ELECTRODEPOSITION OF DISPERSED NANOPARTICLES IN NICKEL MATRIX

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Abstract: *The aim of this work was to obtain nickel nanocomposite layers reinforced with SiC-Si$_3$N$_4$, TiO$_2$ and CNT. The electrodeposition was carried out in the same Watts electrolyte for all types of coatings but the particles size and concentrations were different. The experiments were done with and without ultrasounds. The thickness of the layers depends of the parameters applied during the electrodeposition. The microhardness of the layers was also measured. SEM images of fracture composite were obtained.*

Keywords: *nanocomposite, coatings, electrodeposition, nickel, nanoparticles*

1. INTRODUCTION

Composite electroplating has been identified to be a technologically feasible and economically superior technique for the preparation of such kind of composites [1]. Over the past decades, successful co-deposition of micro-sized particles with metal such as metallic powder, silicon carbides, oxides and diamond have been reported. Their corresponding structures and properties were investigated by many researchers. However, it is only recently that this conventional method has been extended to nano-sized particles [2,3]. The ability to codeposit particulate phase with an electroless nickel matrix is a major step in the development of processes aimed at the engineering of surfaces. The prime objective of incorporating the particulate phase is to improve hardness, wear and corrosion resistance [4].

The present work has the purpose of realization and investigation of nanostructured composite layers obtained by using nanoparticle of SiC-Si$_3$N$_4$, TiO$_2$ and CNT in nickel matrix. The microstructure and the microhardness of resulting composites were investigated with respect to the matrix microstructure.

The utilization of nanoparticles in composite applications depends on the ability to disperse them homogeneously in the matrix. Particles dispersed in a continuous electrolyte are in constant Brownian motion. When two particles approach one - another, energies exists between the particles that determine whether the particles will separate or agglomerate. Generally, particle agglomeration occurs as a result of larger attraction energy than repulsion energy between the articles. The magnitude of the net forces involved in producing an agglomerated structure clearly depends on the conditions and the nature of system [5].

2. EXPERIMENTAL

Three experiments with the aim of obtaining a homogeneous dispersion of phases in metal matrix were carried out. In the first experiment we aimed to codeposit SiC-Si$_3$N$_4$ nanoparticles with electroless nickel on medium carbon steel and evaluate its hardness.

The plating electrolyte is a nickel sulfamate bath. The bath composition and experimental process parameter ranges for the first experiments using SiC-Si$_3$N$_4$ are shown in the Table 1. Low carbon steel (QD 5 cm x 5 cm) was used as a substrate deposit. SiC -Si$_3$N$_4$ particles, commercially called C12 with 40 nm diameter, were in a concentration of 20 g/l in the Ni Watts bath.

Experiments with and without ultrasounds were carried out. The base substrate was treated before in perchlorethylen under ultrasounds for 5 min, in natriummetasilicat x 5H$_2$O + natriumhidroxid at 75 °C for 5

minutes, and in 30% H_2SO_4 bath for 1,5 min. Mechanical stirring and ultrasounds were used for the dispersion of particles in the bath.

Table 1 Experimental process parameter for the incorporation of SiC-Si₃N₄ particles in Ni matrix

Component	Bath composition (g/l)	Parameter	Conditions
$NiSO_4$ X 7H2O	250	Temperature	55 °C
$NiCl_2$ X $6H_2O$	30	pH	4,00→4,2
H3BO3	30	Current density	2; 4; 6 A/dm²
dodecyl sulfate	0,3	Stirring rate	700 rpm

To get metallographic cross sections the samples were cut and mounted in resin. They were ground with abrasive paper and polished with silica suspension. The thicknesses of the coatings were measured with an optical microscope. The samples obtained were analyzed at SEM in order to determinate whether the phases were embedded in the matrix, and if there was an agglomeration or a good dispersion in it.

The second experiment had the purpose to incorporate TiO_2 in Ni matrix. The Ni Watts bath had the same composition as in Table 1. TiO_2 particles commercially called T5 have 21 nm diameters with a concentration of 5 g/l in the Ni bath. The pre-treatment of the base substrate was the same mentioned in the first experiment. Were used ultrasounds for the dispersion of particles in the bath.

The third experiment had the purpose to obtain metal matrix coatings reinforced with carbon nanotubes (CNT). It is known that the utilization of CNT in composite applications depends on the ability to disperse them homogeneously in the matrix. Another problem might be the high length-diameter ratio, which could discountenance their embedment in the matrix.

The carbon nanotubes were prepared through CVD from methane, flowing gas – argon and Fe:Mo:MgO as catalysts, by Al. Biris and D. Lupu, at the Institute of Molecular and Isotopic Technologies from Cluj-Napoca. The nanotubes were purified by 24 hours, reflux in HNO_3 3M and annealed in argon at 1200°C for one hour. The concentration of CNT in Ni Watts bath was 0,42 g/l.

