

Improving tribocorrosion behaviour by electro-codeposition of TiC nano-dispersed particles with nickel as hybrid layers for energy applications

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Abstract. In this paper, the results on the surface morphology, nanohardness and tribocorrosion properties of electrodeposited nanostructured Ni/TiC hybrid layers compared with pure Ni layers are presented. The Ni/nano-TiC hybrid layers were obtained by electro-codeposition of TiC nanoparticles (50 nm mean diameter) with nickel from a Watts type bath, on 316L stainless steel support. The combined fretting-corrosion performance was investigated using a reciprocating ball-on-disk tribometer coupled to an electrochemical cell in an electrolyte which simulates the primary water circuit of Pressurized Water Reactors (PWRs). Open circuit potential, as in situ electrochemical technique was performed before, during and after fretting tests in order to obtain information on the changes in surface conditions induced by fretting. The results clearly revealed enhanced nanohardness, improved tribocorrosion properties and reduced coefficients of friction for Ni/nano-TiC hybrid layers as compared to pure Ni layers. The much improved nanohardness and tribocorrosion behaviour can be attributed to the TiC nanoparticles reinforced into Ni matrix.

1. Introduction

Wear resistance is an important factor governing the industrial application of surface coatings. The objective of applying coating to a surface for any tribology based application is to impart both smoothness and hardness to the surface so that friction and wear are reduced. The minimization of the friction of the coating is a vital need. The friction characteristics are also dependent on the condition of the tribological testing and the counterface material used [1].

The tribocorrosion process represents a material degradation which involves mechanical wear processes and electrochemical and/or chemical corrosion processes. The tribocorrosion phenomenon exists in different areas of the industry (energy production, transportation, mining and metallurgy, offshore industry, biomedical implants) where it causes severe damage and economic losses.

A variety of particles such as: SiC [2-4], TiO₂ [5-7], CNT [8] and WC [9] with mean size diameter from 10 nm to 500 nm, are reported as being incorporated in different metallic matrices such as Ni, Zn and Co to form composite layers and coatings and further to be studied in different friction conditions for diverse applications.



Sun et al [5] investigated the friction and wear properties of the electrodeposited nickel-titania nanocomposite coatings and they report under the same conditions that titania-nickel nanocomposite coatings exhibited smoother surfaces, higher hardness, and lower friction and higher wear resistance as compared with the nanocrystalline nickel coatings electrodeposited at same parameters. Zhou et al. [3] shows in their paper work a lower friction coefficient and better wear resistance of as-codeposited Ni-SiC nanocomposite coatings compared to the as-deposited Ni film, which can be attributed to the incorporation of nanometer SiC particles in the deposit greatly increasing the hardness of the composite coating through grain refinement strengthening and dispersion strengthening. S. K. Ghosh and his collaborators [9] concluded that reciprocating dry sliding tests revealed that a lower coefficient of friction was recorded on CoW-WC coatings than on CoW, with a better wear-resistance compared to CoW alloys.

From special literature the following factors are known to influence the fretting: normal load, amplitude, frequency, number of cycles, relative humidity and temperature, materials involved, roughness [10, 11].

In nuclear power plants, some tribological issues occur due to regular interaction between components (control rod drive mechanisms). Therefore, in order to improve the nanohardness, reduce the friction coefficients and further improve the wear properties in wet conditions of pure Ni layers, Ni/TiC nanostructured hybrid layers were prepared on the surface of stainless steel by electrochemical codeposition process. The present work aims to improve surface mechanical property of pure nickel layers by electro-co-deposition of Ni with dispersed second phase titanium carbide nanoparticles (50 nm mean diameter). It was proved that tribocorrosion resistance of the Ni/nano-TiC hybrid layers were significantly enhanced due to the strong dispersion strengthening effect gained by TiC nanoparticles incorporation into Ni matrix. The results have shown that the TiC nanoparticles reinforcing Ni matrix exhibit a significant higher wear resistance under wet conditions in primary water circuit of Pressurized Water Reactors (PWRs) as compared to pure Ni coatings. The corrosion resistance under fretting conditions was improved and the friction coefficients corresponding to Ni/nano-TiC hybrid layers are reduced compared with the pure Ni electrodeposited layers at all applied forces.

