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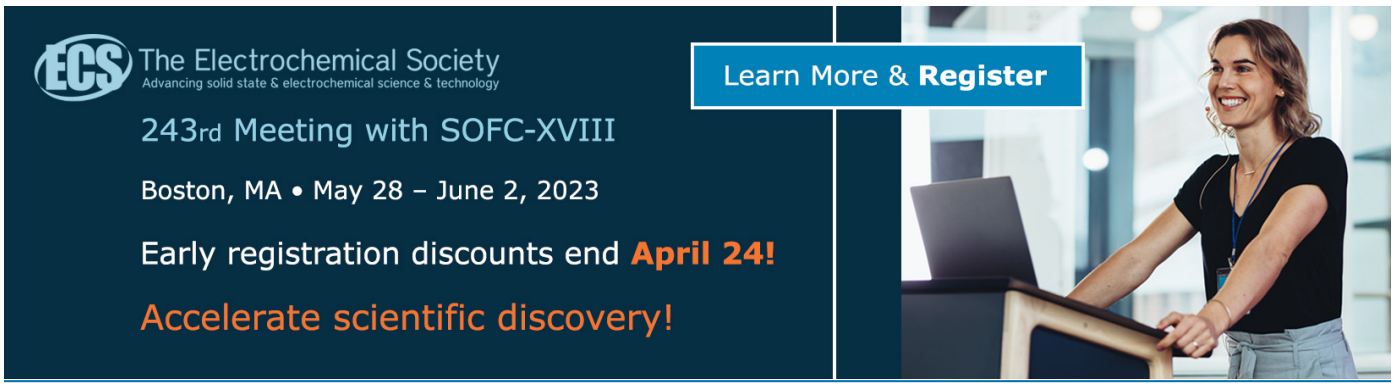

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Electrodeposition and Characterization of Mn-Cu-Zn Alloys for Corrosion Protection Coating

Gigla Tsurtsumia[1], David Gogoli[1], Nana Koiava[1], Izolda Kakhniashvili[1,2], Nunu Jokhadze[1], Tinatin Lezhava[1], Nikoloz Nioradze[1], Dimitri Tatishvili[3]

[1] TSU, Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, 11 Mindeli Str., Tbilisi 0186, Georgia
[2] Georgian Technical University, 69 Kostava Str., Tbilisi 0176, Georgia
[3] G. Tsulukidze Mining Institute, 7 Mindeli Str., Tbilisi 0186, Georgia

giglat@yahoo.com

Abstract. Mn-Cu-Zn alloys were electrodeposited from sulphate bath, containing citrate or EDTA and their mixtures as complexing ligands. The influence of bath composition and deposition parameters on alloys composition, cathodic current efficiency and structural and electrochemical properties were studied. At a higher current density (≥ 37.5 A dm^{-2}) a uniform surface deposit of Mn-Cu-Zn was obtained. Optimal pH of electrolyte (0.3 mol/dm^3 Mn^{2+} + 0.6 mol/dm^3 $(NH_4)_2SO_4$ +0.1 mol/dm^3 Zn^{2+}+0.005 mol/dm^3 Cu^{2+}+ 0.05mol/dm^3 Na_3Cit + 0.15mol/dm^3 EDTA; t=30^0C; τ=20 min) for silvery, nonporous coating of Mn-Cu-Zn alloy was within 6.5-7.5; coating composition: 71-83% Mn, 6-7.8% Cu, 11.5-20% Zn, current efficiency up to 40%. XRD patterns revealed BCT (body centred tetragonal) γ-Mn solid phase solution (lattice constants a=2.68 Å; c=3.59 Å). Corrosion measurements of deposited alloys were performed in aerated 3.5% NaCl solution. The corrosion current density (i_{corr}) of the electrodeposited alloys on carbon steel was 10 times lower than corrosion rate of pure zinc and manganese coatings. Triple alloy coatings corrosion potential (E_{corr}= -1140 mV vs. Ag/AgCl) preserved negative potential value longer (more than three months) compared to carbon steel substrate (E_{corr}= -670 mV vs. Ag/AgCl). Tafel polarization curves taken on Mn-Cu-Zn alloy coating in aerated 3.5% NaCl solution did not show a typical passivation behaviour which can be explained by formation oflow solubility of adherent corrosion products on the alloy surface. Corrosion test of Mn-Cu-Zn electrocoating in chlorine environment shows that it is the best cathodic protective coating for a steel product.

