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Determination of time dependence of coated metal electrical and electrochemical parameters during exposure using principal component analysis

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ABSTRACT

The use of the principal component analysis (PCA) permits the complex and quantitative analysis of the time dependence of electrical and electrochemical parameters of coated metal obtained by fitting impedance data. So far, changes in electrical and electrochemical parameters during exposure were analyzed independently. In this way, some of the information contained in the relationship between changes in parameters over time are lost. In the approach presented, in order to overcome this drawback a correlation analysis using the principal component approach was proposed. The results of this analysis, a 'correlation circle' plot shows a projection of a set of parameters and time onto a two-dimensional plane. The high level of correlation of the given parameter with exposure time means rapid changes in the properties described by this parameter in the system under study, and the low level of correlation indicates small changes and testifies to the durability of the features described by the given parameter. The usefulness of this approach for analysis of time-varying impedance data has been illustrated by example of coating applied on hydrophobic and hydrophilic substrates.

1. Introduction

A typical protective layout: the metal substrate/coating/electrolyte is changing during exposure. These changes can be seen by measuring the impedance spectra during exposure [e.g. 1–7]. Using an appropriate model in the form of an electrical equivalent circuit it is possible to obtain a set of a few or several electrical and electrochemical parameters that change their values during exposure. It is noted that some of the parameters are not independent. However, in practice, the study of time dependence only is encountered. In this way, we lose some of the information that may be useful in assessing the behavior of the protective system. Principal component analysis (PCA) has been used to examine relationship among parameters, and exposure time as well. This new approach was applied to a set of parameters obtained from impedance spectra by fitting using samples of coated titanium with hydrophobic or hydrophilic surfaces. These two model systems were chosen for the study because they are nearly identical, differing only in the state of the substrate surface. The question was whether this one difference will be reflected by the resulting time dependencies of parameters.

Titanium is covered by a thin (nanometric) TiO_2 film, that grows spontaneously on its surface in air [8]. It has been reported that the TiO_2 film can change some of its properties under UV illumination [9–11]. It appears that in dark conditions TiO_2 film exhibits hydrophobic properties. Under sun illumination (UV) TiO_2 film becomes hydrophilic. The mechanism of this phenomena is not fully understood [12] and different explanations exist [13] but it seems that photo-inducted hydrophilicity is connected with an accumulation of photo-excited holes on the surface [14]. This causes weakening of the Ti–O bonds and acceleration the transfer of Ti ions from oxide layer to the aqueous solution. Water can be chemisorbed on oxygen vacancies created during titanium ions transfer. Sakai et al. documented structural changes during the wettability conversion using molecularly thin titania nanosheet [15].

In this paper, using titanium surfaces with hydrophobic or hydrophilic properties covered with organic coatings, a method based on a principal component analysis (PCA) to estimate correlation between equivalent electrical circuit parameters and exposure time was developed.

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Table 1
Compositional specifications for Grade 4 commercially pure titanium products in %.

C	H	O	N	Fe
0.10	0.01	0.4	0.05	0.3

2. Experimental

2.1. Sample preparation

Reproducible layer of TiO_2 on titanium was prepared by oxidation of titanium in an oven in air. Commercially available pure titanium was used for sample preparation. The titanium was of a nominal purity of 99.0% ASTM Grade 4 with alloy additions as specified in Table 1.

After degreasing the samples were immersed for ca. 5 min in HF-HNO_3 (1:5 in volume) solution for surface cleaning. After water rinsing the samples were oxidized at 800 °C for 2 h in air atmosphere. Final temperature was reached with the heating rate of 2 °C/min. At the end of the oxidation the oven containing the samples was cooled in a natural way after switching off. According to the paper by Yusheng et al. [16] rutile TiO_2 is formed on the surface. One group of samples was kept in darkness in order to obtain a hydrophobic surface. The second group of samples was exposed to sunlight irradiation for 2 h at maximum sun radiation (11 a.m.–1 p.m. in July, the light intensity of ca. 100 mW/cm^{-2}) in order to obtain a hydrophilic surface. After that a thin (ca. 25 μm) polyester coating was applied by spraying to both sets of samples.

2.2. Characterization methods

The hydrophilicity of the films was evaluated by screening photos and measuring the contact angle of water droplet. Each measurement was performed at ambient air (22 °C, relative humidity (RH) 40%).

The bare and coated panels were exposed in the laboratory to immersion in 3% NaCl aqueous solution at 22(±1) °C. The impedance measurements were performed using a two electrode system, with a frequency response analyser Solartron 1255 connected to High Impedance Interface Atlas 9181. The impedance measurements were carried out at 10 points/decade over a frequency range from 1 MHz to 0.1 Hz and at 5 points/decade over the range from 0.1 Hz to 0.001 Hz with 20 mV (bare samples) and 60 mV (coated samples) signal amplitude. The selected amplitudes allowed reliable measurement due to improved signal to noise ratio. The exposed painted sheet area was about 5.2 cm^2. Usually, the impedance spectrum was measured automatically every hour during a period of 50 h in full frequency range.

