

Comparative electrochemical characterization of plasma sprayed zirconia and alumina coatings on titanium substrate

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Current ceramic solutions for applications in wear and thermal shock technology is now a necessity. The electrochemical characteristics of yttrium oxide stabilized zirconium oxide (YsZ) and alumina (Al₂O₃) coatings produced on titanium (Ti) targets were investigated in natural seawater. All coatings were produced by plasma spraying deposition. In order to study the electrochemical behaviour, the electrochemical impedance spectroscopy (EIS) and linear potentiodynamic polarization (LPP) performed. Equivalent circuit (EC) was used to modeling EIS data, in order to characterize YsZ and Al₂O₃ coated Ti surface. Scanning electron microscopy (SEM) observations were made before and after the LPP tests. It was found that both YsZ and Al₂O₃ coating showed a good corrosion resistance (polarization resistance and corrosion current density) after 1-day immersion in natural seawater. The Ti substrate was actually passive in these experimental conditions.

(Received August 13, 2014; accepted September 11, 2014)

Keywords: Zirconia, Alumina, Natural seawater, SEM, EIS, LPP

1. Introduction

Titanium (Ti) exhibits outstanding corrosion resistance in a wide variety of environments [1]. For this reason Ti is widely used as construction material in many fields of technology: surgery, aerospace, automotive, power generation, oil and gas extraction [2-10]. Nevertheless, the low wear resistance of this material causes some problems in the service condition. Hence, it is necessary to enhance the surface properties of Ti material. Surface modification is a promising way to increase the surface hardness and wear resistance of titanium.

Hard material coatings such as ceramic have found increasing application in wear technology. ZrO₂ (zirconia) is a ceramic and is investigated as hard coating. However, hard coatings such as zirconia deposited by plasma spraying are often porous and therefore not always corrosion resistant layer. Al₂O₃ (alumina) has a higher hardness than zirconia [11]. Furthermore, the corrosion performance of ceramic coated materials varies with the nature of the substrate [12].

This paper aims to evaluate the electrochemical behaviour of yttrium oxide stabilized zirconium oxide (YsZ) and alumina (Al₂O₃) coated Ti samples by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization study for using the advantages of these coatings in anti-corrosion industrial

application, such as aerospace, black box, medical, dentures, implants, medical devices.

2. Materials and methods

2.1. Materials

Pure titanium (99.9 wt.%) samples were sandblasted on one side to roughen the surfaces. Alumina and zirconia (Sultzter-Metco, USA) coatings were applied on the titanium surface by plasma spray system (SPRAYWIZARD-9MCE, Sultzter-Metco, USA). The spray parameters are listed in Table 1.

Table 1. Parameters used for plasma spray alumina and zirconia coatings.

Feeding mode	Internal
Arc current (A)	500
Arc voltage (V)	50
Working gases	Ar, H ₂
Carrier gas flow rate	Ar: 19%
Torch traverse speed (mm/s)	60 (5 passes)
Spray distance (mm)	150

Argon was employed as the working gas as well as a carrier for the both, alumina and zirconia, into the plasma flame. The both, alumina and zirconia were sprayed continuously by moving the plasma gun, attached to a programmable robot, in front of the titanium substrate.

The uncoated titanium, were mirror-polished (with 400 to 2000 grit emery paper and alumina suspension), washed with distilled water, ultrasonically degreased in ethanol and dried in air.

The coating has around 50-60 μm , because the adhesion by the support to higher values decreases.

2.2. Electrochemical tests

The corrosion medium was natural aerated seawater collected from Black Sea (Constanta zone) having the composition: chloride 0.3; sodium 0.4; sulphate 0.1 mole L^{-1} and other components in very low concentration.

The test specimens were placed in a glass corrosion cell, which was filled with natural seawater. 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 variations of the corrosion behaviour of the samples (coated and uncoated) were studied using the electrochemical impedance spectroscopy (EIS) technique. EIS measurements were performed using a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, USA). The instrument was controlled by a personal computer and specific software (VersaStudio, PAR, USA).

EIS measurements were performed after the uncoated and coated samples were immersed in seawater at 25 ± 1 $^{\circ}\text{C}$, at open circuit potential, for different times (1-hour and 1-day). 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. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data [13]. The impedance representation of CPE is given as:

$$Z_{(\text{CPE})} = \frac{1}{Y_0(j \cdot \omega)^n} \quad (1)$$

where ω is the angular frequency and Y_0 is a constant, and the value of the exponent n indicates the deviation from ideal capacitive behaviour (e.g., when $n = 1$).

