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Electrochemical deposition of black nickel solar absorber coatings on copper substrate for solar thermal applications

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Considerable effort has been expended on developing coatings and absorber materials with solar-thermal conversion efficiency. The characteristics that differences different type of coatings are: the emmisivity, the absorbance and the stability; these are influenced by the composition, the structure and the deposition technique. The article presents a black nickel coating electrodeposited on copper substrates at room temperature. The present work discusses the process optimization based on the growth rate estimated on the potentiodynamic cathodic polarization curves. The effect of the electrolytes is presented and discussed.

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1. Introduction

Efficient conversion of solar radiation into thermal energy requires an economic viable solar absorber coating, which strongly absorbs across the solar spectrum (0.2-2.5 μm) and emits poorly in the infrared region (>2.5 μm). Solar selective surfaces are characterized by high solar absorptance $\alpha_s > 0, 9\%$ in the solar radiation wavelength range, and low emissivity ($\varepsilon_T<0, 1\%$) in the heat radiation wavelength range.

Six main categories are currently accepted (a) intrinsic, (b) semiconductor–metal tandems, (c) multilayer absorbers, (d) multidielectric composite coatings, (e) textured surfaces, and (f) selectively solar-transmitting coatings.

Considerable effort has been expended on developing coatings and absorber materials having high conversion efficiency. The functional characteristics that differences the coatings are: the stability, the simplicity of the structure and the fabrication technique [1].

Cermet materials, metal/dielectric (nano-) composite have appropriate optical properties. They consist of a metal oxide coating containing metal nanoparticles embedded in a dielectric host on a metallic substrate [2].

Black nickel cermet consists of a mixture of Ni: NiO: Ni_2O_3: NiOOH with the composition tailored by the deposition parameters. By using the electrodeposition, process control of the desired characteristics and reproducibility can be achieved [3].

The article presents a black nickel coating electrodeposited on copper substrates at room temperature. The present work mainly deals with the growth rate based on the potentiondynamic cathodic polarization curves. The effect of neutral electrolytes is presented and discussed.

2. Experimental

Samples consisting of 2×2 cm flat pieces were cut from sheets of commercial cooper. The samples were mechanically polished and degreased with a surfactant. By polishing the substrate with different sandpaper different surface morphologies were obtained. Studies were made only on one face of these plates with a 4 cm^2 surface area. Before each experiment, the cooper cathode was mechanically polished with emery paper (600), then washed with distilled water and rinsed with ethanol. A platinum (Pt) plate or a Pt wire was used as anode.

Different electrodeposition baths were studied and they are presented in Table 1 [3, 4]. Nickel sulfate (Merck), nickel chloride (Analar), boric acid, potassium nitrate, and sodium chloride (Reactivul Bucuresti) were used as received, without further purification. Bidistilled water was used for the electrolyte preparation. Direct current was supplied by a Hameg Programmable Power Supply (HM 8142). All potentials were measured relative to a saturated calomel electrode. The reference electrode was connected to the electrolytic bath via a salt bridge.

Table 1. Electrolyte bath deposition composition.

Receipt Component	R1	R2	S1	S2	S3
$NiSO_4$	0.5 m	0.5 m			
$NiCl_2$	0.09 m	0.09 m	0.4 m	0.4 m	0.4 m
H_3BO_3	0.3 m	0.3 m			
KNO_3	0.2 m	0.2 m			
NaCl			0.5 m	0.8 m	1 m
anode	Pt plate	Pt wire	Pt wire	Pt wire	Pt wire

3. Results

For each electrodeposition baths conditions, the potentiondynamic cathodic polarization curves were developed. Also, the growth rate and the deposition potential were evaluated for each case. A comparison between the obtained values was done. The receipt that gave the best results was chosen for further improvement.

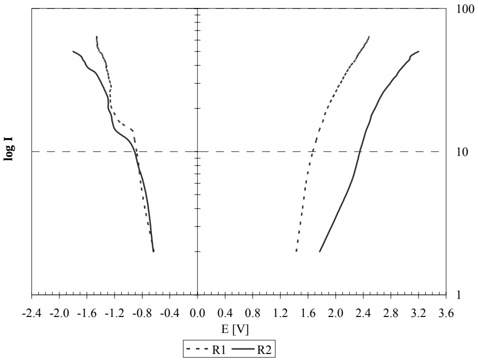

Fig. 1. Polarization curves (for R1 and R2 electrolyte composition).

