COMPOSITION AND MORPHOLOGIES OF Mn-Ni AND Mn-Ni-Cu COATINGS ELECTRODEPOSITED FROM SOLUTION CONTAINING COMPLEXING LIGANDS EDTA AND NTA

D. Gogoli and G. Tsurtsumia

*Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry
of Ivane Javakhishvili Tbilisi State University
11 Mindeli Str., Tbilisi, 0186, Georgia
E-mail: davit.gogoli@tsu.ge*

Abstract:*The effects of complexing ligands -ethylenediaminetetraacetic acid disodium salt (EDTA), nitrilotriacetic acid trisodium salt (NTA) and their mixtures on the composition and morphology of Mn-Ni and Mn-Cu-Ni alloys obtained by electrodeposition were studied. It found that high values of stability constants of conventionally electropositive potential of the nickel ion complexes are not sufficient for obtaining of high-quality manganese-containing alloy coatings by electro-deposition; it is important for complex-containing solution to contain concentrations of metal ions with a definite ratio and additives of definite ligands or ligand mixtures. The formation of hydroxyl ions as a result of concurrent reaction – water reduction occurring in parallel with metals co-deposition has a significant impact on co-deposition processes of metals and on parameters of electro-deposition process.*
Keywords: *electro-deposition, composition, morphology, complexing ligands, stability constants, alloy, current efficiency.*

Introduction

Preparation of new metal alloy coatings capable of protecting steel from corrosion is a major objective of electrochemical deposition and functional galvanotechnics. A growing interest of researchers in alloys electrodeposition is mainly caused by the cost-effectiveness of metal coatings due to inexpensive and eco-friendly electrolytes used. In that regard, of particular interest was the possibility of obtaining manganese alloys characterized by high anti-corrosion performance with suitable mechanical properties [1,2]. Manganese is a metal with high negative standard potential $(E^0_{Mn^{2+}/Mn} = -1.18V, SHE)$. It is produced in the industry through electrolysis and is chemically active and easily reacts with air oxygen and moisture which results in coating the surface with manganese oxides and hydroxides.

Electrocoatings of pure manganese, despite their high effect, are fragile and in case of impact are easily removed from a steel surface to get protected from corrosion. Freshly electrodeposited Mn from the solutions by electrolysis yields a plastic γ-Mn with (body central tetragonal) (BCT) structure. It takes about ten days for electrodeposition of γ-Mn to get it completely transformed into a BCC (body centered cubic), brittle α-Mn at a temperature of 32°C [3-5]. The brittle, α-Mn can be modified in the presence of additives, such as sulfite-ion (SO_3^{2-}) or selenium compounds $(SeO_3^{2-}$ or $SeO_4^{2-})$ obtained from manganese-ammonium sulfates or chloride solutions. The conditions above promote a stable cathodic process with a high current efficiency together with induced deterioration of coatings' mechanical properties.

Many researchers attempted to reduce the chemical activity and brittleness of manganese [1,6,7]. It was suggested that alloying manganese with metals in their more positive standard potentials, e.g., Cu, Zn, Co, Ni and other metals, could stabilize the plastic γ-Mn form. For example, incorporation of 3% Cu into manganese contributes to the stabilization of the γ-Mn form for a long period.

Nickel coatings are widely used in electrodeposition technology due to their tendency toward passivation, in particular, they are chemically stable in the atmosphere, water and many acids. Nickel coatings protect steel mechanically; however, they fail to protect it electrochemically, for they are cathodic with regard to steel (has more positive potential as compared to steel). Nickel and manganese coatings have greater strength and toughness, next come monolithic nickel coatings. Additionally, Ni-Mn alloys enhance resistence to sulfur embrittlement when heated [8].

There is scarce information in the scientific literature about preparing Mn-Ni and Mn-Ni-Cu galvanic (plating) coatings. Ni-Mn alloy coatings for electroforming were obtained from nickel sulfamate-containing solutions in the presence of manganese salts [9-15]. As a result of electrodeposition the manganese content in the coatings was 2wt%. Despite such a small quantity, the coating hardness essentially rose to reach 500Hv even in spite of the fact that the coatings are characterized by more or less internal stress. In the work [16] Ni-Mn alloy coatings are also prepared through electrodeposition in the sulfamate bath, at low current density 1-2 A/dm^2. Obtained coatings are characterized by low internal stress, high leveling power and better corrosion resistance. Proceeding from the results obtained, the Ni-Mn

alloy coatings mentioned above can be regarded as an acceptable electrodeposition system for microelectronic applications.

Thus, according to available literature data, Ni-Mn alloy coatings are obtained through electrodeposition from sulfamate solutions whose manganese content doesn't exceed 6 wt%. Note that Mn-Ni coatings are used for sacrificial protection of steel against corrosion. Besides, their high adhesion to the surface has to be characterized by more negative corrosion potential value as compared to corrosion potential of the steel to be protected. This is achieved by the increase in the content of manganese metal with more negative potential in the coating.