Linear potentiodynamic polarization measurements (LPP) were also carried out in natural seawater at 25 $^{\circ}\text{C}$ using a potentiostat. These measurements were conducted by stepping the potential using a scanning rate of 1 mV/s from -0.8 V to 0.6 V.

2.3. Coating characterization

The surfaces of YsZ and Al_2O_3 coated before and after LPP measurements were investigated using a Quanta 3D scanning electron microscope (model AL99/D8229).

3. Results and discussion

The planar and cross-section SEM images of the YsZ and Al_2O_3 coating are shown in Figs. 1 and 2(a-b). Both metallic surfaces covered by YsZ and Al_2O_3 exhibited many pores and cracks. The topography of the YsZ and Al_2O_3 can also be observed from the inspection of the SEM images taken from cross-sections through the coated films (cf. Fig. 1b and 2b). For both samples, the cross-sections shows no significant variation in the coated layer (around of 50-60 μm).

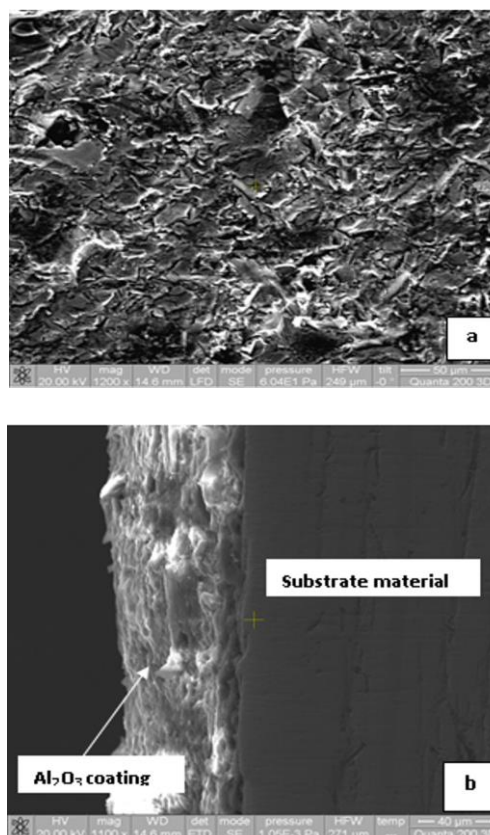


Fig. 1. Planar and cross-section SEM images of the Al_2O_3 -coated titanium: (a) planar image, and (b) cross-section.

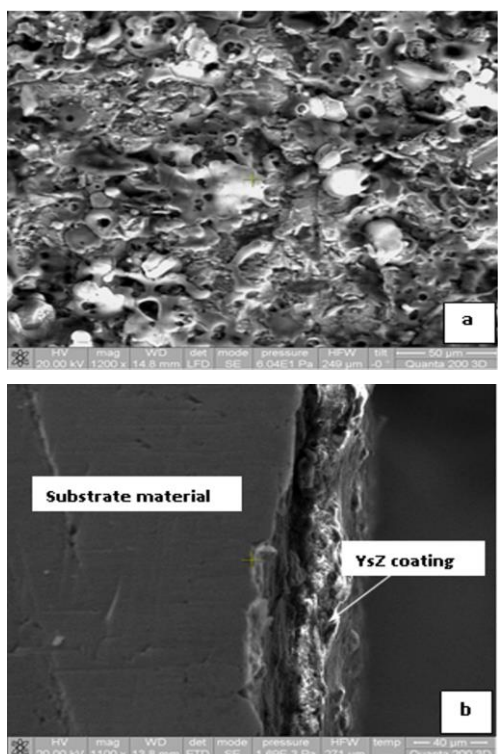


Fig. 2. Planar and cross-section SEM images of the YsZ-coated titanium: (a) planar image, and (b) cross-section.

Electrochemical impedance spectroscopy (EIS) measurements offer useful information regarding the layer of the coated sample. The Bode plot (magnitude and phase of impedance $|Z|$ versus log of frequency) is usually used to represent the result. Fig. 3 shows the Bode plot from the uncoated samples different immersion times in seawater. From the Bode plot, the phase angle is approximately zero at high frequency, indicating that the impedance is determined by solution resistance. The phase angle is close to -70° and slope between $|Z|$ and log of frequency is less than -1 over a medium range of

frequency, independent of time immersion, indicating that the passive film was not fully capacitive.

