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Wear-corrosion response of Cerium oxide reinforced Cobalt hybrid composite layers in biological solution

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Abstract. The research work aims at improving biomaterials surface properties by Co/nano-CeO₂ composite layers obtained by electro-codeposition method from a cobalt sulphate solution containing CeO₂ dispersed nanoparticles. The thicknesses of pure cobalt and Co/CeO₂ hybrid nanocomposite layers are measured versus applied current density and time of the plating process. The tribocorrosion properties of Co/nano-CeO₂ hybrid nanocomposite layers and pure Co layer obtained were comparatively investigated friction sliding tests in a unidirectional tribometer in lubricating conditions using biological solution (Hank). During the tribocorrosion test, the normal force, tangential force, coefficient of friction, number of cycles as well as the electrochemical parameter (potential), were continuously monitored. The results show that the wear - corrosion (tribocorrosion) behavior of Co/nano-CeO₂ hybrid nanocomposite layers are closely related with dispersed reinforcing nano-CeO₂ content. The hybrid nanocomposite layers with all CeO₂ content shows increased wear - corrosion resistance as compared with pure Co layer, by decreasing wear volume loss with increasing nano-CeO₂ particles dispersed into plating electrolyte.

1. Introduction

Among many processing routes, electrodeposition is a simple and economical method to produce metallic or composite films as compared to other techniques, such as plasma spray, sol-gel, chemical vapor deposition, physical vapor deposition and ion implantation [1-4].

Codepositions of fine particles into metallic electrodeposited matrix as the second phase results in enhanced properties like hardness, corrosion and wear resistance of metallic reinforced coatings. Different ceramic nanoparticles including cerium oxide, CeO₂, are reported to be used as dispersed phase during nickel or cobalt electrodeposition [1, 2, 5, 6].

CeO₂ is an oxide of the rare earth metal cerium which has many superior properties, being also biocompatible material. It has been proven that electro-codeposited CeO₂ into metal matrix can significantly improve the surface properties of Ni/CeO₂ nanocomposite coatings by decreasing the friction coefficient in dry conditions (in air at room temperature) [7], or by increasing the corrosion resistance [8].

The tribological performance of Ni-CeO₂ nano composite coatings under non-lubricated conditions was studied [9].



The effects of lanthanide oxides particles on morphology and corrosion properties of cobalt composite coatings was studied also in 0.1 M NaCl solution [1], the authors found a correlation between the corrosion protection properties of the composite coatings and the composition and the morphology of the cobalt matrix.

The effect of current density and ZrO₂ particles, with an average size of 5 µm, on electrodeposition, microhardness, and corrosion behavior of cobalt coatings have been investigated [2]. The influences of electro-codeposition parameters on corrosion resistance of Co/nano-CeO₂ composite layers were studied [5, 6], showing good effect of embedded CeO₂ nanoparticles into cobalt matrix.

However, no investigations have been done intensely on the wear-corrosion response of embedded nano-CeO₂ particles into cobalt matrix and Co/nano-CeO₂ hybrid composite layers obtained in biological solutions.

In the present study, the friction and wear (tribocorrosion) behavior of electrodeposited Co/nano-CeO₂ hybrid composite layers under lubricated conditions are evaluated. The effect of nano CeO₂ particles added to cobalt plating electrolyte on sliding wear resistance at different loading normal forces in Hank biological solution is discussed.

2. Experimental procedures

2.1. Materials and methods

2.1.1. Preparation of nanocomposite layers Co/CeO₂. Hybrid nanocomposite layers have been obtained using different concentration of CeO₂ nanoparticles dispersed into a cobalt-based electrolyte (cobalt chloride and cobalt sulfate). The nanoscale particle of cerium oxide with average sizes of 25 nm (Nanopowder, ≤ 25 nm particles) from SIGMA-ALDRICH were used. Analytical purity chemicals were used to prepare the electrolyte. The hybrid layers were deposited on stainless steel AISI 304L surface using a two electrode cell. The stainless steel plate with an active area of 22 cm² is the cathode and plate of 99,9 % cobalt is the anode.

2.1.2. Layer microhardness measurement. Microhardness measurements were achieved by using an optical microscope Vickers LECO M400-H1 type (Hardness Testing Machine) by applying a force of 0,01 kgf. The layers microhardness was obtained from the average of ten microhardness measurements performed for each sample separately on a 1 cm² area. The applied force was selected so as to avoid any effect of the substrate for the measured microhardness value.

