THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI
FASCICLE IX METALLURGY AND MATERIALS SCIENCE, ISSN 1453 – 083X. N^0. 1 – 2006

IMPROVED HARDNESS AND TRIBOCORROSION PROPERTIES OF NICKEL COATINGS BY CO - DEPOSITING ZrO_2 MICRO - SIZED DISPERSED PHASE DURING ELECTROPLATING PROCESS

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ABSTRACT

The tribocorrosion properties of ZrO_2 – nickel microstrucured composite coatings have been studied in the following conditions:

-Solution: 0.5M K_2SO_4
-Tribo corrosimeter: pin on disc connected with electrochemical cell.
-Normal Force: 10N
-Rotation Speed: 120 tours/min.

The objectives of our study in principal are to fully understanding the tribocorrosion process kinetic and mechanism of composite coatings materials. 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. 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 seconds at 120 rpm (sliding speed 100 mm/second) under 10 N (average pressure 120 MPa for hertzian contact conditions) and then stopped during a latency time (20 or 200 s.). This mechanical solicitation was repeated over 2500 cycles. Some features of these tests reproduce the wear conditions of composite coatings in the intermittent friction, K_2SO_4 0.5M was used as corrosive and passivating electrolyte for tribocorrosion tests.

KEYWORDS: composite, coatings, dispersed particles, zirconium oxide, nickel, tribocorrosion.

1. Introduction

Composite electroplating is a method of co-depositing insoluble dispersed particles of metallic or non-metallic compounds with metals or alloy in a plating bath, to improve the material coating properties such as corrosion resistance, lubrication, hardness or wear-resistance. Such a coating features the properties of both the metal and the dispersed particles. These coatings can be considered to be metal-matrix composites (MMC), obtained through electroplating. Composite coatings obtained by metal co-deposition of various dispersed phases during electrocrystallisation have been given special attention in recent years [1-10]. Nickel, copper, chromium, iron, cobalt, silver, gold were mainly used as a metal matrix. Metals, metal oxides, carbides, borides and polymers as co-depositing dispersed particles were used. Composite Coatings are used in both aqueous and high temperature applications. Electric power generation, and waste incineration involve severe conditions and thick coatings have proved effective. Diesel and gas turbine engines are subjects of the high temperature corrosion and highly beneficial coatings have been developed. Some nuclear power systems also rely on coatings. Factors that must be taken into account include substrate compatibility, adhesion, porosity, the possibility of repair or recoating, interdiffusion, the effect of thermal cycling, resistance to wear and corrosion, and not at last the cost.

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. 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.

However, few are reported on their friction and wear properties as well as wear mechanism in water environment. In particular, during recent years, Ni-ZrO_2 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 composite materials were obtained by using dispersed micro sized ZrO_2 particles (mean diameter 10 μm). The influence of dispersed ZrO2 dispersed particles on the nickel reduction was discussed in the previous papers [4].

Prior to the wear corrosion tests, the composition and surface morphology of coatings were investigated in the scanning electron microscope with the aid of EDS. The presence of particles inside of composite coating was detected by optical microscopy.

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.

However, 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 [3, 11].

The aim of this work is to investigate the influence of ZrO_2 particles dispersion in the Ni matrix on the tribocorrosion behavior of Ni-ZrO_2 composite coatings in aqueous environment.

2. Experimental

2.1. Preparation of nickel zirconia microstructued composite coatings

Pure nickel and nickel zirconium oxide 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 zirconium oxide (ZrO_2) at different concentrations (50 - 100 g/l) was suspended in the electrolysis bath. The average particle size was 10 µm. Thickness of metal and composite deposits were obtained between 50 and 150 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 between 100 and 1500 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

Weighing the electrodes on a microbalance and stripping the deposit we could determine the amount of dispersed phase in the composite coating. The particles were filtered, dried and weighted. The weight percentage of the particles in the composite deposition was calculated by the formula:

$$p\% = \frac{m_p}{m_s}100 \qquad (1)$$

Where: **p% -** represents the weight percentage of the particles in the composite coating;

m_p is the particles mass, in grams;

m_s is the total composite coating mass, in grams.

The uniformity of dispersed phase distribution in the composite coatings was examined by light microscopy in cross section. Scanning electron microscopy (SEM) revealed the comparative surface morphology of coatings and the uniformity of zirconium oxide particles in the composite deposit.

The micro sized composite coatings were deposited on a top of a cylinder having the dimensions: high = 25 mm and diameter = 25 mm (Fig. 1).

