3rd International Conference
″Advanced Composite Materials Engineering ″
COMAT 2010
27- 29 October 2010, Brasov, Romania

CORROSION STUDY OF NANOCOMPOSITE COATINGS OBTAINED BY ELECTRODEPOSITION OF TiO_2, Si_3N_4-SiC AND CNT IN NICKEL MATRIX

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Abstract: *The aim of this study was to evaluate the corrosion resistance of different nanocomposite coatings with nickel matrix. Si_3N_4-SiC (~40 nm), TiO_2 (~20 nm) and CNT with nickel from a basic Watts bath. Corrosion tests were performed in aqueous NaCl (3.5 wt. %) using electrochemical impedance spectroscopy measurements. From experimental data we observed that corrosion resistance is higher for CNT/Ni coatings and smaller for TiO_2/Ni coatings.*
Keywords: *nanocomposite coatings, electrodeposition, corrosion*

1. INTRODUCERE

The scientific investigation and applied research on composite materials can date back to 1940's, and these advanced materials have been introduced gradually in our daily life. Composites are also recognized as high-tech materials, which not only turn up in various sports, such as tennis, golf and sailing, but also constitute an increasing proportion of modern airplane and automobile [1]. The electrodeposition of composite layers is a method of co-deposition of inert dispersed particles, from metallic or non-metallic compounds, and of metals or alloys in a bath with the aim of improving the coating properties like corrosion resistance, strength or wear resistance. Electroplated composite coatings containing micro sized particles are used as wear resistant coatings and corrosion resistant coatings in aqueous and high temperature environments.[2]. The major challenges of the co-deposition of nanoparticles is avoiding the agglomeration of particles suspended in the plating solutions.

In this work nickel composite coatings containing nanoparticles like Si_3N_4-SiC, TiO_2 and CNT have been subjected to examination by electrochemical investigations in order to evaluate corrosion behaviour. Electrochemical impedance spectroscopy (EIS) in a 3.5% wt. NaCl test solution at room temperature were carried out. An equivalent circuit has also been proposed and impedance parameters have been simulated by the Zview software.

2. TECHNICAL REQUIREMENTS

A Watt's bath containing the parameters from table1 was used for the deposition of Ni/ SiC - Si_3N_4 and Ni/TiO_2 composite layers. In order to maintain the pH between 4.0 and 4.2 limits H_2SO_4 was used. SiC - Si_3N_4 (commercially called C12) nanoparticles with 40 nm diameter, had 20 g/l concentration in nickel bath. TiO_2 particles commercial called T5 had 21 nm diameter and 5 g/l concentration in the bath. Regarding the electrodeposition of CNT the electrolyte had the same composition as in table 1. The concentration of CNT in the Watts bath was 0.42 g/l. The experiments were done by respecting the following parameters: magnetic stirring 120-200 rpm; pH-3.7 -4.7;curent density 2.4 A/dm^2; time 50 min.

Table 1: Experimental process parameter for the incorporation of SiC - Si_3N_4 and TiO_2 inanoparticles in Ni matrix

Component	Bath composition (g/l)	Parameters	Conditions
$NiSO_4$ X $7H_2O$	250	Temperature	55 ^oC
$NiCl_2$ X $6H_2O$	30	pH	4,00→4,2
H_3BO_3	30	Current densities	2; 4; 6 A/dm^2
dodecyl sulphate	0,3	Agitation rate	700 rpm

In order to disperse carbon nanotubes in the bath sonotrode was used. The ultrasounds were used for two hours before the introduction of cathode with the aim of defeat van der walls forces.

Electrochemical corrosion tests were done with a Voltalab 10 frequency analyzer potentiostat. The testing solution was 3,5% NaCl at ambient temperature. A standard chemical cell with three electrodes was used with the sample as working electrode, a platinum grill as auxiliary electrode and Ag/AgCl (E=+199 mV/ENH) as reference electrode. The frequency area for every specimen was 10^2-10^6, the scanning speed : 0,2 mV/s and the amplitude 10 mV.

