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## Tribocorrosion behaviour of Ni–SiC nano-structured composite coatings obtained by electrodeposition

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#### ARTICLE INFO

# Article history: Received 1 October 2007 Received in revised form 29 February 2008 Accepted 7 April 2008 Available online 11 June 2008

Keywords:
Nano-structured coatings
Tribocorrosion
Nickel
Silicon carbide nanoparticles
Friction
Electrochemical measurements

#### ABSTRACT

The combined corrosion-wear degradation of nano-structured Ni-SiC coatings in sliding contacts immersed in electrically conductive solutions is investigated in situ by electrochemical techniques (open-circuit potential measurements, EOC, the potentiodynamic polarization measurements, PD, and the electrochemical impedance spectroscopy). The coating thickness was 50 µm, with an average volume of dispersed phases inside nickel of 20%. The samples were tested in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disk tribometer, with the working surface of the specimen facing upwards. Both continuous and intermittent friction tests were carried out. In the intermittent tests, friction was applied periodically: during each cycle, friction was first applied for 2 s at constant sliding speed under constant normal load and then stopped during a latency time of 20 s or 0.5 s. Without friction, the free potential reaches a passive value after immersion in the test solution. When friction force is applied the free potential is shutting down to active values. Under friction the measured current, *I* can be considered as the sum of two partial currents: one generated by the wear track areas, where the passive film is destroyed and the surface is active; the other one linked to the surface not subjected to friction and that remains in the passive state. A localised corrosion process when subjected to friction in 0.5 M K<sub>2</sub>SO<sub>4</sub> was not observed on nano-structured Ni-SiC composite coatings. The mechanical destruction of the passive film occurs in the wear track by friction and subsequent restoration of the film (repassivation) when friction stops. The wear volume loss increases with sliding forces.

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#### 1. Introduction

Tribocorrosion or corrosion-wear describes the material behaviour in systems where interactions between tribological and corrosion processes take place. In such tribocorrosion systems, materials are subjected to mechanical, chemical, and electrochemical loadings.

Tribocorrosion is defined as the chemical–electrochemical–mechanical process leading to a degradation of materials in sliding, rolling or erosion contacts immersed in a corrosive environment. That degradation results from the combined action of corrosion and wear. The mechanism of tribocorrosion is not yet fully understood due to the complexity of the chemical, electrochemical, physical, and mechanical processes involved [1–3]. Examples of the occurrence of tribocorrosion in service are the accelerated corrosion of

steel conveyors exposed to ambient air of high relative humidity, the fall out of electrical connectors in the automotive industry, the degradation of hip prosthesis and dental fillers, the erosion wear of turbine blades, etc. Passive metals are particularly sensitive to tribocorrosion because rubbing can destroy their passive surface film that may enhance both corrosion and wear rate before the surface repassivates. It was observed that the material removal in a tribocorrosion system usually exceeds the sum of mechanical and corrosion contributions measured separately [4,5]. Therefore it is of interest to understand the behaviour of passive metals under tribocorrosion conditions. Over the past few years, the mechanisms of wear and corrosion-wear of stainless steels were studied by different techniques [6–10]. The literature data about tribocorrosion behaviour of micro- and nano-structured coatings are still very poor [11,12].

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

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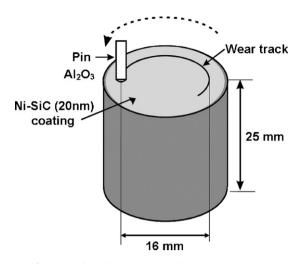


Fig. 1. Sample with nano-structured Ni-SiC coating on top.

in which the properties of a metallic host material are modified with the addition of a second phase (ceramics) by electrodeposition process. In the literature, there is very limited study in the dispersion of inert particles in the metallic matrix and its influence on the mechanical and tribological properties. The aim of this work is to investigate the influence of SiC nanosized particles (20-nm mean diameter) dispersed in the Ni matrix on the tribocorrosion behaviour of Ni–SiC nano-composite coatings in aqueous environment.

The combined corrosion-wear degradation of nano-structured Ni–SiC (20 nm) in sliding contacts immersed in electrically conductive solutions is investigated in situ by electrochemical techniques and additional ex situ methods like high resolution microtopography and scanning electron microscopy. Such electrochemical techniques are the open-circuit potential measurements,  $E_{\rm OC}$ , the potentiodynamic polarization measurements, PD, the electrochemical impedance measurements and the transients of current repassivation versus time after mechanical perturbation.

#### 2. Experimental set-up

Samples with nano-structured composite coatings Ni–SiC (20 nm) were prepared by co-deposition of nanosized SiC with nickel in a Watts plating baths. The composite coatings were deposited on a top face of a stainless steel cylinder (high = 25 mm, diameter = 25 mm) see Fig. 1. The coating thickness was 50  $\mu$ m, with an average volume of dispersed phase inside nickel of 20%. The samples were then installed in a cell, containing the electrolyte and electrodes, and mounted on a pin-on-disk tribometer, with the working surface of the specimen facing upwards, see Fig. 2. For

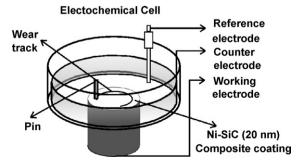


Fig. 2. Electrochemical cell used for tribocorrosion tests.

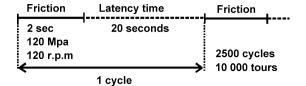


Fig. 3. Schematic tribocorrosion tests.

electrochemical measurements (open-circuit potential, potentio-dynamic 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 = +670~mV/NHE).

The tribocorrosion properties have been studied in the following conditions: solution—0.5 M  $K_2SO_4$ ; normal force: 5–20 N; rotation speed: 30–120 tours/min. The counterbody (pin) was an alumina 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 (disk) 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.

Both continuous and intermittent friction tests were carried out. In the intermittent tests, friction was applied periodically: during each cycle, friction was first applied for 2 s at constant sliding speed under constant normal load and then stopped during a latency time (20 s). This mechanical solicitation was repeated over 2500 cycles (10,000 tours), see Fig. 3. Some features of these tests reproduce the wear conditions of composite coatings in the real conditions of work. Even in the case of continuous friction a latency time of 0.5–2 s could be considered in the rotation speed range from 30 to 120 rpm. This is the time of the pin to reach the same point of the circular drown wear track on the composite surface at constant speed.

#### 3. Results and discussions

#### 3.1. Open-circuit potential measurements

Under unloaded conditions, the free potential variations are quite small and reach stable passive value (Fig. 4a). At the start of the friction–corrosion tests, the potential of the SiC–Ni nano-composite coatings undergoes a significant negative shift in both test conditions: intermittent friction with latency time of 20 s (Fig. 4b) and continuous friction (domain B from Fig. 4c). Under friction the free potential shut down to active values and try to reach the passive values after friction stops. The passive value of the free potential reached after friction stop are more negative that those reached before starting the friction, see Fig. 4b and domain C from Fig. 4c.

The open-circuit potential depends on the following parameters:

- The respective intrinsic open-circuit potentials of the materials in worn and unworn areas. These open-circuit potentials are different because the electrochemical state of the metal is disturbed by the removal of the surface films that may consist of adsorbed species, passive films, or corrosion products, in the sliding contact, and by a mechanical straining of the metal.
- The ratio of worn to unworn areas. In particular, if the extent of the worn area increases, the open-circuit potential of the disk will shift depending on the controlling electrochemical processes, being either the anodic (e.g., the dissolution of the metal) or the

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