Many researchers use the complex compound-containing solutions for obtaining high-quality galvanic coatings for metals and alloys. Today there is no theory or model making it possible to select the solution composition for alloy electrodeposition. There are common approaches only to roughly estimate metals co-deposition. In case of co-deposition of two or more metals, it is necessary to approach their deposition potentials that can be reached through adding the complex-forming ligands into electrodeposition bath. At this time, they usually try to select ligands that form complexes of metal ions with more positive electrode potential whose stability constants (β^0) are higher than stability constants of metal ion complexes with less positive potential. According to the probability model of additive selection of ligands developed by E.G. Vinokurov and V.V. Bondar [17], the following conditions ought to be met for joint electrodeposition of A and B components in the alloy:

$$\lg\beta^0_A / n_A \geq 1.5 \lg\beta^0_B / n_B \text{ or } \lg\beta^0_A / \lg\beta^0_B \geq 1.5 \, n_A / n_B, \qquad (1)$$

where β^0_A, β^0_B and n_A, n_B – stability constants of more electropositive metal A and electronegative metal B and their ions' charges in the complex. Based on this condition, we

selected as complex-forming ligand with one-type aminopolycarbonic acid derivatives, the so-called complex – sodium salt of ethylenediamine tetra-acetic acid Trilon B

(H_2Y^{2-} is a ligand) and trisodium salt of nitrilotriacetic acid NTA (X^{3-} is a ligand) which forms, with metal ions, the complexes with different density and stability constants.

The objective of the work was to select the electrolyte composition for electrodeposition of high-quality Mn-Ni and Mn-Ni-Cu alloy coatings with high content of manganese from the solutions containing ligands (H_2Y^{2-} and X^{3-}) with different density and stability constants. In order to accomplish the task, the impact of cathode current density, solution pH on the current yield of electrodeposited coatings, coating thickness, electrolysis duration, and composition and morphology of alloys were studied.

Experiments

Chemically pure reagents (Aldrich): $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $CuSO_4 \cdot 5H_2O$, Na_2SeO_4, ethylenediaminetetraacetic acid disodium salt dehydrate– $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$(EDTA), nitrilotriacetic acid trisodium salt monohydrate– $C_6H_6NNa_3O_6 \cdot H_2O$ (NTA) were chosen for preparation of electrodeposition solutions.

Distilled water was used for solutions preparation. As is known, for electrodeposition of manganese metal, it is essential to have buffer reagent (additive agent) ammonia sulfate, or selen-containing compounds [18] in small quantities in the electrolyte to inhibit hydrogen evolution process and raise manganese current yield. For this reason, all electrolytes used for obtaining galvanic coatings for manganese-containing alloy provide for ammonium sulfate as a main additive and selenate Na_2SeO_4 in small quantity as well. Solution composition and electrodeposition conditions for separate experiments are indicated in appropriate tables and figures. Electrodeposition was conducted through the use of DC power supply type Power station PE 1018-2 (plating electronic GmbH) in a rectangular bath made of organic glass (polymethyl methacrylate) separated by belting diaphragms into three parts: two anodic and middle cathodic compartments. Catholyte (400ml) was circulated through cathodic chamber by micro-pump and silicon tubes from the reservoir for circulation of solution. The reservoir was equipped with electric heater placed in a quartz pipe for heating the solution (30^0C) and with the glass electrode for pH control (MP5129, Chine). Constant pH in the catholyte was maintained during electrodeposition by drop-wise addition of 50% H_2SO_4 into circulation reservoir. Note that volume of stagnant anolyte (0.5 mol/l Na_2SO_4) was 300ml; electric coatings were obtained on steel (C 0.22%, Mn 0.52%, Si 0.18%, P<0.04%, S<0.05%, As<0.08%) or copper electrodes with total area of 4 cm^2; titan electrodes with 40cm^2 area modified by TiO_2 and RuO_2 were used as anodes.

The thickness of coating was verified by a coating thickness measurement instrument DCFN 3000EZ.

The chemical composition of the coatings was determined by the X-ray-fluorescence analysis method (Delta-Analyzer<Innov-X Systems >USA) and by means of an X-ray energy dispersion micro-spectral analyzer (JSM 6510 LM, Japan). The morphologies of coatings were determined by the SEM,JSM-6510 series JEOL Ltd. Japan.

Current efficiency of alloy coatings' electrodeposition was determined through the use of electrogravimetric method – via definition of cathode weight gain (accuracy of 0.001 g) after passing a known quantity of electricity. Given the alloy composition, the current efficiency(ϕ_{alloy}) was calculated from formula [19]:

$$\Phi_{alloy.} = m_{alloy}/(I \cdot \tau \cdot K(alloy) \cdot 100\%, \quad (2)$$

where, $m_{alloy.}$ – the mass of deposited alloy, g; I – passed current, A; τ– time of electrolysis, h; K(alloy) – electrochemical equivalent of alloy. This value was calculated from general formula:
$$K(alloy) = 1/(\omega_1/K_1 + \omega_2/K_2 + \omega_3/K_3 + ... + \omega_n/K_n),$$
(3)

where, ω_1, ω_2, $\cdots$ ω_n mass content of metals in the alloy, while K_1, K_2, $\cdots K_n$ – their electrochemical equivalents. Coating thickness (δ) was calculated from formula:

$$h = \tau \cdot i_{cath.} \cdot K_{alloy} \cdot \phi_{alloy}/d_{alloy}, \qquad (4)$$

where, $i_{cath.}$ – cathodic current density, A/cm^2; d_{alloy}–alloy density, g/cm^3.

The density of two-component alloy was calculated under the approximate formula:

$$d_{alloy} \approx d_1 d_2/(d_1\omega_1 + d_2\omega_2) \quad (5)$$

The values of coating thickness measured by means of DCFN 3000EZ tool complied with values under the formula (4).