2.1.3. Wear-corrosion (tribocorrosion) investigations. Wear-corrosion tests were performed using a uni-directional tribometer shown schematically in Figure 1 (a, b). The tribometer is modified for working with a three electrode electrochemical cell.

The samples are therefore mounted in horizontal position into electrochemical cell being connected to a potentiostat as working electrode (WE).

A Solartron Instruments 1287 Electrochemical Interface potentiostat/galvanostat with a frequency response analyzer SI 1255 is used to monitor electrochemical parameters during sliding tests. Platinum wire is the counter electrode (CE) and as reference electrode (RE) is used, Ag/AgCl (saturated KCl solution, E = 199mV versus standard hydrogen electrode).

These electrodes are placed in the friction corrosion cell in such a way that only 3 cm² area of the working electrode (WE) was exposed to electrolyte. During the tribocorrosion test, the normal force, tangential force, coefficient of friction, number of cycles as well as the electrochemical parameter (potential), were continuously monitored.

Two types of samples are investigated:

- (i) Co/nano - CeO₂ hybrid composite layers having three content values of dispersed cerium oxide nanoparticles into plating electrolyte, 10, 20 and 30 g/L⁻¹ respectively, named: Co/nano-CeO₂ (10 g/L⁻¹), Co/nano-CeO₂ (20 g/L⁻¹), Co/nano-CeO₂ (30 g/L⁻¹) and
- (ii) Pure Co layer named Co/CeO₂ (0 g/L⁻¹).

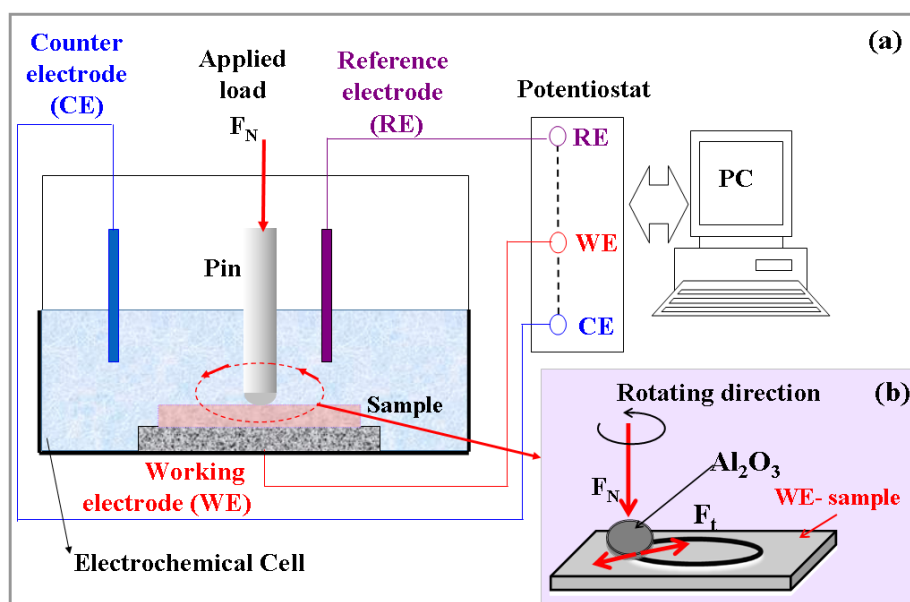


Figure 1. Schematic drawn of tribocorrosion experimental set-up: (a) Electrochemical cell and electrode connections to electrochemical station (potentiostat); (b) Sample with pin rotating direction and wear track on the layer surface.

The sample with layer system is then installed in a tribocorrosion cell, containing the electrolyte and electrodes, with the working surface of the sample facing upwards. The counterbody (pin) is a corundum cylinder (7 mm in diameter), mounted vertically on a rotating head, above the sample [10].

The lower spherical end (radius = 100 mm) of the pin, is then applied against the tested surface with an adjustable normal force (1, 3 and 5N). When rotation is applied, the end of the pin draws a circular wear track (10 mm in diameter) on the working surface, Figure 1 (b).

Tribocorrosion investigations were conducted as follows:

- Measuring the open circuit potential (OCP) of the sample versus reference electrode Ag/AgCl, from immersion for 18 h until it achieve a stable value, without any sliding.
- Friction sliding test during which the OCP of the sample is measured versus reference electrode Ag/AgCl.
- Measuring the open circuit potential (OCP) of the sample after friction sliding is stopped in order to observe the repassivation capacity of tested surfaces.

