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Corrosion protection and mechanical performance of SiO_2 films deposited via PECVD on OT59 brass

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bstract

urpose – To evaluate the corrosion performance and nano-mechanical behaviour of a brass substrate covered by different thick SiO_2 layers deposited y means of plasma enhanced chemical vapour deposition (PECVD) technique.

esign/methodology/approach – The comparison between laboratory and "industrial" objects revealed a very good corrosion behaviour and good iechanical performance of both of them: in particular it was possible to modulate the surface treatment to solve various problems from the industrial oint of view.

indings – It was possible to reduce the Cu migration into the SiO_2 coating during the PECVD deposition at a negligible level and to control it by the eposition; further, the nano-indentation tests revealed the great utility of the coating annealing in obtaining a significant improvement of the iechanical properties of the coated objects.

esearch limitations/implications – Even if some industrial problems were solved (minimization of the presence of the coating defects and ansparency of the coatings), some on the layer hardness (anti-wear behaviour of the industrial objects) has to be better investigated and possibly solved.

ractical implications – The work reports a deposition process that is carried out industrially over a two year period.

riginality/value – This research reports a PECVD process realized on industrial objects: the originality is in the reached corrosion and mechanical erformances that made it possible to realize a satisfactory industrial deposition.

eywords Corrosion protection, Brass, Films (states of matter), Substrates

aper type Research paper

ntroduction

he plasma enhanced chemical vapour deposition (PECVD) by now a technique normally used in industry in many pplications, for example as optics (Tien *et al.*, 1972; Choi *al.*, 2000), corrosion protection layers (Okuara and White, 987; Schreiber *et al.*, 1980), and as barrier films for food ackaging (Fayet *et al.*, 1995). SiO_2 dielectric films are largely mployed in silicon integrated circuit technology as a assivating layer or as intermetallic insulation in multilayer ructures (Sahli *et al.*, 1992; Inagaki *et al.*, 1989; Falcony *et al.*, 1991). Low processing temperatures make it possible to avoid segregation effects and dopant migration within the device (Selamoglou *et al.*, 1989; Patrick *et al.*, 1992).

SiO_2 layers are also used in the anti-wear and anti-corrosion field: increasing attention toward these techniques is due to the fact that now it is possible to coat large surfaces (1 m^2 and more), which make it increasingly attractive to industry (Sahli *et al.*, 1994; Perrin *et al.*, 2000). It has been shown that electrochemical techniques based on surface impedance measurements are very useful when controlling the integrity and quality of coatings (Kittel *et al.*, 2002; Popov *et al.*, 1993; Walter, 1991; Amirudin and Thierry, 1995; Santagata *et al.*, 1998). Studies of corrosion prevention and protection have recently reported the good correlation between electrochemical parameters and several relevant chemical-physical properties of metal surfaces, such as the water adsorption, film resistance and corrosion rate of the coated metal (Kittel *et al.*, 2002).

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After the deposition of very thin, transparent, homogeneous and amorphous SiO_2 films by means of hexamethyldisiloxane (HMDSO) (which provides the best results as a reagent precursor (Yasuda, 1987)), the metallic substrate rarely comes into contact with even the most aggressive external environment, therein assuring high resistance to the corrosive attack. The diffusion of aggressive species through the coating to the metal/coating interface is minimised.

From a physical standpoint, an inorganic coating with high corrosion protection efficiency can be thought of as being 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 the protective coating depends on:

1 its thickness;
2 the absence of defects; and
3 the adhesion of the layer to the substrate.

A coating without mechanical defects, such as micro-porosity, localised cracks or poor local adhesion to the substrate metal, is obtained by tuning the layer deposition process, and, especially, by the pre-treatment, the importance of which was first pointed out by Yasuda (1987).

Plasma deposited amorphous SiO_2 also can be a good candidate to improve the abrasion and wear resistance of the substrate surface. For this purpose, the determination of the surface and near-surface mechanical properties of the film is important in order to evaluate the performance of the coating in service.

The nano-indentation technique is now widely used in evaluating the hardness of small volumes such as thin films, and several studies concerning micro-indentation and nano-indentation analysis of plasma-deposited SiO_2 on different substrates such as polymers (Rats *et al.*, 1999) or Herasil and borosilicate glass (Beck *et al.*, 1998) have been reported. However, no data, at the present, are known for the system SiO_2/brass.

This paper presents an evaluation of the corrosion performance and nano-mechanical behaviour of the brass substrate when covered by different thick SiO_2 layers deposited by means of the PECVD technique. Samples prepared by means of an industrial process were tested in a standard very aggressive solution (aerated 1N H_2SO_4 at 25°C – 1-168 h of it) by means of DC and AC measurements. SIMS analysis was employed to characterise the coating thickness and the homogeneity of the deposition. On the basis of the initial laboratory results, the same deposition process was used to cover some industrial objects, which were tested following ASTM protocols.

Methodology

PECVD treatment

The deposition system consisted of a 13.56 MHz radio frequency source, capacitively coupled (0-1,200 W) to a cylindrical process chamber. The precursor flow was ignited and adjusted to produce the desired pressure. After pressure was stabilised at about 0.1 mbar, the radio frequency energy was applied to the electrode at a power of 600 W. A $0.7 \times 1.0\,m^2$ surface electrode was used as a sample holder. HMDSO and O_2 gases were employed.

