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TRENDS IN
ELECTROCHEMISTRY
AND CORROSION AT THE
BEGINNING OF THE
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Dedicated to Professor Dr. Josep M. Costa on the occasion of his 70th birthday

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An EIS study of the corrosion behaviour of PECVD coated brass substrate

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ABSTRACT

The electrochemical impedance spectroscopy (EIS) was used to analyse the corrosion behaviour of the Ni plated brass (OT59) substrate covered by SiO₂ coatings of different thickness. The specimens were immersed for long time (up to 168h) in a corrosive solution (synthetic swear). Plasma Enhanced Chemical Vapour Deposition (PECVD) technique was used to deposit SiO₂ coatings: the aim was to obtain a surface treatment that prevents the release of Ni, an allergenic metal. The deposition was performed in RF (13.56 MHz) plasma with hexamethyldisiloxan (HMDSO) and O₂ mixture at near room temperature without any solvents and without particular surface pretreatments. Different thickness of SiO₂ film was obtained varying the time of plasma exposure.

The EIS technique was demonstrated to provide a wealth of information on the behaviour of the coated substrate over time, on condition that the obtained data are carefully interpreted. In this study the attention was focused on the equivalent circuit (EC) that models the electrode/solution interface. The electrical circuit elements were interpreted in terms of influence of the coating defects on the substrate corrosion, and to choose the best PECVD treatment.

KEYWORD: EIS, PECVD technique, SiO₂ coatings on Ni plated brass, synthetic swear.

INTRODUCTION

The metal surface modification obtained by the deposition of thin corrosion protective layers by means of Plasma Enhanced Chemical Vapor Deposition (PECVD) technique can be useful in solving industrial problems towards corrosion [1-2]. For example, SiO₂ layers can act as a barrier towards ion diffusion and can be effectively used against metal wear and corrosion [3]. The SiO₂ layer transparency can ensure a good application of this technique to some kind of industrial objects whose previous surface treatment is judged sufficient from the aesthetical point of view. However, the different colours that can be achieved through the control of the coating parameters during the deposition processes, or the use of different gases as precursors, enable an increase also in the decorative PECVD application such as, for example, glass frames, handles, watch cases and sanitary parts.

By means of this technique it was possible to obtain layers resistant to the environment corrosion: the increasing interest for these films is also due to the fact that now it is possible to obtain this kind of treatment on supports whose surface can even be a big one (1 m²) [4, 5].

Recent studies demonstrated that, after the deposition of a very thin, transparent, homogeneous and amorphous SiO₂ film by means of PECVD, the metallic substrate rarely comes into contact with even the most aggressive external environment, so assuring high resistance to the corrosive attack. Further, the diffusion of aggressive species into the metal/coating interface can be minimized [6].

This surface treatment can be applied to prevent the allergies created by metals in direct and prolonged contact with the human body and particularly with the skin. Ni is known to be an allergy-causing factor, and Ni-containing alloys of coated items coming into direct contact with the skin have to be tested to verify their Ni-release before their commerce.

The increasing attention for this industrial problem led to the development of innovative coating which ensure the same brilliant and levelling ability characteristics of Ni-plating [7] or to alternative methods like painting or coating Ni-plated objects to avoid Ni-release from the substrate.

In this paper we present an EIS study on the corrosive behaviour of Ni-plated OT59 brass specimens covered by PECVD SiO₂ coatings in synthetic sweat solution.

EXPERIMENTAL

Thickness measurements

The coating thickness (CT) for all the PT samples was ascertained by means of different surface techniques (SEM, XPS and SIMS). In particular we reported here the SEM measurements that were carried out to study the homogeneity and the thickness of the various coatings with a JEOL apparatus, model JSM 5600 LV, equipped with a detector of back-scattered electrons and an X Ray probe for the element analysis (Oxford Instruments).

PECVD treatment

The deposition system consisted of a 13.56 MHz radio frequency source, capacitively coupled (0-1200 W) to a cylindrical process chamber.

