



WC-Co-Cr COATING ON STEEL SUBSTRATE PROCESSED BY PLASMA SPRAYING METHOD

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Received October 1, 2012

Currently, stainless steel is popular for gears manufacturing and special solicitations. A technological solution for improving wear resistance is covering the surfaces with materials with superior properties. The aim of this study is to investigate the corrosion and mechanical behavior of steel coated using plasma spraying technique. Linear polarization and electrochemical impedance spectroscopy (EIS) have been realized in order to determine the electrochemical behaviour of steel compared to coating. As a result, the coating had a better behaviour than the steel.

INTRODUCTION

Thermally sprayed coatings are used to improve the wear characteristics of surfaces¹. WC-Co-Cr coatings are used to improve the wear resistance and corrosion properties of materials.² This coating has very low porosity, and high hardness. When it is deposited on steel substrate increases its operating life. WC-Co-Cr coatings have good wear resistance from the hard WC grains and good toughness from Co-Cr.³⁻⁵

M.Y.P Costa obtained good results about the WC-Co-Cr coating which decreased the fatigue strength of the substrate.⁶

In last years, most of materials properties have been improved by surface modification. Many machine elements that works in aggressive environments have a short life because of their damages appeared in operating. Mechanical or chemical processes often damage many metallic industrial components, such as gears, nozzles, valves, etc. Damage is presented by selection of a high-grade material that is suitable for industrial

components based on experimental results. Steels type 21TMC12 has good mechanical properties for gears. However, in surface appear defects like cracks or pits.

Tungsten carbide with Cobalt and Chromium, WC10Co4Cr, is recommended for machine elements where required high wear and corrosion resistance.

MATERIALS AND SAMPLE PREPARATION

In our research, we used steel type 21TiMnCr12 as basic material chosen according to the international standards and bought from SC Agmus SA Iași. From specialty literature we have taken information about this material which is an alloyed steel used in gears manufacturing. After the samples have been done, we coated them by plasma spraying deposition with WC10Co4Cr powder. The powder was bought from Durum Durmat, code 105.017, and its composition is 86% WC, 10% Co, 4%Cr, with particles size $-25 \pm 5 \mu\text{m}$,

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and is recommended for machine elements with high wear caused by friction.

Plasma spraying is a thermal deposition process that works with inert gases, which on high voltage discharge, ionizes forming plasma. The temperature and the velocity of plasma jet are very high and when the powder is injected, is melted and projected to the surface, creating the coating.

Plasma spraying deposition process has been accomplished with Sulzer Metco 9MCE Facility in normal conditions of temperature, pressure and humidity and parameters are shown in Table 1. Sulzer Metco 9MCE Facility has a gun, which works on 10000-16000 °C with a speed of plasma jet of more than 3000 m/s, the speed of powder transport being 450-650 m/s.

Table 1

Plasma spraying deposition parameters

Air	6.4 bar
Propane	5.5 bar
Nitrogen	60 l/min
Rotation	4 rpm
Spraying distance	180 mm

Samples obtained have been analyzed with SEM Quanta 200 3D in order to determine the quality of the coating and in Fig. 1 is shown its microstructure. The coating is porous and the layer's thickness is approximately 300 μm .