The SiO_2 coating was deposited after an initial O_2 substrate activation to clean the surface from organic contamination (Yasuda, 1987), to improve the adhesion and reduce the formation of defects (van Ooij *et al.*, 1995). The PECVD treatment was carried out at near room temperature (about 35°C). However, (as expected) an undesirably defined substrate/film interface results because of the use of O_2^+ ions of relatively large energy (Barranco *et al.*, 2001).

Electrochemical measurements

The resulting coatings were electrochemically examined to determine their corrosion resistance in a very aggressive test solution (aerated 1N H_2SO_4 at 25°C). The methodologies used to investigate the corrosion behaviour of the PECVD treated samples included DC (Tafel curves) and AC (EIS) techniques.

Thermostatted double-walled (1 litre) Pyrex glass cells (Green cells) were used in the electrochemical tests. Brass discs of 11.3 mm diameter, (with a nominal composition of: Cu = 59 percent; Zn = 29 percent; Pb = 1 percent), were laser cut from plate. Each sample was mounted on a Teflon holder that left an exposed area of $0.5\,cm^2$, and was the working electrode. Before use, specimens were washed with distilled water, degreased with acetone and dried with a jet of air. The working electrode, a saturated calomel reference electrode (SCE) inside a Luggin capillary probe, and a platinum counter electrode, were placed inside the cell. All the reported potentials refer to SCE. Each test was repeated three times to verify its reproducibility.

The potentiodynamic tests were carried out as follows. Each specimen was immersed until a stable (±2 mV) free corrosion potential (E_{corr}) was attained. At that point, the scan was started from the E_{corr} until a potential $E = (E_{corr}$ – about 400 mV) and recorded with a scanning rate of 1,000 μV/s. The specimen then was replaced and re-immersed inside the electrochemical cell in the same solution. After E_{corr} was reached, the anodic scan was started from the E_{corr} until a potential: $E = (E_{corr}$ + about 200 mV). The data were recorded by means of an SOLARTRON Model 1287 electrochemical interface. Each test was repeated three times on different specimens in three different solutions at the same concentration to verify its reproducibility. E_{corr}, i_{corr} and b_A values for each of the samples were determined by extrapolating Tafel lines using SOLARTRON Corrview software. The DC curve method has been extensively reported previously (Moretti *et al.*, 2002).

EIS measurements were usually performed at the corrosion potential of the brass substrate, by applying a ±10 mV amplitude sinusoidal wave perturbation to the corroding system. The frequency values usually ranged from 10^5 Hz to 10^{-2} Hz, with ten frequency values per decade. At the end of each EIS measurement, potentiostatic polarization was interrupted and the working electrode was allowed to corrode freely until the next EIS measurement (the free corrosion potential, E_{corr}, was determined in the meantime). The data were recorded by means of the electrochemical interface and a SOLARTRON Model 1260 frequency response analyser. The experimental data were interpolated with Solartron Zview software to model the best equivalent circuit to approximate the impedance behaviour. The physical model (discussed below and shown in the Figure 10) and the electrochemical model (shown in the Figure 11) enabled the charge transfer resistance (R_{ct}) and double-layer capacity (C_{dl}) of the corrosion reaction, as well as the pore resistance (R_{pore}) and the coating capacity (C_{coat}) to be determined.

he solution resistance (R_s), is generally negligible (4-$\Omega\,cm^2$) because of the high solution conductivity.

The constant phase element (CPE) was used in place of a real" capacitive value to compensate for the non-omogeneity of the surface caused by, for example, the orrosion process (Jüttner *et al.*, 1988; Growcock *et al.*, 1989).

In the equivalent circuit, a "W" indicated the Warburg iffusion element: it takes into account of the diffusion henomena that can occur inside the coating, depending on, or example, the water uptake. In fact, all coated samples, specially that of higher thickness, presented an almost ectilinear part (at about 45°) in the EIS spectra recorded ithin 24 h (Kendig *et al.*, 1983).

IMS measurements

he obtained coated samples were examined by means of IMS measurements to verify their thickness and the eatment homogeneity. A custom-built instrument (Pagura *al.*, 1992) was used to carry out the SIMS analysis. A ionochromatic (6 keV, ionic current ~400 nA) O_2^+ ion beam, ollimated to 50 μm, was generated in a mass-filtered uoplasmatron ion gun (model DP50B, VG Fisons, UK). he magnification was set to 2,000X, except for the sample of 80 nm for which it was set to 1000 ×, reducing the current ensity of the beam to 25 percent.

A powerful mass-energy analyser (model EQS1000, Hiden, JK), with a high transmission 45° sector field energy analyser nd a quadrupole mass-filter, was used in counting mode for ositive-ion detection. Lens and energy analyser potentials, uadrupole electronic control units and the detection system ere controlled through a Hiden HAL IV interface. Ion depth rofiles were recorded for samples of interest as a function of ombarding time. Border effects were avoided by employing lectronic gating: only a percentage (50 percent, considering ie preliminary level of the investigation) of the rastered area ontributed to the ionic signal, which was restricted to the entral part of the crater. The craters produced by ion ombardment were measured with a surface profiler KLA encor (San Jose, CA) model P10. The surface roughness of iO_2 was measured by scanning 600 μm^2 regions. Three epth-profiles were acquired for each sample, so as to stimate the reproducibility of the process and, therein, the niformity and surface roughness of the silica layers.

lano-indentation measurements

lano-indentation was used to determine film hardness using Nanotest 600 instrument from Micromaterials Ltd with a erkovich (threesided pyramidal) diamond indenter. Several eak loads for each sample in the range: 2.5-100 mN were sed with the same loading and unloading rates: these were aried in proportion to the peak loads starting at a value of .1 mN/s for the 2.5 indentations, while common xperimental conditions as initial (contact) load 0.05 mN nd holding period at peak load 10 s were used for all the ieasurements. The indentations were repeated at least five mes at each load on different regions of the sample surface, 0 μm apart. The hardness (H) and reduced modulus (E_r) ave been determined from these indentation curves using a ietbod originally proposed by Oliver, which fits a power-law inction to the unloading curve (Oliver and Pharr, 1992). he nano-indentation measurements were also carried out on nealed samples: the annealing was performed in oxygen mosphere at 500°C (1 h).

