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Thickness-properties synergy in organic–inorganic consolidated melting-gel coatings for protection of 304 stainless steel in NaCl solutions

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ABSTRACT

Homogeneous and crack-free methyl-substituted organic–inorganic hybrid glass coatings (thickness up to 10 μm) were deposited on AISI 304 stainless steel. Different hybrid glasses obtained from consolidation of the diluted melting gels with various methyltriethoxysilane (MTES)/dimethyldiethoxysilane (DMDES) ratios were evaluated considering chemical structure, coating adhesion and corrosion protection. The 70MTES/30DMDES (molar%) melting-gel coating provided improved corrosion protection for this steel due to the synergy of different properties: a highly cross-linked inorganic structure, a coating plasticity based on the hybrid network, and a good adhesion to the substrate through hydroxyl groups. Electrochemical results show a good barrier film with a passive range of 500 mV, a low anodic current density (0.03 nA cm^{-2}) and impedance values of $10^{9.5} \Omega \text{ cm}^2$ after two months of immersion in 3.5 wt.% NaCl solution.

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1. Introduction

Stainless steels have excellent corrosion resistance in neutral and alkaline media due to the formation of a surface passive oxide layer based on chromium oxides from chromium in the alloy. This layer is developed at the initiation of the corrosion process and its high stability and density effectively limits subsequent corrosion. However, the presence of chloride ions in the surrounding environment generates localized pitting corrosion due to breakage of the passivation layer based on chromium compounds [1–3]. Therefore additional corrosion protection systems are necessary for the use of stainless steels in environments containing chloride ions. Coatings based on Cr (VI) compounds have been widely used for corrosion protection of different metal substrates based on their high efficiency and low cost. However, its high toxicity leads to the search for alternative coatings that can provide similar protective characteristics.

The sol-gel method is a chemical synthesis technique which allows the preparation of inorganic and organic–inorganic hybrid coatings through hydrolysis and polycondensation reactions of alkoxide groups. High homogeneity and purity of the coating composition and excellent adhesion to metal substrates are some of the main advantages in its application as protective coatings against corrosion of metals. However, the presence of defects in the densified coatings, such as cracks or residual porosity, has limited significantly a practical industrial application in the field of corrosion protection of metal substrates. The number of these defects is higher in coatings with increased inorganic character due to the smaller capacity for releasing stress during the drying and sintering processes. Thin pure silica coatings using tetraethyl orthosilicate (TEOS) as precursor have been prepared on AISI 304 stainless steel with a reduction of the current densities in polarization tests. In general, the improvement provided by inorganic sol-gel coatings is limited because of the small thickness and residual defects [4–6]. For the silicon-based sol-gel coatings, the incorporation of alkoxy-silanes with organic groups attached to the silicon atom has reduced the presence of defects, allowing the preparation of crack-free coatings with thickness greater than 2 μm [7–12]. Other oxides compositions have been evaluated for corrosion protection of this stainless steel [13–23], but their inorganic nature leads to limited protection due to their low thickness and to the presence of defects coming from their inherent brittleness. In contrast, the incorporation of commercial colloidal

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suspension of silica and the electrophoretic deposition (EPD) for the preparation of coatings on AISI 304 stainless steel has allowed the synthesis of thicker coatings with improved corrosion protection properties [24,25].