The precursor flow was ignited and adjusted to produce the desired pressure. After pressure stabilization at about 0.1 mbar, the radio frequency energy was applied to the electrode at a power of 600 W.

A 0.7x1.0 m² surface electrode was used as a sample holder. HMDSO and O₂ gases were employed: HMDSO proving to perform the best in this kind of plasma [8].

After an initial O₂ activation of the substrate to clean the surface from organic contamination [8], improve the adhesion and reduce the formation of defects [9], the SiO₂ coating was deposited.

The PECVD treatment was carried out at near room temperature (about 35 °C).

Electrochemical measurements

Tafel curves

The potentiodynamic Tafel curves obtained with the Ni plated brass (OT59) specimens covered by SiO₂ coatings of different thickness, were carried out in synthetic sweat (NaCl: 0.5wt%; DL-lactic acid: 0.1wt%; urea: 0.1wt%) and recorded after a 1 - 168h immersion time (IT) with an Electrochemical Interface SOLARTRON Mod. 1287 interfaced with a PC.

The experimental part of the potentiodynamic curves method has been reported elsewhere [10].

Each test was repeated three times to verify its reproducibility. The average values of the obtained electrochemical data reported in Table 1 include: free corrosion potential, E_{corr} (mV_{SCE}; all the E_{corr} here reported refer to the SCE); corrosion current density, i_{corr} (μAcm^{-2}); anodic Tafel slope, b_A (mVdec⁻¹).

EIS measurements

AC impedance spectra for the PECVD coated Ni-plated brass samples were recorded using a SOLARTRON 1260 Impedance Gain-Phase Analyzer coupled with a SOLARTRON 1286 ECI.

EIS measurements were performed in synthetic sweat at 37°C in a three-electrode thermostatted Green cell, as described elsewhere [10].

When a stable E_{corr} was reached, a sinusoidal AC perturbation of 5mV amplitude was applied to the working electrode over the frequency range 0.01 - 10,000 Hz.

The impedance spectra were collected as a function of exposure time, up to seven days of immersion. Finally, the data were analyzed with the ZView Solartron software.

RESULTS AND DISCUSSION

From a physical standpoint, an inorganic coating with high corrosion protection efficiency can be thought as an electrically insulating barrier that, by preventing the contact of electrochemically active species with the metal surface, hinders the occurrence of corrosion processes. The "impermeability" of a protective coating depends on: i) its thickness; ii) the absence of defects; and iii) the adhesion of the layer to the substrate. A coating without mechanical defects, such as micro-porosity, localized cracks or poor local adhesion to the metallic substrate, can be obtained by tuning the layer deposition process, and especially the pre-treatment, the importance of which was first pointed out by Yasuda [8]. But generally the "industrial" treatment is more "rough", so that it is important to study the effect on the corrosion prevention of a PECVD industrial treatment. Existing growth defects in the coating are detrimental to the corrosion resistance of a coated metal: these defects are particularly dangerous as they provide direct paths for corrosive electrolytes to reach the coating/substrate interface, where the localized corrosion can be initiated due to the corrosion potential difference between the coating and the metallic substrate [11].

The EIS technique has shown its usefulness to study the localized corrosion of coating/metal systems, and offers a number of advantages over conventional electrochemical polarisation techniques [12-15]. However, modelling and interpretation of EIS spectra become the key to extracting useful information on the details of the corrosion reaction, especially in long time tests. EIS modelling is usually carried out through an equivalent circuit (EC) which is an assembly of circuit elements, representing the physical and electrical characteristics of the electrochemical interface. Presently the assessment of the proper assignation of circuit elements to some interface characteristics is made easier by numerous works on the application of the EIS technique to the corrosion behaviour study of coated metals and alloys in different aggressive environments.

For these reasons in this paper the data obtained from the Tafel curves were compared to those obtained from the EIS measurements.

SEM analysis

PT samples were also studied by SEM technique to analyse the homogeneity and possible presence of defects, as well as confirm the coating thickness (CT). In the images of the 30' PT sample, reported as an example in Fig. 1, the absence of "macroscopic" defects can be noted. The homogeneity of the coating obtained was also good, but only for 30 - 45' PT specimens: some non-homogeneity was found in the PECVD samples treated for a shorter time.

