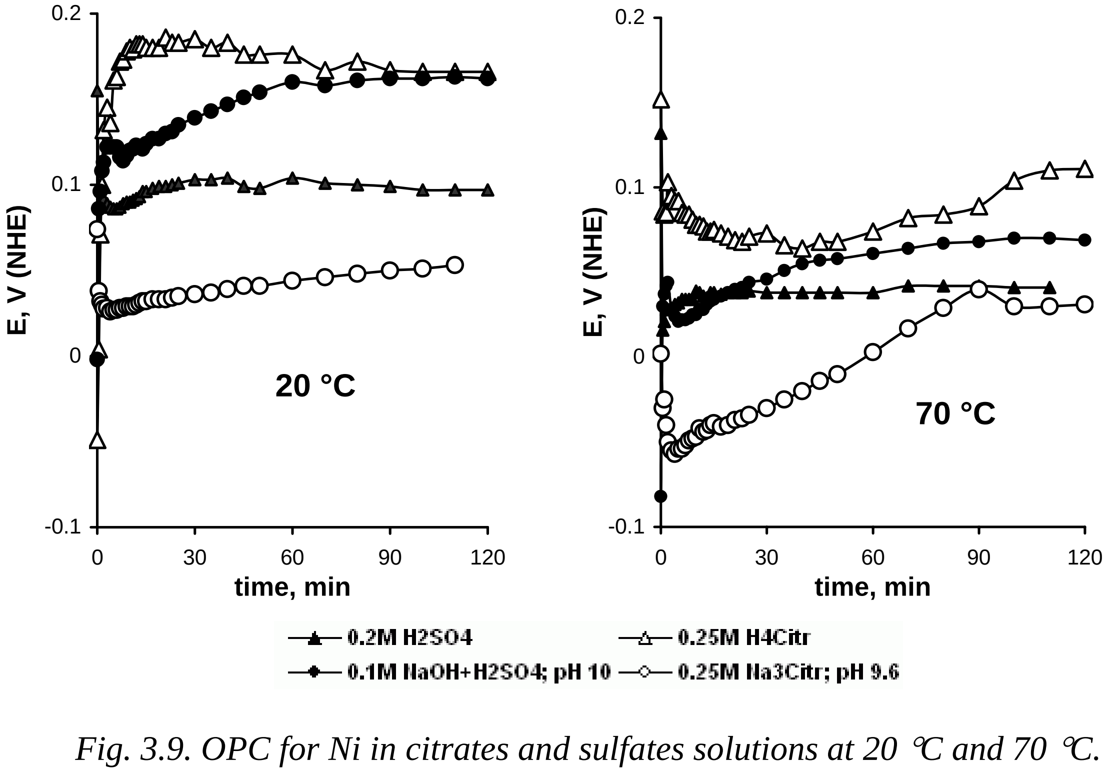
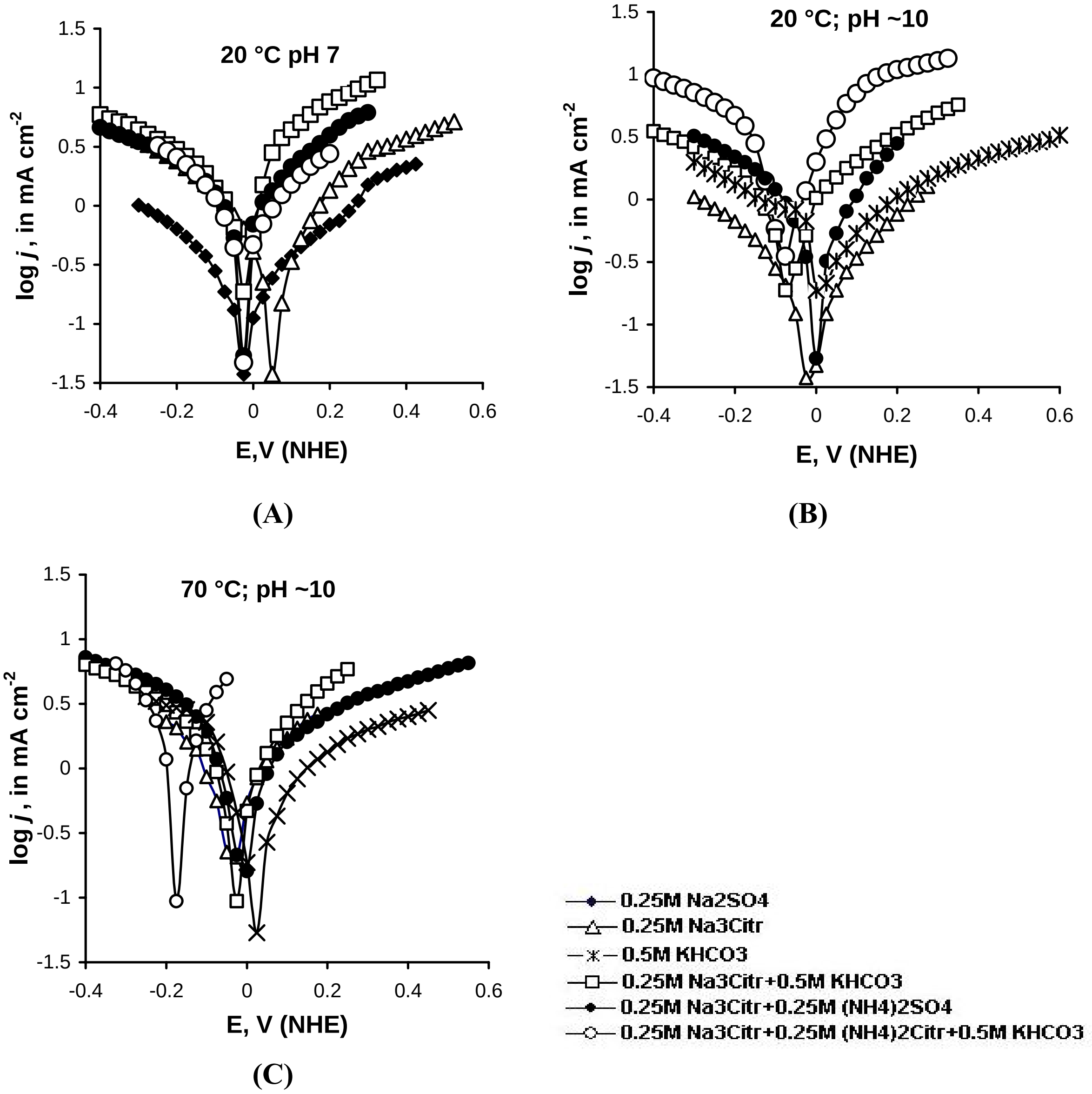