1. Introduction

Thanks to abundance of manganese and its high negative standard potential ($E^0_{Mn2+/Mn}$ = -1.15 V), researchers are interested in development of manganese galvanic coatings and its alloys as protective materials. Manganese alloys with copper, zinc, cobalt, and nickel are characterized by high corrosion protective properties and their technical and economic efficiencies are equal to known protectors prepared on the bases of aluminium and magnesium [1]. However, wide use of pure manganese galvanic coatings is restricted due to their relatively high chemical activity and brittleness, caused by change of crystalline modification. Plastic γ-Mn tetragonal face-centred structure is obtained by electrodeposition. After short time, γ-Mn transforms into stable, brittle, body-centred cubic α-Mn [2]. Chemical activity and brittle form of α-Mn can be reduced by alloying it with metals such as copper, zinc, cobalt, nickel, iron and others having a lower negative standard potential. Alloying metals such

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as copper, iron, nickel, cobalt, stabilize γ- Mn modification. For example, addition of 3% copper in manganese provides stability of γ-Mn modification for a long time [3-5].

In literature, there is widely available information as about production as well as about corrosion resistance of binary manganese containing galvanic coatings. Special interest attracts Zn-Mn binary coatings because Zn-Mn alloy coatings with high Mn content (10-30% at. Mn) are characterized with the highest corrosion resistance among other zinc alloys [6,7]. Due to high plasticity and corrosion resistance characteristic to binary Mn-Cu and Mn-Zn alloys, it was interesting to combine their characteristics in one triple Mn-Cu-Zn alloy. Different composition, but similar triple galvanic coating alloy (Zn-Ni-Mn) was obtained from sulphate solutions, in which content of Mn did not exceed 3.7% [8].

In the presented work, electrodeposition of high quality triple alloy Mn-Cu-Zn coatings from sulphate solution containing complexing ligands of citrate, EDTA and their mixtures is described. Also, influence of electrolyte composition, pH and cathodic current density on galvanic alloy coating chemical composition, current efficiency, corrosion stability, morphology and structure is studied.

2. Experimental procedure

Electrodeposited coatings of manganese-containing alloys were obtained using electrolytes of various compositions. Electrolytes were prepared from analytical grade reagents: $MnSO_4 \cdot H_2O$, $(NH_4)_2SO_4$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$, sodium citrate ($Na_3C_6H_5O_7 \cdot 5.5H_2O$) and EDTA ($Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$). Electrolyte preparation, electrolysis conditions and calculation of alloys cathode current efficiency are described in detail [9].

Electrochemical characterization techniques such as linear and Tafel polarization studies were carried out to evaluate the corrosion properties of the Mn-Cu-Zn alloys. The experiments were performed at room temperature with a ПИ-50-1.1 potentiostat system (Russia). The potentiodynamic measurements were done in the 3-electrode electrochemical cell containing aerated 3.5% NaCl solution, which was appropriate for studying corrosion due to the presence of corrosion activators (chloride ions). In electrochemical measurements, active surface areas of used samples were 0.5 cm^2. Potentials were measured vs Ag/AgCl electrode. Morphology and structure of deposits were studied by scanning electron microscope (SEM), (JSM-6510 series JEOL Ltd. Japan) and X-ray diffraction (Russian origin, copper anode Kα-emission, λ =1.54184 Å). Chemical composition of coating was determined by X-ray-fluorescence analysis method (Delta-Analyzer < INNOV-X SYSTEMS >USA) and by X-ray energy dispersion micro-spectral analyser (JSM 6510 LM, Japan). The thickness of the deposited alloy has been approximately estimated from the current efficiency of alloys and the densities of alloys [9] and confirmed by SEM (cross-section).