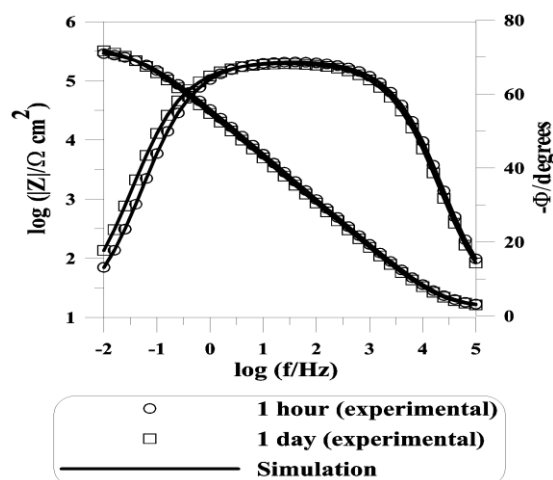


Fig. 3. Measured (discrete points) and fitted (solid lines) Bode impedance spectra of uncoated Ti samples exposed to natural seawater for different immersion times.

The electrochemical response of the uncoated sample is the best simulated employing the equivalent circuit, $R_{sol}(R_1Q_1)$, as shown in Fig. 4a. 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. Table 2 shows the results of the fitting. The Randle's model is usually used to simulate the oxide film [14-17]. In this model, R_{sol} corresponds to solution resistance. The R_{sol} of the test electrolyte, equals $60 \pm 5 \Omega$, was observed for the specimens, indifferent of the immersion time, and was not inserted in Table 2.

Table 2. Electrochemical parameters obtained from EIS spectra using the selected ECs for the samples after different immersion time in natural seawater at open circuit potential.

Titanium samples	Immersion time	$10^5 Q_1$, S/cm ² s ⁿ	n_1	$10^{-4} R_1$, Ω cm ²	$10^5 Q_2$, S/cm ² s ⁿ	n_2	$10^{-4} R_2$, Ω cm ²
Uncoated	1-hour	1.7	0.81	23.4	-	-	-
	1-day	1.7	0.82	29.1	-	-	-
YsZ coating	1-hour	2.4	0.81	8.9	-	-	-
	1-day	3.5	0.80	1.2	1.9	0.79	9.1
Al ₂ O ₃ coating	1-hour	1.8	0.81	15.3	-	-	-
	1-day	3.7	0.80	1.3	1.7	0.80	21.2

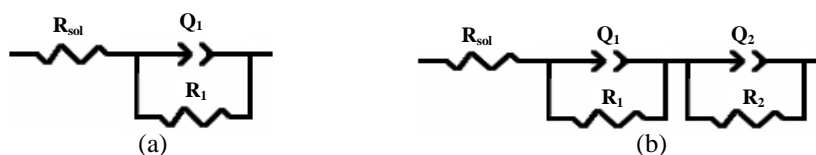


Fig. 4. Equivalent circuits used for fitting the measured impedance spectra.

The parameters R_1 and Q_1 describe the proprieties of the passive oxide layer formed on uncoated sample. For the uncoated sample after 1-hour immersed in natural seawater, the values of R_1 , representing the polarization resistance, is relatively high, about $2 \cdot 10^5 \Omega \text{ cm}^2$. The R_1 obtained from EIS spectra increases with immersion time indicating a growth of the passive layer in time.

Bode plots of the YsZ and Al_2O_3 coated titanium immersed for different periods in natural seawater are shown in Fig. 5(a-b).