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 = +670 mV/ NHE), see Fig. 1. The electrodes were connected to a PAR273A potentiostat controlled through a computer by using Corrware 2.2 (Scribner) software.

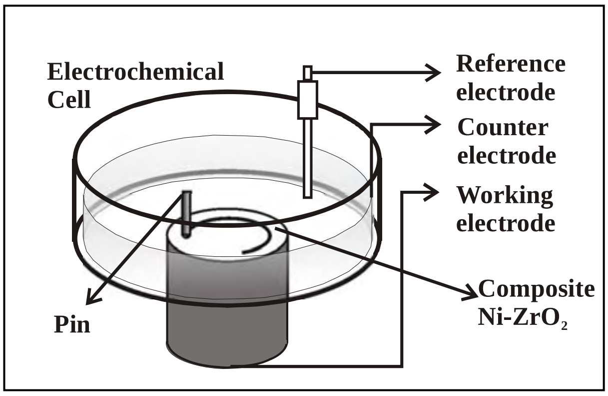


***Fig. 1**. Schematic set-up for electrochemical measurements on a working electrode as Ni-ZrO_2 composite coating (WE)*

The tribocorrosion properties have been studied in the following conditions:

Solution: 0.5M K_2SO_4.

Tribo corrosimeter: pin on disc connected with electrochemical cell.

Normal Force: 10N.

Rotation Speed: 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.

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). 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 seconds at 120 rpm (sliding speed 100 mm/second) under 10 N (average pressure 120 MPa for hertzian contact conditions) and then stopped during a latency time (20 or 200 s.), see Fig. 2. This mechanical solicitation was repeated over 2500 cycles. Some features of these tests reproduce the wear conditions of composite coatings in the intermittent friction. K_2SO_4 0.5M was used as corrosive and passivating electrolyte for tribocorrosion tests.

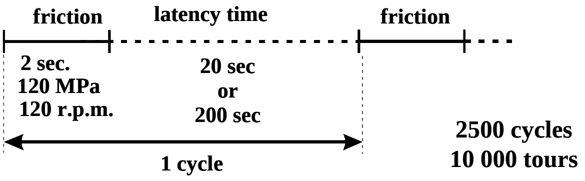


***Fig. 2.** Schematic tribocorrosion tests*

After triboccorosion tests the surface of samples was analysed by SEM and EDS systems.

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.

3. Results and discussion

3.1. Structural aspects of zirconia nickel matrix composite coatings

Micrographies presented allow comparison between a pure nickel coating (Fig. 3) and nickel with zirconium oxide composite coatings (Figures 4, 5, 6 at different magnification), carried out with 100 gl^{-1} of ZrO_2 in the plating bath.

The pure nickel deposit has a rather regular surface, whereas the composite coating develops in a nodular disturbed surface structure. The zirconium oxide particles are clearly visible on the surface with a homogeneous distribution (white particles). The X-ray disperse energy analysis spot on a white particle have revealed a spectra with zirconium but also with nickel (Figure 7). This can suggest that particles are not free on the coating surface but they have a thin layer of nickel. The nickel layer can be done from the reduced nickel ions at the cathode. The surface structure morphology of composite coating obtained by two scanning electronic microscopy techniques is presented on the Figure 8. The surface analysis of composite coatings is not the most suitable method to determine the presence of zirconium oxide in the nickel matrix, but it is appropriate to observe the morphology and surface structure changes. One of the most reliable methods to observe the distribution of zirconia particles in the nickel matrix consists of studying the cross section of a deposit.

The microstructure performed shows the presence and distribution of zirconium oxide particles (8 mass %) in the nickel matrix see Figure 9.