3. Results and discussions

The colour of as such prepared electrolyte for electrodeposition of Mn-Cu-Zn (0.3 mol/dm^3 Mn^{2+}+0.6 mol/dm^3 $(NH_4)_2SO_4$ + 0.1 mol/$dm^3$$Zn^{2+}$+ 0.005 mol/$dm^3$ Cu^{2+} + 0.2 mol/dm^3 Na_3Cit, pH 6.5-7.5) is greenish-emerald, after delay on air, colour of electrolyte moved to greenish-yellow. It should be noted that colour of electrolyte isolated from atmospheric air did not change and pH in both cases were constant. At high current densities ($i_k \geq 37.5$ A/dm^2) and pH 6.5-7.5, silvery, fine-grained, dense and non-porous Mn-Cu-Zn alloys can be obtained. At low current densities, black sponge-coated alloyswere obtained, which were easily removed from cathode surface.

Chemical composition of silvery, solid, fine dispersed triple Mn-Zn-Cu alloy with corresponding current efficiencies according to electrolysis conditions (current density and pH) is shown in figure 1; catholyte composition: 0.3 mol/dm^3 Mn^{2+} + 0.6 mol/dm^3 $(NH_4)_2SO_4$ + 0.1 mol/$dm^3$$Zn^{2+}$+ 0.005 mol/$dm^3$ Cu^{2+} + 0.2 mol/dm^3 Na_3Cit.

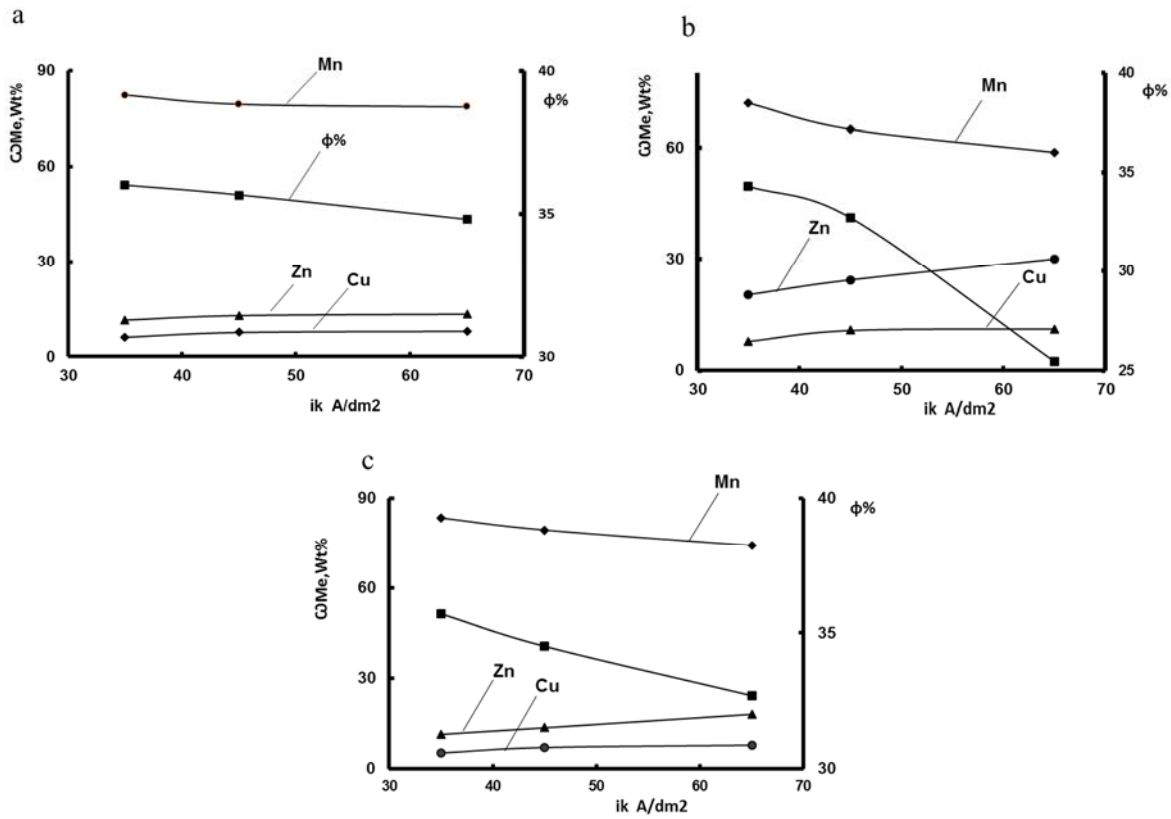

Figure 1. Change ofMn, Zn and Cu content (ω_{Me}) and current efficiency (Φ) in Mn-Cu-Zn deposit as function of cathodic current density (i_k) and different pH (a - 6.5, b - 7.0, c - 7.5); t=30^{0}C; τ=20 min.