2. Materials and methods

2.1. Fabrication of Ni/TiC nanocomposite coatings

A standard Watts' nickel plating bath containing nickel sulphate 200 gL⁻¹, nickel chloride 50 gL⁻¹ and boric acid 30 gL⁻¹ was used as electrolytic solution. TiC particles with mean diameters of 50 nm used in this work were purchased from Hefei Kaier Nanometer Technology & Development Co. Ltd. and the crystalline structure of this nanopowder was cubic with >99.0 % purity. The concentration of TiC nanoparticles in the electrolyte bath was 10 gL⁻¹.

A pure Ni sheet was used as the anode, 304 stainless steel sheets with area of 25 cm² were used as the cathode and a saturated calomel electrode (SCE - Hg/Hg₂Cl₂, KCl saturated solution, E=+244mV vs. standard hydrogen electrode) was used as the reference electrode. Before the electrodeposition, cathode was degreased with 5M NaOH and 1:1 HCl, washed in distilled water, and then immersed immediately in the electroplating bath.

The pH of solution was kept at 4.04 ± 0.2. The electrodeposition was carried out at 45 ± 1 °C temperature, by applying a constant current density of 40 mA/cm² and a time of 15 min. The temperature was kept constant by using a double walls glass cell having 450 mL plating solution. The suspension of TiC nanoparticles was maintained in the bath by continuous agitation using a stirring rate of 450 rpm. Pure Ni layers were also produced under the same experimental conditions for comparison.

The surface morphology and the elemental composition of the pure nickel and nanostructured Ni/TiC hybrid layers obtained electrochemically were characterized by scanning electron microscopy (SEM-Philips XL 30 FEG) with energy dispersive X-ray spectroscopy (EDX).

2.2. Nanohardness tests

The pure Ni layer and nanostructured Ni/TiC hybrid layer were tested by nanoindentation tester (CSM-instruments equipped with a Berkovich diamond indenter) in order to extract elastic modulus (E), indentation hardness (H), Vickers nanohardness (Hv) and maximum depth penetration of the specimen material from load–penetration depth measurements. The applied loading force was 10 mN, with a 5 s pause time after each measurement.

2.3. Tribocorrosion test apparatus and solution

Before the morphological, elemental characterization and also tribocorrosion tests, all the electrodeposited samples were ultrasonically cleaned in ethanol for 10 min and then in distilled water.

Experimental set-up for tribocorrosion experiments (figure 1) consisted in a conventional three-electrode cell composed of: working electrode – pure Ni layer and Ni/TiC nanostructured hybrid layers, reference electrode – Ag/AgCl microelectrode with KCl saturated solution ($E = +200$ mV vs. standard hydrogen electrode) and auxiliary electrode – Pt foil. The active surface area of the working electrode exposed to the solution was 1 cm^2 .

The fretting tests were performed in wet conditions, at room temperature ($23\text{ }^{\circ}\text{C}$) on reciprocating fretting motion using a ball-on-plate geometry by applying the normal forces of 1 N and 2 N, a frequency of 1 Hz, under linear displacement amplitude of $200\text{ }\mu\text{m}$ for 10000 numbers of fretting cycles. As a test solution in the tribocorrosion experiments was used an electrolyte which simulates the primary water circuit of Pressurized Water Reactors (PWRs) with the following composition 5.72 gL^{-1} LiOH and 0.4485 gL^{-1} H_3BO_3 , having a pH of 8.3 [12]. The alumina balls with 10 mm diameter (CERATEC Technical Ceramics BV) were used as a counterbody during the tribocorrosion tests. The friction coefficients versus fretting distance were recorded automatically during the test.