The application of electrochemical impedance spectroscopy were performed in representations Nyquist diagrams (imaginary component of impedance based on real component), which were processed using specialized software version 2.80 ZView. Based on overlapping curves modeled with the experimental data representations, the type of circuit with the best correlation coefficient was selected, determining values of said electric circuit components.

3. RESULTS AND DISCUSSIONS

The proposed circuit was chosen due to the best fitting quality with the experimental data. Fig. 1 represents the equivalent circuit which describes the electrochemical behavior of Ni/ Si_3N_4-SiC, Ni/TiO_2 and Ni/CNT composite layers and in table 2 are the calculated values for the analyzed samples. The circuit is a simple one with a sub circuit consisting of an electrical resistance in parallel with a constant phase element. This circuit is a simple model of the corrosion process involving the corrosion reaction, surface capacity and solution resistance.

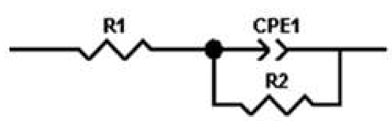

Fig.1 Equivalent circuit which schematically describes the electrochemical behavior of Ni/Si_3N_4-SiC, Ni/TiO_2 and Ni/CNT coatings

To better interpret the results we have summarized below the results in terms of certain realization parameters of composite coatings to observe their influence on corrosion resistance

Table 2 Impedance parameters of the analyzed samples obtained with 2.80 ZView software

The sample	R1	R2	CPE	
			CPE-t	**CPE-p**
Ni/Si_3N_4-SiC (4 A/dm^2)	1570	6,031*10^{13}	1,7832*10^{-5}	0,78314
Ni/Si_3N_4-SiC (6 A/dm^2)	1532	5,569*10^{13}	1,7076*10^{-5}	0,86086
Ni/TiO_2 (2 A/dm^2)	1846	1,1708E^6	4,3364E^{-7}	0,83248
Ni/TiO2 (4 A/dm^2)	1580	1,1718E^6	2,2525E^{-7}	0,86332
Ni/CNT (19 μm)	1240	2.2079E^6	7,9359E^{-7}	0,86332
Ni/CNT (24 μm)	1550	2,0468*10^7	1,9143*10^{-5}	0,80783

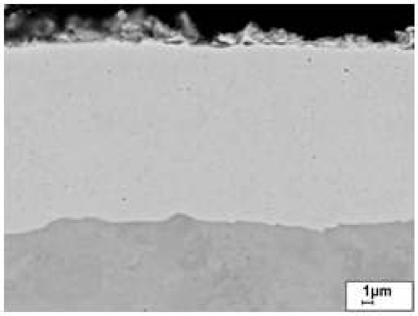

Fig. 2 Scanning electron micrograph of the $Ni/SiC\text{-}Si_3N_4$ cross-section coating

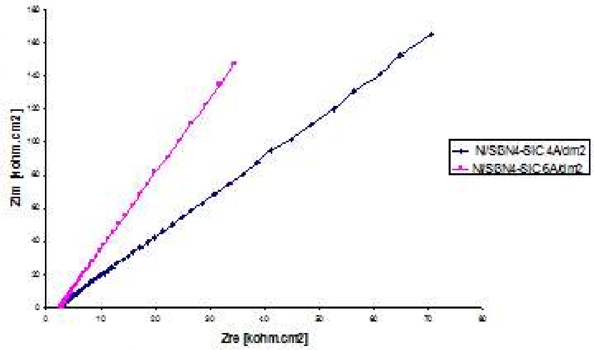

Fig. 3 $Ni/Si_3N_4\text{-}SiC$ electrochemical impedance curves

In the case of $Ni/Si_3N_4\text{-}SiC$ specimens (figs. 2, 3) the difference of the current density used the electrodeposition of the coatings explains the difference between the corrosion resistance of the two samples analyzed. The corrosion resistance is higher for the sample made under $4A/dm^2$ than for the sample made under $6\ A/dm^2$. The coatings layer was 23µm thickness for both samples.