Fig. 3.9. OPC for Ni in citrates and sulfates solutions at 20 °C and 70 °C.

The determined Evans diagrams are presented in Fig 3.10 The values of pH in the range 8 to 10 of the investigated solutions were chosen, because the citric complexes of Ni(II) dominate at pH 8-9, whereas the ammonia and citrate complexes of Ni(II) are in comparative amounts at pH ~ 10. The adding of complexing agents (citrates, ammonia) caused an increase in the both cathodic and anodic current densities in comparison with obtained in Na_2SO_4 solutions. Notably, at pH 7 the cathodic currents are obtained similar, and differences is evident just in the anodic part of voltammogram (Fig. 310, A). At pH~ 10 the currents on the Evans diagram in the presence of $(NH_4)_2SO_4$ are higher due to additional amount of the complexing agents (citrates + NH_3) (Fig. 3.10, B and C).



(A) (B)

(C)

Fig. 3.10. Evans diagrams for Ni obtained in various solutions.

From the obtained data follows that any addition to citrates causes an increase in corrosion current exceptionally additions of ammonia sulfate at 20 °C, and can reach values of 2 mA/cm^2.

Addition information about corrosion behavior of Ni dependently on the immersion time was received by means of EIS. The R_p ($\equiv R_{corr}$) as a function of time after Ni was immersed into solution is shown in Fig. 3.11. As it can be seen, the obtained R_p values for Ni in acidic solutions are significantly less than (and corrosion rate could be higher) that obtained in alkaline solutions. Moreover, in alkaline solutions the fast increase in values of R_p is evident after 5-15 minutes of the Ni electrode immersion, whereas in the acidic media the values of R_p change weakly with time. The R_p values sudden increase when OCP becomes relatively positive in alkaline media, i.e. approx. -0.05÷0.0 V. Such sufficient increase of R_p values at certain potentials might indicate the formation of passive film onto Ni surfaces.