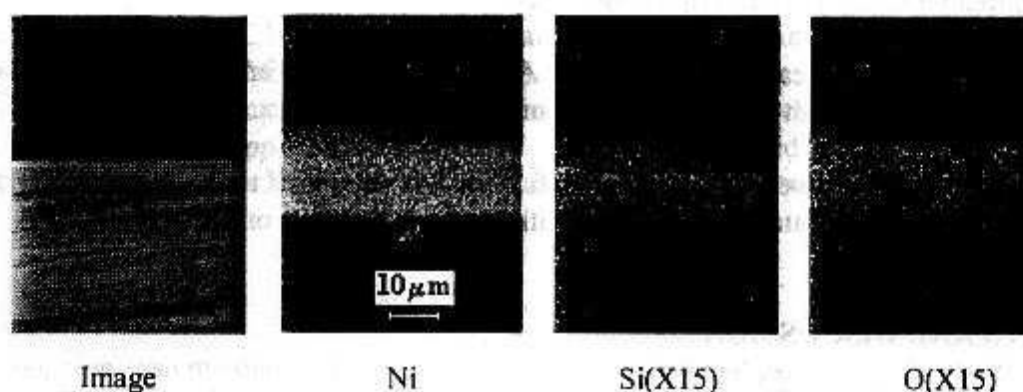


Fig. 1. SEM analysis of a PT (30') specimen. The maps of Si and O are magnified (x15) to show the homogeneity and the absence of defects.

Electrochemical tests

Tafel data

Table 1 reports potentiodynamic data obtained from Tafel curves after 168h IT of the PECVD treated (PT) specimens [5, 15, 30 and 40' of treatment time corresponding respectively to a CT of 0.5, 1.0, 1.5 and 2.0 μ] in synthetic sweat at 37°C.

One can note that the corrosion current densities, i_{corr} , obtained with the specimens whose thickness was 1.0, 1.5 and 2.0 μ , came out significantly lower than that of untreated one, thus

indicating the advantageous effects on the corrosion prevention of the PT samples also in the long time tests (168h). The unique kind of specimens that resulted to have an i_{corr} similar to that of untreated ones was that 5' PT, i.e. 0.5 μ thick (15.6 compared to 17.8 μAcm^{-2}).

After 1 week IT the 40' PT specimens (2.0 μ of CT) reached, on average, the lowest i_{corr} , 2.3 μAcm^{-2} , that is almost one order of magnitude lower than the i_{corr} of the untreated samples (17.8 μAcm^{-2}).

Table 1. Potentiodynamic data obtained from Tafel curves after 168h immersion time (IT) in synthetic sweat solution at 37°C. The TT = 0 refers to untreated Ni-plated brass samples (TT: PECVD treatment time; CT: SiO₂ coating thickness.).

TT	CT	E_{corr}	i_{corr}	b_a
min	μ	mV	μAcm^{-2}	mVdec ⁻¹
0	0	-435	17.8	68
5	0.5	-440	15.6	82
15	1.0	-442	4.2	90
30	1.5	-412	2.5	94
40	2.0	-417	2.3	95

It can be noted that, as the thickness increased, the E_{corr} became clearly more positive for the coated samples: this suggests, as expected, that the anticorrosion performance of the PT samples increases as the CT increases [16].

Also the b_a shifted towards higher values as the TT increased (from 68 to 95 mVdec⁻¹): this is clearly correlated with the effect of the layer on the anodic dissolution and indicates that the PECVD treatment influences, also at lowest TT, the anodic part of the corrosion reaction.

The tests carried out after one week with 30 and 40' PT samples demonstrated that with these CT almost the same i_{corr} value was reached (nearly 2.4 μAcm^{-2}). These first results allow to conclude that:

- i) the stationary state reached in the water uptake of the SiO₂ coatings [6, 17] through pores and defects permits corrosive media to penetrate into the substrate and provoke a small but detectable corrosion current (inversely proportional to CT);
- ii) probably the 30' PECVD treatment is sufficient to obtain a good prevention of the corrosion reaction.