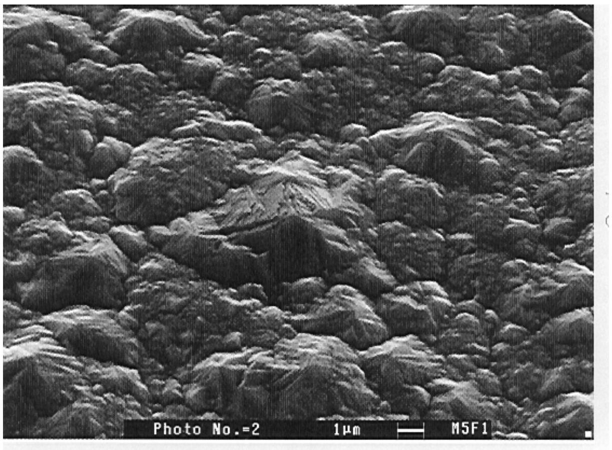


***Fig. 3.** SEM morphology of pure nickel coating*

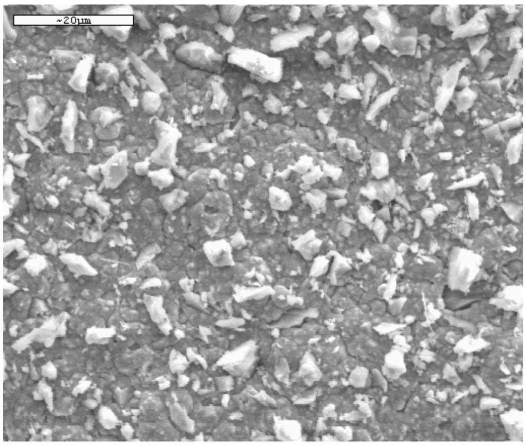


***Fig. 4.** SEM Surface morphology of ZrO_2 + nickel composite coating*

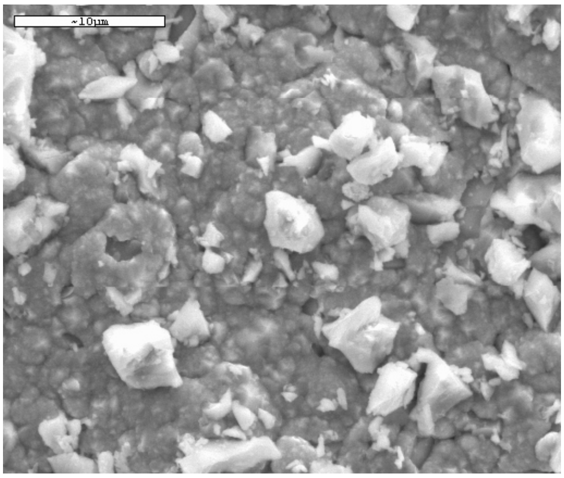


***Fig. 5.** SEM Surface morphology of ZrO_2–Ni composite coating*

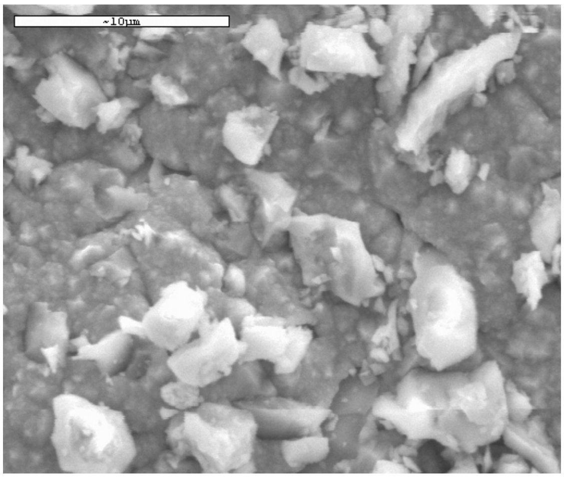


***Fig. 6.** SEM Surface morphology of ZrO_2–Ni composite coating*

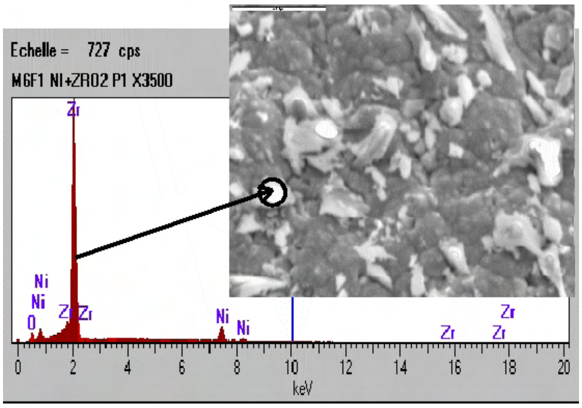
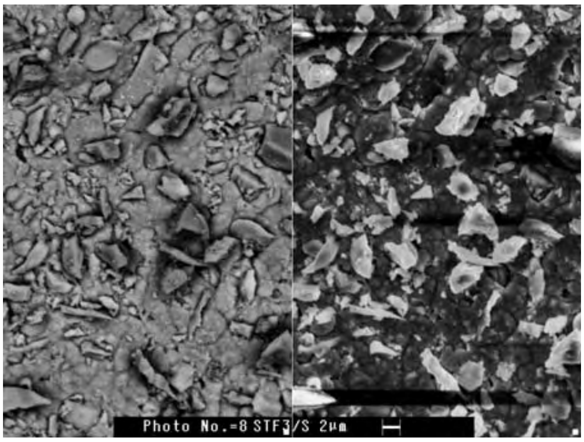