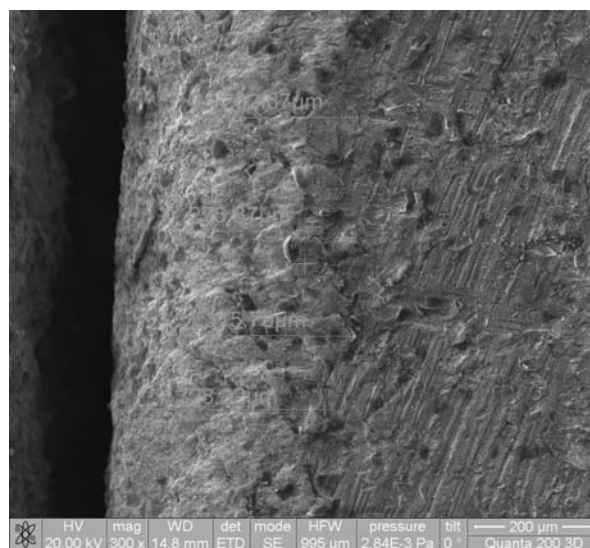
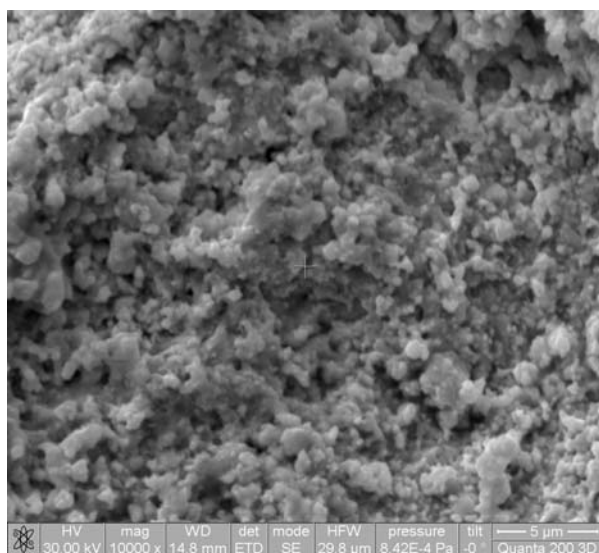


Fig. 1 – SEM observation of WC-Co-Cr coating:
(a) overview at 10000x magnification, and (b) transversal section at 300 x magnification.

EXPERIMENTAL

1. Tribological method

Samples coated by plasma spraying were subjected to fretting test in order to establish their friction coefficient. For fretting test, we used Frethme facility projected and realized from the researchers of Karlsruhe Institute of Technology, Germany. Samples have been subjected to a sliding force of 50 N, with 75 μm amplitude and a frequency of 10 Hz under a load of 150 N, for more than 10^6 cycles, in dry contact. The fretting test has been accomplished at normal conditions of pressure, temperature and humidity.

2. Electrochemical method

Corrosion tests were performed electrochemically at room temperature ($\sim 25^\circ\text{C}$) in a 3.5% NaCl in distilled water.

The tests specimens was placed in a glass corrosion cell, which was filled with freshly prepared electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode

and a platinum coil as the counter electrode. All potentials referred to in this article are with respect to SCE. The measurement was managed by a PAR 263A potentiostat controlled by a personal computer with dedicate software (PowerCorr).

For both samples (coated and uncoated) linear potentiodynamic polarization measurement was performed. These tests were conducted by stepping the potential using a scanning rate of 1 mV/s from -1000 mV (SCE) to +500 mV (SCE).

EIS measurements were performed after the samples were immersed in both electrolytes at $25\pm 1^\circ\text{C}$, at open circuit potential, for different period of times. The alternating current (AC) impedance spectra for samples were obtained with a scan frequency range of 100 kHz to 10 MHz with amplitude of 10 mV.

In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used. The usual guidelines for the selection of the best-fit EC were followed: a minimum number

of circuit elements are employed and the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the error associated with each element was up to 5%. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data.⁷

RESULTS AND DISCUSSION

1. Tribological characterization

Friction coefficient of WC-Co-Cr coating main value is 0.56 after more than one million cycles. Comparing to steel's the friction coefficient value, is similar because in dry contact, steel has the value 0.5.