Our work is based on “melting gels” coatings within the field of materials prepared by sol-gel. The softening behavior of the organic–inorganic melting gels was initially observed by Matsuda et al. [26], who prepared poly(benzylsilsesquioxane) particles, which were then electrophoretically deposited onto an indium tin oxide (ITO) substrate. After heat treatment, continuous thick transparent films were obtained. Later, the melting gel preparation was reported also for systems contain different ratios between a mono-substituted and a di-substituted alkoxides. An example is the system obtained by using phenyltriethoxysilane and diphenyldiethoxysilane [27–29]. Our studies [30,31] were focused on the formation of the melting gels and their organic–inorganic hybrid glasses in the system using methyltriethoxysilane (MTES) along with dimethyldiethoxysilane (DMEDES). The defining property set of these hybrid organic–inorganic melting gels is that they are solid at room temperature, become fluid at a temperature T_1 ($\sim 110^\circ\text{C}$), and can be re-softened many times. However, after consolidation at a temperature T_2 ($T_2 > T_1$), the gels are consolidated and transformed in hybrid glasses. The consolidation temperature appears to correspond to cross-linking of the silica chains in three dimensional networks [29–31]. Curing these gels to temperature T_2 increases the reactivity of retained alkoxy and/or hydroxyl groups allowing cross-linking to the point of forming an irreversible glass network. As a result of the heat treatment at the consolidation temperature, the gels cross-link and densify. The process of softening-becoming rigid re-softening can be repeated many times, as long as the cross linking is not completed by increasing the temperature to T_2 . This property can be used advantageously in processing after preparation of the coatings.

Our previous work [32] in the field of corrosion protection of metal substrates in NaCl solutions was focused on the preparation and characterization of very thick (more than 0.5 mm) hybrid glasses coatings on stainless steel. They showed very good behavior against corrosion in NaCl solutions. However, this high thickness limited the potential industrial applications of this coating. For this reason, the main objective in this work is the preparation of new hybrid glass coatings based MTES and DMEDES on stainless steel, which have a small thickness that can be easily applied as a single layer and is able to maintain excellent anti-corrosion properties. The main obstacle in obtaining thin coatings using the melting gels prepared using MTES and DMEDES is the high viscosity of those gels [33]. In order to overcome this issue the melting gels were diluted with the parental solvent which allowed us to obtain coatings with a controlled thickness by dip coating. An important point in this work is to evaluate the influence of the coating composition (MTES/DMEDES ratio) on the structure, adhesion and corrosion protection provided in NaCl solutions.

2. Experimental section

2.1. Materials and reagents

Two alkoxides were employed, one mono-substituted methyltriethoxysilane (MTES) (Sigma-Aldrich, Milwaukee, WI) and a di-substituted one dimethyldiethoxysilane (DMEDES) (Fluka, Milwaukee, WI). Hydrochloric acid (Fisher Scientific, Atlanta, GA) and ammonia (Fluka, Milwaukee, WI) were used as catalysts while anhydrous ethanol (Sigma-Aldrich, Milwaukee, WI) was used as solvent. Dry acetone (Spectralab, Sigma-Aldrich, Milwaukee, WI) was used to remove ammonium chloride.

2.2. Synthesis procedure and preparation of coatings

The preparation of melting gels was reported before [30,32]. Briefly, the melting gels were prepared as follows (Fig. 1). Four melting gels

Fig. 1. Flowchart for the preparation of the hybrid glass coatings.

with compositions between 60MTES/40DMEDES and 75MTES/25DMEDES (concentration expressed in mol%) which are listed in Table 1 have been prepared for this study. The synthesis had three different steps. First, the water was mixed with hydrochloric acid and with half of the ethanol. Separately, the MTES was mixed with the other half of the ethanol. Then, the solution MTES and ethanol were added dropwise to the water solution under continuous stirring. The container was sealed, and the mixture was stirred at room temperature for 3 h. The molar ratios of MTES:EtOH:H₂O:HCl were 1:4:3:0.01. In the second step, the di-substituted alkoxide DMEDES was diluted with ethanol in a molar ratio of DMEDES:EtOH = 1:4. The DMEDES–EtOH mixture was added dropwise to the first mixture. This resulting solution was kept under continuous stirring in the sealed container at room temperature for two more hours. In the third step, ammonia was added to the mixture, which was stirred for one more hour in the sealed container. The molar ratio of (MTES + DMEDES):NH₃ = 1:0.01. The final solution was stirred for 48 h at room temperature in an open container until gelation occurred. Ammonium chloride was formed as a byproduct during gelation. To remove this, 10 ml of dry acetone was added to the samples. The ammonium chloride was removed by filtration. Then the clear solution was stirred in an open beaker until all the acetone was evaporated. This was followed by a heat treatment at 70 °C for 24 h to remove any remaining acetone and ethanol, followed by another heat treatment at 110 °C for removal of un-reacted water.