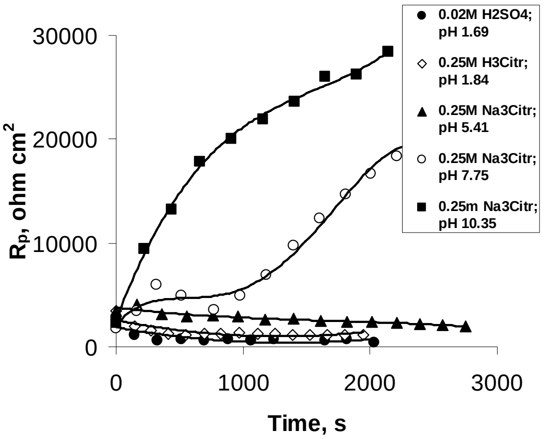
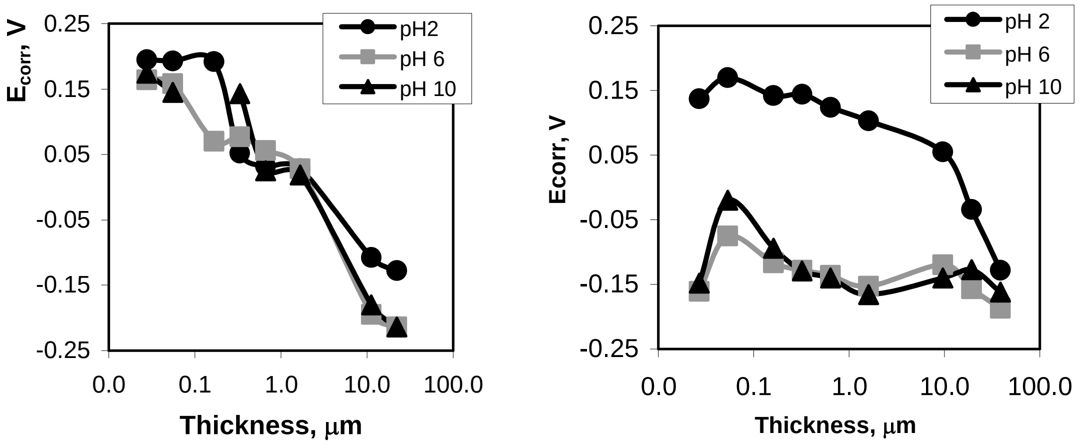


Fig. 3.11. R_p as a function of time obtained for Ni in the various solutions.

3.6. Corrosion study of Ni-Mo alloys electrodeposited from pyrophosphate solutions

Electrodeposition of metals and alloys usually is performed onto foreign substrates. If coating is porous, the galvanic pairs can form and make influence on the corrosion behavior. Therefore the corrosion behavior of Ni-18 at.%Mo was investigated and obtained results was compared with Ni electrodeposits. Corrosion potential as a function of Ni-Mo thickness is presented in Fig. 3.12. As it can be seen, E_{corr} becomes more and more negative with increasing in thickness of electrodeposits. The potential for Ni-Mo is less sensitive to thickness than that for Ni. The values E_{corr} reach the regular values for this Ni-Mo alloy when the thickness of deposits exceeds 0.1 μm. However, the values of corrosion resistance R_{corr} reach the typical values for Ni-Mo, if thickness of electrodeposits exceeds 5-10 μm.