2. Electrochemical characterization

Fig. 3 displays the linear polarization curves, in semi-logarithmic scale of current densities corresponding to WC-Co-Cr coating and uncoated steel type 21TiMnCr12 samples in 3.5% NaCl solution at 25°C traced between -1000 mV to 500 mV with 1 mV/s potential sweep rate. Fig. 3 indicates that the sample coated with WC-Co-Cr presents a similar anodic behaviour in comparison with the uncoated sample curve, but there is a

small shift to higher currents. No passive region was observed, the anodic current density continuously increased. Such effect has been associated to the diffusion of small Cl^- ions than that oxygen, which makes difficult for the surface to be homogeneously passivated. However, the anodic curves for the coated sample are shifted one order of magnitude towards higher values than the substrate one. It means that the uncoated sample is more reactive and, as a consequence, the anodic currents increase greatly during the anodic sweep. The average values zero corrosion potential (ZCP) and corrosion current density (i_{corr}) from polarization curves determined by the PowerCorr software are presented in Table 2.

The linear polarization curves of WC-Co-Cr coating showed a shift of ZCP to more positive value (-735 mV) compared with uncoated sample (-809 mV). The higher ZCP exhibited for coated sample, probably can be associated with the positive contribution of the coating in the formation of the formed film. The corrosion current density for uncoated sample is ca. two times higher than for coated samples. Thus, the results indicated that the uncoated sample is most easily corroded.

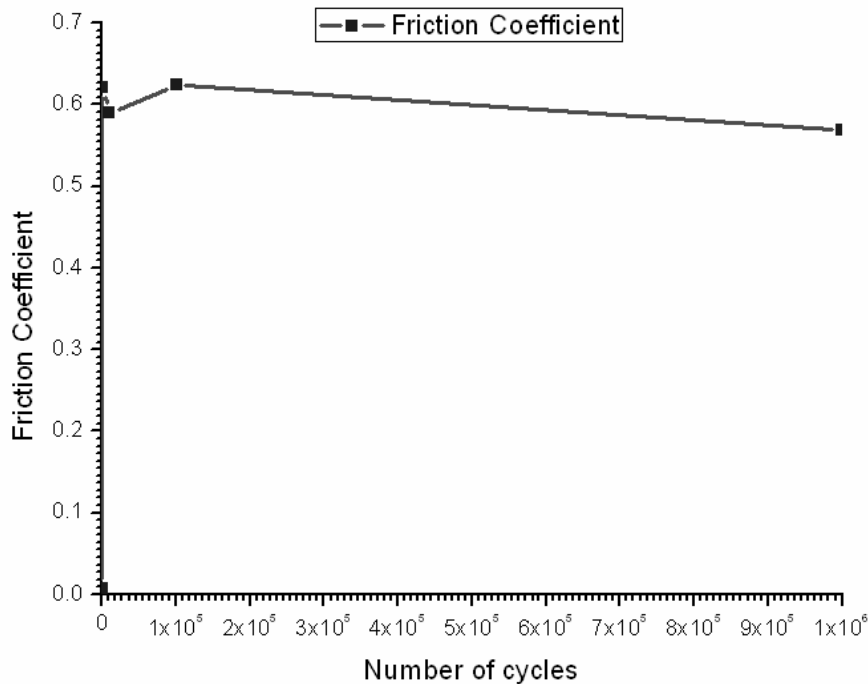


Fig. 2 – Variation of friction coefficient of WC-Co-Cr coated after running.