From a typical synthesis there are obtained 8.9 ml of melting gels. All the melting gels listed in Table 1 were diluted with 10 ml of the parental solvent, absolute ethanol. The complete dissolving of the melting gels in ethanol took ~ 36 h under a continuous stirring. The consolidation temperatures for each composition are a function of the mol% between MTES and DMEDES. At these temperatures the melting gels are

Table 1

The chemical compositions of the diluted melting gels prepared in the MTES–DMEDES system and their temperature of consolidation.

Sample	Composition		Volume of Ethanol for dilution (ml)	Temperature of consolidation (°C)	Thickness of the hybrid glass coating (μm)
	MTES (mol%)	DMEDES (mol%)			
1	75	25	10	135	5.5 ± 0.3
2	70	30	10	140	4.0 ± 0.3
3	65	35	10	150	4.0 ± 0.3
4	60	40	10	155	10.5 ± 0.3

transformed in hybrid glasses. Those temperatures were established empirically in a previous study [31] and were listed in Table 1.

Coatings have been prepared on AISI 304 stainless steel coupons ($5 \times 7 \text{ cm}^2$). Previously, the metal substrates were degreased, washed with distilled water, rinsed in ethanol and dried at room temperature. The coatings were obtained using a MTI Desktop Dip Coater (Richmond, CA, USA) with adjustable speed. The support was immersed in the solution for 1 min and withdrawn with a speed of 10 cm/min. The coatings were dried at room temperature for 1 h and then dried for 17 h at the temperature of consolidation listed in Table 1.

2.3. Morphological and structural characterization

Dynamic viscosity has been determined via rotational rheometry on an AR-G2 rotational rheometer (TA instruments). The tests were performed using standard DIN concentric cylinders, sample volume 10 ml per test. The first test was performed to check viscosity variation over a range of stress values, 0.001–50 Pa. The test has been performed two ways, increasing applied stress values from 0.001 Pa to 50 Pa, followed by decreasing stress from 50 to 0.001 Pa; each ramp duration was one minute. Steady state of samples was achieved after stress reached 4 Pa up to 50 Pa, after the latter value, applied stress became too high. Subsequently, the second type of tests was conducted to determine viscosity variation over time, by applying a constant stress on the sample, for a certain length of time, stress values being chosen within previously determined “steady state” range, 10 Pa and 50 Pa, respectively. The constant stress was applied for 10 min each for both values.

Standard tests for measuring coatings adhesion by tape test was accomplished using ASTM D3359. Evaluation of thickness and homogeneity on cross-sections of the coated metal substrates was performed by scanning electron microscopy (HITACHI S-4700 field emission) and elemental chemical analysis through energy dispersive X-ray spectroscopy (EDX, NORAN system six). Coated substrates were cut and immersed in a resin; after solidification of the resin, a slide was cut and the “fresh” surface was polished. Then, the surface was sputtering with gold for SEM observations. ToF-SIMS (Time of Flight Secondary Ions Mass Spectrometer) has been used to study the elements distribution depth profile of the coatings (TOF-SIMS⁵ – ION TOF equipment). The analysis was performed over a $26 \times 26 \mu\text{m}$ area using a pulsed 25 kV Bi⁺ ion source. Sputtering was achieved with a 2 kV oxygen beam, and data acquisition and post-processing analyses were carried out using Ion-Spec software. FTIR spectra for the hybrid glass coatings were recorded on a Perkin Elmer Spectrum 100 spectrometer using the Attenuated Total Reflectance (ATR) accessory with a resolution of 2 cm^{-1} . Micro-scratch tests were used in order to analyze the influence of the coating composition on the adhesion of the layers to the substrate. The tests were performed in a “progressive load” mode (Model APEX-1, CETR equipment) with a Conical type diamond (5 mm tip radius), a normal load up to 50 mN, and a scratch of 2 mm length made in 80 s. Normal load applied (Fz), tangential force (Fx), apparent friction coefficient (Fx/Fz) and scratch depth (Z) vs. horizontal displacement (Y) were recorded. The evaluation of the coatings adhesion was complemented by the observation of the residual scratch patterns using scanning electron microscopy (HITACHI S-4700 field emission). All assays were made at least in duplicate in order to confirm repeatability.

