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NANOSTRUCTURED SiC-Ni COMPOSITE COATINGS OBTAINED BY ELECTRODEPOSITION – A TRIBOCORROSION STUDY

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ABSTRACT

The tribocorrosion properties of SiC (20nm) - Ni nanostructured coatings have been studied in pin on disc tribocorrosimeter connected with an electrochemical cell. The objectives of our study in principal is to fully understanding the tribocorrosion process kinetic and mechanism of modified surfaces by co-depositing nano silicon carbide particles with nickel. The samples with coating on a top of a cylinder were installed in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disc tribometer, with the working surface of the specimen facing upwards. The counterbody (pin) was a corrundum cylinder (7 mm in diameter), mounted vertically on a rotating head, above the specimen. The lower spherical end (radius = 100 mm) of the pin, was then applied against the composite surface (disc) with an adjustable normal force. When rotation was applied, the end of the pin draws a circular wear track (16 mm in diameter) on the working composite surface. Continuous friction tests were carried out. Different friction forces were applied during 10000 tours with a rotation speed of counterbody from 30 to 120 tours/min. Some features of these tests reproduce the wear conditions of composite coatings in real conditions. K_2SO_4 0.5M was used as corrosive and passivating electrolyte for tribocorrosion tests.

KEYWORDS: composite, coatings, dispersed particles, tribocorrosion, wear.

1.Introduction

In industry, e.g. automotive applications, there is always the risk of material touching each other under sliding conditions. In many cases, these industrial components, e.g. bearings, pumps, rolling mill bearings, are required to operate in aqueous environments (corrosive media) in which water is either deliberately introduced as a coolant or present as a working fluid. The combined action of wear and corrosion, named tribocorrosion, often results in a significant increase in the total material loss. Thus, there are required materials having the desired corrosion, friction, and wear properties. Accordingly, many efforts have been made to develop suitable materials to aqueous environment. Composite coatings obtained by metal co-deposition of various dispersed phases during electrocrystallisation have been given special attention in recent years [1-10]. Ni-based alloys, which are in general designed for uses at high temperature, possess some extraordinary characteristics such as excellent mechanical properties, good thermal stability, chemical inertness, and high wear resistance. The Ni-based composites are successfully used due to their capability of having self-lubricating property in a wide temperature range, for instance, the turbine engines used in aviation and electric industries, the radiator sealing systems of the automobile engines, and the mechanical devices in the atomic reactors [1-3]. However, few are reported on their friction and wear properties as well as wear mechanism in water environment [3,11]. In particular, during recent years, Ni-SiC composites have been widely investigated and successfully commercialized in the automotive and aerospace industry as a result of their improved mechanical and tribological properties. The metal-matrix composites are materials in which the properties of a metallic host material are modified with addition of a second phase (ceramics) by electrodeposition process. The second phase can be hard oxide (Al_2O_3, TiO_2, SiO_2) or carbides particles (SiC, WC), or diamond, or solid lubricant (PTFE, graphite or MoS_2), or even liquid containing microcapsules [4]. Most composite coatings contain micron-sized particles. The major challenges with the codeposition of second phase particles are the achievement of a high level of codeposition and avoiding the agglomeration of particles suspended in the electrolytes. The aim of this work is to investigate the influence of nano-sized SiC particles dispersed in the Ni matrix on the tribocorrosion behavior of Ni-SiC nanostructured coatings in aqueous environment.

2. Experimental

2.1. Preparation of nano SiC - Ni composite coatings

Nickel silicon carbide co-depositions were made in common nickel plating electrolytes (sulfate and chloride). The electrolyte was prepared from p.a. chemicals and distilled water, which provided the required purity for the potentiodynamic investigations and characterizations of the coatings obtained. Pure dispersed nano sized silicon carbide at different concentrations ($50gL^{-1}$) was suspended in the electrolysis bath. The average particle size was 20 nm. Thickness of composite deposits were obtained at 50 µm and were verified by measuring the weight before and after deposition and also by light microscopy on cross section. The particles were kept in suspension by mechanical or magnetic stirring at a rotation rate at 200 r.p.m. A saturated calomel electrode was used as reference electrode (SCE) in order to determine the influence of the dispersed phase on nickel electrodeposition.