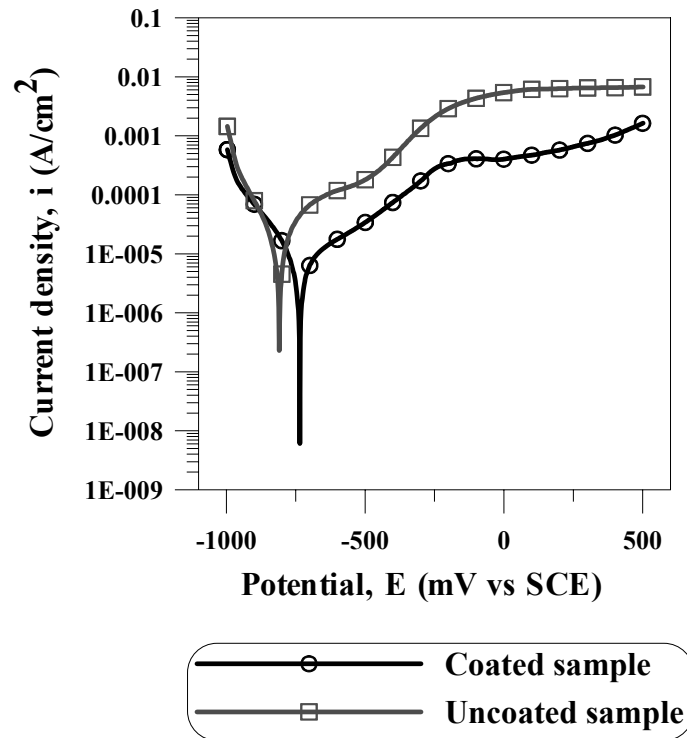


Fig. 3 – Linear potentiodynamic polarization curves measured for coated and uncoated specimens after immersion in 3.5% NaCl.

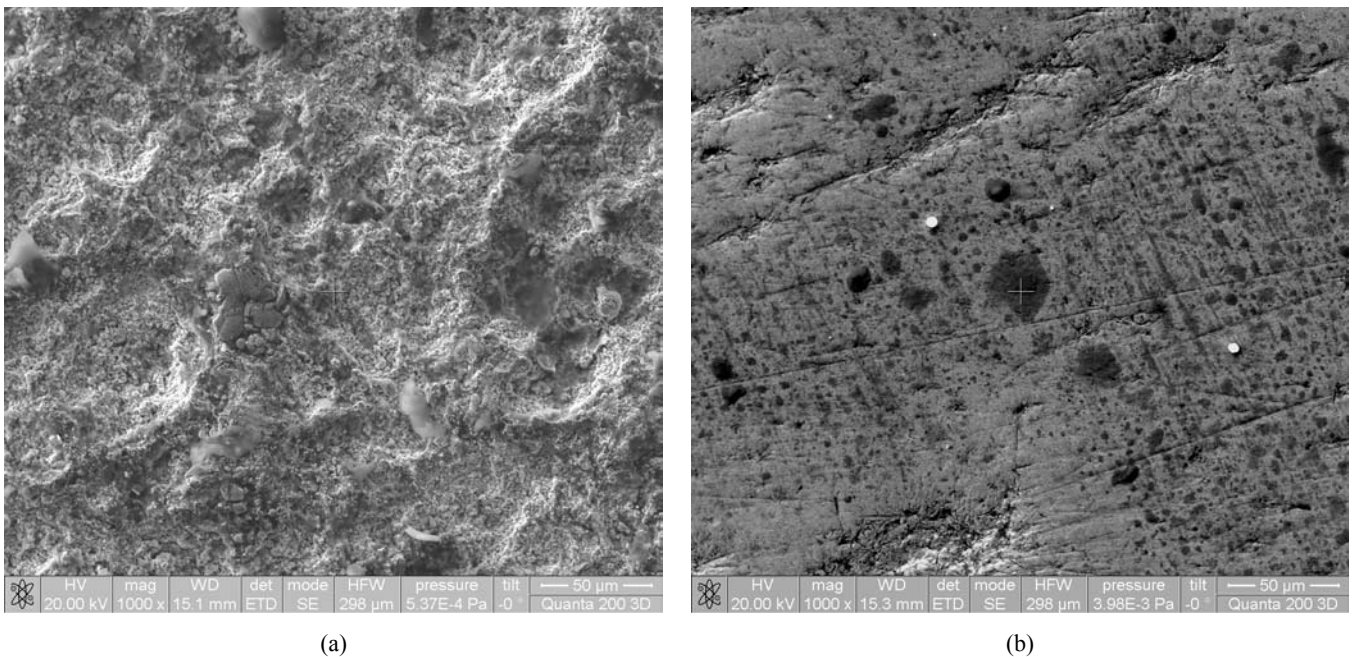


Fig. 4 – SEM observation of the:
(a) WC-Co-Cr coated, and (b) uncoated samples after linear polarization test in 3.5% NaCl solution.