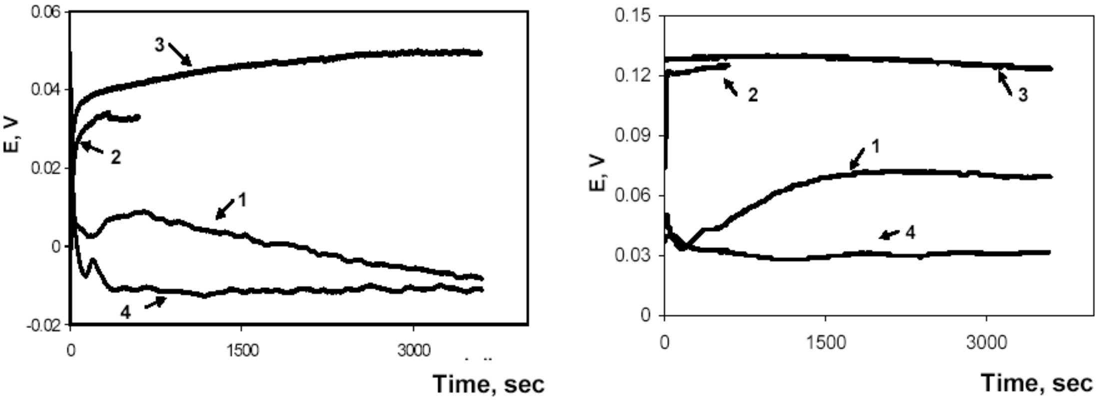
Ni **Ni-Mo (18 at.% Mo)**

Fig. 3.12. E_{corr} *vs thickness of electrodeposits Ni and Ni-Mo (18 at.% Mo, obtained from pyrophosphate bath. Corrosion media 1M* Na_2SO_4*+0.1M NaCl.*

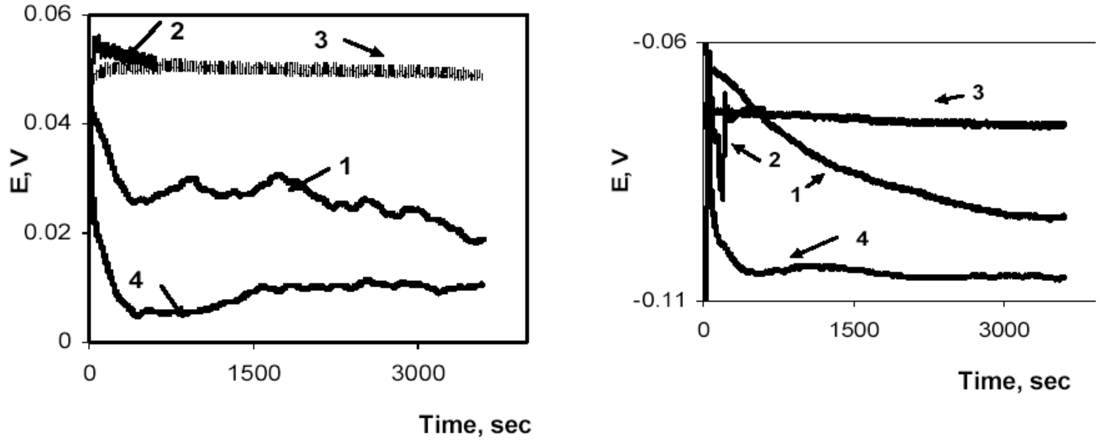
3.7. Tribocorrosion study of self-passivated W and Mo alloys

The number of nanocrystalline W and Mo alloys has been investigated in corrosion media consisting on 1 M Na_2SO_4: Fe-26 at.% W, Co- 28 at.% W; Co- 4,5 at.% P-20 at.% W; Co-25 at.% Mo. All of these alloys were electrodeposited onto polished steel.

The synergistic effect of friction and corrosion (tribocorrocion) evidently appears when treated metal or alloy is in the passive state. However, all of these freshly electrodeposited alloys are in active state or are not so passive, that it evidently influences on the corrosion potential (OCP). These alloys do not show sufficient passivity even after one month had been kept in open air. Only after 6 months the corrosion potentials of these alloys shifted toward positive values at 0.4-0.5 V compared with values of corrosion potential for freshly electrodeposited alloys. The changes in OCP before tribocorrosion test, during test and after is presented for investigated alloys are shown in Fig. 3.13.



Fe-W CoW



CoPW CoMo

Fig. 3.13. OCP vs time of immersion into corrosion media obtained for investigated alloys (marked below graph), had been kept in open air for 6 month. 1- Changes of OCP prior troibocorrosion test; 2- Changes of OCP after measuring system had been switched ON; 3- Changes of OCP during tribocorrosion test with mechanical loading; 4- Changes of OCP after unloading.