***Fig. 7.** X-ray spectra analysis on a zirconium oxide (white) particle embedded in a nickel matrix*



(a) (b)

***Fig. 8.** (a) Back - scattering SEM image; (b) Diffuse electron image*

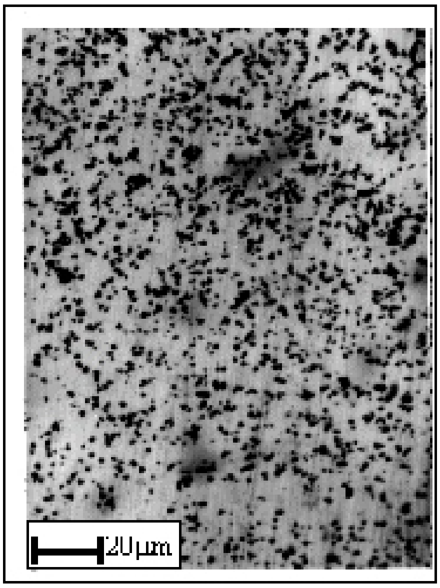


Fig. 9. *Optic microstructure of composite coatings with 8% ZrO_2. Cross section of the coating, magnification 500x*

On optic microscopy the zirconium oxide appear as black points and are uniform distributed inside of the composite coating. The corrosion and tribocorrosion properties of composite coatings could be improved comparative with pure nickel coating.

3.2. Microhardness of nickel – zirconia composite coatings

The microhardness of the plated layers of composite coatings have been determined by optic microscopy on the samples surface. The Vickers microhardness of zirconium oxide composite coatings comparatively to pure nickel electroplating is presented on Table 1.

Table 1. *Results of Vickers microhardness testing on pure nickel and nickel matrix composite coatings with ZrO_2 particles.*

Type of coating	**Load grams**	**D_1 μm**	**D_2 μm**	**HV**
Pure Ni	200	42.3	41.5	211
	100	24.9	32.4	226
	200	41.3	41.4	217
Ni+ ZrO_2 20% mass.	300	25.4	27.1	808
	300	22.5	31.5	763
	300	26.9	26.7	775
Ni+ ZrO_2 46 % mass.	300	20.5	29.0	909
	300	20.3	25.5	1059
	300	24.5	20.3	1110

3.3. Tribocorrosion studies

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.

The open circuit potential recorded during uni-directional 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.

One must be aware that a galvanic coupling between worn and unworn parts on the disk surface may take place [12, 13, 14]. Consequently, 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 matrix) or the cathodic reaction (e.g., the reduction of hydrogen or dissolved oxygen),

-The relative position of worn and unworn areas. As a result of the galvanic coupling, a current is flowing between anodic and cathodic areas. The ohmic drop may induce a non-uniform distribution of potential and current density over the disk surface.

The measured open circuit potential is thus an average value depending on that distribution,

-The mechanism and kinetics of the anodic and cathodic reactions in worn and unworn areas.

The evolution of the open circuit potential is shown in Figures 10. The evolution of the open circuit potential was measured under unloaded and mechanically loaded conditions.

During the latency time, a competition between repassivation and dissolution occurs.

At the end of the periods of friction, during the stages of latency, the increase of E_{OC} indicates the restoration of the passive film on the areas where it was removed by friction