2.4. Electrochemical characterization

Analysis of the corrosion protection provided by the coatings was performed using direct current and alternating current electrochemical measurements. The tests were performed in 3.5 wt.% NaCl solution at room temperature using an electrochemical unit (Multichannel Potentiostat VMP3 from Bio-Logic SAS, Low Current channel) with a maximum current resolution down to 76 fA. A three electrode cell was employed using a saturated calomel electrode (SCE) as reference, a platinum mesh as counter electrode and the coated samples as working

electrode with 0.785 cm^2 of exposed area to the testing solution. Potentiodynamic polarization curves of bare and coated metal substrates were performed at a scan rate of 0.167 mV s^{-1} after three hours and two months of immersion in the electrolyte. Electrochemical Impedance Spectroscopy (EIS) was recorded as a function of the immersion time sweeping frequencies from 40,000 to 10^{-3} Hz and modulating 0.015 V (rms) around the open circuit potential. Both tests were made at least in duplicate in order to confirm repeatability.

3. Results and discussion

3.1. Rheological study of precursor solutions

As a general trend, viscosity of all samples varies ever so slightly with the applied stress. The increase in viscosity is more pronounced for the sample with the lowest DMDDES content (25%), while variation becomes less significant when the content of MTES decreases. Yet, analyzing the actual viscosity values change with applied stress (of the order of magnitude of $10^{-3} \text{ Pa}\cdot\text{s}$), presented in Table 2, it can be stated that shear does induce only minor differences in overall viscosity. It is expected that the most important factor in the viscosity change to be samples' composition, as it has been previously observed for the undiluted melting gels. Yet, as seen very clearly in the data presented in Table 2, three of the samples (DMDDES percent range 40–30%) display surprisingly close viscosity values, from 0.013 to 0.015 $\text{Pa}\cdot\text{s}$ at 10 Pa, and from 0.020 to 0.021 $\text{Pa}\cdot\text{s}$ at 50 Pa. What is more, comparing the viscosity values for samples with 40% DMDDES and 30% DMDDES, it is observed that the starting viscosity value at 10 Pa is the same for both (0.013 $\text{Pa}\cdot\text{s}$), while at 50 Pa, samples display only minor difference in viscosity values, 0.021 $\text{Pa}\cdot\text{s}$ for the sample with 40% DMDDES and 0.020 Pa for the sample with 30% DMDDES. The main difference in viscosity values is displayed by the sample with the lowest DMDDES content, this sample stands out by displaying the highest viscosity values at both applied stress (0.045 $\text{Pa}\cdot\text{s}$ at 10 Pa and 0.048 $\text{Pa}\cdot\text{s}$ at 50 Pa). In addition, viscosity values for this sample do not change much between 10 Pa and 50 Pa, a behavior that is different from the rest of the samples. The outstanding feature of the melting gels is however, that their dilution in ethanol does not induce thixotropy, as seen from the measurements performed at constant stress values, 10 Pa and 50 Pa, respectively, meaning that their viscosity remains constant over time when the stress is applied. The non-thixotropic character of the pure and undiluted melting gels was identified previously.

3.2. Cross-section analysis and structural properties of coated substrates

The adhesion of the coatings to the metal substrate was evaluated by scratching the coated surface following ASTM D3359 standard test. All the coatings show a very good adhesion, “the edges of the cuts are completely smooth, and none of the squares of the lattice is detached (Classification 5B)”. As an example, Fig. 2 shows the magnified view of the lattice for the 65MTES/35DMDDES coating; other coatings show the same behavior.