EIS results

Equivalent circuit (EC)

The relative EC which better fitted data for coated samples is shown in Fig. 2.

The parallel-connected elements $C_{\text{sub}}-R_{\text{sub}}$ were introduced to describe the electrical charge transfer at the interface substrate/coating: C_{sub} is the substrate capacity and R_{sub} the substrate charge transfer resistance referred to electrochemical behaviour of the substrate, respectively. The non-ideal electric behaviour is taken into account by introducing a constant phase element (CPE) such as a coating capacity. In series with R_{sub} and C_{sub} , R_{pore} is the pore resistance to the ionic current through the pores; C_c represents the coating capacity. R_s , the solution resistance, completes the circuit.

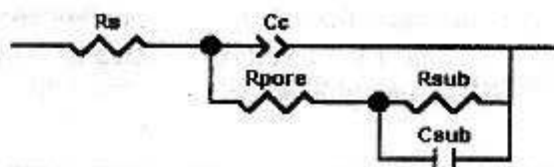


Fig. 2. The EC used to interpret the EIS data.

While nickel-plated samples are active substrates, and corrosion takes place in form of anodic dissolution from the exposed area in a one-time constant process, corrosion of PECVD coated samples is usually localised at the pores and defects, where the electrolyte is able to penetrate up to the substrate. The coating itself can act as a capacitor, so that Bode spectra of EIS data showed two time constants. For example in Fig. 3 are reported the EIS spectra and the fitting results of the experimental data obtained with the 40' PT sample after 48h of IT in synthetic swear solution ($T=37^\circ\text{C}$), using the EC reported in Fig. 2.

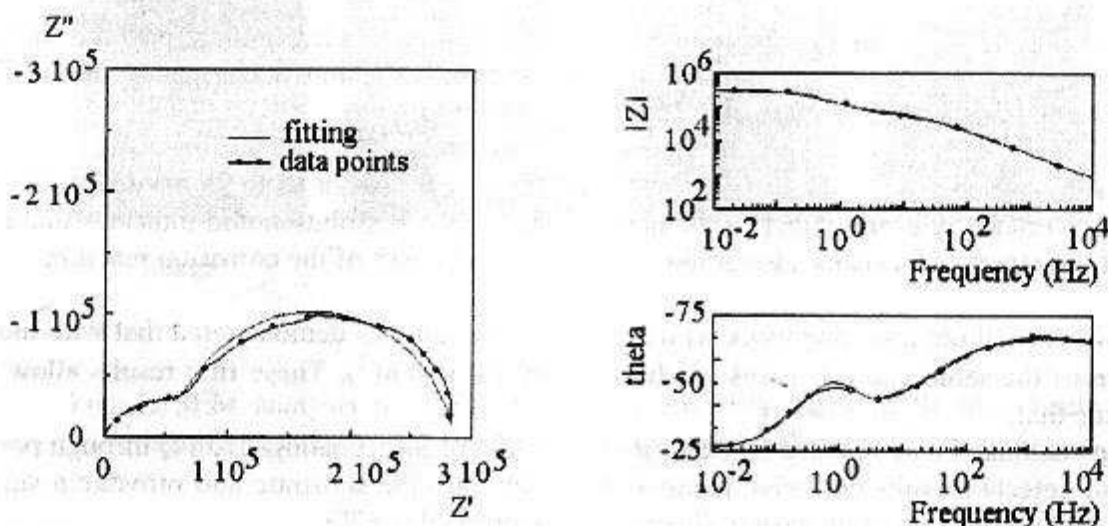


Fig. 3. The fitting results of the experimental data (40' PT sample; IT in synthetic swear solution: 48h; $T = 37^\circ\text{C}$) obtained using the EC reported in Fig. 2.

The interface substrate/coating behaves as a two time-constant system, as one can note both in the Nyquist and Bode spectra. As one can note, the used EC well interprets the experimental data.