Results and discussion

Complexons selected as additives in solutions meant for preparation of Mn-Ni and Mn-Ni-Cu galvanic coatings for manganese-containing alloys' dissociate: Trilon B is dissociated in a weak acid medium, predominantly in the H_2Y^{2-} anionic form:

$$Na_2H_2Y \leftrightarrows 2\,Na^+ + H_2Y^{2-} \qquad (6)$$
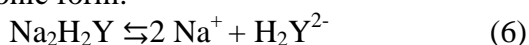
In general, the generated anionic form depends on pH, however, complex formation with Ni^{2+}, Mn^{2+}, Cu^{2+} and other ions occurs in one stage and metal-ligand ratio (1:1) in the complex doesn't change:

$$Me^{2+} + H_2Y^{2-} \leftrightarrows MeY^{2-} + 2H^+ \qquad (7a)$$

$$Me^{2+} + X^{3-} \leftrightarrows MeX^- \qquad (7b)$$
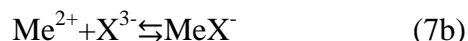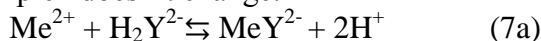
Ligand – ethylenediamine tetra-acetic acid anion Y^{4-} is hexadentate ligand (due to availability of 4-carboxyl, 2-amino group). Nitrilotriacetic acid anion X^{3-} is tetradentate ligand (due to availability of 3-carboxyl and 1 amino group) to form the complexes with formula MeX by means of Ni^{2+}, Mn^{2+} and Cu^{2+}ions. Stability constant values of these metal complexes with ligand Y^{4-} are characterized by higher magnitudes as compared to ligand X^{3-} (Table 1) [20].

Table 1. Logarithms of stability constants ($lg\beta^0$) of Mn^{2+}, $Ni^{2+}$and Cu^{2+} ions complexes with ligands and their values $lg\beta^0/n$

Ligand	$lg\beta^0_{Mn}{}^{2+}$	$lg\beta^0_{Mn}{}^{2+}/n$	$lg\beta^0_{Ni}{}^{2+}$	$lg\beta^0_{Ni}{}^{2+}/n$	$lg\beta^0_{Cu}{}^{2+}$	$lg\beta^0_{Cu}{}^{2+}/n$
Y^{4-} (EDTA)	13.56	6.78	18.56	9.28	18.80	9.4
X^{3-}(NTA)	7.44	3.72	11.26	5.63	12.68	6.34

As is seen from Table 1, given the both ligands, the values of logarithms of stability constants of complexes decrease in $lg\beta^0_{Cu}{}^{2+}>$ $lg\beta^0_{Ni}{}^{2+}>$ $lg\beta^0_{Mn}{}^{2+}$ series. Conditions of the above mentioned equation (1) $lg\beta^0_{Cu}{}^{2+}/n>lg\beta^0_{Ni}{}^{2+}/n>lg\beta^0_{Mn}{}^{2+}/n$ are complied with; however, the ratio is not more than 1.5 like a model of simultaneous electrodeposition of alloys requirements [17].

The external appearance and composition of Mn-Ni coatings obtained through the electrodeposition with EDTA additive from solutions containing nickel and manganese sulfates substantially depends on molar ratio of nickel and EDTA (in terms of unchangeable concentration of other components) (Fig. 1).

Fig. 1 shows that selenium and carbon are incorporated in the coating of the steel electrode. Coatings are silver-colored only due to the increase of nickel sulfate concentration up to 25 g/l (0.089 mol/l); however, they are obtained in lamellar (flake) form. Manganese is deposited on the electrode with molar ratio 0.1:0.15 together with simultaneous rise in nickel sulfate and EDTA concentrations in the solution to be electrodeposited (Fig. 2). Crystals of electrodeposited manganese are of spherical shape and grown as a column.
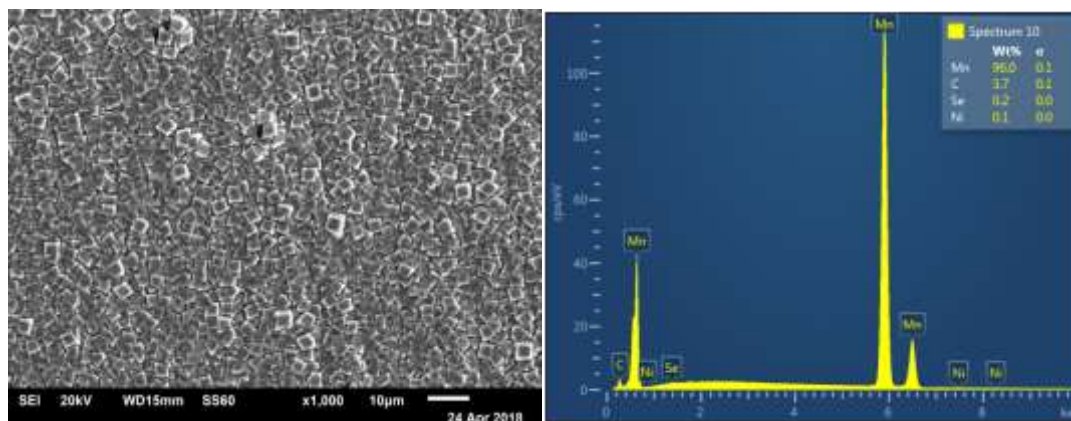
Fig.1.SEM and chemical composition of the coating obtained from the solution: 5g/l (0.0178 mol/l) $NiSO_4 \cdot 7H_2O$ + 9.75g/l (0.026mol/l) EDTA + 0.33g/l Na_2SeO_4 + 52.85g/l(0.35mol/l)$MnSO_4$ + 79.2g/l (0.6 mol/l) $(NH_4)_2SO_4$; conditions of electrodeposition on steel electrode: 0.15A/cm^2; pH 3.5; t=30^{0}C; electrodeposition time 15 min.
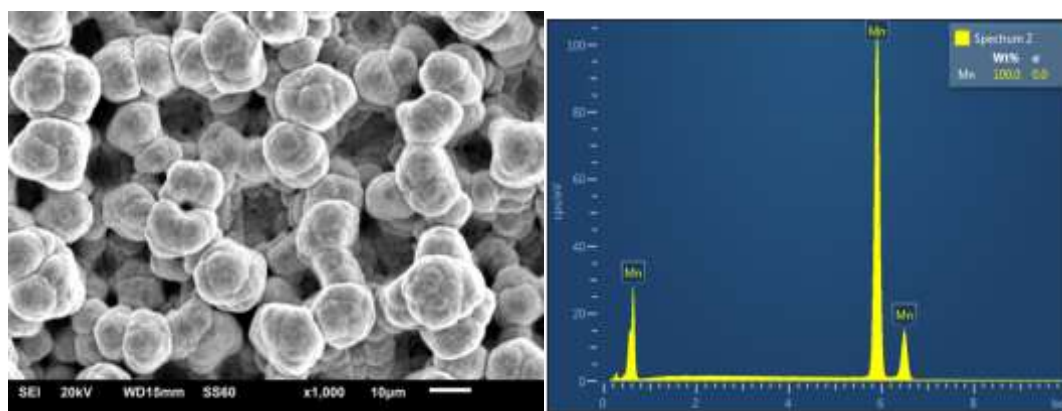