Results

Electrochemical tests – DC results

Figure 1 shows some typical "i vs E" curves (Tafel curves) obtained with different SiO_2 (from 180 to 1,950 nm thick) specimens after 1 h of immersion time in aerated 1N H_2SO_4 at 25°C, compared to the sample of untreated brass substrate. Figure 2 shows the same curves obtained with the same samples at 168 h of immersion time (1 week) in the same experimental conditions. Table I summarises the electrochemical DC results.

Figure 1 Some typical Tafel curves obtained with uncoated and SiO_2-coated brass (in aerated 1N H_2SO_4 at 25°C; after 1 h)

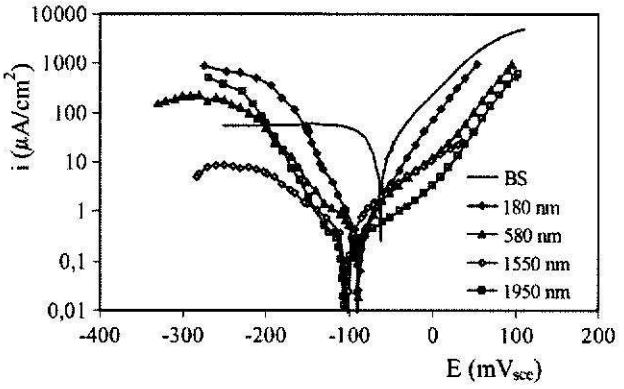


Figure 2 Some typical Tafel curves obtained with uncoated and SiO_2 coated brass (in aerated 1N H_2SO_4 at 25°C; after 168 h)

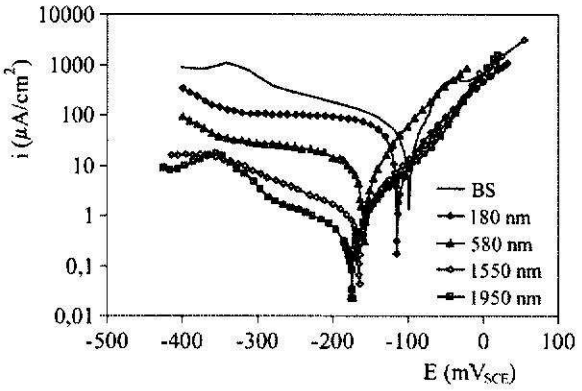


Table I Electrochemical data obtained in the DC tests

Immersion time (h)	Coating thickness (nm)	E_{corr} (mV$_{sce}$)	b_A (mV/dec)	i_{corr} (μA/cm^2)
1	0	−107	45	16.1
	180	−83	56	1.3
	580	−89	73	1.0
	1,550	−100	86	0.4
	1,950	−97	90	0.2
168	0	−104	31	20.2
	180	−122	72	0.5
	580	−143	70	0.3
	1,550	−155	72	0.4
	1,950	−159	72	0.3

After 1 h all the PECVD treatments influenced the corrosion current (i_{corr}) (Table I). All the curves of the treated specimens were clearly shifted to lower i_{corr} values, with respect to those of the brass substrate (Figure 1). In these experimental conditions, the i_{corr} value of the brass was about 16 μA/cm^2, whereas those calculated for the different coatings were significantly lower (at least one order of magnitude), ranging from 1.3 to about 0.2 μA/cm^2 (Table I). In the short term tests, the 1,950 nm thick layer reached, on average, the lowest i_{corr}, 0.2 μA/cm^2, and was almost two orders of magnitude lower than that of the brass substrate.

In the short immersion tests, as the PECVD treatment time and, consequently, the thickness of the SiO_2 layer increased (Table I). The average E_{corr} values seemed not to be significantly influenced, ranging from around -90 to -100 mV$_{sce}$.

At the end of the experiments (168 h) the various PECVD treatments behaved in a quite different way. Actually, after 168 h, the corrosion reaction mechanism seems to be almost the same for the various coatings, as evidenced by the curve shape that is very similar for the various specimens. As reported in Table I, the anodic Tafel slopes for the coated samples ranged all around 70 mV/dec. Thus, the E_{corr} values became as much more negative as coating thickness increased (from -113 to -174 in comparison with -98 mV$_{sce}$ – Table I).

AC (EIS) results

The EIS results are summarised in Table II. Figures 3 and 4 show the capacitance and resistance trends over time. The charge transfer resistance (R_{ct}) and the pore resistance (R_{pore}) trends vs coating thickness were very similar in all cases (Figure 3): though higher values were found with the 1,950 nm coating thickness.

Their values increased with time to a maximum after 1-48 h and then slowly diminished reaching a stable value in 72-168 h of immersion time (Table II).