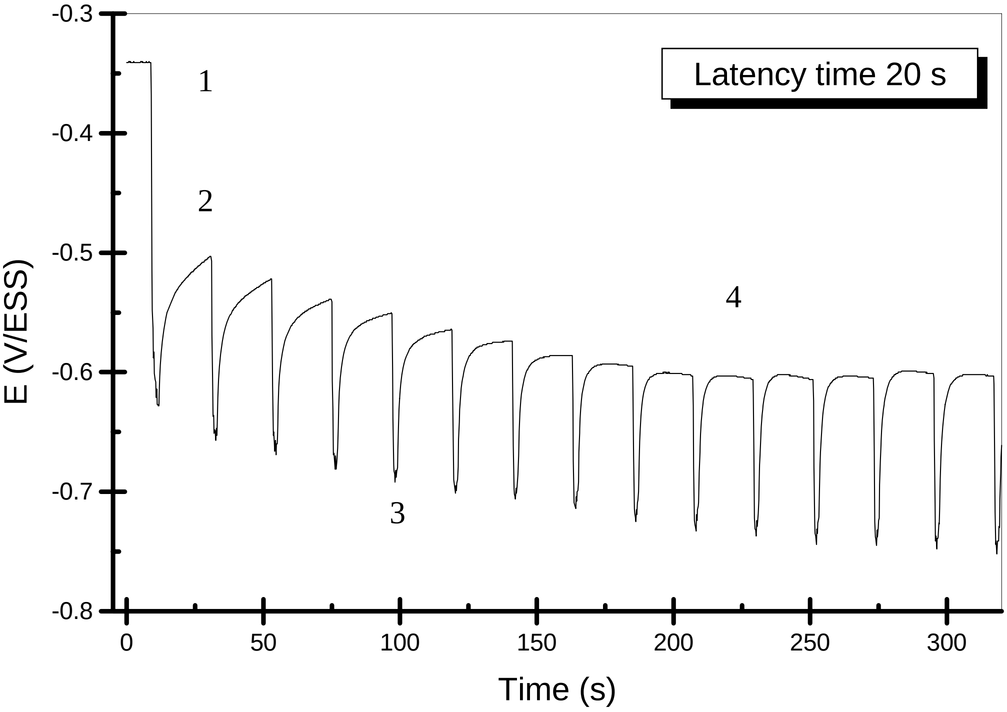


Fig. 10. *Variation of the open circuit potential of Ni-ZrO2 composite coating immersed in 0.5 M K_2SO_4 before (e.g. area 1 and 2), during (e.g. area 3), and after loading (e.g. area 4), during intermittent friction tests.*

Polarization diagrams

The polarization curves of ZrO_2-Ni composite coatings in 0.5 M K_2SO_4 were recorded under continuous friction (10 N; 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 11.

If the composite surface of the sample is not subjected to rubbing (black curve no rubbing), hydrogen evolution and oxygen reduction are the only reactions detected in the potential domain A. In domain B and C, the composite surface is passivated, the current remaining very small and the zero-current potential lying between -0.8 and -0.6 V/SSE. After domain C the anodic current must increases with the applied potential, revealing the dissolution of the alloy, induced by oxydation of the passive film, giving soluble species.

When friction is applied (red curve), the shape of the polarization diagram changes: hydrogen evolution on composite surface is not modified in domainA, but an anodic current of about 3 mA appears in the potential range from [-0.5 ; -0.3] V/SSE, indicating a dissolution of the coating. A first approch for interpreting the polarization curve under friction can be developed on the following considerations, based on a concept of "*active wear track*" [13].

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.

-At the zero-current potential where I=0, a galvanic coupling is established. I_t and I_p are different from zero, and $I_p=-I_t$. These partial currents flow between the active wear track areas and the rest of the surface. On the wear track, where dissolution of the material and the formation of a new passive film occurs, I_t is anodic. On the remaining surface, I_p is cathodic and is related to reactions as dissolved oxygen reduction or hydrogen reduction.