The wear tests were carried out by applying three normal forces: 1N, 3N and 5N at constant speed of 120 rpm during 5000 cycles.

Table 1. Chemical composition of the biological Hank electrolyte.

Compounds	[g L ⁻¹]
NaCl	8.8
KCl	0.4
CaCl ₂	0.14
NaHCO ₃	0.35
C ₆ H ₁₂ O ₆	1
MgSO ₄ x 7H ₂ O	0.2

In the present investigation freshly prepared simulated body fluid (SBF) solution was used for each experiment with chemical composition presented in Table 1, having a pH equal to 7.4. Tests were performed at room temperature (25°C).

The wear volume was determined using a microtopograph, STIL with high resolution, equipped with optical fiber for light signal capture and intensity analysis with a side resolution of 1 μm and a vertical resolution of 30 nm.

The image is then transformed into a 2D profile surface and 3D surface with Surface Map software.

3. Results and discussion

3.1. Layer thicknesses

From Figure 2 it can be seen that with the increase of the electrodeposition time, the thicknesses of the obtained layers also increase. With the increase of the CeO_2 nanoparticles into electrolyte the thicknesses of the hybrid composite layers slightly increase as compared with pure cobalt layer at the same deposition time, proving the cerium oxide incorporation into cobalt matrix.

For tribocorrosion investigations were chosen layer thicknesses of 20 μm for all layer systems, in order to avoid the influence of the support material. The depth of the resulted wear tracks ranges between 0.5 and 1.5 μm .

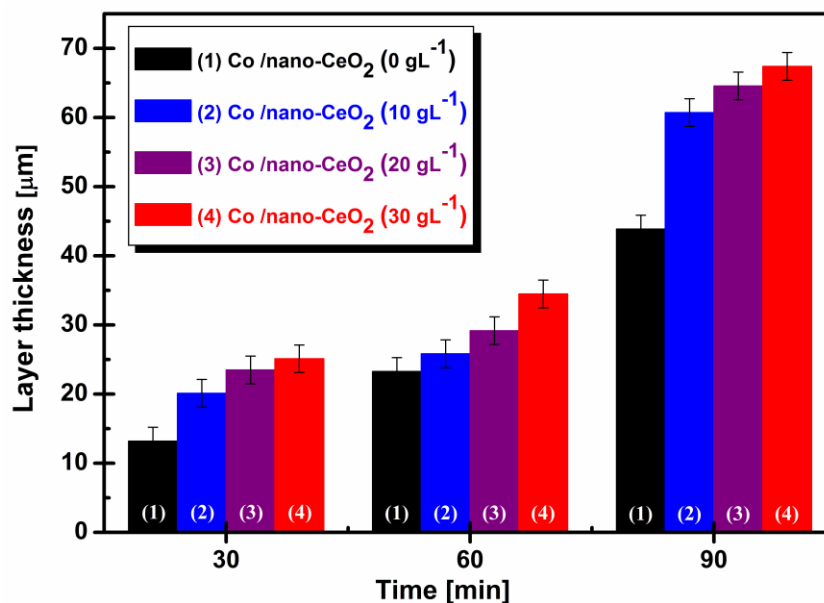


Figure 2. Layer thicknesses of pure cobalt layers and hybrid Co/nano- CeO_2 (10-30 gL^{-1}) composite layers versus time of electrodeposition process at constant current density of $23 \text{ mA} \cdot \text{cm}^{-2}$.

3.2. Microhardness of hybrid composite layers

Figure 3 shows the relationship between the microhardness of the obtained layers and the content of dispersed CeO_2 nanoparticles into electrolyte versus time of electrodeposition.

It is seen that, the microhardnesses of the Co/nano- CeO_2 hybrid composite layers are higher than that of pure Co layers obtained at same deposition time, proving the hardening effect of cerium oxide incorporated into cobalt matrix.

The microhardness of the composite layers increases with the increase of CeO_2 nanoparticles content in the cobalt plating electrolyte being almost constant with increase of deposition time.

The enhancement in the hardness of Co/nano-CeO₂ hybrid composite layers is related to the dispersion-strengthening effect caused by CeO₂ nanoparticles embedded into composite layers, which impede the motion of dislocations in metallic cobalt matrix [6].