The Ni Watts bath has the same composition as in Table 1. The substrate was prepared as mentioned before. Was used a sonotrode bar, 20% amplitude, in order to disperse the CNT in the bath. The ultrasounds were applied for 50 min before for the reason of dispersing the nanotubes and to defeat the Wan der Walls forces that keep the nanotubes together.

During the experiment process was used: - magnetically stirring → 200 rpm; - pH of the electrolyte between 4,347 – 5,382; current density → 2,4 A/dm²; time 50 min; temperature 48°C. It was used a lower stirring than it was used for the other experiments because of the lower density of carbon nanotubes which is 1,1 – 1,3 g/cm^3 [6].

3. RESULTS AND DISCUSSIONS:

Coatings between 9,4 µm and 22,8 µm were obtained. The thickness of the layer is growing with the growing of the current density. The percent of the particles embedded in the matrix is very low as it can be seen in the picture below (Fig.1), and within the experiments made without using ultrasounds there is no track of particles. The black grains that can be seen in the pictures are some agglomeration of particles. In order to achieve a good dispersion of the particles in the Watts bath were effectuated experiments on the same composition with ultrasounds using sonotrode bar, and magnetically stirring. The SEM analyses are shown in the fig.2.
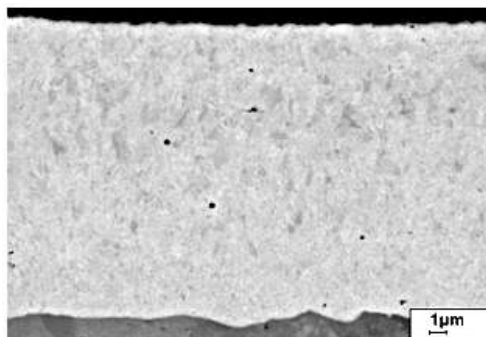

Fig.1 Scanning electron micrograph of the Ni/SiC-Si₃N₄ cross-section coating made using bath ultrasounds
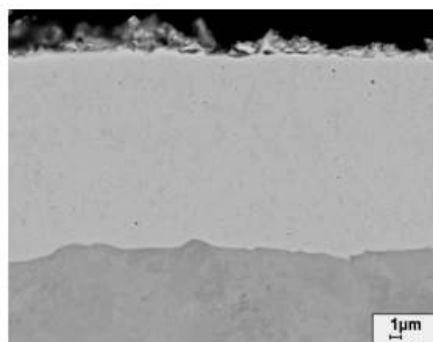
Fig.2 SEM analyse of Ni/SiC-Si₃N₄ dispersion coating made using sonotrode ultrasounds

Some agglomerations of the particles in the Ni matrix but we obtained a better dispersion than on the specimens realized using bath ultrasounds.

The distribution of TiO_2 particles in the cross-section of composite coatings are shown in the Figs.3 and 4. It can be seen that TiO_2 particles appear well dispersed in the Ni matrix for the coatings made under ultrasonic agitation, but for the coatings without ultrasonic agitation we can distinguish just a few TiO_2 particle. This indicates that the ultrasound method to disperse the particles in nickel bath is effective. There is no difference in the coatings dispersion between the two methods of ultrasound used, bar respectively bath ultrasounds.
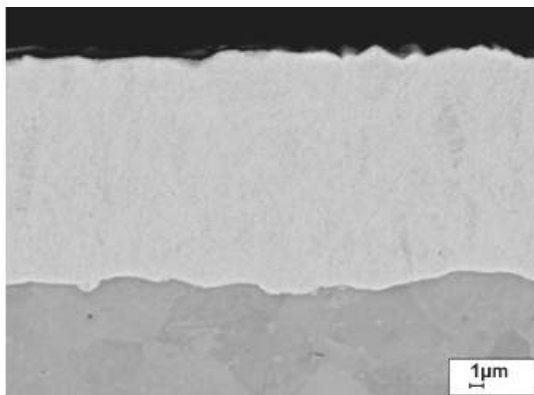

Fig. 3 Ni/TiO_2 (21 nm) deposit without ultrasounds. There are just a few particles in the Ni matrix.
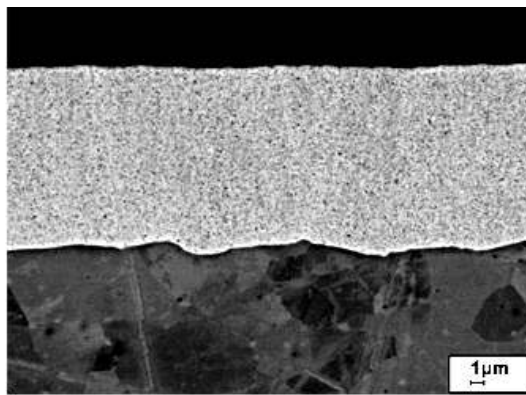