Fig.2. SEM and chemical composition of the coating obtained from the solution: 28.1g/l (0.1mol/l)$NiSO_4 \cdot 7H_2O$ + 55.825g/l (0.15 mol/l) EDTA + 0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$ + 79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on steel electrode: 0.15 A/cm^2; pH 6.5; t=30^{0}C; electrodeposition time 15 min.

Adding NTA ligand instead of EDTA drastically changes coating structure and composition of the electrode – very thin coating with 25% current yield is obtained, main component of which is nickel (Fig. 3); coating thickness is 5-7μm.

It is seen in SEM picture that silver-colored coating is so much thin that copper electrode impact is noticeable on the chemical composition graph. Manganese content increases in the thin coatings at pH = 3,5 and at high current densities, but the strain in coatings also increases, so cracks become visible (Fig. 4). Results of the experiment show that a higher value of nickel complex stability constant as compared to manganese complex with EDTA provides the electrodeposition of manganese in the coating only. At the same time, in case of NTA ligand due to relatively low values of stability constants of complexes, nickel content

in thin coatings prepared through electrodeposition exceeds significantly the

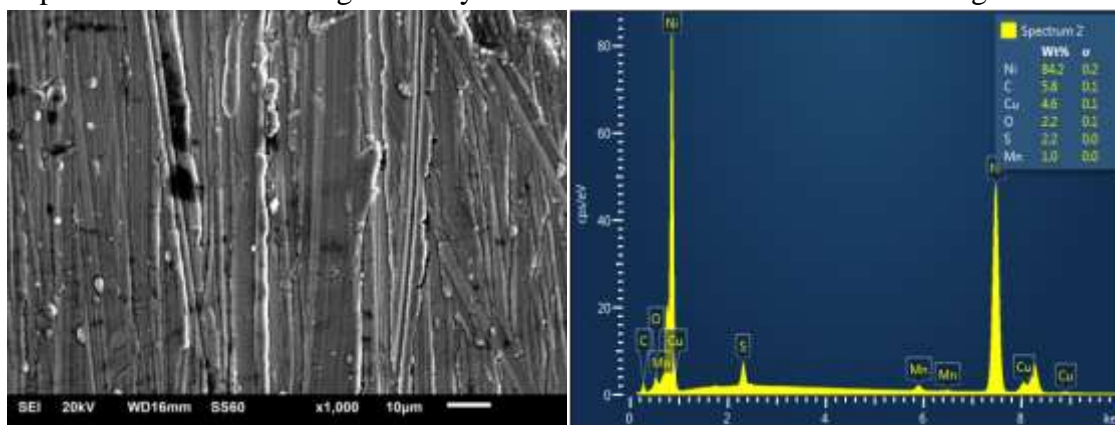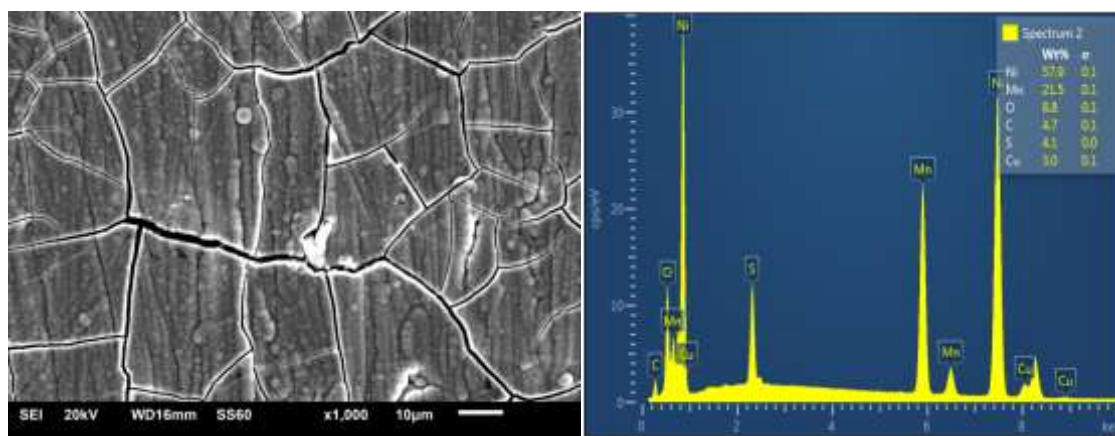manganese quantity; however, in parallel the tension increases in the coating.