2.2. Structural and chemical analyses

Nano SiC (20nm) amount in the composite coating by surface and cross section analysis was performed with X-ray disperse energy system (EDX). Nano SiC content in the coating was obtained at 8.99 as weight % or calculated at ~25 as volume %.

2.3. Wear - corrosion studies

For electrochemical measurements (open-circuit potential, potentiodynamic polarization) a three-electrode set-up was used, with the sample as working electrode, a circular platinum gauze as counter electrode and a "Hg/Hg_2SO_4/saturated K_2SO_4 solution" as reference electrode (SSE=+670mV/NHE), see Fig. 1. The electrodes were connected to a PAR273A potentiostat controlled through a computer by using Corrware 2.2 (Scribner) software.

The tribocorrosion properties have been studied in the following conditions:

Solution: 0.5M K_2SO_4.
Normal Force: 10N – 15N.
Rotation Speed: 30-120 tours/min.

The samples were then installed in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disc tribometer, with the working surface of the specimen facing upwards.

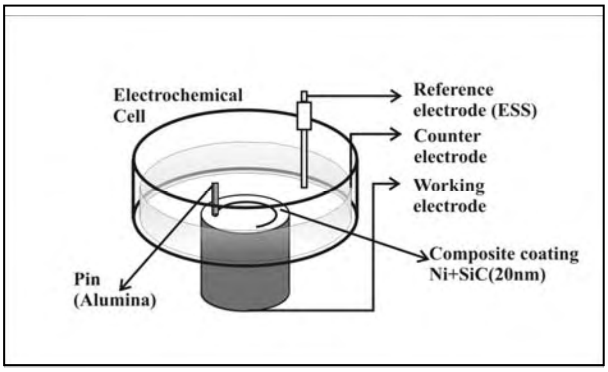

Fig. 1. *Schematic set-up for electrochemical measurements on a working electrode as Ni-SiC composite coating (WE).*

The counterbody (pin) was a corrundum cylinder (7 mm in diameter), mounted vertically on a rotating head, above the specimen. The lower spherical end (radius = 100 mm) of the pin, was then applied against the composite surface (disc) with an adjustable normal force. When rotation was applied, the end of the pin draws a circular wear track (16 mm in diameter) on the working composite surface (Fig. 1).

3. Results and discussion

3.1. Open circuit potential measurements

This method gives information on the electrochemical state of a material, for example active or passive state. However, open circuit potential measurements provide limited information on the kinetics of surface reactions.

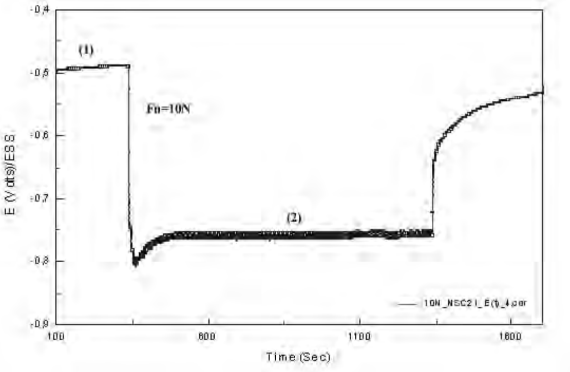

Fig. 2. *Variation of the open circuit potential of Ni-SiC nanostructured coating immersed in 0.5 M K_2SO_4 before(area 1), and during sliding tests (area 2)*

3.2. Polarization diagrams

The open circuit potential recorded during unidirectional pin-on-disk sliding tests in which the disk is the material under investigation, is a mixed potential reflecting the combined state of the unworn disk material and the material in the wear track [12,13,14]. An example of the evolution of the open circuit potential before and during sliding is shown in Figure 2.

The polarization curves of Ni-SiC nanostructured composite coatings in 0.5 M K_2SO_4 were recorded under continuous friction (applied load 10N and 15N; 120 rpm), and without applied friction, by direct potentiodynamic scan from the hydrogen evolution potential domain up to the beginning of transpassive dissolution domain. These curves are presented in Figure 3.

