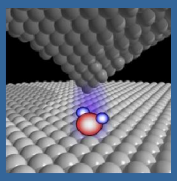
ELECTRODEPOSITION OF Co AND NiCo ALLOYS COATINGS USING CHOLINE CHLORIDE BASED IONIC LIQUIDS – EVALUATION OF CORROSION BEHAVIOR



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Cobalt and Ni-Co alloys represent significant engineering materials widely used in various industrial applications, due to their strength, good corrosion performance and electrocatalytic activity. Usually, electrodeposition of Co and Ni-Co alloys from aqueous based electrolytes suffers from hydrogen embrittlement.
Room temperature ionic liquids (RTILs) are promising electrolytes for the electrodeposition of various metals and alloys because of their wide electrochemical potential windows, nonvolatility and high thermal stability.
Recently a novel ionic medium with interesting perspectives in metals and alloys electrodepositionhas been developed, based on choline chloride eutectic mixtures with different hydrogen bond donor compounds, including ethylene glycol.
Detailed investigations are still required to implement these novel electrodeposition procedures, in order to optimize operation parameters and deposits characteristics. Additional information in this field may significantly contribute to the extension of the practical applications of these systems.
Some preliminary experimental results are thus presented, regarding the electrodeposition and corrosion behaviour of Co and Ni-Co alloy coatings from some choline chloride based ionic liquids containing Co and Ni salts.

EXPERIMENTAL

Accelerated corrosion tests:

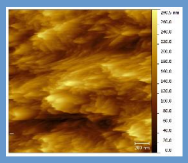
(i) continuous immersion in 0.5M NaCl at 25 °C for 240 hours with intermediary visual examinations and recording of corrosion potential;
(ii) potentiodynamic polarization curves (3 mV/s, against Ag/AgCl reference electrode and a Pt counterelectrode; WE = the investigated coating with a geometrical constant surface of 0.63585 cm^2)
(iii) impedance spectra at open circuit potential, in 0.5M NaCl;
- All electrochemical tests have been performed using a PGSTAT 12 electrochemical equipment, Metrohm Autolab
-min. 3 pcs. of each coating type deposited onto copper metallic support (50x50 mm);
-the Co and Ni-Co coatings had thicknesses of 10-12 μm

Electrolytes composition and operating parameters

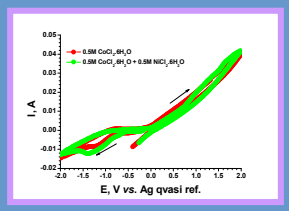
Coating type	Electrolyte composition	Electrodeposition duration [min.]	Current density [mA/cm^2]	Temperature [°C]	Coating aspect
Co	0.5 M $CoCl_2.6H_2O$ in ILEG (ILEG = choline chloride:ethylene glycol 1:2 molar ratio)	30 – 120	8 - 12	70 – 75	Bright, light gray uniform deposition, good adhesion
Ni-Co	0.5 M $CoCl_2.6H_2O$ + 0.5 M $NiCl_2.6H_2O$ in ILEG (ILEG = choline chloride:ethylene glycol 1:2 molar ratio)	30 - 120	6-20	65-75	Bright, light gray uniform deposition, good adhesion

RESULTS AND DISSCUSSION

Co coatings

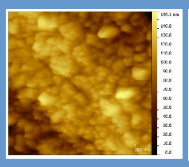


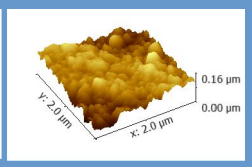
3D and 2D AFM images and profile of the electrodeposited Co coating (0.67 A/dm^2, 70°C, under mild stirring)



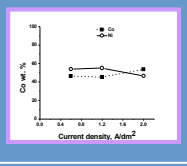
Comparative cyclic voltammograms on Cu working electrode for single ILEG-$MeCl_2$ (Me = Co) and binary ILEG-$CoCl_2$-$NiCl_2$ systems at 0.5M metals salts concentration at a temperature of 70°C (scan rate: 100 mV s^{-1}; S_{WE} = 0.2 cm^2)

Ni-Co alloy coatings

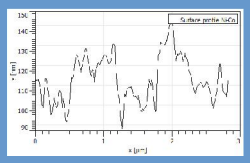


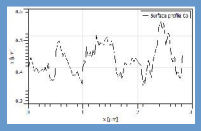


The Ni-Co alloy coatings composition against the applied current density for ILEG containing 0.5M $CoCl_2$ and 0.5M $NiCl_2$