Figure 1 (a,b,c) shows that chemical composition of Mn-Zn-Cu alloy obtained at pH 6.5-7.5 and their current efficiencies are practically identical and common regularity is revealed: increase of current density decreases manganese content, increases copper and zinc content and the current efficiency of alloy is decreased. Coatings are silvery and nonporous (negative effect at checking for porosity by the reagent $K_4[Fe(CN)_6]$) (figure 2).

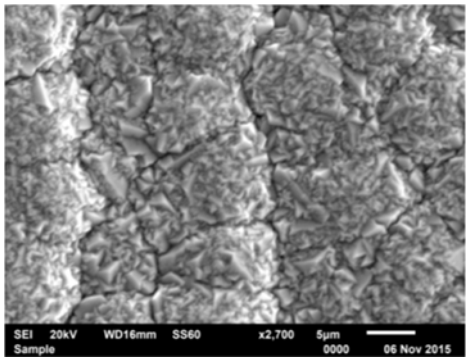

Figure 2. SEM micrograph of Mn-Cu-Zn alloy coating from the electrolyte: 0.3 mol/dm^3 Mn^{2+} + 0.6 mol/dm^3 $(NH_4)_2SO_4$ + 0.1 mol/dm^3Zn^{2+}+0.005 mol/dm^3 Cu^{2+}+0.2 mol/dm^3 Na_3Cit; pH 6.5; i_k=37.5 A /dm^2 ; t=30^{0}C; τ=20 min.

Increase or decrease of concentration of metal salts in electrolytes yielded blackish coatings. Increase of concentration of additive – sodium citrate over 0.2 mol/dm^3 practically had no effect on the

electrodeposition process and on the external look of a coating. But after increase of catholyte pH, in particular, over pH 8, external look of coating was worsened drastically and became black. XRD patterns of coating obtained under controlled pH 6.5 and 7.0 (figure 3) showed only BCT γ-Mn – solid phase solution with copper and zinc (lattice constants a=2.68 Å; c=3.59Å).