Coatings are transparent and homogeneous without visual evidence of defects. Fig. 3 presents the cross-section SEM micrographs of the four coatings on the metal substrate, showing crack-free layers with a thickness of 10.5 μm for the 60MTES/40DMDDES coating, and thickness

Table 2
Viscosity values for samples measured at 10 Pa and 50 Pa (constant stress measurements).

Sample	Viscosity (Pa·s) 10 Pa	Viscosity (cP) 10 Pa	Viscosity (Pa·s) 50 Pa	Viscosity (cP) 50 Pa
75MTES/25DMDDES	0.045	45	0.048	48
70MTES/30DMDDES	0.013	13	0.020	20
65MTES/35DMDDES	0.015	15	0.021	21
60MTES/40DMDDES	0.013	13	0.021	21

Fig. 2. Optical microscope image of the lattice for the 65MTES/35DMEDES coating after standard test for measuring adhesion by tape test (ASTM D3359).

between 4.0 and 5.5 μm for the other three coatings (Table 1). EDS analysis allows the identification of coatings and substrate; and the study of the interface indicates some interaction between the metal substrate and the coating with diffusion of the elements in both directions. The ToF-SIMS depth profiles of the 70MTES/30DMEDES coating on the metal substrate (Fig. 4) show a homogeneous distribution of silicon in the coating. The metal/coating interface can be located by the intersection of the Si^+ line and Cr^+ and Fe^+ lines. In the case of silicon line, it can be seen how the concentration gradient is wider in the interface area. This behavior can be probably associated with an elements inter-diffusion confirming the EDS results, although the sputtering to reach the interface can also interfere the concentration profile in this area.

Fig. 5 shows the FTIR spectra of coatings in the range of 4000–2800 cm^{-1} and 1600–600 cm^{-1} . The spectra containing the typical

absorption band of OH groups around 3400 cm^{-1} is shown only for the 70MTES/30DMEDES coating. The absence of the stretching frequency of O—H bond can be ascribed to the interactions between hydroxyl groups and hydrolyzed ethoxy groups, creating ion-dipole interactions [34]. In order for the coating to attach to the exposed surface of the stainless steel, OH groups in the 70MTES/30DMEDES are needed. The OH groups probably lead to bonding between the coating and substrate through interaction between Fe and Si oxides/hydroxides, which contributes to the resistance against corrosion. Bands at 2967 and 2938 cm^{-1} are associated to asymmetric and symmetric CH_3 -stretching, and the band at 2911 cm^{-1} in the 70MTES/30DMEDES coating is assigned to asymmetric CH_2 stretching band from residual ethoxy groups [30]. The intensity of $\nu_{\text{asym}} \text{CH}_3$ is unusually enhanced for 70MTES/30DMEDES composition comparing with $\nu_{\text{sym}} \text{CH}_3$. That fact could be related to a higher degree of crosslinking that produces a steric impediment facilitating asymmetric vibration modes [35]. The absorption peaks at 1408 cm^{-1} ($\delta_{\text{as}} \text{CH}_3$) and 1268 cm^{-1} ($\delta_{\text{s}} \text{CH}_3$) confirm the presence of methyl groups. Si—C bonds are detected for all compositions considering the absorbance peaks of $\nu \text{Si—C}$ (686 cm^{-1}) and $\delta \text{Si—C}$ (857 cm^{-1}) [36–38]. The characteristic vibrations bands for a silica network were identified at 760 cm^{-1} for $\nu_3 \text{Si—O—Si}$ and 1001 cm^{-1} for $\nu_{\text{as}} \text{Si—O—Si}$ (TO). The interaction between Si—OH and Fe—OH to produce Si—O—Fe bonds can cause the broadening and downshifting of the band frequency of the asymmetric Si—O—Si stretching (997–978 cm^{-1}) vibration compared to the same vibration in pure Si—O network (1045 cm^{-1}) [39,40]. This band indicates a covalent bond between the metal substrate and the coating [41,42], in agreement with the elements inter-diffusion showed by EDS analysis. On the other hand, TO mode present a higher intensity and shift to higher wave numbers (up to 997 cm^{-1}) for 70MTES/30DMEDES coating involving a strengthening of the band that can be interpreted as a higher degree of network crosslinking [43]. Both effects take place at the same time, being so difficult to confirm the presence of Si—O—Fe bonds due to the proximity of both bands (only 7 cm^{-1}), even after spectra