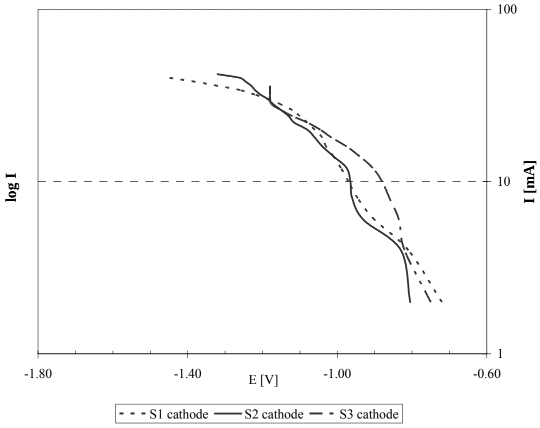

Fig. 2. Polarization curves (for S1, S2 and S3 electrolyte composition).

4. Discussion

As Fig. 1 shows, there is no significant difference in the cathodic process, when using the Pt plate or Pt wire on the anode side. In the case of R1 samples, at the anode there is only one process which corresponds to the specie with the lowest potential. From the usual anions, HO^- presents the lowest standard potential, but, due to the oxygen over potential on Pt, the presence of Cl^- induced Cl_2 formation, which was identified as anodic reaction product. On the other side, for sample R2, two anodic processes can be registered: in the beginning O_2 is released and at higher values of the current, Cl_2 is formed. The cathodic curves present two slope changes which correspond to the metal deposition (nickel) in the first phase and, while increasing the current, second nickel oxides are forming.

A black coating is obtained in both cases, but the surfaces are not homogeneous because of the hydrogen release at the cathode. The process of blackening the cooper plate is simultaneous with the hydrogen formation which leads to small white spots. Therefore, we have tried to avoid the hydrogen formation by removing the boric acid (S1, S2, and S3), while optimizing the ionic strength.

For the second group of experiments the NaCl concentration was varied. Sodium chloride has the role of decreasing the electrolyte internal resistance and thus increasing the growth rate.

From the cathodic curves (Fig. 2) it can be clearly observed that increasing the ionic strength at high NaCl concentrations, leads to one single deposition process which is bright nickel formation (S3). In the S1 sample, the nickel formation is transforming at higher current density in nickel oxide. The sample S2 shows three different slopes on the kinetic curve, associated with Ni, Ni^{II} and Ni^{III} compounds formation. The aim of the study is to obtain a cermet as a mixture of metal and metal oxides, therefore, S2 receipt, with NaCl 0.8m, was chosen for further improvement.

Tabel 2 presents the estimate growth rate (as current densities) and the growth potential, for S2 samples. Values were compared with these obtained in the R1 case. R1 was chosen as comparison because of the anode process, although the present composition does not lead to the formation of mixed oxides.

The electrochemical deposition rate (the current density) for the metal oxide is increasing with the nickel valence. The deposition potential is also increasing. The standard electrod potential for nickel given in tables (25 ^oC, 1 atm, a=1) is ε_o= - 0.25 V [5]. The values obtained in this case are larger due to the over potential on the electrode.

Table 2. Growth rate and deposition potential.

		Ni	NiO	Ni_2O_3
R1	E, [V]	-0.3891	0.0703	
	J, [mA/cm^2]	0.1232	0.2648	
S2	E, [V]	-0.6309	0.0062	0.2995
	J, [mA/cm^2]	0.0089	0.0451	0.0985

5. Conclusions

Different receipts for obtaining black nickel coatings by electrodeposition technique were studied. The effect of electrolytes for increasing the ionic strength was studied and the optimum concentration of NaCl was determined. Based on the potentiondynamic cathodic polarization curves growth rate and the deposition potential were calculated.

The aim of the study is to obtain a cermet as a mixture of metal and metal oxides. Although from the cathodic polarization curves, in the S2 case a mixture of nickel oxides was obtained, R1 receipt gave better results on the coatings aspects. Further work will continue on S1 receipts to obtain a adherent, homogenous coating.

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