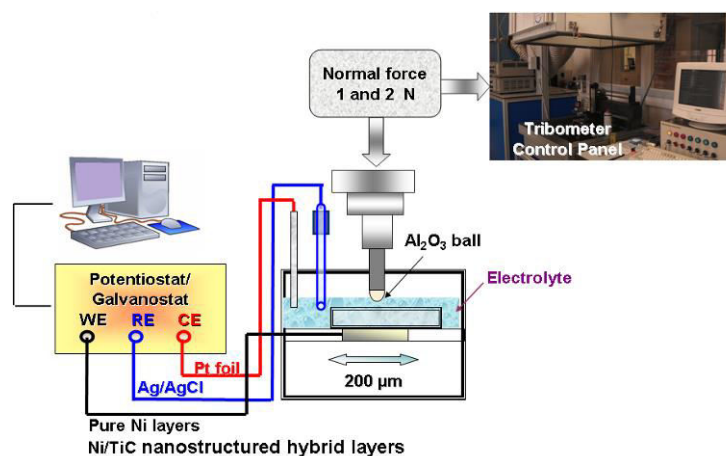


Figure 1. Schematic view of the experimental set-up used for tribocorrosion tests.

After the fretting tests, the debris and the wear track morphology was investigated by SEM analysis using a Philips model XL 30 FEG.

3. Results and discussion

3.1. Morphological and elemental characterization

The nanocomposite layer with good adherence to stainless steel support, having a thickness of 10 micrometers and about 5.16 wt % of titanium carbide included into nickel matrix was characterized by SEM-EDX, nanoidentation and to tribocorrosion process in bidirectional fretting conditions in water +Li+B solution simulating the cooling water from PWR.

The surface morphology and chemical composition of Ni/nano-TiC nanocomposite layers are

presented in figure 2 (b, c) comparatively with pure nickel layers obtained at same electrodeposition parameters, figure 2 (a, b). TiC nanoparticles are homogeneously dispersed in the Ni matrix. This means that nickel ions from the electrolyte are adsorbed on TiC nanoparticles and then are reduced on the TiC surface and their deposition on the surface is uniform. The SEM morphology of nanostructured Ni/TiC hybrid layers also reveals a cauliflower structure, comparatively with pure nickel electrodeposited layers which show defined grain crystallites.

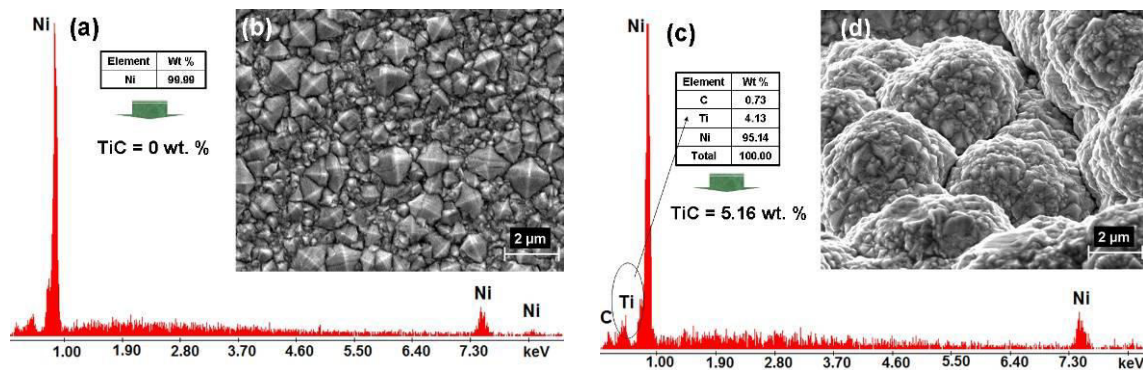


Figure 2. EDX spectrum and elemental analysis collected from the entire surface of: (a) pure Ni layer corresponding SEM micrograph (b) and (c) Ni/TiC nanostructured hybrid layers corresponding SEM micrograph (d).

The incorporation percentage of TiC into Ni matrix is determined by transformation of average Ti element wt % in molecular mass of TiC, considering the standard atomic weight of Ti element which is 47.86. The weight percentage for Ti element included into Ni matrix, as shown in figure 2c was determined by EDX analyses being equal to 4.13 wt % (mean value). Therefore the wt. % of TiC reinforcing nanostructured Ni/TiC hybrid layers resulted at an average value of 5.16, percentage that improved the properties of the nanostructured hybrid layer.