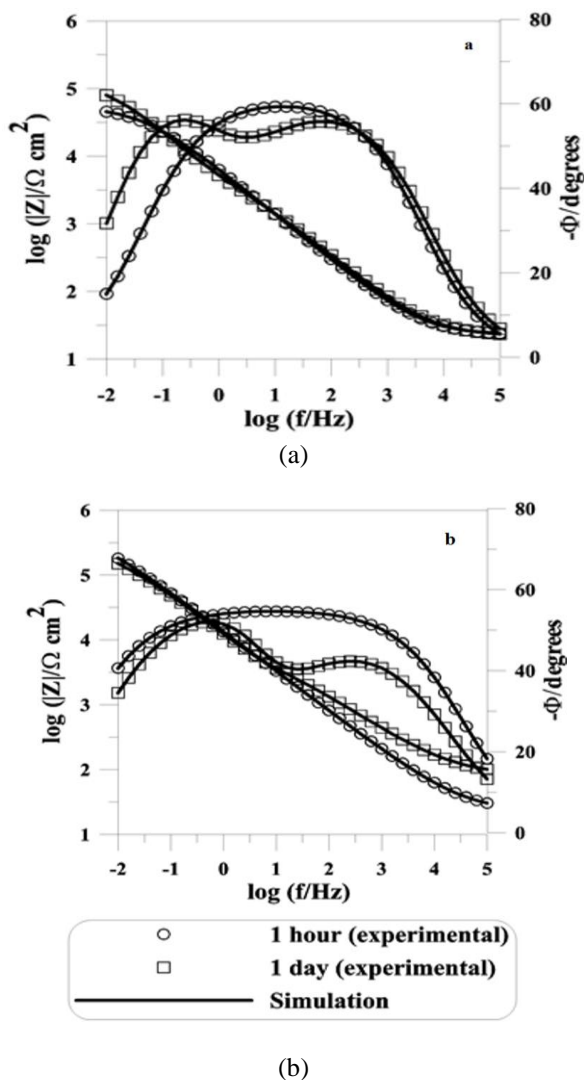


Fig. 5. Measured (discrete points) and fitted (solid lines) Bode impedance spectra of: (a) YsZ and (b) Al_2O_3 coated Ti samples exposed to natural seawater for different immersion times.

According to the impedance diagram, YsZ and Al_2O_3 coated Ti samples after 1-hour immersion, the Bode-phase plots are in agreement with an EC with one time constant (Fig. 4a). In fact, 1-hour immersion period is too short to reveal any degradation of the substrate.

The impedance spectra were fitted using the ZSimpWin software and the resultant EIS parameters are

given in Table 2. The R_1 and Q_1 parameters describe the processes occurring at electrolyte/coating layer. R_1 is the charge transfer resistance associated with the penetration of the electrolyte through the pores or pinholes existing in the coated layer and Q_1 correspond to capacitance of the coating layer. R_{sol} is the ohmic resistance of the electrolyte.

When the immersion period is greater than 1-day, the phase shift is different to that of 1-hour. The low-frequency domain evidences the processes taking place at the substrate/electrolyte interface. Such behavior is typical for a metallic material covered with a porous film, which is exposed to an electrolytic environment.

In this case, the electrochemical interface can be subdivided into sub-interfaces: electrolyte/coated layer and electrolyte/substrate. This type of EIS spectra is best modeled by an equivalent circuit (EC) proposed for the two sub-electrochemical interfaces, as shown in Fig. 4b.

The parameter R_2 coupled with Q_2 describes the processes at the substrate layer at the electrolyte/substrate layer interface. R_2 is the polarization resistance at the electrolyte/substrate interface in the pores or pinholes and Q_2 to the capacitance at the electrolyte/substrate layer interface which seems to be associated to the double layer formation. The values of the electrochemical parameters from equivalent circuits that fit best the experimental data are presented in Table 2. For both coated samples after 1-day immersed in seawater, the values of R_2 are relatively high (around of $10^5 \Omega \text{ cm}^2$). The resistance of the uncoated composed of R_1 (passive oxide layer resistance) is in the same order of magnitude than the R_2 of both coated samples. This behavior confirming the hypothesis of the existence of passive film on the titanium surfaces, which prevents corrosion process at the substrate.

Corrosion may occur at pores as the result of the metal being directly exposed to the aggressive attack of the electrolyte. The decrease of R_1 as immersion time increases imply that increased number of opening pinholes and pores the coating layer became more conductive. Usually in this process, some pitting can be produced at the interface between the coating layer and substrate.

Table 2 indicates that the Al_2O_3 always presents slightly higher R_2 values than YsZ, though they exhibit a similar trend with time. The value of polarization resistance indicates that the sample maintained 1-day in seawater is still highly resistant to corrosion.

3.1. Linear potentiodynamic polarization tests

Fig. 6 and Table 3 shows the results of the electrochemical polarization measurements on coated and untreated samples in natural seawater at 25 °C. The zero current potential (ZCP) and corrosion current density (j_{corr}) values were determined by Tafel analysis of both anodic and cathodic branches of the polarization plots.

Table 3. Zero current potential (ZCP) and corrosion current density (j_{corr}) for the untreated and coated specimens recorded in natural seawater after 1-day exposure at 25 °C.