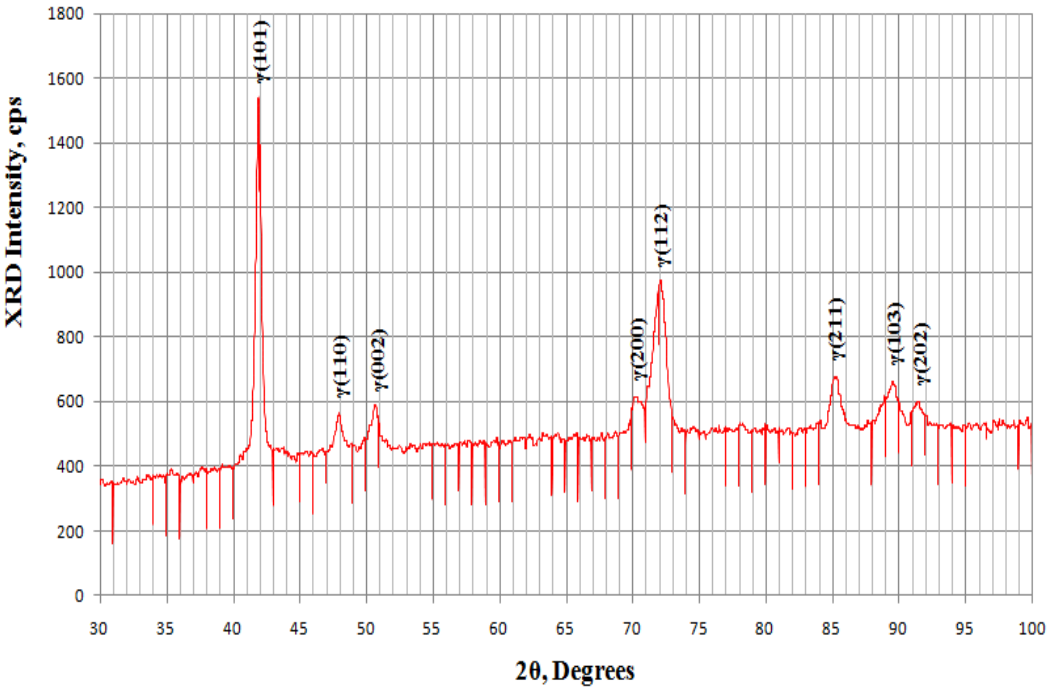

Figure 3. XRD pattern of Mn-Cu-Zn alloy coati ng from the electrolyte: 0.3mol/dm^3 Mn^{2+}+ 0.6mol/dm^3 $(NH_4)_2S0_4$ + 0.1mol/dm^3 Zn^{2+}+0.005 mol/dm^3 Cu^{2+} + 0.2mol/dm^3 Na_3Cit; pH 6.5; i_k = 37.5A/dm^2; t=30 ºC; τ=20 min.

When EDTA was used as a complexing agent instead of a citrate, precipitate was formed during preparation of electrolyte. But when both complex agents were taken at equal quantities (each 0.1 mol/dm^3) electrolyte turned out stable. Electrodeposition yielded silvery, nonporous deposit. Chemical composition of electrodeposited triple alloys obtained using electrolytes with various concentrations of complex ligands is shown in table 1.

Table1. Influence of additives–Na_3Cit and EDTA on Mn–Cu-Zn alloy chemical composition; catholyte: 0.3 mol/dm^3 Mn^{2+} + 0.6 mol/dm^3 $(NH_4)_2SO_4$ + 0.1 mol/dm^3 Zn^{2+}+0.005 mol/dm^3 Cu^{2+}+Xmol/dm^3 ligand; i_k=37.5A/dm^2; pH 6.5;t=30^{0}C; τ=20 min.

Concentration of ligand, X mol/dm^3	ω_{Mn}, wt.%	ω_{Cu}, wt.%	ω_{Zn}, wt.%	ω_C, wt.%	ω_O, wt. %
0.2 mol/dm^3 Na_3Cit	80.32	4.35	10.47	2.62	2.24
0.1 mol/dm^3 Na_3Cit +0.1 mol/dm3 EDTA	77.59	5.42	11.95	2.66	2.38
0.05 mol/dm^3 Na_3Cit+0.15 mol/dm3 EDTA	84.54	4.41	7.35	2.44	1.25

Obtained coatings are relatively fine grained (figure 4).

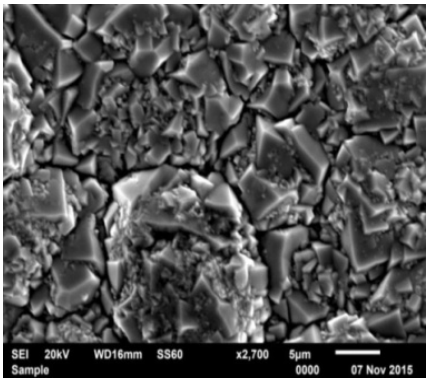

Figure 4. SEM micrograph of Mn-Cu-Zn alloy coating obtained from the electrolyte: 0.3 mol/dm^3 Mn^{2+} +0.6 mol/dm^3 $(NH_4)_2SO_4$ +0.1 mol/dm^3 Zn^{2+}+0.005 mol/dm^3 Cu^{2+}+ 0.05 mol/dm^3 Na_3Cit + 0.15mol/dm^3 EDTA ; pH 6.5; i_k =37.5A/dm^2; t=30^{0}C.

The XRD pattern of obtained alloys are the same and only body centred tetragonal structure of γ-Mn solid phase solution is identified. X-ray energy dispersion microanalysis (figure 5) shows that silvery, dense Mn – Cu – Zn coatings contain non-metal components - carbon and oxygen.