Fig. 3. Cross-section SEM micrographs of coatings on the stainless steel: a) 75MTES-25DMEDES, b) 70MTES-30DMEDES, c) 65MTES-35DMEDES, and d) 60MTES-40DMEDES. The white lines indicate the interface between coating and substrate based on the results of EDS.

Fig. 4. ToF-SIMS (Time of Flight Secondary Ions Mass Spectrometer) depth profiles of the stainless steel substrate protected with the 70MTES-30DMDES coating.

deconvolution. The vibration ν_{as} Si—O—Si in mode LO can be observed at 1101 cm^{-1} . The higher intensity of those peaks for the 70MTES/30DMDES composition appears to be a result of a higher degree of polycondensation in this composition, generating a highly crosslinked hybrid network. The absence of a band at 896 cm^{-1} related to δ Si—O—C is an indication that most of the ethoxy groups are completely hydrolyzed. However, the 70MTES/30DMDES coating shows a small shoulder in this location, in agreement with the band observed at 2911 cm^{-1} for this composition [32].

Using ^{13}C and ^{29}Si NMR spectroscopy the molecular structures of the hybrid glasses were identified [44]. Quantitative ^{29}Si NMR of the hybrid glasses samples shown characteristic signals to D^1 , D^2 , T^2 , and T^3 . In this study the quantitative measurements were used to identify the final ratio between the mono substituted species $\text{CH}_3\text{-SiO}_3$ and the di-substituted species $(\text{CH}_3)_2\text{-SiO}_2$ which are present in each studied hybrid glass. The NMR spectra revealed the presence of unhydrolyzed Si—OEt groups which in good agreement with the FT-IR data for the sample with composition 70MTES/30DMDES. In addition using a two-dimensional ^{29}Si NMR it was shown more extended structural motifs within the framework, which seems to reveal that two distinct types of T^3 Si environments (the dominant type of Si sites in both materials) exist, that

correspond to Si atoms located in regions with different extents of framework condensation [44].

An additional structural characterization was done using Small Angle X-ray Scattering (SAXS). The SAXS data revealed that the mono substituted species $(\text{CH}_3\text{-SiO}_3)$ and the di-substituted species $((\text{CH}_3)_2\text{-SiO}_2)$ that are coming from hydrolysis and polycondensation of the MTES and DMDES are homogeneously mixed and do not separate to form a well-defined phase structure. In addition, the SAXS data confirmed the absence of any nano- or micro-pores.

Evaluation of adhesion is an important issue for the development of efficient protective coatings on metal substrates, and the under-layer corrosion through blistering can be reduced significantly with well-bonded coatings. Fig. 6 displays the results of the micro-scratch tests (normal load applied (F_z), tangential force (F_x), apparent friction coefficient, F_x/F_z (COF) and scratch depth (Z) vs. horizontal displacement (Y)) and SEM micrographs of the scratch patterns for the four coatings. F_z is the force applied by the equipment that increases gradually and normal to the surface from almost zero to 50 mN. This gradual load is applied on the coating over 2 mm (Y), generating tangential forces (F_x) that the equipment is able to measure. The coefficient of friction (COF) is the relationship between F_x and F_z , and is drawn because in

Fig. 5. FTIR spectra of coatings in the range (a) $4000\text{--}2800\text{ cm}^{-1}$ and (b) $1600\text{--}600\text{ cm}^{-1}$.