For all alloys the OCP are in the range of 0.0 V, that is related with passive state. During test all OCP variations fit the interval of 120 mV that can be considered as relatively stable passive state, and can not be destroyed by means of applied load. However, EIS measurements performed simultaneously show sufficient changes in resistance of corrosion – see Fig. 3.14-3.16 for W alloys. The highest value of corrosion resistance before tribocorrosion test was obtained for Co-W alloy. However, during test the resistance decreases almost 4 times. The decrease in corrosion resistance at ~4 times was obtained for Co-Mo too, however values of ones was sufficiently smaller both before and during tribocorrosion test in comparison with investigated W-containing alloys. In contrary, the resistance of corrosion for Fe-W does not changes sufficiently, some more it changes in case of Co-P-W alloys. During tribocorrosion test the corrosion resistance of Fe-W remains almost unchanged, slightly reduced in case of Co-P-W.

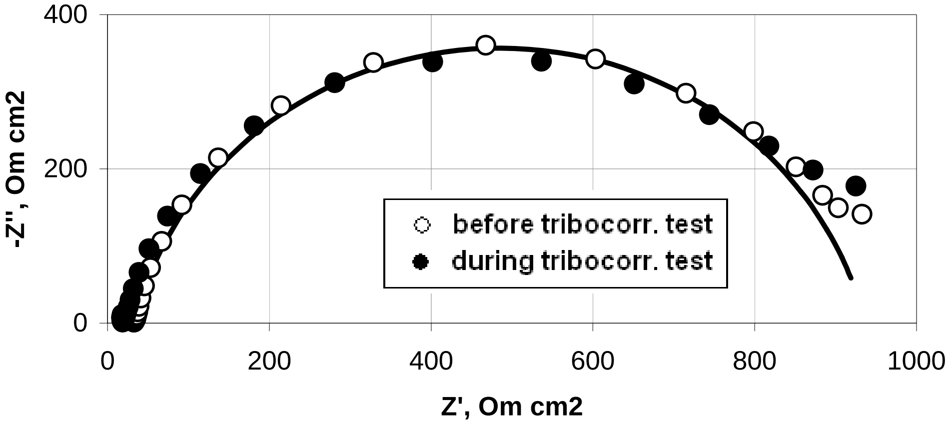


Fig. 3.14. Nyquist plot for Fe-W determined before and during tribocorrosion test. Circles – experimental data, lines – fitting results to the equivalent circuit described on p. 13.

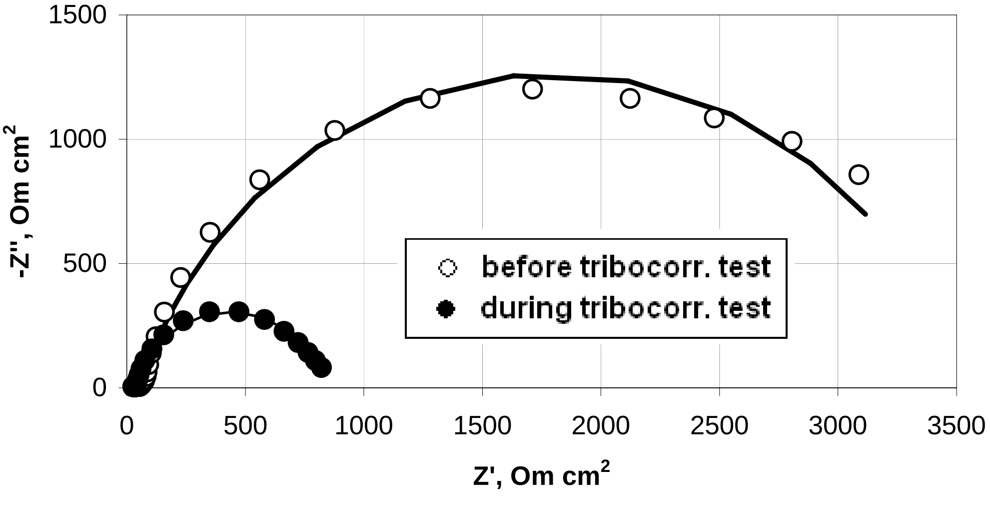


Fig. 3.15. Nyquist plot for Co-W determined before and during tribocorrosion test. Circles – experimental data, lines – fitting results to the equivalent circuit described on p. 13.