EIS data

In Fig. 4 the time progress of the EIS spectra obtained with a 15' PT sample immersed in synthetic swear solution at $T=37^{\circ}\text{C}$ is reported. Two time constants are observable but only until 24h: one at high frequencies, representing the dielectric characteristic of the coating, and one at low frequencies, corresponding to the behaviour of the active substrate in the pores.

From the Bode (frequency vs θ) diagram one can observe that the position of the two peaks does not remain unchanged with IT, thus indicating an instability of the coating property over time [18]. After 24 h the situation changes: generally we can observe only one peak. These facts support the hypothesis that the dielectric coating property may be affected by the IT.

In addition, at an IT higher than 24h, the peak heights do not significantly change with the exposure time, indicating that the capacitive response reached an almost steady state. This agrees with the localized corrosion reaction into the pore that increases over time: as IT increases, the pores permit the solution to penetrate up to the Ni layer causing localised corrosion. Thus, current flow through defects becomes significant, even if almost constant after 48 h [11].

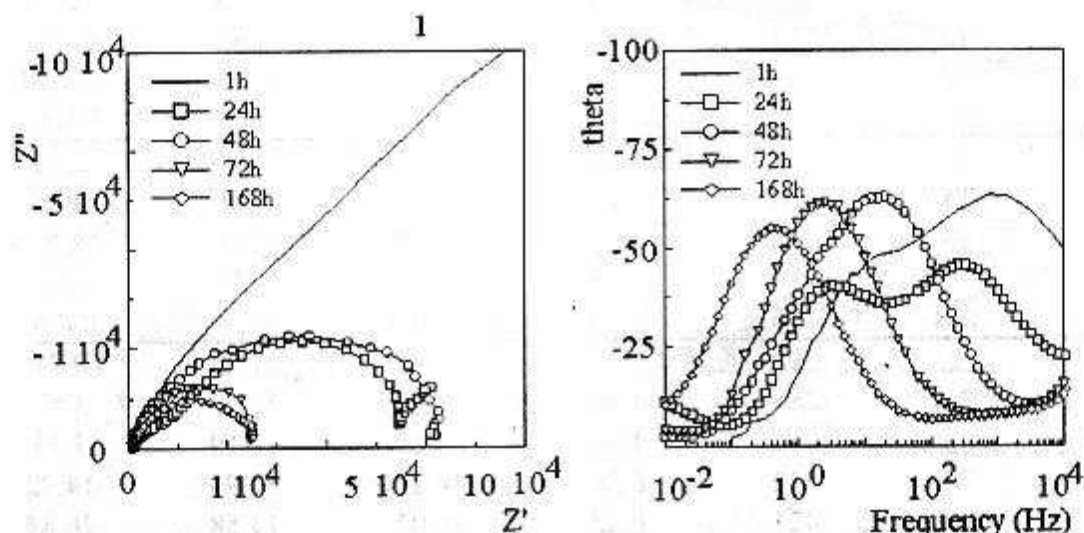


Fig. 4. EIS spectra (Nyquist format on the left and Bode - frequency vs θ - on the right) obtained with a 15' PT sample immersed in synthetic swear solution at $T=37^{\circ}\text{C}$.

Since one can affirm that Ni coatings on brass substrate are relatively passivated, the electrochemical response of Ni layer (the substrate) is often hardly distinguishable from that of an "inert" PECVD coating, such as the SiO_2 here used. It is expected that the response from the Ni-layer existing at the bottom of the pores is also capacitive as it is passivated. This passive layer is normally an inert thin oxide film with a relatively low conductivity [19], which results in a capacitive response which is similar to that obtained from SiO_2 layers, at least up to $1\ \mu$ thick. For this reason with thin SiO_2 coatings we obtained EIS data that can be also interpreted with a one-time constant EC [18] (Fig. 4). On the other hand, samples with 1.5 and $2.0\ \mu$ CT showed EIS spectra with a better separation between the two time-constants (see below). It is evident that the electrolyte comes into a thicker coating with a greater difficulty than into a less thick layer.