Fig. 6. Micro-scratch tests of the coated substrate, showing normal load applied (F_z), tangential force (F_x), apparent friction coefficient, F_x/F_z (COF) and scratch depth (Z) vs. horizontal displacement (Y): a) 75MTES-25DMDES, b) 70MTES-30DMDES, c) 65MTES-35DMDES, and d) 60MTES-40DMDES.

some cases the change between a linear and a saw-shaped behavior indicates the rupture and/or detachment of the coating. Finally, Z is an indication of how the tip penetrates the coating as the load increases, which in some cases allows the detection of the coating detachment depending on the hardness of coating and substrate. All the coatings present a similar behavior, with a smooth trend for F_x and COF curves at low loads, and a rough trend at higher loads. The behavior at low loads is associated with deformation and cracking of the coatings without detachment of films; and the rough behavior at higher loads can be attributed to spallation of the coatings. The changing trend highlights a critical load at which coating peeling occurs widely. The normal load applied for this point is 23, 28, 11 and 10 mN for 75MTES/25DMDES, 70MTES/30DMDES, 65MTES/35DMDES, and 60MTES/40DMDES coating, respectively. The SEM micrographs confirm the location of the critical load for

the coating detachment, leaving visible the metal substrate under the coatings. The 70MTES/30DMDES coating presents improved adhesion to the metal substrate, probably because this composition combines synergistically enough OH groups which improve the bond with the substrate and a suitable ratio of organic and inorganic components which provides flexibility to the coating to deform without causing spallation from the substrate.

3.3. Electrochemical evaluation of bare and coated substrates

For the purpose of analyzing the influence of the percentage of mono- and di-substituted alkoxy silane in the corrosion protection provided by these coatings, polarization curves and impedance measurements as a function of immersion time in 3.5 wt.% NaCl were

recorded. Fig. 7 shows the potentiodynamic polarization curves of the protected substrates after three hours and two months of immersion in comparison with the bare substrate after three hours and 28 days of immersion. As shown in Fig. 7a, the curves of the coated substrates present very long passive ranges (1.2 V) without significant differences between them, suggesting similar resistance of the coatings to the movement of the ions after three hours of immersion. The anodic currents measured on the coated stainless steel are also low: $0.2 \cdot 10^{-3} \text{ nA cm}^{-2}$ for the 60MTES/40DMDES composition, and around 0.2 nA cm^{-2} for the other three compositions. The lower current density of the former is probably associated with the higher thickness of this coating ($10.5 \mu\text{m}$). These results indicate an improvement of 800 mV for the passive range and a reduction of more than three orders of magnitude in the anodic current densities in comparison with the stainless steel reference. The coatings seem to provide an effective barrier protection of the steel substrate, reducing significantly the active area exposed to the aggressive solution. The curves of the coated substrates after two months of immersion (Fig. 7b) show a slight deterioration of the corrosion protection system with a reduction of passive ranges and an increase of current densities as a consequence of electrolyte penetration through residual pores. However, it should be emphasized that both properties have better values compared to the bare substrate after 28 days of immersion. Regarding the behavior of the coatings considering their composition, a trend change is revealed by comparison of the curves obtained after three hours of immersion. The 60MTES/40DMDES coating shows a greater increasing in the anodic current density values after two months of immersion, reaching about 4.0 nA cm^{-2} , despite its higher thickness. The coatings with higher content of mono-substituted alkoxy silane present a slower increasing of anodic current densities probably associated with a higher level of cross-linking which can oppose a better barrier against permeation of the electrolyte (0.62 nA cm^{-2}). The 70MTES/30DMDES coating presents the lowest anodic current density after two months of immersion (0.028 nA cm^{-2}). This behavior can be associated with a good combination of a high level of cross-linking in the structure and adhesion to the substrate, in agreement with the results obtained in IR and micro-scratch tests.