By the comparison between the double-layer capacity (C_{dl}) as well as the coating capacity (C_{coat}) values, one can note that, on average, the C_{dl} values were significantly lower than were those of C_{coat} (ranging from about 100 to 200 μF/cm^2 for all thicknesses – Table II): in fact the coatings act as a substrate insulator, and even if the solution penetrated in the layer defects, the C_{coat} remained significantly higher than the C_{dl}. After 168 h of immersion time, the C_{coat} values, on average, decreased. At 168 h the minimum C_{coat} value was only reached by the 1,950 nm coating (about 1,200 μF/cm^2).

SIMS results

The thickness of SiO_2 layers deposited on the brass samples was measured by the SIMS technique that made it possible to obtain also the depth-profiles of the most representative elemental – or molecular – ions, associated to deposited SiO_2, interface regions and substrate. Table III presents the thickness data obtained for the different PECVD treatments; Figures 5 and 6 show the element profiles obtained for the 180 and 1,950 nm layer thicknesses.

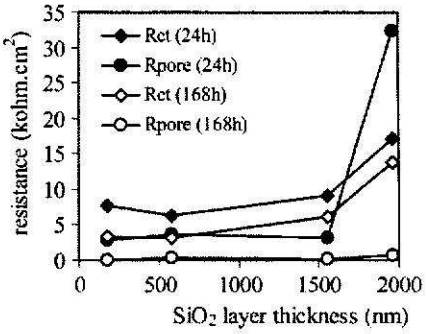
There was evident proportionality in the thickness of SiO_2 as a function of the PECVD treatment time. The sample exposed to plasma for only 5 min (180 nm thick) showed an uncertainty of about 40 percent, probably due to the residual roughness of the substrate and intrinsic defects in the analysis, such that due to the crater walls, generated by the technique, that are irregular and discernible with care. The resulting thickness was obtained considering the maximum intensity of the $^{11}B^+$ signal as an indicator of the silica-brass interface.

When the PECVD treatment was carried out to reach 1,550 or 1,950 nm of coating thickness (for 30 and 45 min, respectively), Cu migrated in the SiO_2 layer during the deposition: for the 1,950 nm specimen, for example, the Cu started to migrate from the brass surface into the coating (up to 1 μm of the thickness) (Figure 6). Notwithstanding this fact, corrosion activity did not increase (see discussion).

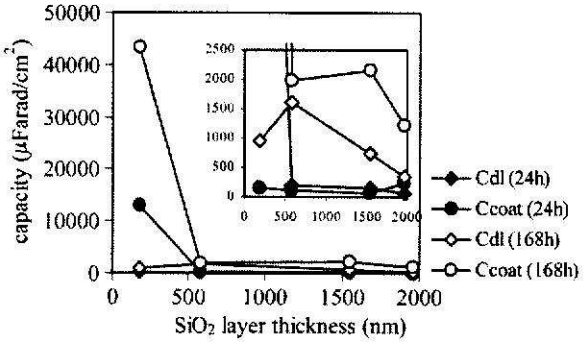
Table II The EIS data obtained for the PECVD treated samples in aerated 1N H_2SO_4. R_{ct}: charge transfer resistance; C_{dl} double-layer capacity; R_{pore}: pore resistance; C_{coat}: coating capacity

Coating thickness (nm)	Immersion time (h)	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	R_{pore} (Ω cm^2)	C_{coat} (μF/cm^2)
0	1	830	63		
	24	220	426		
	48	205	859		
	72	108	1,796		
	168	97	12,342		
180	1	5,450	162	2,857	12,954
	24	7,620	62	3,747	11,114
	48	5,744	283	5,449	14,213
	72	5,971	409	5,985	11,669
	168	3,350	952	651	43,292
580	1	4,207	109	3,699	196
	24	6,280	85	4,207	3,152
	48	6,351	170	4,850	33,198
	72	6,199	208	5,400	37,205
	168	3,110	1,606	300	1,955
1,550	1	1,950	62	3,220	3,567
	24	9,098	266	3,240	1,047
	48	3,058	358	3,254	1,243
	72	2,554	457	2,238	1,476
	168	6,090	742	260	2,152
1,950	1	19,902	249	9,281	63
	24	17,129	221	32392	59
	48	24,212	203	28,786	181
	72	20,472	160	22,530	267
	168	13,883	358	676	1,217

Figure 3 R_{ct} and R_{pore} trends vs the layer thickness in aerated 1N H_2SO_4 (25°C) at 1 and 168 h of immersion time



igure 4 C_{dl} and C_{coat} trends vs the layer thickness in aerated 1N I_2SO_4 (25°C) at 1 and 168 h of immersion time



able III The thicknesses of the PECVD treated samples obtained from ıe SIMS technique

hickness (nm)	Uncertainty (per cent)	Roughness (Å)
80	40	365
80	25	270
,550	25	280
,950	15	190

Jano-indentation measurements

The nano-indentation measurements were performed on the urface of both uncoated and PECVD-treated brass surfaces, ı order to determine their hardness. Figure 7 shows a omparison of indentation load-depth curves, carried out at ıe peak loads of 5 mN, on bare brass substrates and for two iO_2 films of different thicknesses (580 and 1,950 nm).