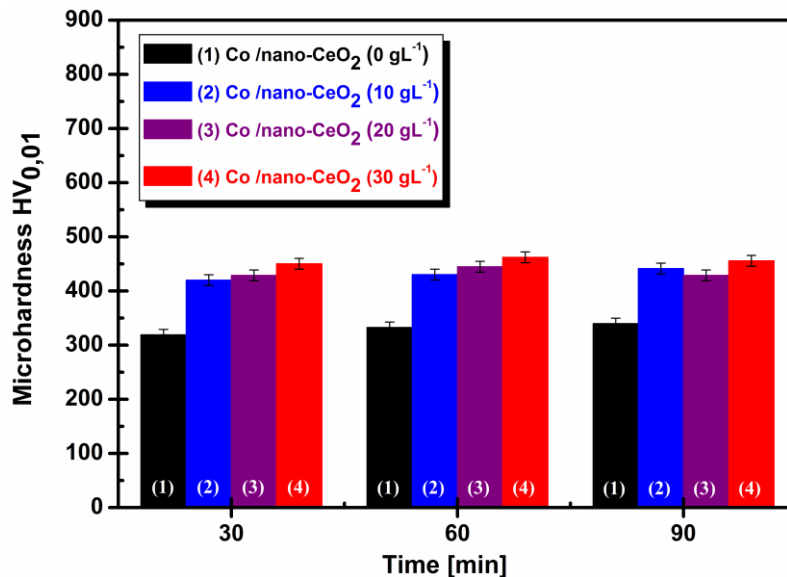


Figure 3. Vickers microhardness measurements on pure cobalt and Co/nano-CeO₂ hybrid composite layers versus electrodeposition time at constant current density of 23 mA · cm⁻².

It is very encouraging to note that the Co/nano-CeO₂ hybrid composite layers exhibit higher hardness value at increased content of the codeposited CeO₂ nanoparticles. Accordingly, the improved friction and wear properties are expected from the hardened matrix.

3.3. Tribocorrosion studies

3.3.1. Open circuit potential measurements. The open circuit potential recorded during uni-directional pin-on-disc sliding tests, in which the surface layer is the material under investigation, is a mixed potential reflecting the combined state of the un-worn surface area of layer and the layer surface in the wear track. The evolution of the open circuit potential is shown in Figure 4. After immersion in the biological Hank solution the open circuit potential tends slowly to a more positive value indicating the passivation state of the pure cobalt layer and Co/nano-CeO₂ hybrid composite surfaces.

It is noted that when the force is applied and friction starts, the surface of the layers are degraded.

This degradation leads to a sudden potential drop in the cathodic direction values indicating the occurrence of a surface activation process.

This layer degradation is more significant in Figure 4 for pure cobalt layer as compared to the hybrid composite layers. The potential drop to more negative values is lower for hybrid composite layers due to the embedded cerium oxide nanoparticles into composite layers which ennobled their electrochemical behavior and therefore increase their resistance to wear-corrosion process.

Some authors [11] found that the OCP value during the tribocorrosion tests decreases and reaches almost the initial OCP value measured for the base material when immersed in the test solution, before passivation state. After wear tests when friction is stopped, OCP values increased sharply since the layers are repassivated with a thin layer of cobalt oxide that forms on the surface instantly when the applied force was stopped.

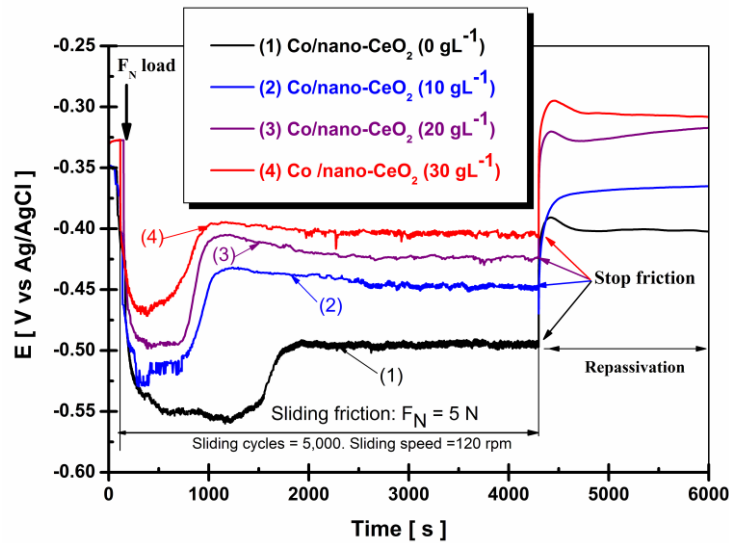


Figure 4. Open circuit potential evolution of: (1) Co/nano-CeO₂ (0 gL⁻¹); (2) Co/nano-CeO₂ (10 gL⁻¹); (3) Co/nano-CeO₂ (20 gL⁻¹); (4) Co/nano-CeO₂ (30 gL⁻¹) measured as a function of time before sliding, during friction with an imposed normal load of 5N (5000 cycles) and after friction was stopped showing repassivation of surfaces.