The AFM images were acquired in contact mode using the SPM Integra Aura system by NT-MDT. All calculations were conducted using the Microsoft Office Excel and XLStat (Addinsoft, USA) programs.

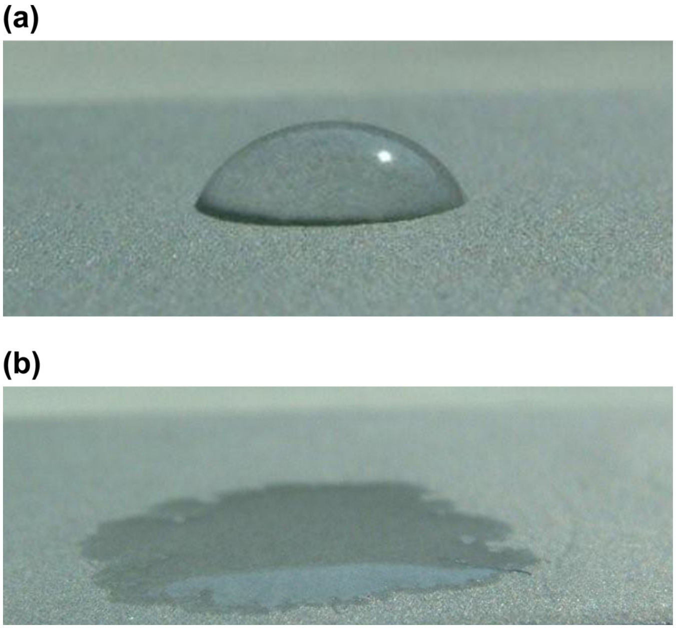

Fig. 1. Water droplet with diameter of ca. 2 mm on TiO_2 film on titanium after keeping in darkness (a) and after 2-h sunlight exposure (b).

3. Results and discussion

The Ti/TiO_2 substrate was tested before organic coating application. Water contact angles on the TiO_2 film were measured for samples kept in darkness and after sunlight irradiation. The water contact angle was 62 (±1)° in darkness. After sunlight irradiation, the water contact angle became to 3 (±2)°. Fig. 1 presents images of water droplet on TiO_2 films. The angle dependence suggests that the surface of the metallic titanium kept in darkness becomes hydrophobic and the one exposed to sunlight hydrophilic. These results are in agreement with previous studies [9–11,13,16].

Morphological features of the TiO_2 film were investigated also by AFM. Fig. 2 presents the representative images of the samples

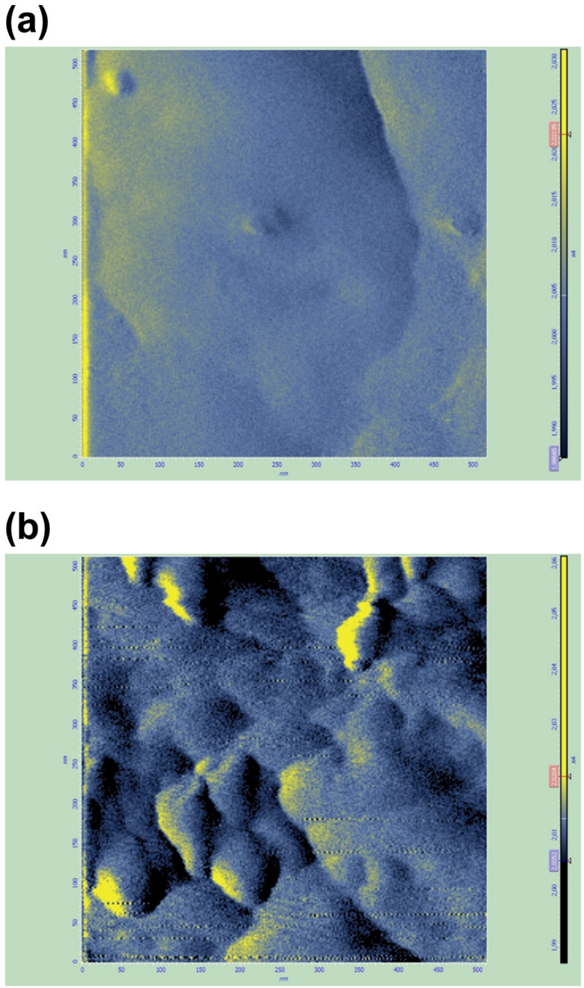

Fig. 2. Topography of the dry TiO_2 film on titanium kept in darkness (a) and after sunlight irradiation (b). Scanned area 500 nm × 500 nm.

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