The uncoated brass sample exhibited a smaller indentation epth and a lower amount of creep deformation during the 0 s hold period at maximum load: this implied that its ardness was higher. In addition, different samples exhibited ery little variation in hardness, as evidenced by the small ifferences in the depth obtained at the maximum load. It was lso interesting to observe the slope of the unloading segment f the load-displacement graphs and to assess the elastic ecovery on unloading. For brass, the slope of the unloading segment was almost vertical, typical of a ductile plastic material such as most metals. This indicated that the elastic strains during indentation were small compared with the plastic strains, so that most of the indenter displacement was accommodated plastically, giving little elastic recovery of the indentation depth (10 per cent). In the case of the coated samples, a larger indenter depth was recovered as the load was removed, indicating that the composite systems presented a larger degree of elastic recovery during unloading (36 per cent for the thickest). The shape of the paths related to the SiO_2/brass systems quickly approached that of the brass substrate as the thickness of the SiO_2 coatings decreased, indicating that the surface and near-surface mechanical properties of the SiO_2/brass system, in the examined range, depended from the coatings thickness.

Table IV reports the calculated average values of hardness for the uncoated and coated brass, together with the average values of reduced modulus and elastic recovery, determined by unloading curves for maximum peak load of 5 mN.

The substrate surface presented a hardness value in good agreement with that previously reported (Doerner and Nix, 1986) and resulted slightly harder than the SiO_2 films, whose hardness values changed only very little with the thickness. Instead, the elastic properties depended on the coating thickness and the composite systems resulted stiffer when the SiO_2 coating decreased.

In any case a remarkable improvement of the surface mechanical properties of the SiO_2/brass system was obtained by annealing the thickest coating at 500°C in O_2 atmosphere (1 h). Figure 8 shows a comparison of indentation load-depth curves for the uncoated brass, and the SiO_2 layer (1,950 nm thick) on brass substrate as deposited and after annealing, for a single indentation carried out to peak loads of 5 mN.

The difference of the three samples is immediately clear, as evidenced by the difference of the indentation depths (obtained at the maximum load) and from the slope of the unloading segment. For the annealed sample, these data indicated, respectively, a higher hardness value and a larger degree of elastic recovery during unloading. The calculated hardness and elasticity values, reported in Table IV, indicated that the annealed sample was ~180 per cent harder and ~140 per cent stiffer than the as-deposited one. For this

igure 5 The element profiles obtained for the 180 nm PECVD treated specimen by the SIMS technique

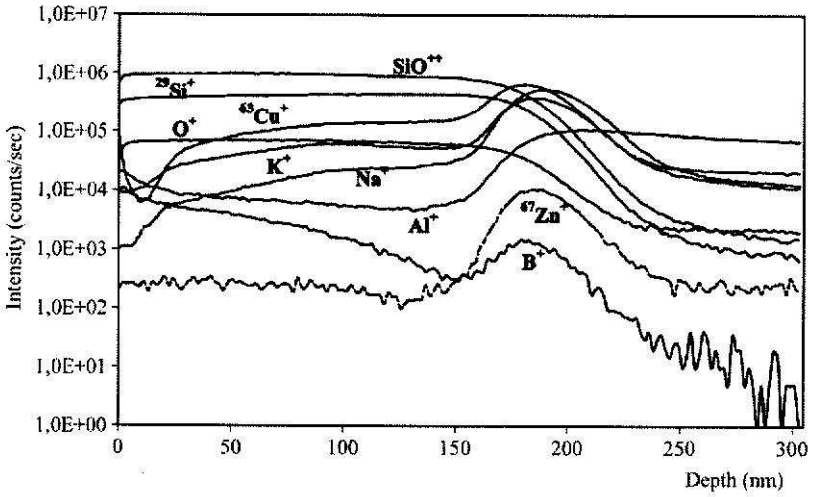


Figure 6 The element profiles obtained for the 1,950 nm PECVD treated specimen by the SIMS technique

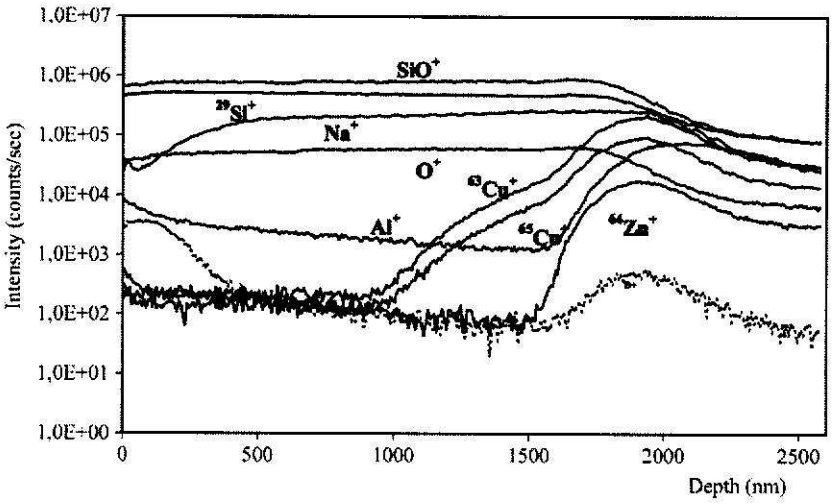


Figure 7 Load-displacement curves for: (a) uncoated brass; (b) SiO_2 coating 580 nm thick; (c) SiO_2 coating 1,950 nm thick