3.2. Nanohardness properties

The nanohardness properties of the pure Ni layers and nanostructured Ni/TiC hybrid layers were measured by nanoindentation technique using a diamond Berkovich indenter at normal load of 10 mN. The hardness values reported are the statistical average of 3 indentations. From load–penetration depth measurements were extracted and plotted in figure 3 the following parameters: indentation hardness (H), Vickers nanohardness (HV), elastic modulus (E) and maximum depth penetration of the specimen.

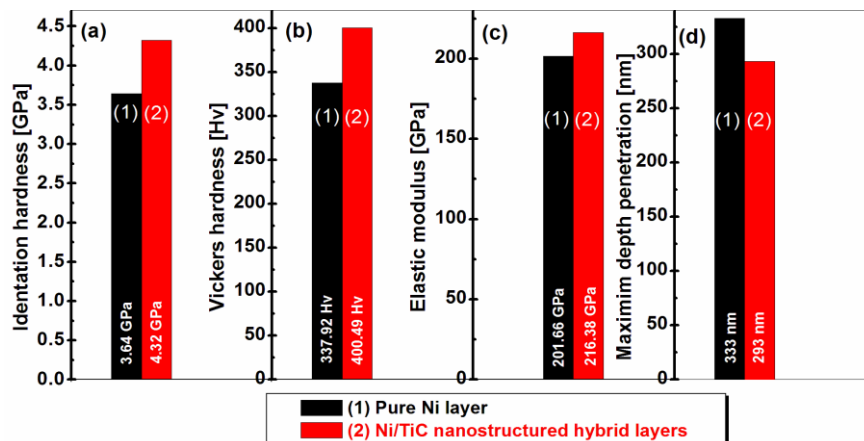


Figure 3. Nanoidentation results as (a) indentation hardness, (b) Vickers hardness, (c) Elastic modulus and (d) maximum depth penetration of (1) pure Ni layer and (2) Ni/TiC nanostructured hybrid layer.

As it is shown in figure 3, the higher nanohardness, Vickers hardness and elastic modulus values correspond to nanostructured Ni/TiC hybrid layers compared with pure Ni layers. Also it can be seen that the maximum depth penetration of the indenter corresponding to nanostructured Ni/TiC hybrid layers reveal a value of 293 nm, while for pure Ni layers show a value of 333 nm.

These results demonstrate the beneficial effect of TiC nanoparticles incorporation into Ni matrix. The inclusion of TiC nanoparticles provokes new nucleation sites on the surface and therefore the grain boundaries expand and obstruct the dislocation.

3.3. Tribocorrosion experiments

3.3.1 Open circuit potential

The measurement of open circuit potential for materials and coatings gives information on the electrochemical state of a material or coating, for example if the material is in active state and dissolution occurs or if it is in passive state and the dissolution is slowed down by the passive film formed over the surface in the given solution. However, open circuit potential measurements provide limited information on the kinetic and mechanism of surface reactions occurring on the studied material. The open circuit potential recorded during bi-directional friction tests, in which the disc (Working Electrode) from figure 1 is the pure nickel or Ni/TiC nanostructured hybrid layer under investigation, becomes a mixed potential reflecting the combined state of the unaffected material surface and the material from the wear track. A galvanic coupling between rubbed and unrubbed parts on the layer surface may take place. The measured open circuit potential is then an average value depending on current density distribution over the whole layer surface exposed to corrosive environment.

The evolution of the open circuit potential was measured under free surface in the solution without friction and under friction mechanically loaded conditions with two applied normal forces as it is shown in figure 4a for pure nickel layer and figure 4b for Ni/TiC nanostructured hybrid layer.