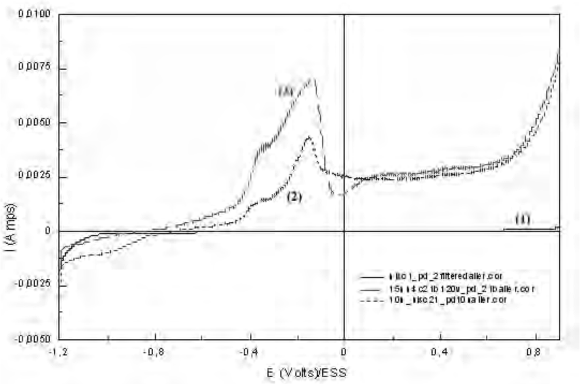

Fig. 3. *Potentiodynamic polarization curves of Ni-SiC nanostructured composite coating immersed in 0.5 M K_2SO_4 recorded by direct potential scan at 0.1 V per minute. Black Curve(1): no friction applied; Blue Curve (2): continuous friction (10 N; 120 rpm);Red Curve(3): Continuous friction (15N, 120 rpm).*

When friction is applied (red and blue curves), the shape of the polarization diagram changes: hydrogen evolution on composite surface is not modified, but an anodic current appears in the potential range from [-0.8 ; -0.0] V/SSE, indicating a dissolution of the coating.

A first approach for interpreting the polarization curves under friction can be developed on the following considerations, based on a concept of "*active wear track*".

The measured current, I can be considered as the sum of two partial currents I_t and I_p ($I=I_t+I_p$). I_t is the current originated from the wear track areas where the passive film is destroyed and metal is active, and I_p the current linked to the surface not subjected to friction and that remains in passive state.

3.3. Current evolution during sliding at different potentials

The current during sliding change from cathodic (without sliding) to an anodic one, and slow variation versus applied load. In Figure 4 it is shown the evolution of current during sliding (Red diagram at 15 N applied force, black diagram at 10 N applied force) at imposed potential of E=-0.710V/ESS.

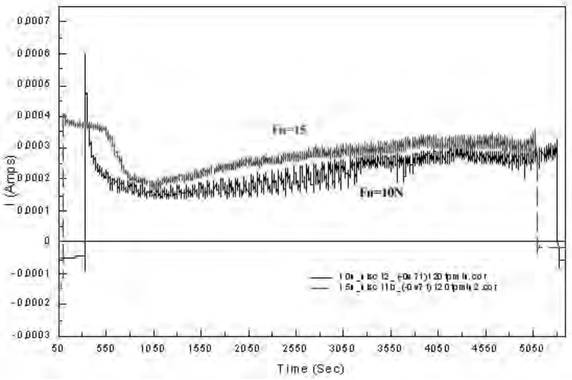

Fig. 4. *Current evolution diagrams under sliding for Ni-SiC nanostructured composite coating immersed in 0.5 M K_2SO_4 recorded under sliding: Red Curve (1): continuous friction (15 N; 120 rpm); Black Curve (2): Continuous friction (10N, 120 rpm).*

3.4. Microtopographic survey of the worn surface

Local wear in the wear track was also measured. It was deduced from surveys of the wear track recorded with an optical high resolution microtopograph, with a lateral resolution of 1 µm and a vertical resolution of 30 nm: the volume of the wear track was measured and the corresponding weight loss was calculated. On Figures 5 and 6 are presented a 3D surface and a profile measured after intermittent sliding test on Ni-SiC nanostructured composite coating, with 15N sliding force and 120 rpm, after 10000 cycles.