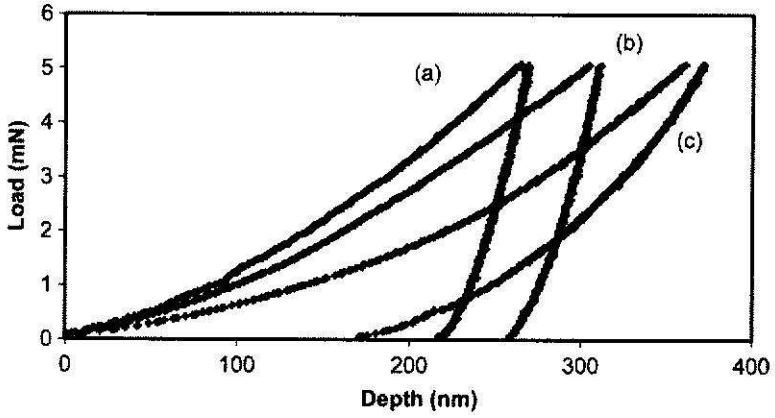


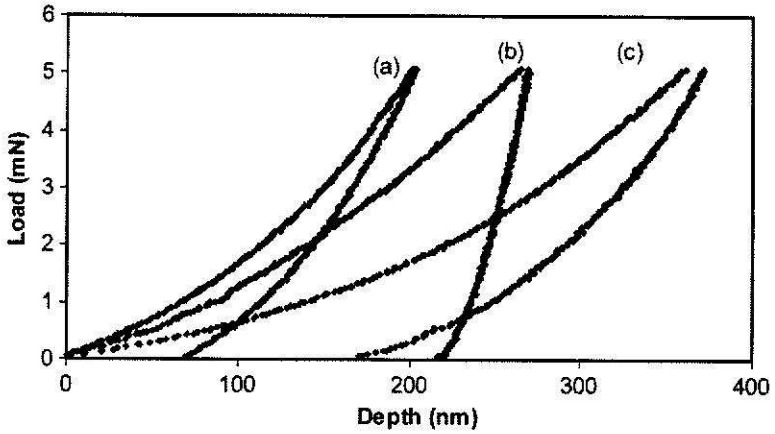
Table IV Summary of evaluated mechanical properties of SiO_2 coatings of substrate and of SiO_2/brass composite system

Sample	Hardness (GPa)	Reduced modulus (GPa)	Elastic recovery
Brass	3.03	109.46	0.10
SiO_2 (180 nm thick)	2.49	84.91	0.08
SiO_2 (580 nm thick)	2.34	48.96	0.17
SiO_2 (1,550 nm thick)	2.28	27.07	0.29
SiO_2 (1,950 nm thick)	2.53	24.46	0.36
Annealed SiO_2 (1,950 nm thick)	7.17	57.85	0.44

situation, where a hard film covered a softer substrate, it was possible to determine the intrinsic hardness value for coating material only when the indentation depth was considerably smaller than the film thickness, since for larger indentation depths a composite hardness that also included a contribution from the substrate will be measured (Saha and Nix, 2002). This behaviour is well depicted in Figure 9, which shows the variation in hardness with depth for uncoated and annealed SiO_2 coated brass (1,950 nm thick; calculated from the indentations, covering the loading range 2.5-100 mN).

The curve of the coated sample showed a first region, at low indentation depth, where the coating hardness was almost constant, and a second region at greater indentation depths, where a decrease in the hardness – as the indentation depth increased – could be detected. This was due to a progressively increasing contribution from the substrate material, typical for a hard film on a softer substrate: the range of the hardness plateau depended on the coating thickness and the average of the values obtained in this plateau region were used to calculate the intrinsic value of the hardness of the baked SiO_2

Figure 8 Load-displacement curves for: (a) annealed SiO_2 coating 1,950 nm thick; (b) uncoated brass; (c) as-deposited SiO_2 coating 1,950 nm thick



coating (Ahn and Kwon, 2000). The average hardness result was 7.24 ± 0.10 GPa, which is in good agreement with those reported previously for as-grown PECVD SiO_2 coatings deposited on fused SiO_2 and borosilicate glass (Beck *et al.*, 1998).

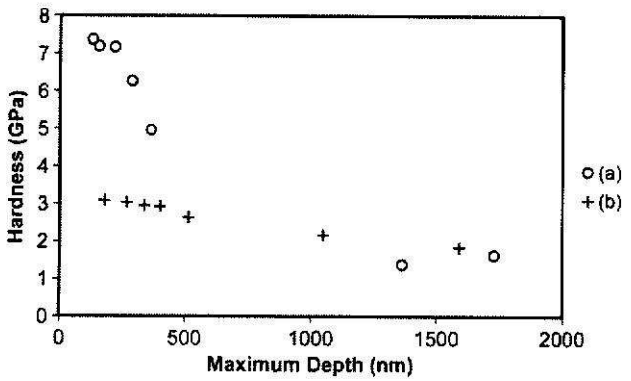
Other technical tests

After the laboratory tests, the PECVD process was used to coat some industrial objects with SiO_2 anti-corrosion and anti-wear layers. Some of these objects were submitted to technical tests to determine the quality of coating achieved (e.g. exposure to the salt spray (fog) chamber test (following the ASTM B117/97 protocol). The results confirmed that the best PECVD treatment was that of the coating 1,950 nm thick, which resisted more than 800 h of salt spray fog, even at 1,550 nm thick the performance was quite good – especially from the point of view of industrial application. These industrial specimens also passed ultraviolet exposure (ASTM G53), adhesion (ASTM D3359), bending (ASTM D522), impact (ASTM 2794) and chemical (ASTM D4652) tests.

Discussion

To analyse the different thick PECVD coatings, especially when the aim is to optimise an industrial process, it is important to have the results of experimentation as soon as possible. Apart from the physical properties (for example, the mechanical properties), the evaluation of the ability of a coating deposit to protect a metallic substrate can be usefully characterised by means of electrochemical techniques. When considering this, the differing nature of direct and alternate current techniques is complementary. Data drawn from the electrochemical techniques – "laboratory" data – can be compared with that obtained from other tests, for example, results from certain ASTM tests are important for the industrial point of view. From this comparison it is possible to have, for example, a life-time prediction of the proposed PECVD treatment.