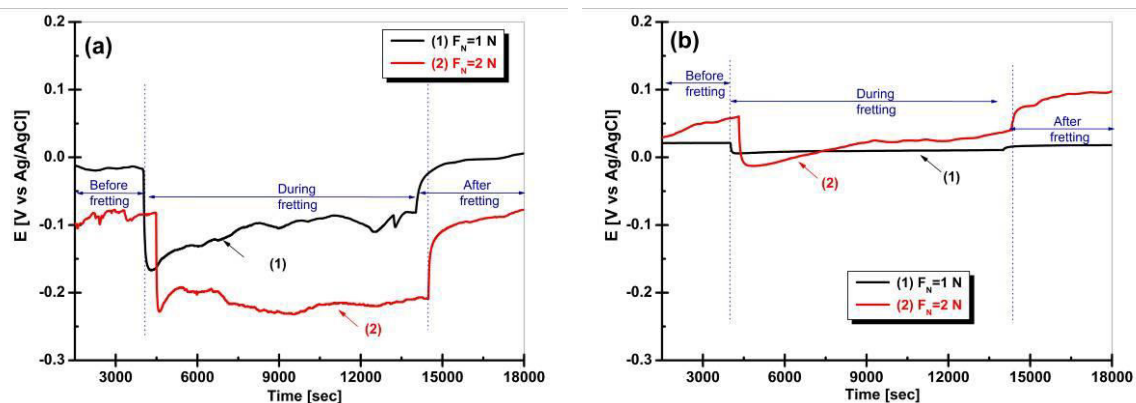


Figure 4. Electrochemical measurements of open circuit potential (E) recorded before, during, and after bi-directional fretting test in water +B+Li solution with two applied normal forces of 1 N and 2 N, 200 μm displacement amplitude, 1 Hz fretting frequency and 10000 cycles for: (a) Pure Ni layer, (b) Ni/TiC nanostructured hybrid layer.

From figure 4a it is observed that the open circuit potential of pure nickel layer in fretting contacts is quite sensitive to the loading conditions in aqueous solution. The open circuit potential of pure nickel layer is shifted down during fretting with about 145 mV at a normal force of 1N and 152 mV at applied normal force of 2 N.

The open circuit potential of Ni/TiC nanostructured hybrid layer is not such sensitive to loading conditions and the shutting down of the potential during starting the fretting is only with few mV (0.015 mV) at 1N loading force and increase very slowly at 2 N loading force at about 0.072 mV, as it

is shown in figure 4b.

Accordingly, the potential variations in Figs 4a and 4b suggest that the tested Ni/TiC nanostructured hybrid layers fretting against corundum under the considered test conditions mainly undergo a removal of their passive surface film at the start of friction, removal which is much more evident for pure nickel layer. The layers surface remains partly active during the fretting test, and finally progressively reactivates when fretting is stopped (unloading conditions).

This indicates the re-establishment of a passive state on the surface of Ni/TiC nanostructured hybrid layers and pure nickel layers in the worn area. It should be underlined that the rate at which the open circuit potential is shutting down when loading the normal force and increases on unloading conditions is totally different for the two types of layers. The underlying processes are thus different in both cases and have different mechanism and kinetics. Indeed on loading, the mechanical destruction of the passive surface film is taking place, while on unloading the repassivation takes place at a rather limited oxidation rate. After unloading, only a small part of the disc surface in the wear track is active, and a galvanic coupling takes place between this small rubbed active area and the rest of the disc surface, which remain in a passive state. This coupling induces an anodic polarization of the active area, resulting in an increase of the repassivation rate, and a smaller repassivation time constant for Ni/TiC nanostructured hybrid layers.

3.3.2. Friction coefficients

Figures 5 (a and b) provides the coefficients of friction monitored in wet conditions as a function of normal forces of 1 N and 2 N, at the fretting frequency of 1 Hz, for number of cycles equal to 10000 and 200 μm displacement amplitude corresponding to pure Ni layer (5a) compared to Ni/TiC nanostructured hybrid layers (5b).