Fig.3. SEM and chemical composition of the coating obtained from the solution: 28.1g/l (0.1mol/l) $NiSO_4 \cdot 7H_2O$ + 27.5g/l (0.1 mol/l) NTA + 0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$ + 79.2g/l$(NH_4)_2SO_4$; conditions of electrodeposition on copper electrode: 0.05 A/cm^2; pH 6.5; t=30^{0}C; electrodeposition time 15min.

Fig.4. SEM and chemical composition of the coating obtained from the solution: 28.1g/l (0.1mol/l)$NiSO_4 \cdot 7H_2O$ +27.5g/l (0.1 mol/l) NTA + 0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$ +79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on copper electrode: 0.15 A/cm^2; pH 3.5; t=30^{0}C; electrodeposition time15min.

Given the different effect of ligand additives on structure and composition of coatings, it'd be interesting to conduct the electrodeposition process in the presence of ligand additives in the electrodeposition solution. There were ready solutions where molar ratios of ligands changed only.
Fig. 5 below shows SEM and chemical composition of alloy coatings that are obtained

on the copper cathode from the solution with molar ratio of EDTA:NTA ligands = 0.05:0.1. As shown in Fig.5, Mn–Ni coatings are of low quality and copper electrode impact on composition spectrum of thin coating is noticeable. Within the cathode current density range of 0.15 – 0.25A/cm^2, the coatings are silver-colored and the value of alloy current
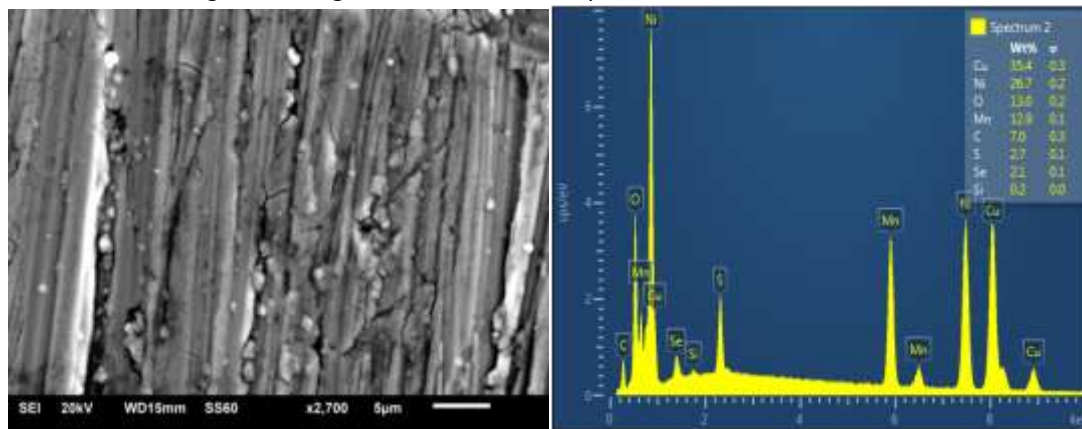
yield was 20% in average; coating thickness – 5-   7μm.

Fig.5. SEM and chemical composition of the coating obtained from the solution: 28.1g/l (0.1mol/l) $NiSO_4 \cdot 7H_2O$ + 18.625g/l (0.05 mol/l) EDTA + 27.5g/l (0.1 mol/l) NNA +0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$+ 79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on copper electrode: $0.15A/cm^2$; pH 3.5; t=30^0C; electrodeposition time 15min.

Coatings obtained in the electrodeposition solution in terms of 0.1:0.05 molar ratio EDTA: NTA ligands are of good quality and manganese content prevails therein (Fig. 6).
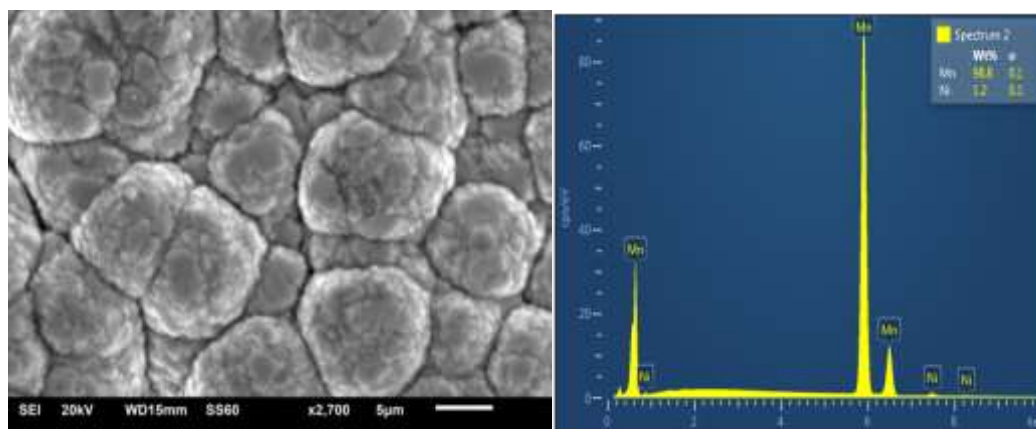

Fig.6. SEM and chemical composition of the coating obtained from the solution: 28.1g/l(0.1mol/l) $NiSO_4 \cdot 7H_2O$ + 37.25g/l (0.1mol/l) EDTA+ 13.775 g/l (0.05 mol/l) NTA+0.33g/lNa_2SeO_4 + 52.85g/l $MnSO_4$+ 79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on copper electrode:$0.2A/cm^2$; pH 3.5; t=30^0C; electrodeposition time is 15 min.