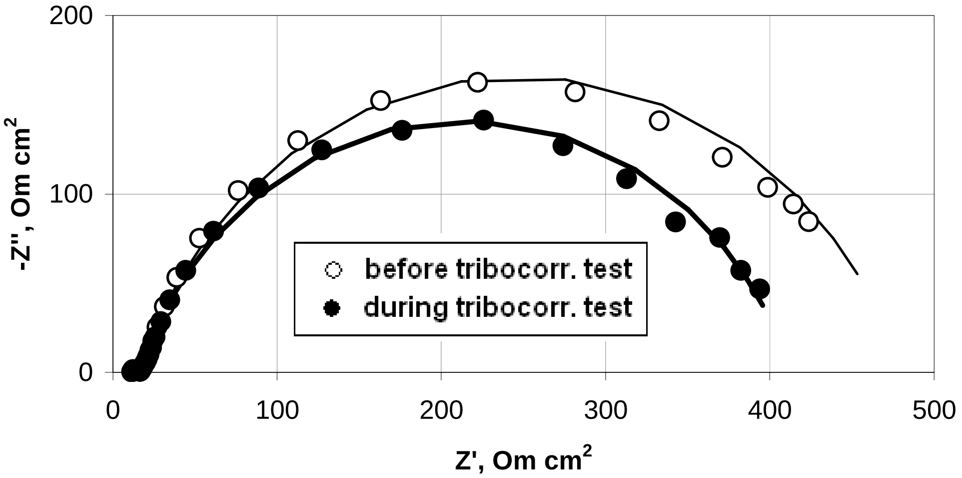


Fig. 3.16. Nyquist plot for Co-P-W determined before and during tribocorrosion test. Circles – experimental data, lines – fitting results to the equivalent circuit described on p. 13.

The clear criteria for tribocorrosion stability of materials are absent. If criteria is higher corrosion resistance during friction (during tribotest), therefore the tribocorrosion resistance decreases in sequence: FeW>CoW>CoPW>CoMo.

4. CONCLUSIONS

1. The difference in corrosion properties between cast iron-group metal and electrodeposited corresponding metal was detected. The values of corrosion potential (open circuit potential - OCP) are more negative for the electrodeposited metals than that for the corresponding cast metal, as well as higher corrosion currents were obtained for electrodeposited metals. The difference in corrosion properties between cast iron-group metal and electrodeposited corresponding metal in acidic media (0.5M H_2SO_4) decreases in sequence Ni<Co<Fe, whereas in neutral media (1M Na_2SO_4) the sequence is a following: Co<Ni<Fe, i.e. in all cases the corrosion resistance of electrodeposited Fe is worse than that for cast Fe
2. The corrosion rates in neutral and acidic media for nanocrystalline W-containing alloys (>20 at% of W) with Ni, Co and Fe electrodeposited from citrate-ammonia baths were evaluated. The corrosion current of electrodeposited nanocrystalline W alloys (>20 at.% of W) in acidic media decreases in sequence CoW>FeW≈Ni-W, whereas in neutral media the sequence is a following: CoW >FeW>NiW.
3. The corrosion of Ni in citrate and citrate-ammonia – carbonates solutions at 20 and 70 °C was detected that at higher temperature the corrosion potential is more negative. Each additive forming complex with Ni sufficiently cause the increase in corrosion current. At 70°C the values of ones can reach 2 mA/cm^2, that is 2-3 times higher than obtained at 20°C. Such corrosion current should be considered in technological processes utilizing pulse current or potential electrodeposition mode.
4. The corrosion properties (corrosion current, OCP or corrosion resistance) of Ni-18%Mo alloys electrodeposited from pyrophosphate bath onto Cu substrate depends on the thickness of electrodeposit up to 5-10 μm, further the values become independent on thickness.
5. The tribocorrosion resistance of electrodeposited and further self-passivated W and Mo alloys (Fe-26 at.% W, Co- 28 at.% W; Co- 4,5 at.% P-20 at.% W; Co-25 at.% Mo) decreases in sequence FeW>CoPW>CoW>CoMo.