For Ni/TiO_2 (fig.4, 5) specimens we observed the same behavior for both layers despite the fact that the layers are made under different current conditions ($2\ A/dm^2$ and $4\ A/dm^2$).

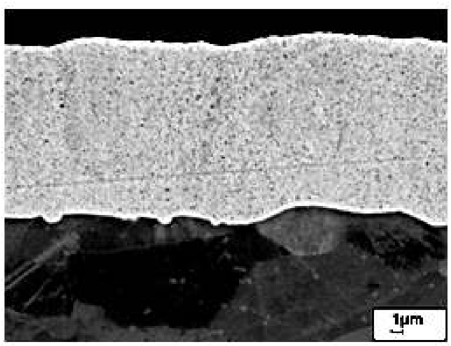

Fig. 4 Scanning electron micrograph of the Ni/TiO_2 cross-section coating

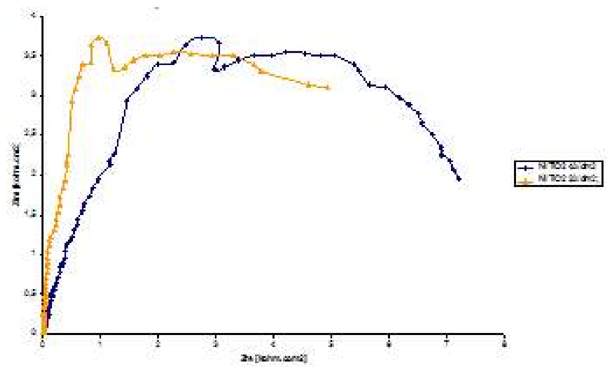

Fig. 5 Ni/TiO_2 electrochemical impedance curves

Also the thickness of the layers are different, the specimen made under $2A/dm^2$ has 14µm thickness, while the specimen made under $4\ A/dm^2$ has 19,6 µm thickness. It might be possible that the thickness of the layers would influence the polarization resistance too.

It is very clear that for Ni/CNT (figs. 6,7) the corrosion resistance grows with the augment of the thickness of the layer because all the deposition parameters are the same for both samples analyzed..

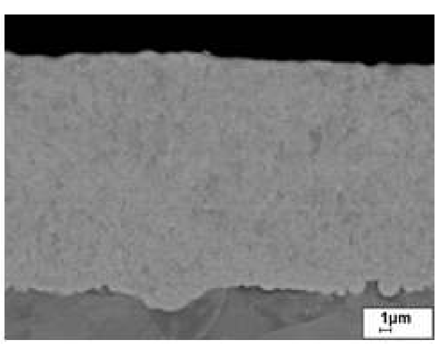

Fig. 6 Scanning electron micrograph of the Ni/TiO_2 cross-section coating

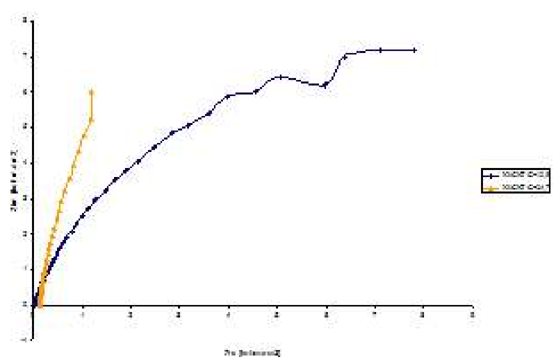

Fig. 7 Ni/TiO_2 electrochemical impedance curves

CONCLUSIONS

There were realized coatings of nickel matrix reinforced with different types of nanoparticles. These coatings were made under different current conditions and were subjected to corrosion tests in order to see if there is any relation between the deposition parameters and electrochemical corrosion behaviour

After corrosion tests we conclude that the deposition parameters of composite layers have a direct influence over the electrochemical properties of the coatings. The Ni/Si_3N_4-SiC layers have the highest corrosion resistance while the Ni/TiO_2 have the smallest corrosion resistance.

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