The figure 5 (a, b) keeps the same general behaviour, namely that the friction coefficients recorded under wet condition of Ni/TiC nanostructured hybrid layers are smaller than that of pure Ni layers for both applied normal forces. For instance, the average value of friction coefficient for Ni/TiC nanostructured hybrid layers at the normal force of 2 N is equal to 0.19 and with 0.28 respectively for pure Ni layer. This could be attributed to the incorporation of the hard TiC nanoparticles into nickel matrix which impedes the damage of the nickel oxides passive film formed on pure Ni layer. Similar observation was made previously by Lekka et al. [13], who compared the performance of pure nickel and Ni-SiC nano-structured composite coatings as far as corrosion, wear and abrasion resistance.

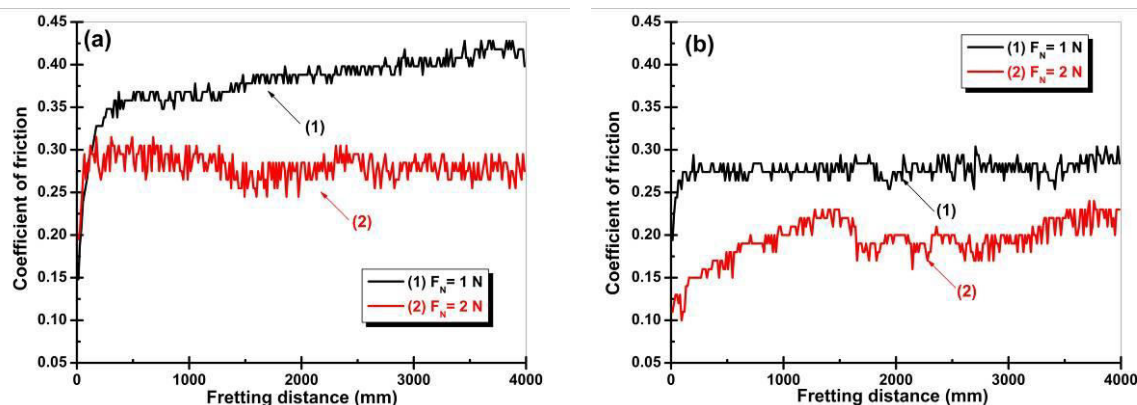


Figure 5. Evolution of friction coefficients during bi-bidirectional fretting test in water +B+Li solution with two applied normal forces of 1 N and 2 N, 200 μm displacement amplitude, 1 Hz fretting frequency and 10000 cycles for: (a) Pure Ni layer, (b) Ni/TiC nanostructured hybrid layer.

3.3.3. Wear tracks analysis

In figure 6 are shown the wear tracks corresponding to pure Ni layer (a, c) and Ni/TiC nanostructured hybrid layer (b, d) at different magnifications view. The wear track of Ni/TiC nanostructured hybrid

layer (figure 6b) is significantly smaller compared with that of pure Ni layer (figure 6a). From figure 6d it can be seen that there are no cracks on the wear track of Ni/TiC nanostructured hybrid layer like in the case of pure Ni layer (figure 6c), rather occurred only the flattening of the surface roughness.