Electrodeposited Mn-Ni coatings within the density limit 0.2-0.3 A/cm^2 were dense and coating thickness was 25-30 μm in average, while current yield was 43-45%.
SEM and chemical composition of obtained electrocoatings together with the solution of both ligands and equal molar ratio EDTA:NTA=0.1:0.1 are shown in Fig. 7.

As shown in Fig 7, electrocoatings obtained from solutions with equal molar ratio of ligands consisting of crystals with unequal size, and small-sized cracks are noticeable between separate agglomerates. Manganese (98.2%) dominates in the alloy coating. According to the experimental results, it is virtually impossible to obtain quality Mn-Ni

alloy coatings from sulfate solutions containing the definite composition of nickel-manganese with addition of one ligand - either EDTA or NTA. However, due to their different density, it was possible to conduct electrodeposition of quality Mn-Ni alloy with 42-45% current yield by adding ligands in certain molar ratio (EDTA:NTA=0.1:0.05) where the electronegative manganese prevails.
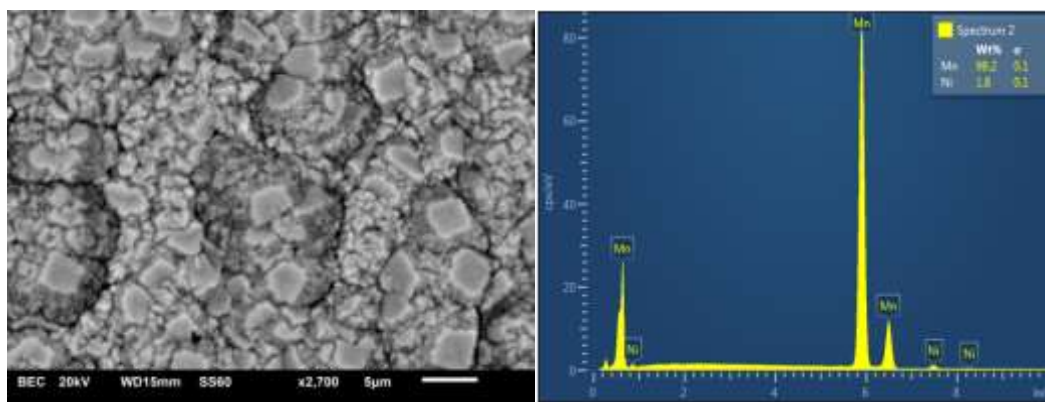

Fig.7.SEM and chemical composition of the coating obtained from the solution: 28.1g/l (0.1mol/l) $NiSO_4 \cdot 7H_2O$ + 37.25g/l (0.1mol/l) EDTA+ 27.5 g/l (0.1 mol/l) NTA + 0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$ + 79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on copper cathode:0.15A/cm^2; pH 3.5; t=30^{0}C; electrodeposition time 15min.

Thus, the so-called anomalous electrodeposition takes place [21] that means the preferred deposition of electronegative metal as compared to electropositive metal. We assume that the preparation of Mn-Ni coating with high manganese content might be caused by high value of electrochemically active nickel complex stability constant and, respectively, by its low reduction rate. Where both ligands added, presumably certain balance is achieved in the solution between metal complexes:

$$MeY^{2-} + X^{3-} \leftrightarrows MeX^- + Y^{4-}, \qquad (8)$$
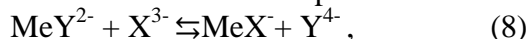
where equilibrium concentrations have a significant impact on composition and morphology of the electrodeposited coating. We tried to obtain a ternary Mn-Ni-Cu alloy coating with copper sulfate salt additive from a solution with the given content of nickel-manganese sulfates where the molar ratio of EDTA and NTA mixture was 0.1:0.05, i.e. in case where high-quality Mn-Ni coating was obtained. As is known, the introduction of electrodeposited copper into Mn-Ni alloy raises the corrosion stability of ternary Mn-Zn-Cu alloy and coating adhesion ability to the electrode [22].

Preparation of Mn–Ni-Cu coatings became possible due to high current densities (0.3-1.4 A/cm^2) through the reduction of coating duration to 7 minutes and under pH 6-7.5. Current yield of the alloy varied within limits of 31-38% while the coating thickness was 16-20μm. Mn-Ni-Cu alloy morphology and chemical composition are shown in Fig. 8 below.