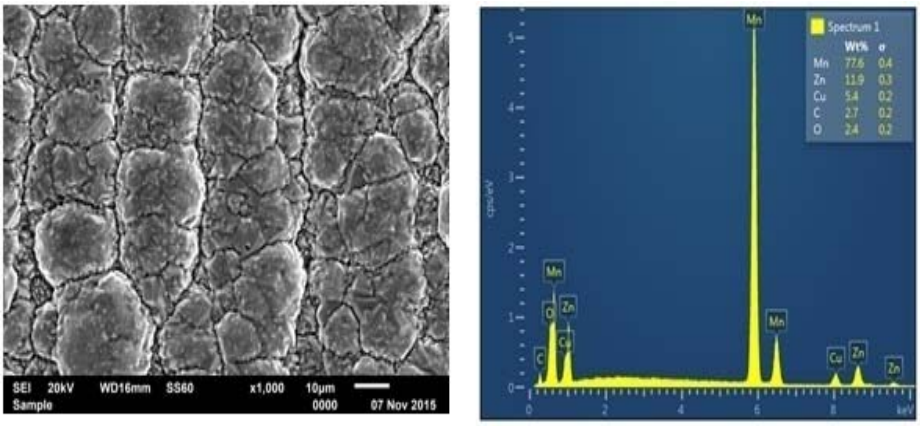

Figure 5. SEM micrograph and X-ray energy microanalysis of Mn-Cu-Zn alloy coating from the electrolyte: 0.3mol/dm^3 Mn^{2+}+0.6 mol/dm^3 $(NH_4)_2SO_4$+0.1mol/dm^3 Zn^{2+}+0.005mol/dm^3 Cu^{2+}+0.1 mol/dm^3 Na_3Cit+0.1 mol/dm^3 EDTA

The polarization curves were not possible to obtainin in our experiments because of the methodological difficulties. Intensive evolution of hydrogen couses high IR drop and in this condition it is impossible to reproduce polarization curves. Irrespective of intense evolution of hydrogen, silvery coating of triple alloys at high cathodic current density on copper or steel cathodes are characterized by high adhesion and plasticity.

It should be noted that manganese which has a more negative standard potential prevails in electrodeposited triple alloys. In literature, this fact is called anomalous codeposition [10], which is characteristic for electrodeposition ofalloys of iron group metals (Fe, Co, Ni) and for iron group metals with Zn and Cd [11,12]. It is determined that anomalous codeposition happens when metal hydroxides are formed on the electrode surface. In our experiments, at high current density, it is possible to form hydroxides on cathode surface due to parallel intensive hydrogen evolution reaction and liberation of OH^-. Formation of the similar hydroxide films, during alloys electrodeposition

process is known in numerous scientific works [13], where kinetic studies proved participation of hydroxide forms in cathodic process.

The time of electrodeposition effects on the external look of surface of triple alloys coating. After 25 minutes, silvery coating is not obtained. Coating surface is covered with blackish metallic oxide and hydroxide. Despite intensive evolution of hydrogen, alloy coating electrodeposited at high cathodic current density on copper or steel cathode is characterized with high adhesion and plasticity. In different conditions, thickness of electrodeposited alloys varies within 50-60 nm.

To study corrosion stability of obtained triple Mn-Cu-Zn alloys electrodeposited on steel cathode, potentiodynamic curves were obtained in solution of 3.5% NaCl. For comparison, the analogous curves were obtained on the same steel cathode without coating, with deposited manganese and zinc (figure 6).