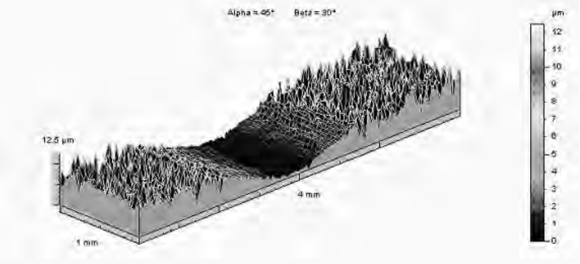

Fig. 5. *3D microtopograph image of wear track area aftercontinuous sliding of Ni-SiC nanostructured composite coating (Fn=15N, 120 rpm, 10 000 cycles)*

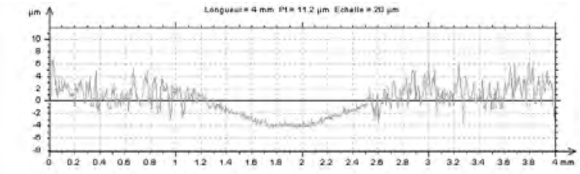

Fig. 6. *2D microtopograph profile of wear track area after continuous sliding of Ni-SiC nanostructured composite coating (Fn=15N, 120 rpm, 10 000 cycles)*

Surface roughness parameters in the middle of the scar (mean value) are: R_a= 0,96 μm; R_t= 5.63μm compared with the non rubbed surface with a R_a= 1.65 μm and R_t=12.4 μm. The introduction of a harder reinforcing phase in the ductile matrix by a certain volume fraction can reduce ductility of the matrix material in the contact region and wear of the matrix can be reduced as a result. The results have to be more worked to have the real conclusions.

Scar surface profiles of pure Ni coating showed higher debris and higher roughness parameters [15]. The experimental data have to be more worked in order to have the conclusion and comparaison with others published data.

3.5. SEM surface morphology after continuous friction

After triboccorosion tests the surface of samples was analysed by SEM and EDS systems. On Figs 7-10 there are the SEM images (at different magnifications) of unrubbed surface (near area along the track) and wear track after continuous friction tests with a normal force of 15 N and 120 tours/min, after 10000 tours of friction.

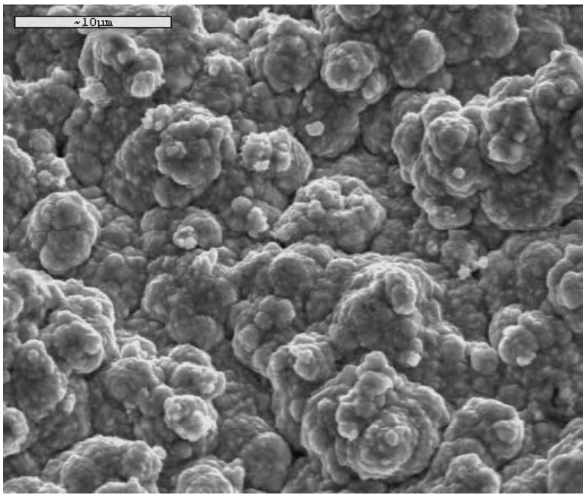

Fig. 7. *SEM image of nanostructured SiC-Ni coating on un- rubbed surface*

On the unrubbed nano structured composite surface (Fig. 7) we observe the nodular disturbed growth of layer with high roughness. The general overview of track area is presented on Fig. 8. The details of wear track are presented on Figs. 9 and 10.

The mechanical damage of the sample surfaces induces an activation of the metal structure, which is well described by the corrosion potential. However the trend with time shows a further increase in the corrosion potential towards more noble values. The equilibrium between the mechanical damage and the electrochemical processes at the metal surface needs some time to be reached.

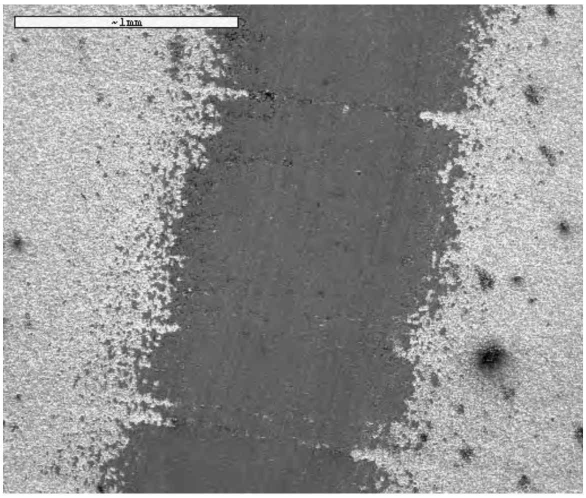

Fig. 8. *SEM image of Wear track after continuous friction test with a normal force of 15 N and 120 tours/min, 10000 tours of friction*