Fig. 4 displays the SEM images of coated and uncoated surface samples after linear potentiodynamic polarization test at 500 mV in 3.5% NaCl solution.

Note the presence of pits distributed at different areas on the uncoated sample surface, and no pit observed for the coated sample. The common

susceptible sites for pits are known to be the inclusions, second phase precipitates, processing defects such as pores, cracks, etc. The coated sample did not present pitting in their surface, although they have presented an anodic current density one order of magnitude higher than the uncoated sample.

The Nyquist impedance diagrams for WC-Co-Cr coated and uncoated sample in .5% NaCl solution as a function of immersion time are shown in Fig. 5 a-b.

All the diagrams for coated and uncoated samples show a capacitive arc. In both cases of coated and uncoated samples, the capacitive arc could be relating the electric double layer capacitance at the electrode/solution interface, which includes the formed film-solution interface. The diameters of the semicircles correspond to the polarizing resistance (R_p) indicative of the kinetics of the charge transfer reactions or rate of dissolution. It could be observed from the Figs. 6 a-b that after 1 day of immersion in 3.5% NaCl solution, the diameter of the semicircle of both samples (coated and uncoated) decreased. The decrease in diameter indicates a decrease in corrosion resistance.

Fig. 6 a-b shows the Bode diagrams for the same systems.

Within the intermediate frequency range, the Bode diagrams show straight lines with slopes smaller than the value -1 and a phase angle smaller than 90° . These features as well as flat capacitive arcs

are relating with the frequency dispersion and can be attributing to inhomogeneities of the solid surface.

According to the impedance diagram, the Bode-phase plots are in agreement with an EC with one time constant (Fig. 7).

The impedance spectra were fitted using the ZSimpWin software and the resultant EIS parameters are given in Table 3. The fitting quality of EIS data was estimated by both the chi-square (χ^2) test (between 10^{-4} and 10^{-5}) values and the comparison between error distribution versus frequency values ($\pm 5\%$ for the whole frequency range) corresponding to experimental and simulated data. In this EC, R_{sol} is the ohmic resistance of the electrolyte (around $25 \Omega \text{ cm}^2$), R_p represents the polarization resistance and Q is the impedance related to a constant phase element (CPE). The more the value of polarization resistance increases, the more the sample will resist corrosion.

From Stern-Geary equation,⁸

$$i_{\text{corr}} = \frac{B}{R_p}$$

with B constant determined by Tafel slope tests, it follows that the higher the R_p , the lower is the corrosion rate.

Table 2

The mean values of parameters measured and calculated for the samples in 3.5% NaCl solution (25 °C)

Sample	ZCP (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)
Uncoated sample	-809	19.1
WC-Co-Cr coated sample	-735	8.4