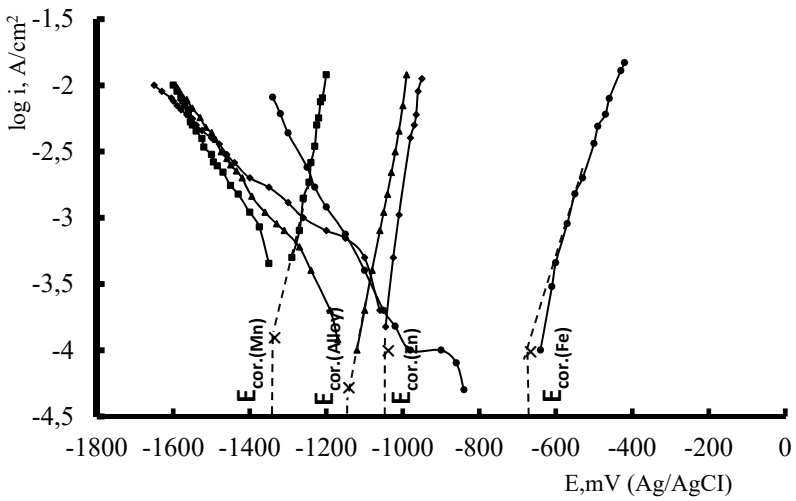

Figure 6. Cathodic and anodic potentiodynamic polarization behaviours of Mn, Zn, steel and electrodeposited Mn-Cu-Zn alloy in 3.5%NaCl solution; potential scan rate1.0 mVs^{-1}; t=30ºC; τ=20min.

The corrosion current density (i_{corr}) was determined by using extrapolation of anodic polarization curves to establish corrosion potential (E_{corr}). It can be seen that the E_{corr} for Mn-Cu-Zn alloy is more negative then E_{corr} of steel base, so its deposition offers sacrificial cathodic protection. The values of corrosion current density i_{corr} of alloy deposits are smaller than those of pure Zn and Mn coatings on steel.

The corrosion behaviour of Mn-Cu-Zn alloys was determined also by monitoring the corrosion potential during exposure of sample to aerated 3.5% NaCl solution, until the corrosion potential of steel substrate was reached. The corrosion potential of bare steel surface in 3.5% NaCl was – 670 mV vs. Ag/AgCl.

After submergence of Mn-Cu-Zn alloy in solution of 3.5% NaCl its corrosion potential (E_{corr}) at the beginning was -1140 mV, which moved slowly towards positive value and coating was getting blackish-silvery colour. After two months, corrosion potential E_{corr} stabilized and became -870 mV vs. Ag/AgCl. More negative corrosion potential of alloys than steel shows that coating is an ideal cathodic protective coating for a steel product. Typical passive regions were not observed on Tafel anodic polarization curves in case of triple alloy coating as well as on manganese and zinc coatings. However, slower dissolution rate of alloy could be assigned to formation of adherent corrosion products with low solubility.

4. Conclusions

Silvery, non-porous triple alloy of Mn-Cu-Zn was obtained at high current densities ($i_k \geq 37.5$ A/dm^2) in electrolyte 0.3 mol/dm^3 Mn^{2+} +0.6 mol/dm^3 $(NH_4)_2SO_4$ + 0.1 mol/dm^3 Zn^{2+}+0.005 mol/dm^3Cu^{2+}+0.2 mol/dm^3 Na_3Cit; t=30^{0}C; τ=20 min; pH 6.5-7.5; coating composition: 83%-71%Mn, 6.0%-7.8% Cu, 11.5%-20% Zn; current efficiency up to 36 %. The electrodeposition of Mn-Cu-Zn exhibited the phenomenon of anomalous type code position at the studied current density from 37.5 A/dm^2 to 65 A/dm^2. At pH 8, external look of coating suffers drastic worsening, it becomes black. XRD patterns reveals BCT γ-Mn solid phase solution (lattice constants a=2.68 Å; c=3.59Å).

In case of application of EDTA instead of citrate as a complexing agent it was observed formation of precipitate in the solution, but if both complexing agents were used in equal concentrations (each 0.1 mol/dm^3) electrolyte turned out stable. Electrodeposition yielded silvery, nonporous deposit and current efficiency of Mn-Cu-Zn triple alloy increased up to 40 %. Solid silvery Mn-Cu-Zn coating contained non-metal component-carbon and oxygen. Non-metals were in lower concentration in coatings where manganese content was high, zinc content was low and ligand EDTA prevailed in electrolyte. Thickness of the coating was within 50-60 nm. Silvery coating was not obtained when electrodeposition time exceeded 25 min. Production of silvery triple alloys at high current density is related to discharge of metallic hydroxide complexes on the surface of cathode. Corrosion test of Mn-Cu-Zn electrocoating in chlorine environment shows that it is the best cathodic protective coating for a steel product.

Acknowledgment

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