Figure 9 Variation of hardness with depth for: (a) Annealed SiO_2 coating 1,950 nm thick; (b) uncoated brass substrate



In the present work, the same samples were examined using both in DC (Tafel curves) and in AC (EIS) to have a better vision of the whole picture. The DC technique gives an image of the entire corrosion process.

Considering the whole corrosion process, by analysing the short time test results (Figure 1), the shape of the obtained Tafel curves evidenced that both the cathodic (oxygen reduction) and the anodic (metal dissolution) part of the corrosion reaction were involved. In fact, as indicated for the anodic reaction, the anodic Tafel slope, b_A, significantly increased in the short time tests (Table I): the average b_A value obtained for the uncoated substrate was 45 mV/dec, while it increased (until 90 mV/dec for the max thickness) for the treated samples, doubling in the case of the 1,950 nm sample. This means that, at least for short immersion times, the anodic part of the corrosion reaction was greatly influenced by the PECVD treatment.

The same can be said for the cathodic part of the corrosion mechanism. While for the uncoated substrate the oxygen reduction reaction was almost unchanged – depending on the oxygen diffusion rate, due to the aerated environment, for coated specimens a different corrosion mechanism (i.e. a curve shape) was evident, see Figure 1. After 168 h, the corrosion reaction mechanism seemed to be almost the same for the various coatings, as evidenced by the curve shape that is very similar for the various specimens. As reported in Table I, the anodic Tafel slopes for the coated samples ranged all around 70 mV/dec. This could indicate, first of all, the reached homogeneity of the PECVD deposition at the various treatment time (Moretti *et al.*, 2002). The i_{corr} seemed to indicate that only the 1,550 and 1,950 nm thick coatings resisted the corrosive attack in this environment (Table I) and it was only for these samples the corrosion rates measured

after a week were one order of magnitude lower than samples with thinner coatings (about 1 $\mu A/cm^2$ in comparison with about 10 $\mu A/cm^2$). This finding was confirmed by the fact that it was only these specimens that appeared visually not to have sustained "damage" (i.e. not attacked from the corrosion point of view) after a week of immersion.

The E_{corr} values became as much more negative (from -113 to -174 in comparison with $-98\,mV_{sce}$ – Table I), as coating thickness increased, indicating the more cathodic behaviour of the coated samples as the layer thickness increased, compared with that of the uncoated substrate. After 24 h of immersion, all treated samples reached a similar steady-state in the corrosion reaction: this is thought to be due to the reaching of a pseudo-stationary state in the water uptake of the SiO_2 layers (Yin and Lu, 2002; Moretti *et al.*, 2002). The EIS data (see below) confirmed this conclusion. The use of EIS in evaluating the degradation, for example, of SiO_2 coatings and their interaction with aqueous environment, provides useful information that cannot be obtained with traditional DC techniques. First of all a model of equivalent circuit that represents the metal/coating behaviour in the chosen aggressive environment can be hypothesized: this allows the circuit analogy in the EIS spectra interpretation to be applied (Kendig *et al.*, 1983). EIS data analysis is often accompanied by an equivalent circuit modelling, which is an assembly of circuit elements that may represent the physical and electrical characteristics of the electrochemical interface. The equivalent circuit design, and the consequent interpretation of the EIS spectra of the coated brass, can encompass many considerations about the involved corrosion reactions, the physical properties of both coating and metal surface, and the chemical characteristics of the materials.

The physical model assumed to describe the phenomena due to the diffusion process of the reagents from the bulk solution toward the metal surface is shown in Figure 10. On the basis of this model the equivalent circuit shown in Figure 11 was chosen in accordance to the literature (Kendig and Scully, 1990). Because of the EIS is not a very

Figure 10 The physical model chosen to interpret the brass/SiO_2 system behaviour in aerated 1N H_2SO_4 (25°C)

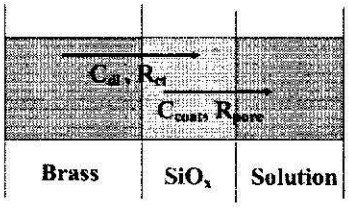
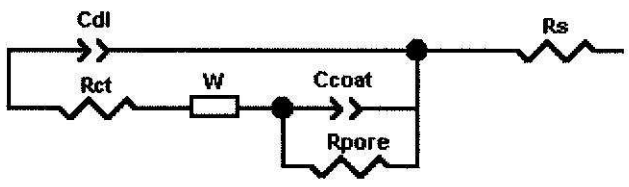


Figure 11 The equivalent circuit used to fit the EIS data of the PECVD coated specimens. C_{dl}: double-layer capacity; R_{ct}: charge-transfer resistance; W: Warburg element (diffusion parameter); C_{coat}: coating capacity; R_{pore}: pore resistance of coating; R_s: solution resistance



"perturbative" technique, the relative contributions of different electrochemical components of the circuit are easier to distinguish than is the case with dc polarisation. Further, it is possible to determine the different frequency zones at which electrochemical effects take place, and link these with the different phenomena occurring to the metal/coating and coating/solution interfaces.