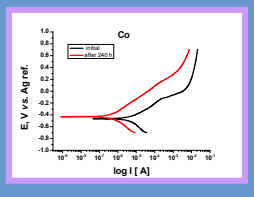
3D and 2D AFM images and profile of the electrodeposited Ni-Co alloy (46.5 wt.% Co) coating (0.8 A/dm^2, 70°C, under mild stirring)

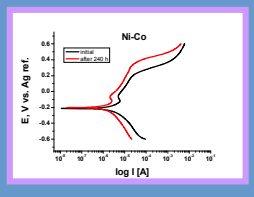


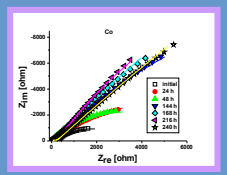


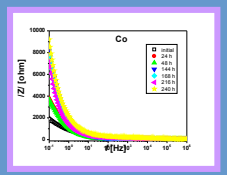
AFM analysis (contact mode, ambient atmosphere, using a home-built system controlled by commercial electronics-SPM1000 and PLLPro2 from RHK Technologies and standard contact mode tips-PPP-CONTR, from Nanosensors) **evidenced that** Co deposits were formed by multiple compact acicular crystallites of about 200..250 nm x 20..40 nm. AFM images also allowed the calculation of surface roughness parameters: values of 28 nm (Ra) and 35.5 nm (RMS) were determined analyzing deposit areas of 1 μm×1 μm.
Ni-Co deposits (46.5 wt. % Co) are composed by multiple relatively equally sized grains with spherical shape of about 35…55 nm. The analysis of surface roughness showed values of 11-12 nm (Ra) and 13-14 nm (RMS) (deposit areas of 1 μm×1 μm).

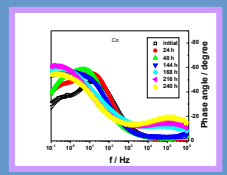
Corrosion behaviour of Co and Ni-Co alloy coatings obtained from choline chloride based ionic liquids

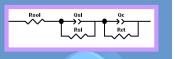




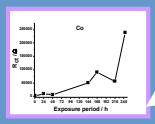




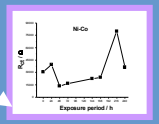


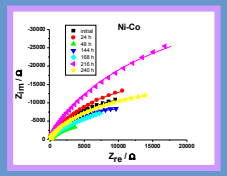


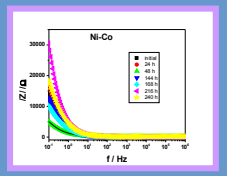
Coating type	Initial		After 240 hours	
	Ecorr, V/Ag	Icorr, μA/cm^2	Ecorr, V/Ag	I cor, μA/cm^2
Co	-0.464	5.57	-0.432	0.65
Ni-Co (46.5 wt.% Co)	-0.200	3.36	-0.182	1.91

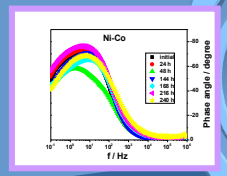


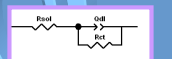
Dependence of R_{ct} against immersion period for Co and Ni-Co alloy coatings











CONCLUSIONS

- Adherent, uniform Co and Ni-Co alloy coatings have been electrodeposited from ILEG based electrolytes;
- The Ni-Co alloys contained about 45-55 % Co, with a very slight variation against the applied current density domain.
- Based on the preliminary experimental results Co coatings deposited from ILEG based electrolytes showed a better corrosion performance as compared with the aqueous electrolytes, materialized in corrosion currents of 0.6 – 6 μA/cm^2 and polarization resistances of 3-60 kΩ, with even higher values after 168 h of immersion, suggesting the gradual formation of a passive film on the surface.
- Ni-Co alloy coatings (46.5 wt.% Co) deposited from ILEG based electrolytes showed a good corrosion performance in corrosion currents of 2-3 μA/cm^2 and polarization resistances of around 20-40 kΩ after 144-240 hours of conditioning.
- It is worth to mention that after 240 hours of continuous immersion in chloride containing aggresive medium the exposed specimens didn't exhibited any major surface modification and no pits have been evidenced.
- The good corrosion behaviour may be correlated with the developed quite compact morphologies of the coatings when choline chloride based ionic liquids are used as electrolytes.

Acknowledgements
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