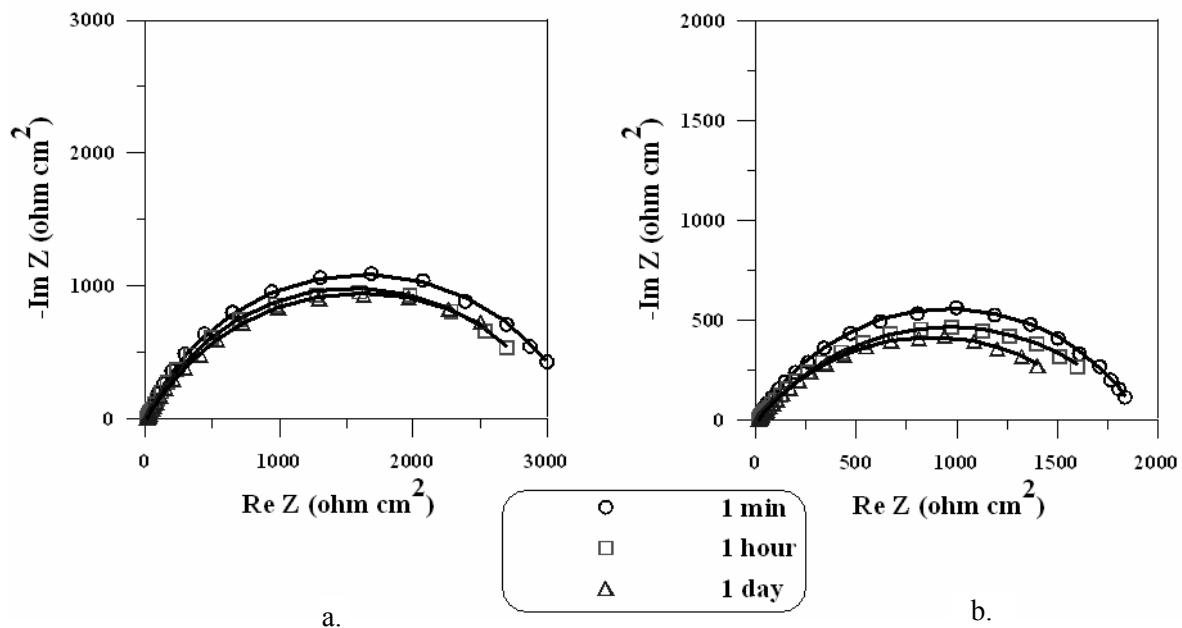


Fig. 5 – Electrochemical impedance diagrams for: (a) WC-Co-Cr coated and (b) uncoated samples as a function of immersion time in 3.5% NaCl solution at open circuit potential.