6. The list of Original Publications by the Author

Articles in journals

1. V. Kublanovsky, O. Bersirova, A. Dikusar, Zh. Bobanova, H. Cesiulis, **J. Sinkeviciute**, I.Prosycevas. Electrodeposition and corrosion properties of nanocrystalline Fe-W alloys // *Physicochemical Mechanics of Materials* (ISSN 0430-6252), 2008, No. 7, p.p. 308-314.
2. H. Cesiulis, **J. Sinkeviciute**. The Study of Ni Corrosion in Dependence of Time // *Materials Science (Medziagotyra) (ISSN 1392–1320). 2006, Vol. 12, No. 1, p. 19-21.*
3. H. Cesiulis, **J. Sinkeviciute**. Corrosion of Ni in citrate-ammonia baths // *Physicochemical Mechanics of Materials* (ISSN 0430-6252), 2004, No. 4, p. 128-132.

Published contributions to academic conferences

1. Materials Engineering 2007. International Baltic Conference. October, Kaunas, Lithuania 2007
2. Chemistry 2005. 7th National Lithuanian Conference didicated to prof. Daukšas centenary. Vilnius, February 25, 2005
3. Materials Engineering 2005. 14th International Baltic Conference. October 6 – 7, Kaunas, Lithuania 2005
4. European Congress of Young Chemists. YpungChem 2004. October 13th – 17th 2004. Jurata. Poland
5. Respublikinė studentų mokslinė konferencija. Chemija ir cheminė technologija. Vilnius, 2004 m. gegužės 7 d

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Elektrochemiškai nusodintų W ir Mo lydinių su geležies grupės metalais korozijos tyrimas

SANTRAUKA

Buvo tiriama grynų geležies grupės metalų Ni, Co ir Fe (metalurginių ir jų elektrocheminių dangų) bei jų nanokristalinių lydinių su W arba Mo korozinės savybės, o taip pat šių užsipasyvavusių lydinių tribokorozinė elgsena. W lydinių pavyzdžiai buvo nusodinami iš citratinių-amoniakinių elektrolitų, o Ni-Mo – iš pirofosfatinio elektrolito.Ni ir Ni-Mo lydiniai nusodidami iš pirofosfatinių elektrolitų. Pagrindiniai tyrimai atlikti voltamperometrijos ir elektrocheminio impedanso metodu. Koroziniams tyrimams buvo naudojamos ne plonesnės nei 10 µm dangos.

Nustatyta, kad rūgštinėje korozijos terpėje skirtumai tarp metalo dangos ir metalurginio metalo korozijos savybė mažėja tokia seka: Ni<Co<Fe, o neutralioje terpėje: Co<Ni<Fe. Tuo tarpu geležies grupės metalų lydinių atveju rūgštinėje terpėje korozijos srovės didėja (atsparumas korozijai mažėja) tokia seka: CoW>FeW»Ni-W, o neutralioje: CoW>FeW> NiW.

Tiriant Ni koroziją citratiniuose - amoniakiniuose - karbonatiniuose tirpaluose, bei jų mišiniuose, 20^{o}C ir 70^{o}C temperatūroje. Gauta, kad bet koks šiame darbe tirtas priedas citratiniuose tirpaluose didina korozijos srovę, ypač $(NH_4)_2SO_4$ 20°C temperatūroje. Aukštesnėse temperatūrose korozijos srovės yra ~ 2 mA/cm^2, ir yra 2 – 3 kartus didesnės nei 20°C temperatūroje.

Dangų storio įtaka korozinėms savybėms tirta Ni-Mo lydiniui, kuris nusodinamas iš pirofosfatinio elektrolito. Gauta, kad korozijos potencialas arba varža priklauso nuo dangos storio, kai jis neviršija 5-8 µm. Kai danga storesnė, atsparumas korozijai nuo storio nepriklauso.

Ant plieno elektrochemiškai nusodintų ir savaime užsipasyvavusių W ir Mo lydinių (Fe-26 at.% W, Co- 28 at.% W; Co- 4,5 at.% P-20 at.% W; Co-25 at.% Mo) tribokorozinis atsparumas mažėja tokia seka: FeW>CoPW>CoW>CoMo.