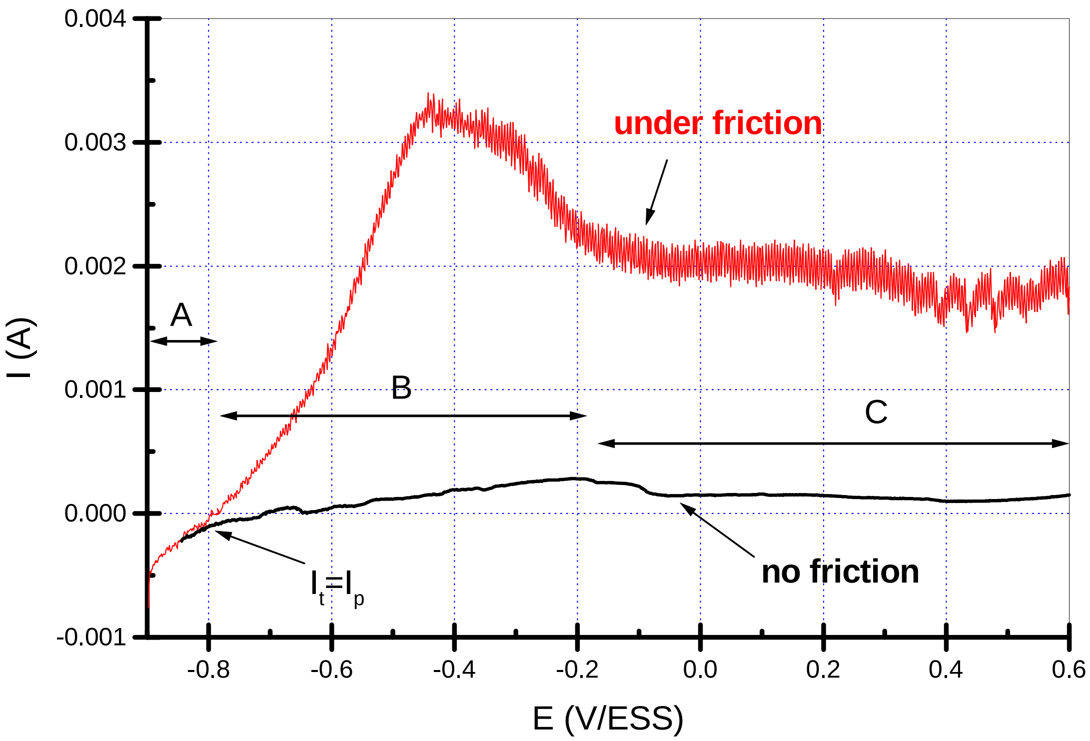


Fig. 11. *Potentiodynamic polarization curves of Ni-ZrO2 composite coating immersed in 0.5 M K_2SO_4 recorded by direct potential scan at 0.1 V per minute. Black Curve: no friction applied; Red Curve: continuous friction (10 N ; 120 rpm).*

-When the potential increases, the galvanic coupling is broken and I_t is no longer equal to $-I_p$. Both I_t and I_p increase. As a result, the measured current I, flowing between the specimen and the counter electrode increases. On the surface not subjected to friction and in passive state, I_p can not exceed the value of the current measured at the same potential on the unrubbed specimen. By comparing the values of I in both conditions (see figure 10), it can be deduced that, under friction, $I = I_t$ (from -0.78 to 0.6 V/SSE). The total current measured under friction and its evolution with applied potential, are characteristic of the behaviour of composite surface in the wear track. The steep increase of the current with potential around the zero-current potential, indicates that a rapid dissolution occurs in the wear track.

-The further decrease of the dissolution current above -0.3 V/SSE reveals the effect of repassivation in the active wear track. The rate of this reaction, occurring in the areas where the passive film is removed, increases with potential. This induces a lowering of the total depassivated area, and thus a decrease of the dissolution current.

Thus, polarization curves reveal the occurrence of depassivation and dissolution of the composite surface induced by friction in the wear track, and give the opportunity of quantitative measurements concerning the variation of the active wear track area with tribological parameters (normal load, sliding speed, etc.).

The depassivation of these areas along the wear track was interpreted as the result of the potential distribution generated over the surface of the specimen by the galvanic coupling between the anodic active wear track areas (having low specific corrosion potential) and the cathodic passivated surrounding surface (having higher specific rest potential).

SEM surface morphology after continuous and intermittent friction fretting

After triboccorosion tests the surface of samples was analysed by SEM and EDS systems. On Figs 12 and 13 there are the SEM images (at different magnifications) of wear track after continuous (Fig. 12) and intermittent friction (Fig. 13) tests with a latency time of 20 seconds.

The chemical analysis after tribocorrosion tests on continous friction (FC) evidenced a different content of zirconium particles on the area near of the wear track compared with the wear track area. On the unrubbed surface the content of zirconium was 13, 07 % (mass percent) whereas inside of the track was around 22,18 %. This can suggest a preferential dissolution of nickel matrix on the surface in the narrow area along the trace.