The equivalent circuit proposed is formed by two parallel resistive/capacitive circuits:

1 The first circuit (for the high frequency part of the EIS spectrum) is characterised by the pore resistance (R_{pore}) and the coating capacity (C_{coat}) (Kendig and Scully, 1990; Mansfeld, 1993). From the electrical standpoint, the oxide layer which covers the metal surface acts as the dielectric of a condenser. The oxide film is usually represented by an RC circuit: it depicts the phenomena due to the ionic conduction through pores in the oxide film and the reactions occurring in the SiO_2 layer, which may also be influenced by the presence of the Cu ions, migrating from the substrate into SiO_2 layer. The presence of Cu ions inside the film was confirmed by the SIMS spectra (Figure 6). The presence of these ions was responsible of a very low – but significant – corrosion current in the silica coating. In series with these RC components, the W element, relates to the influence of diffusion phenomena on the system, (Lillard *et al.*, 1995).
2 The second circuit (for the low frequency part of the EIS spectrum) is characterised by the charge transfer resistance (R_{ct}) and the double-layer capacity (C_{dl}), taking into account the corrosion reaction (Faradic current) on a modified coated-brass surface (Bastidas *et al.*, 2000).

The non-ideal electrical behaviour takes into account constant phase elements (CPE) and the already-introduced diffusional impedance element (W) (Liu *et al.*, 2003). After short immersion times (up to 24 h) the EC may become more complicated, because, for example, part of the aggressive solution could penetrate not in a uniform way through coating pores or defects. This heterogeneous distribution of the conducting media can lead to two RC circuits in parallel, as reported by other authors (Castela and Simões, 2003).

For longer immersion times, greater than 24 h, water uptake was completed (this took, on average, at least one day of immersion): and the corrosion proceeded at pores and defects in the coating, according to the hypothesis of almost uniform electrical properties of both film and brass surface. In this way, the EIS spectrum could be simply explained.

The values reached after a week, especially for the thickest layer, indicated good anti-corrosion protection. The most significant R_{ct} value obtained at the end of the exposure period was about 14 $k\Omega\,cm^2$ for the 1,950 nm specimen (168 h), which even at 48 h had already reached about 24 $k\Omega\,cm^2$ (Table II).

These results appeared quite different to those obtained in the DC experiments. Furthermore, *r* the R_{ct} value for the 1,550 nm specimens also diminished over time. This was confirmed by the R_{pore} data trend. Additionally, in this case, the EIS technique was much more useful than the conventional DC techniques, because it permits to obtain more precise information on the corrosive process to be obtained during a long term test, even if localised corrosion

degradation phenomena (for example: pitting) were not evident from visual inspection of the sample.

After 168 h of immersion, a decrease in the C_{coat} value was evident, perhaps due to the hindering of migration of the reaction products in solution that had penetrated into the film. This also meant that the water uptake was essentially complete when C_{coat} no longer varied significantly (Castela and Simões, 2003). At 1 week of exposure the minimum C_{coat} value was only reached by the 1,950 nm coating (about 1,200 μ F/cm^2).

Thus, a result of the electrochemical tests was that a coating 1,950 nm thick, deposited on a brass substrate, successfully resisted the onset of corrosion for at least a week of immersion in the aerated 1N H_2SO_4. All of the other coating thicknesses exhibited lower different performances, though the 1,550 nm layer thickness achieved results that in general were comparable with those from the 1,950 coating. This was a satisfactory result as according to the findings from the salt spray fog test an industrial brass object should resist atmospheric corrosion for at least 10 years if covered by 2 μm of SiO_2 coating.

From the mechanical point of view, the silica film deposited has to maintain both its anti-corrosion and anti-wear layer performance. For this reason the same samples were subjected to the nano-mechanical test. The result was that the as-deposited SiO_2 coating on the brass substrate presented poor mechanical properties, probably due to a high residual film stress, which decreased as the coating thickness was reduced. This behaviour probably could explain the increase of the reduced modulus and the consequent decrease of the elastic recovery observed with lower thickness of silica coating, as reported in Table IV. A significant improvement of the mechanical properties of the SiO_2 coatings was obtained after annealing in oxygen atmosphere at 500°C (1 h). This treatment produced a densification process that smoothed the surface morphology (confirmed also by SEM analysis). Further experimentation and analyses are to be carried out to optimise the annealing procedure.

Conclusions

- "Laboratory" samples of brass coated by SiO_2 were tested by means of electrochemical techniques in a standard very aggressive solution (aerated 1N H_2SO_4 at 25°C) for 168 h. The surface treatment lowered the i_{corr} by almost two orders of magnitude, especially in the case of 1,550-1,950 nm coating thicknesses (1-168 h DC tests).
- AC electrochemical tests (EIS) carried out on samples in the same solution and experimental conditions showed very significant increases in R_{ct} and decreases in C_{coat} only for the samples with a 1,950 nm thick coating. Equivalent circuit modelling gave plausible interpretation of the different components of the degradation process over time (i.e. Cu migration into the SiO_2 coating during the PECVD deposition – water uptake – metal/coating interface).
- SIMS analyses, carried out on "laboratory" samples, made it possible to manage the different parameters of the deposition system and to obtain information on homogeneity and thickness (180-1,950 nm) of the coatings as well as to exclude possible defects of the layers, at least for the thicker coatings.
- Nano-indentation tests revealed large differences in the mechanical properties of as-grown and annealed SiO_2 coatings. The latter exhibited significantly higher hardness and elastic modulus, presumably due to its higher smooth surface structures. Further experimentation and analyses are to be carried out to optimise the annealing procedure for best corrosion and wear properties.

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