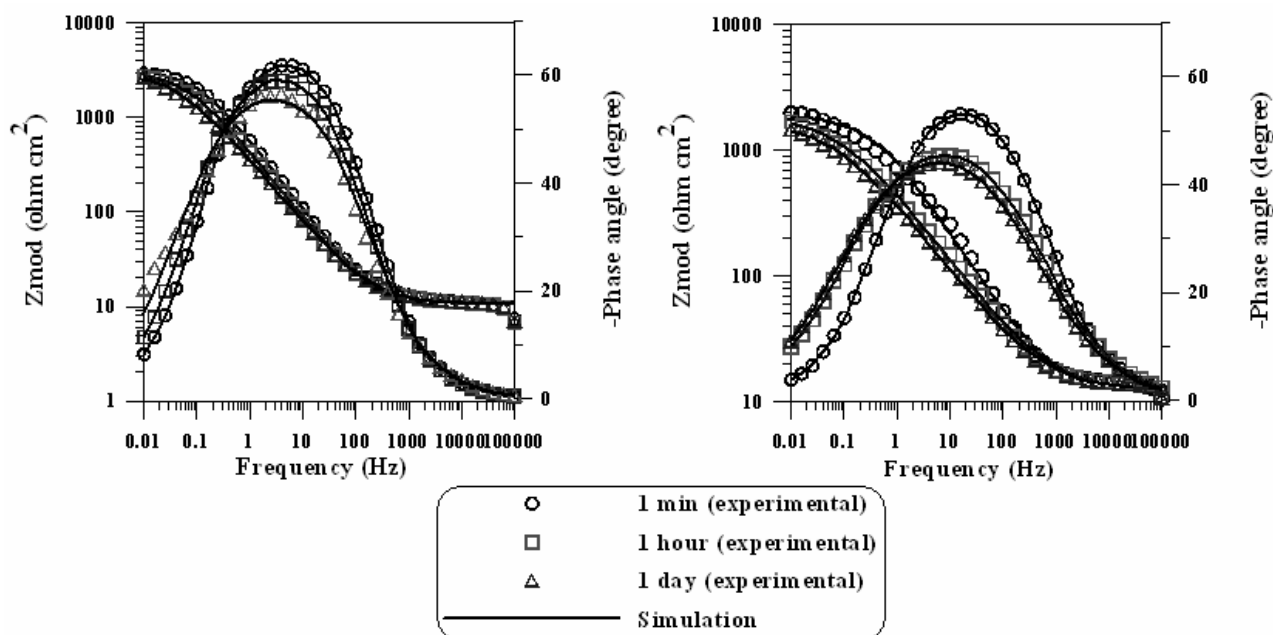


Fig. 6 – Bode plots for EIS data:

(a) WC-Co-Cr coated and (b) uncoated samples maintained different time periods in 3.5% NaCl solution at open circuit potential.

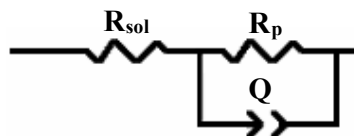


Fig. 7 – Equivalent circuit (EC) used for fitting the measured impedance spectra.

For both WC-Co-Cr coated and uncoated samples, the EIS spectra indicate that the formed film is affected by the solution with the increase of immersion time, as suggested by the decrease of polarization resistance (R_p) values. The coated R_p values are higher than of uncoated sample's, showing that the formed film on coated sample is more corrosion resistant than the one formed on uncoated sample.

The Q values increase by increasing the immersion time assuming values characteristics of

the electric double layer. These results indicate that the solution reaches both the WC-Co-Cr coated and uncoated sample surface because of the formed film dissolution causing the decrease of the total systems impedance. This hypothesis could be confirmed by the decreasing time of the capacitive arcs in the Nyquist diagrams (Fig. 5).

Therefore, the coating treatment increases the mechanical properties without altering the corrosion properties of the substrate.

Table 3

Electrochemical parameters obtained from EIS spectra using the selected EC for the WC-Co-Cr coated and uncoated samples after different immersion time in 3.5% NaCl solution at open circuit potential

Samples	Immersion time	$10^4 Q$, $S\ cm^{-2}\ s^n$	n	$10^{-3} R_p$, $\Omega\ cm^2$
WC-Co-Cr coating	1 min	1.2	0.80	2.9
	1 hour	3.8	0.79	2.8
	24 hours	4.2	0.78	2.6
Uncoated sample	1 min	2.7	0.79	1.9
	1 hour	6.1	0.78	1.7
	24 hours	7.5	0.76	1.3

CONCLUSIONS

The aim of this paper is the improving of materials properties by coating. In our researches we have accomplished some experiments to establish some properties of the materials obtained. On fretting test, we obtained the friction coefficient that is similar to. Friction coefficient is directly proportional to wear rate, so in tribology is very important to obtain low value of friction in order to obtain low wear. In this case, its value is approximately equal to the steel even if the coating is porous and the surface is rough.

The electrochemical behavior of plasma sprayed WC-Co-Cr coatings on 21TiMnCr12 was evaluated by means of linear polarization and EIS in 3.5% NaCl solution, at 25 °C. The zero corrosion potential (ZCP) of an coated sample is nobler than of uncoated one, and the corrosion current density (i_{corr}) of uncoated sample is more than two times larger than that of coated one. In a 3.5% NaCl solution, at 25 °C, abundant pitting corrosion occurs for the only uncoated sample. For both WC-Co-Cr coated and uncoated samples, the polarization resistance (R_p) values obtained from EIS spectra decreases with the time of electrode

immersion. In 3.5% NaCl solution, at 25 °C, the WC-Co-Cr coating sample surface has a corrosion behavior similar or better to the substrate sample. Results presented here show that it is possible to produce WC-Co-Cr coating layer on the 21TiMnCr12 with better mechanical characteristics, without degradation of the corrosion resistance, by using the plasma sprayed process.

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