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

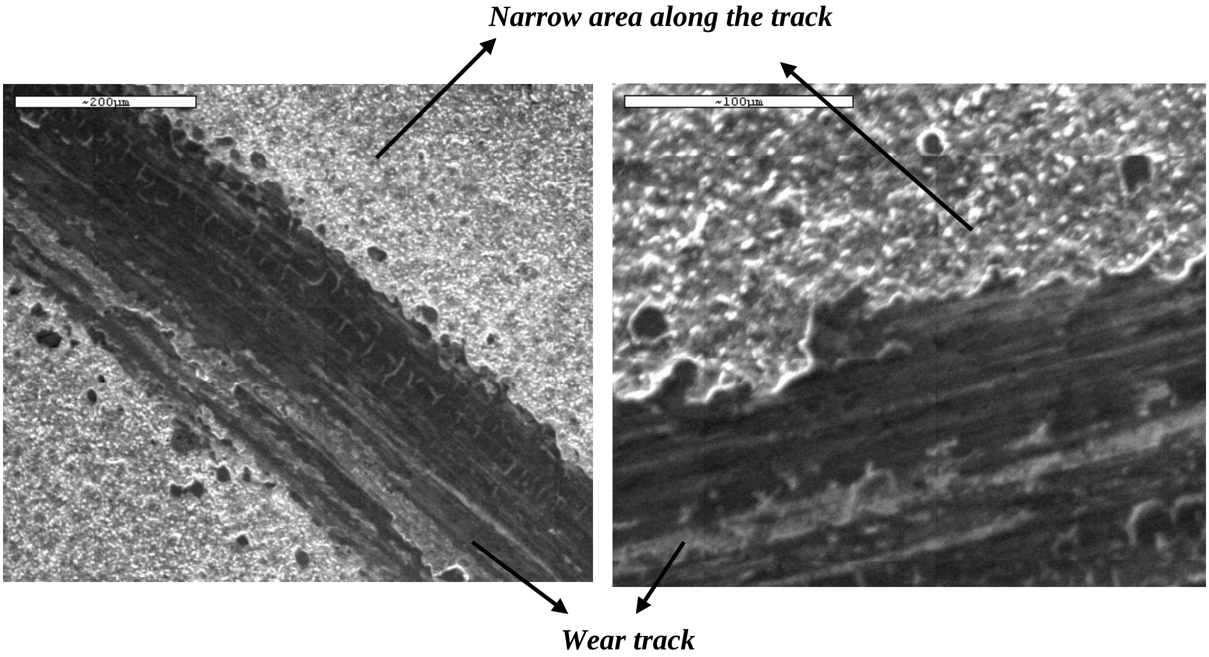


Fig. 12. *SEM Structure of composite surface after continuous friction tests (FC)*

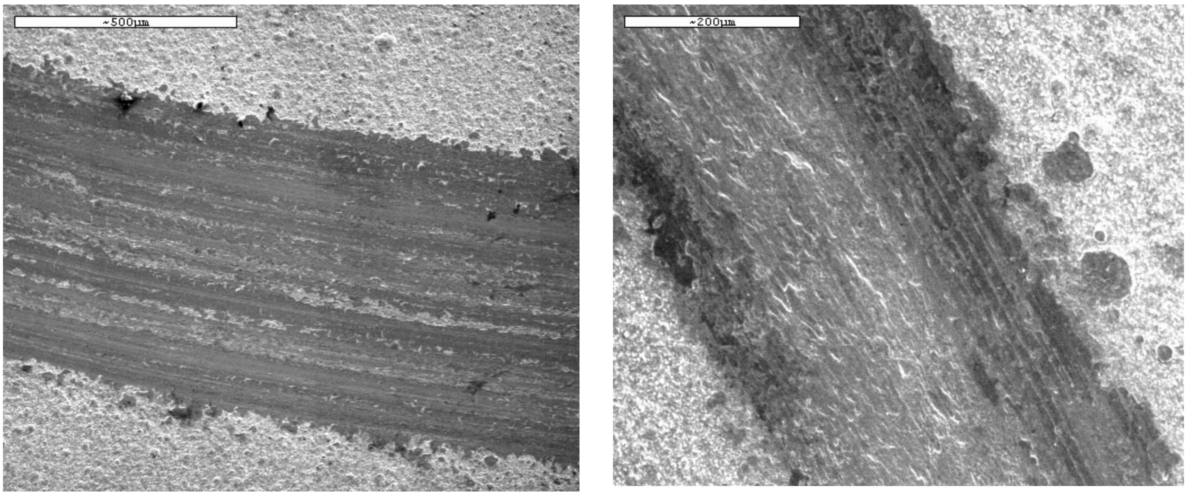


Fig. 13. *SEM surface morphology of Ni-ZrO$_2$ composite coating after intermittent friction tests (latency time 20s)*

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 14 and 15 are presented a 3D surface and a profile measured after intermittent friction test on Ni-ZrO_2 composite coating.