Fig.4 Scanning electron micrograph of the cross-section of Ni/TiO_2 coatings made by electrodepositing under bar ultrasonic agitation

The results of the carbon nanotubes / nickel coatings experiment can be seen in the images below. The images made with the scanning electron microscope (figs.4,5) do not show the embedment of particles in the Ni matrix, and the hardness test confirmed the same thing, the hardness being comparable with a simple nickel coating. The next experiments that have the purpose the incorporation of carbon nanotubes are following. It would be necessary to modify the parameters to see if it modifies somehow the result. For the future experiments it should be figured out if it is necessary to find a surfactant or to activate the nanotubes by milling in order to obtain a good dispersion in the matrix. Also the variation of the parameters could indicate a possible "wetting" of particles.
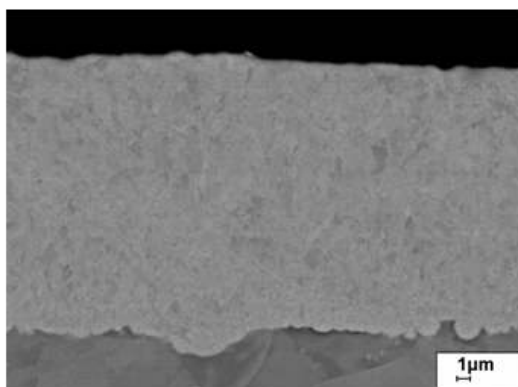

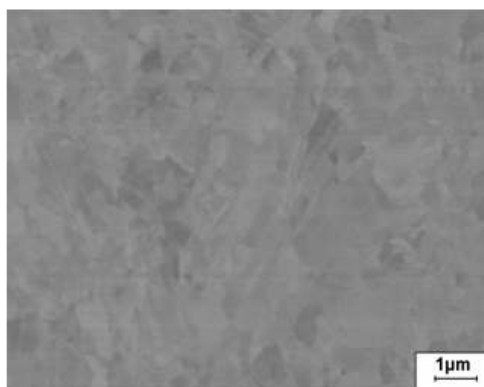Fig.5 SEM micrograph of Ni/CNT composite coating (magnitude 3000k)

Fig.6 SEM micrograph of Ni/CNT composite coating (magnitude 10000k)

Hardness measurements were carried out using Fischer Martens Hardness Tester employing a load of 50 mN for 30 s. Five lines were taken on each deposit and the values were then averaged. There were micro hardness tests effectuated in order to be compared with simple Ni coating. We obtained results like 407,09 HV for Ni/SiC-Si_3N_4 composite coating while the simple Ni coatings have 317 HV. For Ni/TiO_2 we obtained a micro hardness of 395 HV, while for Ni/CNT we obtained 277 HV. In the figure 6 it is illustrated the variation of the depth in function of the load applied for all three types of composites. As it can be seen the incorporation of TiO_2 and SiC-Si_3N_4 improve the micro hardness of the coatings.
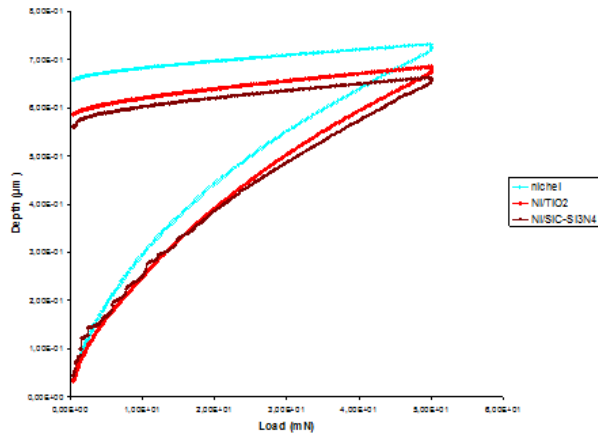
Fig.6 Variation of the depth in function of the load applied.

4. CONCLUSIONS

Electroplated Ni coatings with incorporated phases were studied.

The agglomeration tendency of particles in sulfamate bath was a major problem during the experiments. Successful incorporation of SiC-Si$_3$N$_4$ and TiO$_2$ with a homogeneous dispersion in the matrix has been established despite the problems. CNT incorporation in metal matrix might have been done, but we need further analyze to conclude this aspect.

The hardness of dispersion coatings was compared with the hardness of pure Ni coatings. The incorporation of discrete phases improved the micro hardness of the coating.

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