Note that Mn–Ni-Cu coating crystals are of spherical shape and grow like columns with cavities, which presumably indicate the formation of passive surface of steel cathode. When electro-deposition duration is above 7 minutes, the coating is blackish due to metal hydroxides which are presumably formed as a result of electrochemical concomitant reactions of the interaction of obtained hydroxyl ions and metal complex ions in the adjacent layer:
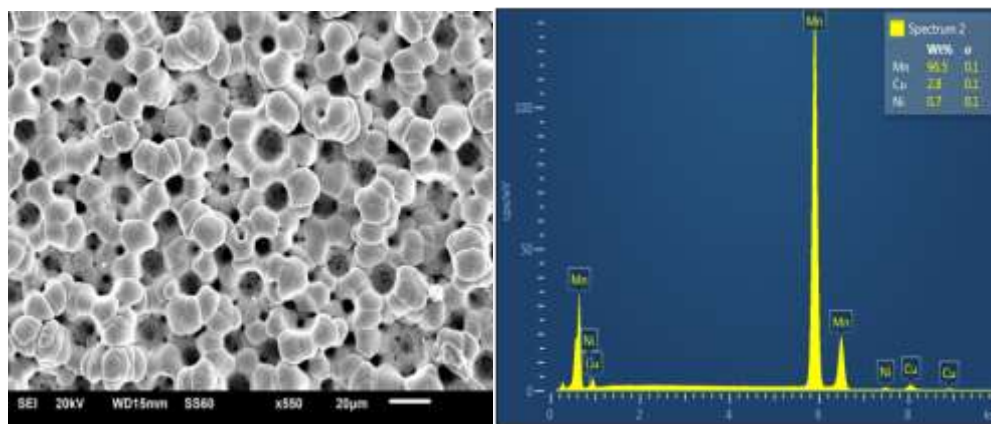
$$2H_2O + 2e \rightarrow H_2 + 2OH^- \qquad (9)$$
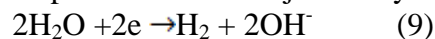
Fig.8. SEM and chemical composition of the coating obtained from the solution: 2.5g/l $CuSO_4 \cdot 5H_2O$+28.1g/l $NiSO_4 \cdot 7H_2O$ + 37.25g/l (0.1mol/l) EDTA + 13.775 g/l (0.05 mol/l)NTA + 0.33g/l Na_2SeO_4 + 52.85g/l $MnSO_4$ + 79.2g/l $(NH_4)_2SO_4$; conditions of electrodeposition on steel cathode:0.15A/cm^2; pH 6.5; t=30^{0}C; electrodeposition time 5 min.

In case of one ligand addition from solutions of mentioned composition in the wide range of cathode current densities, the coatings are black and easily removed from electrode surface. This indicates that in the electro-deposition process of metal alloys, the key role is assigned to hydroxyl ions originating from the cathode surface via water molecules reduction reaction. Hydroxyl ions lead to the formation of metal hydroxides that manifests itself in blocking the electrode surface and terminating the metal electro-deposition process. Experimental justification of this opinion is a goal of further research.

Conclusions

The quality coatings of Mn(98.2%)-Ni and Mn(96.5%)-Cu-Ni alloys with relatively high content of manganese are obtained by stationary electrolysis in sulfate solutions of corresponding metals with addition of mixture of complex-forming ligands EDTA and NTA (with molar ration 0,1:0,05) and surface-active substances (Na_2SeO_4). It found that a complex-containing solution selected for electro-deposition of quality Mn-Ni and Mn-Cu-Ni alloy coatings contains definite ratio of metal ions concentrations and additives of definite ligand or ligand mixture. The formation of hydroxyl ions as a result of concurrent reaction of water reduction taking place in parallel with metals co-deposition has a significant impact on the composition, external appearance of alloy coatings, as well as the parameters of electro-deposition process (current density, solution pH, electrolysis duration).

It revealed that a higher stability constant of nickel complex with EDTA as compared to the stability constant of corresponding manganese complex provides the electro-deposition of manganese only that is impossible from solutions without ligand additives.

References

1. Gong J. & Zangari G. Electrodeposition and characterization of manganese coatings. *J.Electrochemical Society*. 2002, vol.149, no. 4, pp. C209-C217.
2. Gong J., Zangari G. Increased metallic character of electrodeposited Mn coatings using metalion additives. *Electrochemical and Solid-State Letters*. 2004, vol. 7, no. 9, pp. C91- C97.
3. Dean R.S. Electrolytic manganeseand its alloys. New York: The Ronald Press Company.1952. p.125.
4. Lu J., Dreisinger D., GlückT. Manganese electrodeposition. A literature review. *J. Hydrometallurgy*. 2014, vol. 141, pp.105–116.
5. Sulcius A., Griskonis E., Kantminiene K., Zmuidzinaviciene N. Influence of different electrolysis parameters on electrodeposition of γ- and α-Mn from pure electrolytes – review with special reference to Russian language literature. *J. Hydrometallurgy*. 2013, vol. 137, May, pp. 33-37.
6. Gong J. & Zangari G. Electrodeposition and Characterization of Sacrificial Copper-Manganese Alloy Coatings. *J. Electrochemical Society*. 2004, vol. 151, no. 5, pp. C297-C306.
7. Mpoyo L.M., Degrez M., and Winand R. High Speed Electrodeposition of Alloys. Part 1: Manganese-Copper Alloys. Oberflachen Werkstoffe. 1993, vol.4, pp. 7-11.
8. Malone G.A. New developments in electroformed nickel-based structural alloys. *Plating And Surface Finishing*. 1987, vol. 74, pp. 50-56.
9. Stephen A., Ananth M.V., Ravichandran V., and Narashiman B.R.V. Magnetic properties Of electrodeposited nickel-manganese alloys: effect of Ni/Mn bath ratio. *J. Appl. Electrochem*. 2000, vol. 30, no.11, pp.1313-1316.
10. Goods S.H, Kelly J.J., and Yang N.Y.C. Electrodeposited nickel-manganese: an alloy For microsystem application. *Microsystem Technologyies*. 2004, vol.10, no.6-7, pp. 498-505.
11. Marquis E.A., Talin A.A., Kelly J.J., Goods S.H., and Michael J.R. Effects of current density on the structure of Ni and Ni-Mn electrodeposits. *J. Appl. Electrochem*. 2006, vol. 36, no. 6, pp. 669-676.
12.Atanassov N. and Mitreva V. Electrodeposition and properties of nickel-manganese layers. *Surface and Coatings Technology*. 1996, vol. 78, no. 1-3, pp. 144-149.
13. Kelly J.J., Goods S.H., and Yang N.Y.C. High performance nanostructured Ni-Mn alloy for microsystem applications. *Electrochemical and Solid-State Letters*. 2003. vol. 6, no. 6, pp.C88-C91.
14. Cheng K.H, Chen F.J., Lee C.Y., Lin C.S., Huang J.T, Lan C.C., Tsou P.H., and Ho T.I. Fabrication of Ni-Mn microprobe structure with low internal stress and high hardness Byemploying DC electrodeposition. *Adv. Mat. Science and Engineering*. 2014, vol. 2014, Article ID 890814, 6 pages.
15. Stephen A. Corrosion behavior of electrodeposited Ni-Mn alloys – electro-chemicallimpedance measurement. *Anti-Corrosion Methods and Materials*.1999, vol. 46, no. 2, pp.117- 121.
16. Lee C.Y., Cheng K.H., Wu M.W. The mechanical and electrochemical properties of DC-electrodeposited Ni-Mn alloy coating with low internal stress. *Int. J. Mechanical and Mechatronics Engineering*. 2015, vol. 9, no.7, pp.1336-1340.
17. Vinokurov E.G., Bondar V.V. Models for describing and predicting the processes of electrodeposition of alloys. 2009. Moscow: VINITI.(In Russian).
18. Fan X., Xi, S., Sun D., Liu Z., Du Jun, Tao C. Mn-Se interactions at the cathode interface during the electrolytic-manganese process. *J.Hydrometallurgy*. 2012, vol. 127-128, pp. 24-28.