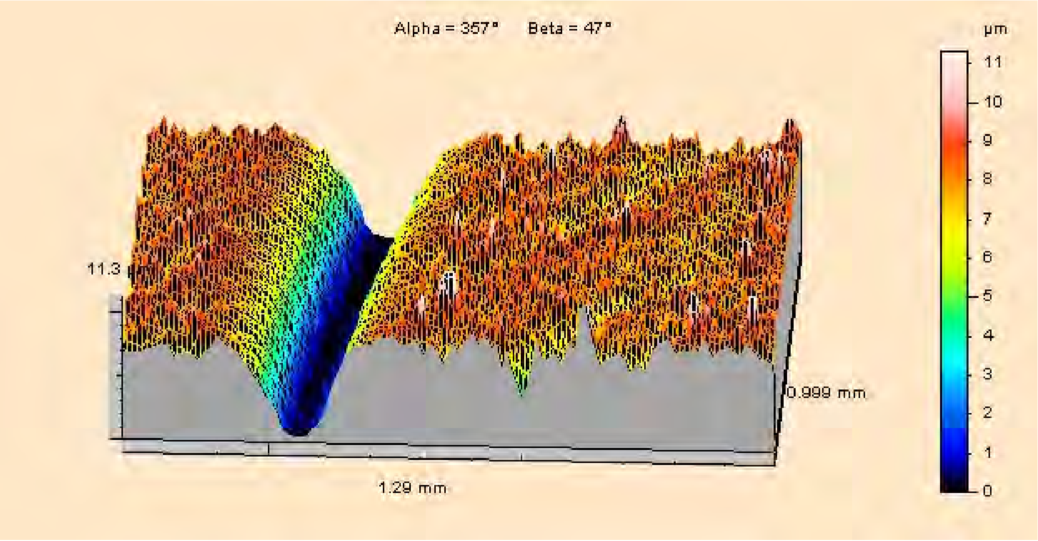


Fig. 14. *3D Microtopograph image of wear track area after intermittent friction (20s latency time) of Ni-ZrO_2 composite coating*

When a tribo-element is made of a ductile element such as Al, Cu, Ni, Fe or an alloy with a combination of them, material in the contact region plastically deforms severely under the combined stresses of compression and shear.

Large plastic deformation generally introduces large wear rate since wear surface tends to become rough and protective surface layers are easily destroyed. Scar surface profiles of pure Ni coating showed higher debris and higher roughness parameters [15].

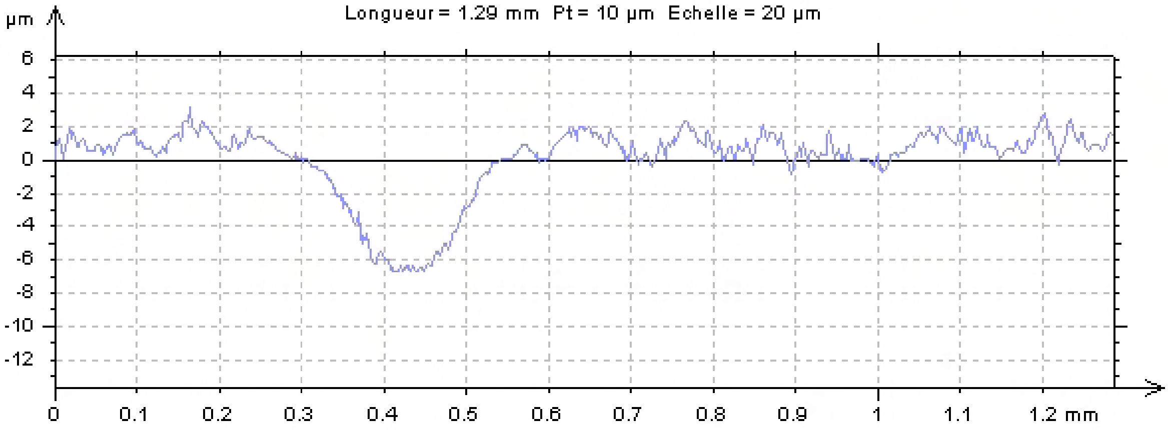


Fig. 15. *2D Microtopograph profile of wear track area after intermittent friction (20s latency time) of Ni-ZrO_2 composite coating*

Surface roughness parameters in the middle of the scar (mean value) presented in the paper [15] are: R_a= 8.19 µm; R_q= 9.67 µm; R_p= 28.50 µm; R_v= 29.50 µm. In the case of ZrO_2-Ni composite surface these values are under 1 micron as we can see on Fig. 15.

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.

4. Conclusions

The tribocorrosion behaviour of Ni-ZrO_2 microstructured 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 – zirconia microstructured composite coating is affected by a tribocorrosion process when subjected to intermittent friction in 0.5 M H_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

We would like to thank COST-STSM-532-00455 and the bilateral scientific project Romania-Flanders (contract BIL 02/26) for the financial support.

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