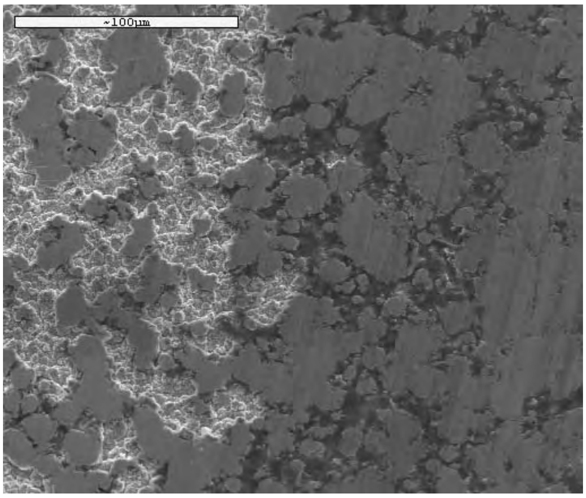

Fig. 9. *SEM image of Wear track details after continuous friction test with a normal force of 15 N and 120 tours/min, 10000 tours of friction.*

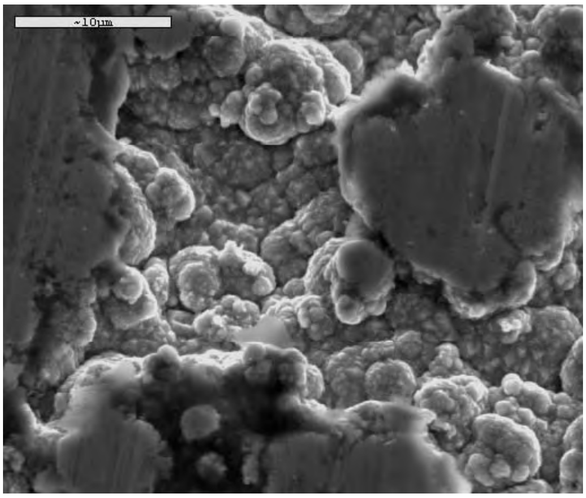

Fig. 10. *SEM image of near area along the track (15 N and 120 tours/min, 10000 tours of friction)*

At the beginning, the mechanical wear induces a rapid deterioration of the protective surface layers, which causes a drastic decrease of the corrosion potential.

4. Conclusions

The tribocorrosion behaviour of nanosized dispersed SiC - Ni-ZrO_2 composite coatings in a pin on disk sliding system in 0.5 M K_2SO_4 solution was investigated combined with *in-situ* electrochemical (potential and polarization diagrams) measurements and *ex-situ* SEM –EDS and microtopographic surveys.

This overview points out the capabilities of electrochemical methods like open circuit potential measurements, polarization curves measurements, for the *in situ* investigation of materials used under tribocorrosive conditions in sliding contacts. They can provide not only essential information on the surface conditions of composite surface in sliding contacts, but also on the kinetics of reactions that control the corrosion component in the material loss during tribocorrosion tests.

Aspects of the tribocorrosion mechanism that can be clarified in this way are the nature of electrochemical reactions, the formation of protective passive surface films, the interactions between electrochemical reactions and friction. Information can also be gained on kinetics such as corrosion rate, rate of depassivation by mechanical action in the contact area, and rate of repassivation.

Nickel – nano silicon carbide composite coating is affected by a tribocorrosion process when subjected to friction in 0.5 M K_2SO_4. This tribocorrosion process involves mechanical destruction of the passive film on the contact areas by friction, and subsequent restoration of the film (repassivation) when friction stops.

The surface morphology of composite layers are different compared with pure nickel coating. The surface structure is disturbed by dispersed particles. The crystal growth of nickel matrix result in a preferentially random than, in an oriented one.

Acknowledgements

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