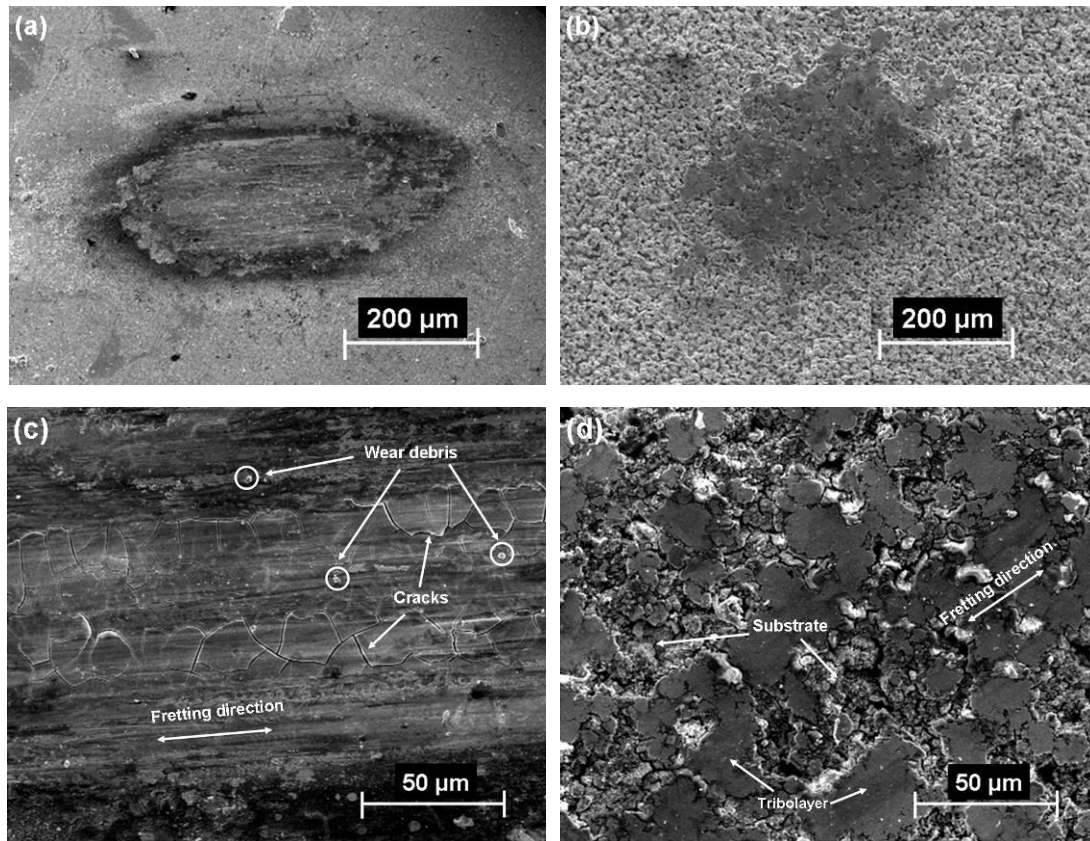


Figure 6. SEM worn analysis corresponding to pure Ni layer (a, c) and Ni/TiC nanostructured hybrid layer (b, d) of the entire wear tracks (a, b) and a zoom inside the wear tracks (c, d).

The magnified view of the wear track corresponding to pure Ni layer (figure 6c) reveals the severe deterioration suffered, being obvious small cracks and wear debris caused by the ploughing action of Al_2O_3 ball.

From the worn surface analyses it can be concluded that TiC nanoparticles have a good effect on Ni/TiC nanostructured hybrid layer revealing improved resistance to wear in wet conditions as compared with pure nickel layer.

4. Conclusions

The TiC nanoparticles could be electro-codeposited with nickel to reinforce the obtained Ni/TiC nanostructured hybrid layer. The inclusion of TiC nanoparticles into nickel matrix during electroplating process was proved by SEM - EDX analysis. The mean wt. % of TiC obtained was 5.16.

By comparatively testing the Ni/TiC nanostructured hybrid layer and pure nickel layers by nanoidentation using 10 mN force the results show higher values for nanohardness, Vickers hardness and elastic modulus induced by TiC nanoparticles reinforcing nickel matrix.

The tribocorrosion behaviour of tested layers in simulating cooling water from nuclear power plant is dependent of surface characteristics.

The open circuit potential is much less influenced by fretting of Ni/TiC nanostructured hybrid layer as compared with pure nickel layer due to higher hardness and formation of a more compact passive

protective layer.

The values of friction coefficients recorded in wet conditions also reflect a better behaviour of Ni/TiC nanostructured hybrid layer being smaller at both applied normal forces compared with pure Ni layer.

Acknowledgements

UEFISCDI – Ministry of Education and Research is acknowledged for the financial support to Competences Centre Interfaces – Tribocorrosion and Electrochemical Systems (CC-ITES) – Dunarea de Jos University of Galati – Research Project: HyBioElect, contract 10 /30-08-2013 (2013 – 2016) in the frame of National Research Programme Romania – PN II PCE.

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