In Table 2 EIS data for PECVD coated Ni-plated samples, compared to the uncoated one, are reported.

Table 2. EIS data obtained during a 1-168h IT for PECVD coated Ni-plated samples, compared to the uncoated one (CT: SiO₂ coating thickness; IT: immersion time).

CT	IT	E _{corr}	R _{pore}	C _c	R _{sub}	C _{sub}
μ	h	mV _{sec}	kohm.cm ²	μFcm ⁻²	kohm.cm ²	μFcm ⁻²
0	1	-449			1.83	62.81
	24	-463			1.22	426.00
	48	-458			1.07	858.68
	72	-459			1.08	1796.01
	168	-452			0.97	1234.00
0.5	1	-390	0.78	0.79	2.63	2.01
	24	-391	0.35	3.41	3.36	42.70
	48	-412	0.30	7.53	2.99	91.83
	72	-435			6.32	358.81
	168	-440			6.07	274.00
1.0	1	-382	0.19	0.09	44.48	2.60
	24	-388	0.89	1.60	5.71	18.67
	48	-428	0.10	34.70	7.85	3.43
	72	-418	0.06	55.21	3.25	80.25
	168	-435	0.39	398.93	6.20	368.62
1.5	1	-298			27.88	0.71
	24	-385	1.93	21.85	22.43	3.87
	48	-403	1.02	24.67	21.19	3.95
	72	-412	0.56	38.21	30.95	14.72
	168	-421	0.48	89.02	13.58	26.87
2.0	1	-380			756.00	0.04
	24	-381	56.88	0.04	212.18	0.41
	48	-400	90.24	0.50	195.92	1.79
	72	-412	51.09	43.71	304.86	0.37
	168	-414	42.40	5.64	147.14	0.68

By examining the data reported in Table 2 we can note that the E_{corr} trend derived from the Tafel curves is confirmed: in fact at 168h the E_{corr} of the untreated samples is -452 mV_{sec}, while those of PT samples are, respectively, -440, -435, -421 and -414 mV_{sec}. But at same time one can see that all the PT samples showed a characteristic trend over time: this is clearly determined by the "water (synthetic sweat solution) uptake" of each coating that increased and favoured the corrosion reaction over time. This is confirmed by the complementary trend of the R_{pore} values.

At 168h IT the capacity values (C_{sub}) diminished as well as the polarization resistance (R_{sub}) increased with CT for all PT samples. The C_{sub} reached values at least one order of magnitude lower compared to uncoated samples, showing the good corrosion resistance properties of this kind of coating, especially for 2.0 μ layer thickness.

But EIS technique permits to reach a more precise conclusion than those obtained by means of DC measurements. In fact we obtain R_{sub} values for samples having a 2.0 μ CT respectively one order of magnitude greater than those having a 1.5 μ CT.

Prolonging IT, one can observe a great change in the electrochemical behaviour from untreated or low PT (until 1 μ) samples, and those of 1.5 and 2.0 μ thickness: these last behave almost similarly and have less time-depending electrochemical properties.

In Fig. 5 are reported the time progress of the EIS spectra obtained with a 40' PT sample immersed in synthetic swear solution at $T=37^\circ\text{C}$.