This OCP increasing values are observed for all layers being more positive for hybrid composite layers being due to a mixed oxide formed by cobalt oxide and cerium from their surfaces. This behavior was observed for other applied normal forces of 1N and 3N, the potential drops being smaller for all layers system.

3.3.2. Wear volume loss. In Figure 5 is shown the wear volume loss calculated from each wear track of: (1) Co/nano-CeO₂ (0 gL⁻¹), (2) Co/nano-CeO₂ (10 gL⁻¹), (3) Co/nano-CeO₂ (20 gL⁻¹), (4) Co/nano-CeO₂ (30 gL⁻¹) versus the three types of normal applied forces: 1N, 3N, respectively 5N.

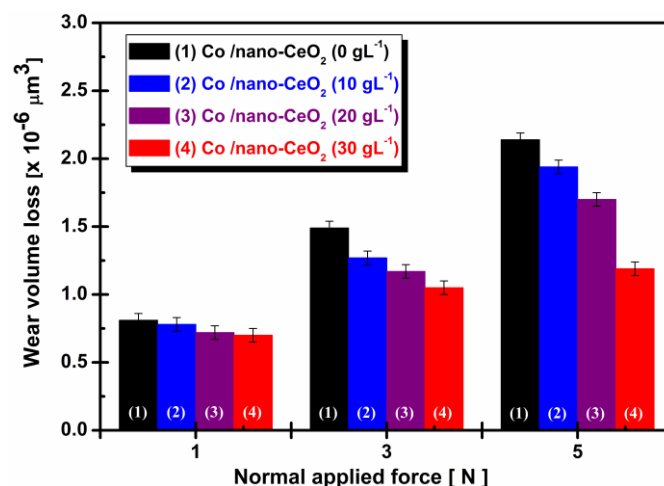


Figure 5. Wear volume loss calculated from each wear track after tribocorrosion investigations of pure cobalt and hybrid composite layers.

From Figure 5 it can be seen that the wear volume loss from the wear tracks of the all layers surface increases with the increasing of normal applied force.

By increasing the content of dispersed cerium oxide into cobalt plating electrolyte the wear volume loss from the wear tracks of hybrid composite layers was found to decrease being much lower than that of the pure cobalt layer tracks under the all applied normal forces, confirming once more the improvement of tribocorrosion performances by adding CeO₂ nanoparticles into cobalt matrix under lubricated conditions.

4. Conclusion

With the increase of the electrodeposition time, the thicknesses of the obtained layers also increase. By increasing the CeO₂ nanoparticles into cobalt plating electrolyte the thicknesses of the hybrid composite layers slightly increase as compared with pure cobalt layer at the same deposition time, proving the cerium oxide incorporation into cobalt matrix.

By increasing the concentration of CeO₂ nanoparticles into plating electrolyte the microhardness of resulted Co/nano-CeO₂ hybrid composite layers increase as compared with pure cobalt layer. The addition of the CeO₂ nanoparticles to the electrolyte led to a slight increase of the microhardness of hybrid composite layers comparatively with pure Co layers obtained with the same imposed parameters.

The open circuit potential measured before sliding tests of Co/nano-CeO₂ hybrid composite layers is more noble (positive) than that of pure cobalt layer, thus leading to a significant anticorrosion effect of CeO₂ nanoparticles embedded into cobalt matrix.

The shift of potential toward the cathodic domain with the onset of sliding is smaller for Co/nano-CeO₂ composite layers than that for pure cobalt layer, due to the presence of embedded CeO₂ nanoparticles.

For Co/nano-CeO₂ hybrid composite layers, the repassivation process is more pronounced even during sliding as compared with pure cobalt layer.

The wear track became deeper for pure Co layers as compared with Co/nano-CeO₂ composite layers, resulting in a lower material loss for Co/nano-CeO₂ hybrid composite layers.

The addition of the CeO₂ nanoparticles into cobalt matrix leads to a decrease a wear volume loss into wear tracks of Co/nano-CeO₂ hybrid composite layers as compared with pure cobalt layer at same friction parameters (applied normal force, rotation speed and number of sliding cycles).

5. References

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