19. Gamburg Y.D. and Zangari G. Theory and Practice of Metal Electrodeposition. 2011, Springer, New York, pp. 235-240.
20. Martell A.E. and Motekaitis R.J. Determination and Use of Stability Constants.1989.VCH Publishers, New York, NY, USA, p.27.
21. Brenner A. Electrodeposition of Alloys. Principle and Practice. Akademic press, NewYork.1963, pp.102-152.
22. Tsurtsumia G., Koiava N., Gogoli D., Kakhniashvili I., Lezhava T., Jokhadze N., Kemoklidze E. Study of the influence of the electrolysis parameters on Mn-Zn, Mn-Cu and Mn-Cu-Zn alloys coating from electrolytes containing complexing ligands. *J. Chem. Chem. Eng.,* 2016. vol.1, pp. 13-27.

EDTA И NTA TƏRKİBLİ MƏHLULLARDAN ELEKTROÇÖKDÜRMƏ YOLU İLƏ ALINAN Mn-Ni VƏ Mn-Ni-Cu ÖRTÜKLƏRİNİN TƏRKİBİ VƏ MORFOLOGİYASI

D.Q. Qoqoli və Q.S. Tsurtsumiya

Tbilisi Dövlət Universitetinin Qeyri-üzvi və Elektrokimya İnstitutu
0186 Tbilisi, Mindeli küç., 11, e-mail: davit.gogoli@tsu.ge

Kompleks əmələgətirən EDTA və NTA liqandların və onların qarışığının elektroçökdürmə yolu ilə alınan Mn-Ni və Mn-Ni-Cu örtüklərinin tərkib və morfologiyasına təsiri öyrənilmişdir. Müəyyən edilmişdir ki, keyfiyyətli örtük yalnız məhlulun tərkibində metall ionlarının və liqandların qatılığı müəyyən nisbətdə olduqda alınır. Metalların birgə elektroçökdürmə prosesinə və onun parametrlərinə (cərəyan sıxlığı, məhlulun pH-ı, elektrolizin müddəti) yan reaksiya nəticəsində əmələ gələn hidroksil ionları da təsir edir.
Açar sözlər: elektroçökdürmə, tərkib, morfologiya, liqand, manqan, nikel

СОСТАВ И МОРФОЛОГИЯ ЭЛЕКТРООСАЖДЕННЫХ ПОКРЫТИЙ Mn-Ni И Mn-Ni-Cu ИЗ РАСТВОРОВ, СОДЕРЖАЩИХ КОМПЛЕКСООБРАЗУЮЩИЕ ЛИГАНДЫ EDTA И NTA

Д.Г. Гоголи и Г.С. Цурцумия

Институт неорганической химии и электрохимии им. Р. Агладзе
Тбилисского государственного университета им. И. Джавахишвили
ул. Миндели 11, Тбилиси, 0186, Грузия, e-mail: davit.gogoli@tsu.ge

Изучено влияние комплексообразующих лигандов EDTA и NTA и их смесей на состав и морфологию полученных электроосаждением сплавов Mn-Ni и Mn-Cu-Ni. Установлено, что высокое значение константы устойчивости комплексов никеля не является достаточным условием для получения качественных покрытий; необходимо, чтобы комплексосодержащий раствор содержал определенное соотношение концентраций ионов металлов и добавок лиганд или смесей лигандов. Значительное влияние на процессы соосаждения металлов и его параметры (плотность тока, pH раствора, продолжительность электролиза) оказывают ионы гидроксила, образующиеся в результате побочной реакции восстановления воды, протекающей параллельно соосаждению металлов.
Ключевые слова: электроосаждение, состав, морфология, лиганд, константа устойчивости, марганец, никель, сплав, выход по току.