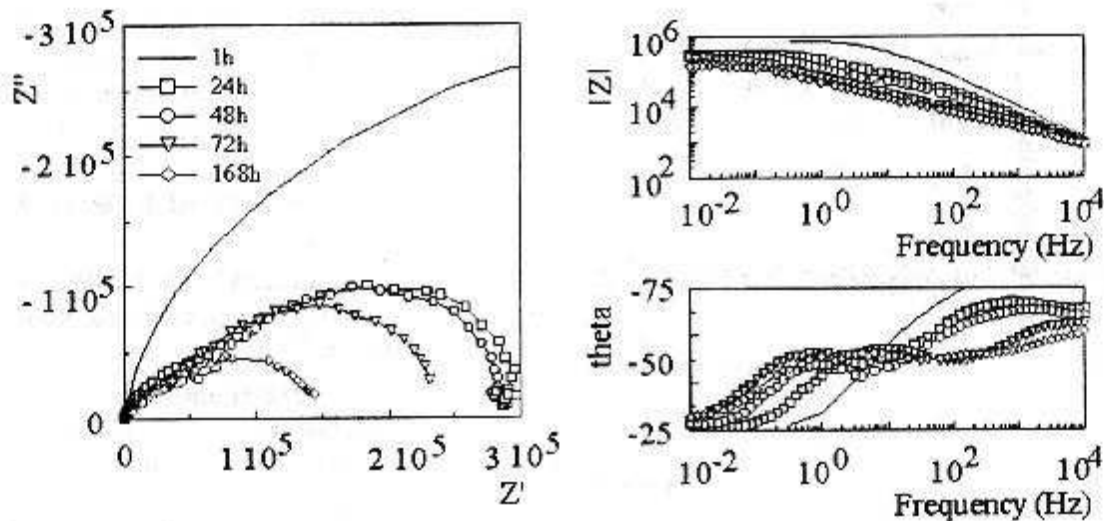


Fig. 5. EIS spectra obtained with a 40' PT sample immersed in synthetic swear solution at $T=37^\circ\text{C}$.

The differences between the spectra reported in Fig. 4 and Fig. 5 are evident. For the 40' PT samples we can note that, after an initial induction period in which the solution penetrates into the pores (1h), two peaks (two time-constants) appear (see, in particular, the Bode format frequency vs θ). Further, the position of the two peaks remains almost "unchanged" with IT indicating a greater stability of the coating property over time. The dielectric coating property of the coating seems not to be affected significantly by the IT.

The peak heights do not significantly change with the exposure time and the capacitive response seems to be more steady.

In Fig. 6a and 6b the trend of the C_{sub} and R_{sub} over time are reported.

The C_{sub} trend well indicates the "water uptake" progress over time: the different behaviours of the various PT samples are here evidenced. What is happening during the test time can be seen as a number of pores more and more gradually revealing because of the solution penetration.

In fact, the 0.5 μ PT sample already after 48 h shows the corrosion reaction effect inside the pores due to the lowest thickness of the coating. This behaviour is evident only after 72h for the 1.0 μ PT sample, while that one of the 1.5 μ PT sample is less evident, even constant. Finally, the 2.0 μ PT sample does not seem to have a "considerable" corrosion reaction result. This is a significant result, because it made it possible to well distinguish among the different tested surface treatments, especially in the case of the thickest ones.

Even the R_{sub} data confirm this conclusion: but in this case only the water uptake progress of the 0.5 μ PT sample was evidently depicted.