Sample	ZCP, mV	j_{corr} , nA/cm ²
Uncoated titanium	-376	316
YsZ coated titanium	-259	417
Al ₂ O ₃ coated titanium	-211	384

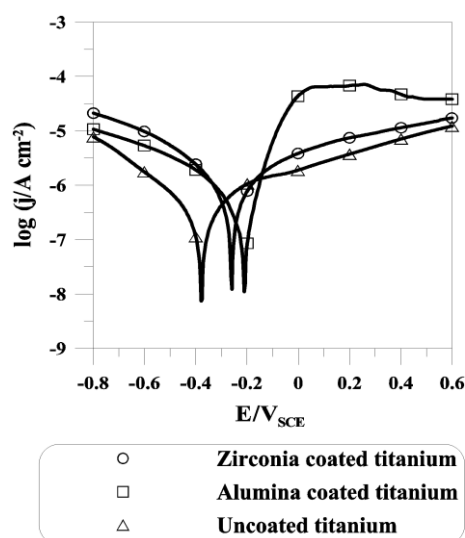


Fig. 6. Linear potentiodynamic polarization curves measured for: zirconia (YsZ)-coated and alumina (Al₂O₃)-coated Ti samples after 1-day immersion in natural seawater.

Significantly, more negative values were determined for the ZCP with the untreated samples after 1-day immersion in seawater. A slow shift of ZCP to noble values was observed for both coating sample. However, similar values of corrosion currents were obtained for uncoated and coated samples in seawater. The polarization results are in agreement with EIS data.

3.2. SEM analysis of corroded surfaces

Typical SEM micrographs of uncoated and coated samples after polarization in natural seawater terminated at 0.6 V are shown in Fig. 7(a-c). The YsZ and Al₂O₃ coating failed due to the localized corrosion in the coating. It revealed that the uniform oxidation occurred on uncoated titanium sample (Fig. 7c). Except the presence of polishing scratches, no pitting, cracks, or other defects appeared on the substrate surfaces after polarization in natural seawater.

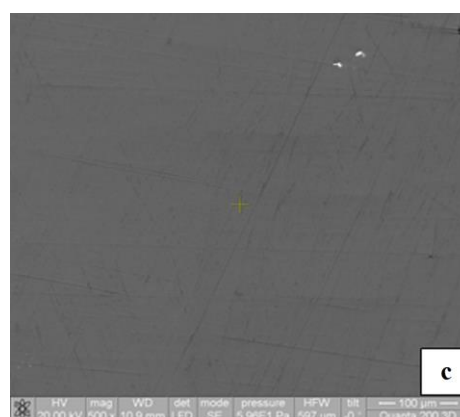
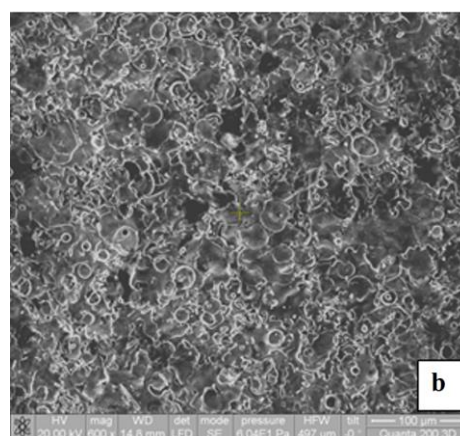
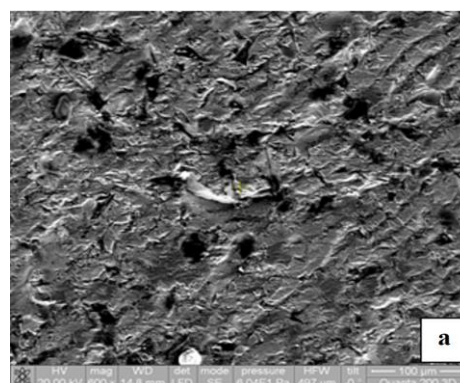


Fig. 7. SEM observation of the: (a) YsZ coated, (b) Al₂O₃ coated and (c) uncoated samples after linear polarization test in natural seawater.

4. Conclusions

The plasma spray method can create an effective ceramic layer on the surface of titanium. Two different physical models with related equivalent circuits are devised to simulate the EIS results for coated titanium. EIS results give the experimental evidence that both coatings are not very dense. After 1-day exposure to seawater, the solution penetrated into interface through the opening pinholes and pores and the coating layer became more conductive. However, the passive oxide layer resistance of the uncoated is in the same order of magnitude than the

polarization resistance at the electrolyte/substrate interface in the pores or pinholes of both coated samples. This behaviour described above that the hypothesis of the existence a passive film on the titanium surfaces is confirming, which prevents corrosion process at the substrate.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0218.

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