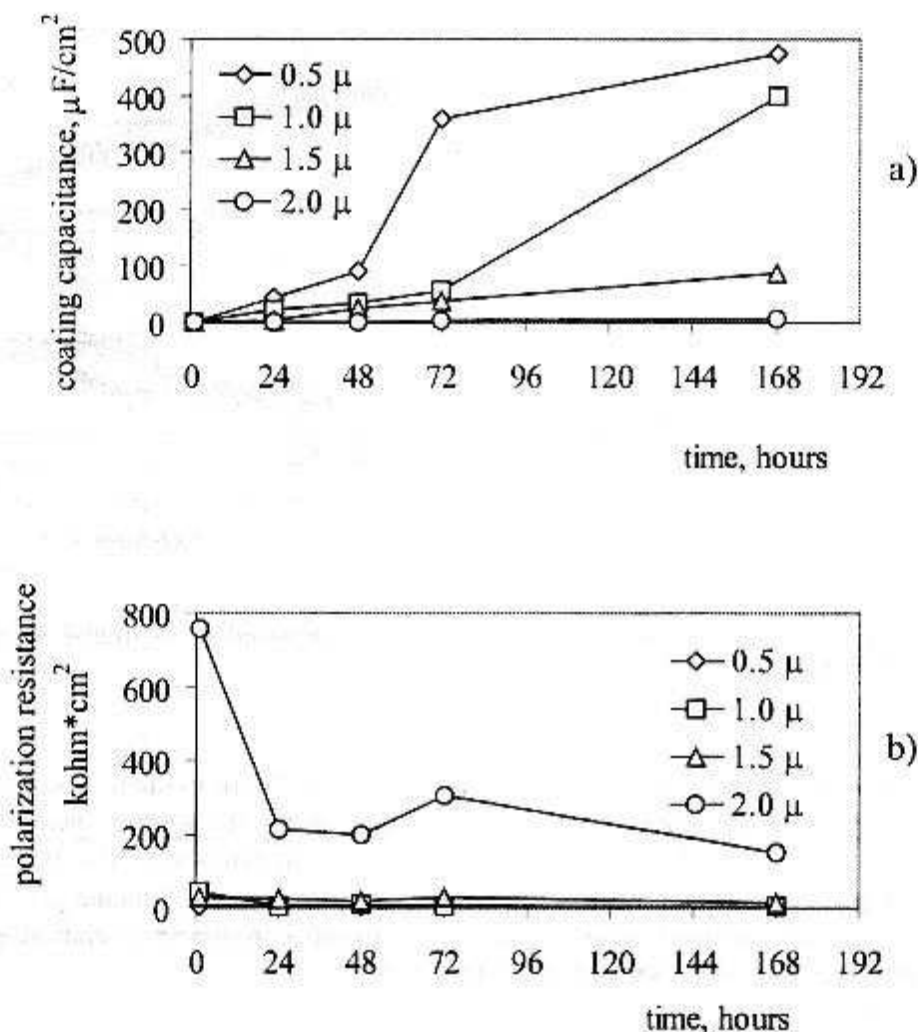


Fig. 6. 6a) the trend of the C_{sub} over time; 6b) the trend of R_{sub} over time (PT samples immersed in synthetic seawater solution at $T=37^\circ\text{C}$).

4. CONCLUSIONS

The electrochemical impedance spectroscopy (EIS) was used to study the corrosion behaviour of the Ni plated brass (OT59) substrate covered by SiO₂ coatings of different thickness until 168h IT. Plasma Enhanced Chemical Vapour Deposition (PECVD) technique was used to deposit SiO₂ coatings: different thickness of SiO₂ film was obtained varying the time of plasma exposure (5, 15, 30 and 40' of TT corresponding respectively to a CT of 0.5, 1.0, 1.5 and 2.0 μ). The tested EC made it possible to obtain information on the water uptake of the various coating and the corrosion performance over time. The conclusions are the following:

1. all PT samples have an initial "induction time" during which the test solution (synthetic sweat) penetrates into the pores. This phenomenon takes at least 1 day and was followed by the corrosion reaction of the substrate (oxidized Ni);
2. it was possible to distinguish between different phenomena occurring on the interface by means of the EC parameters. Especially for the highest CT, two time constants clearly appear: the one at high frequencies represents the dielectric characteristic of the coating, the other at low frequencies corresponds to the substrate in the pores;
3. the non-ideal electric behaviour is taken into account by introducing a constant phase element (CPE) as a coating capacity;
4. the best surface treatment was that obtained after 40' of PECVD treatment corresponding to a CT of 2.0 μ.

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Nomenclature

b_A	anodic Tafel slope $mVdec^{-1}$
C_c	coating capacity
CPE	constant phase element
C_{sub}	substrate capacity
CT	SiO ₂ coating thickness
DC	direct current
EC	equivalent circuit
E_{corr}	free corrosion potential (mV_{SCE})
EIS	electrochemical impedance spectroscopy
HMDSO	hexamethyldisiloxane
i_{corr}	corrosion current density (μAcm^{-2})
IT	Immersion Time
PECVD	Plasma Enhanced Chemical Vapour Deposition
PT	PECVD Treated samples
R_{pore}	pore resistance
R_s	solution resistance
R_{sub}	substrate polarisation resistance
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
TT	PECVD Treatment Time
XPS	X-Ray Photoelectron Microscopy

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