The impedance results confirm the behavior observed previously with the polarization curves (Fig. 8). The four coatings present high total impedance values (around $10^{10} \Omega \text{ cm}^2$) at 10^{-3} Hz during the first day of immersion in the NaCl solution, indicating again the good barrier properties of these coatings in this aggressive electrolyte. The increase of the immersion time up to two months leads to a slow reduction of this total impedance as a result of the electrolyte permeation. The 70MTES/30DMDES coating presents an improved behavior with a slower decreasing of impedance ($10^{9.5} \Omega \text{ cm}^2$), confirming the excellent result shown in the polarization test after two months of immersion. The opposite case corresponds to the 60MTES/40DMDES coating, which has the fastest decreasing reaching the lower impedance value

at 10^{-3} Hz ($10^{7.3} \Omega \text{ cm}^2$). Again, this result agrees with the results of polarization test after two months of immersion that also showed the worst behavior for this coating. The two other coatings, 75MTES/25DMDES and 65MTES/35DMDES, show an intermediate response compared with the previous ones. In order to evaluate in a greater detail the electrochemical behavior of the four coatings, Fig. 9 shows the variation of the impedance modulus at 1 mHz as a function of the immersion time in the NaCl solution showing the values of all tests performed. The results confirm those previously observed in the impedance curves for selected immersion times (Fig. 8). The most important differences between the four coatings occur during the first period of immersion, where a more pronounced reduction in the value of the impedance modulus is observed. In this period, the 60MTES/40DMDES coating shows the fastest impedance reduction, followed by the 75MTES/25DMDES and 65MTES/35DMDES coatings, and finally the 70MTES/30DMDES coating which has the slowest impedance reduction with the immersion time. These results reaffirms that the 70MTES/30DMDES coating combines the proper properties to obtain an efficient corrosion protection system for this stainless steel in NaCl solutions: a high content of mono-substituted alkoxy silane, that produces a high cross-linking in the structure and a good barrier; a sufficient amount of methyl groups attached to the silicon atom, which provides the necessary plasticity to reduce stress and limit the occurrence of defects in the coating; and a good adhesion to the substrate by a combination of both: a well-bonded metal/substrate interface through hydroxyl groups and flexible coatings.

Analyzing the phase angle plot of the four coatings, it is possible to observe that only the 70MTES/30DMDES coating shows values between -50° and -90° . This result indicates a highly capacitive behavior associated with a coating almost free of defects that provides an excellent barrier against the electrolyte permeation. The response of the 70MTES/30DMDES coating during the first day of immersion shows only two time constants, more clearly separated in the phase angle plot. The time constant at frequencies higher than 1 Hz can be associated with the melting-gel coating properties. The slope of the impedance modulus in this region is -0.96 , very close to the value for an ideal capacitor (-1), and a signal of a very good barrier. The second time constant appears below 1 Hz and can be attributed to the passive oxide film on the stainless steel surface. The increase of the immersion time up to 24 days of immersion originates the presence of three time constants: the one at high frequencies associated to the melting-gel coating, and two at lower frequencies attributed to the oxide film and initiation of a charge transfer process at the metal-coating interface. The increase of the immersion time (51 and 66 days) for this coating composition does not cause any changes in the number of time constants, and there is only a shift in the frequency values. However, the electrolyte permeation leads to a reduction of the slope in the high frequency range up to -0.89 after 66 days of immersion. This behavior is also

Fig. 7. Potentiodynamic polarization curves of the coated substrates after (a) three hours and (b) two months of immersion in comparison with the bare substrate after (a) three hours and (b) 28 days of immersion in 3.5 wt.% NaCl solution.

Fig. 8. Electrochemical Impedance Spectroscopy (EIS) measurements of the coated stainless steel substrates after different times of immersion in 3.5 wt.% NaCl solution: a) 75MTES-25DMEDES, b) 70MTES-30DMEDES, c) 65MTES-35DMEDES, and d) 60MTES-40DMEDES in comparison with the bare substrate after one and 28 days of immersion.

observed in the phase angle plot with change from -86° to -73° after one and 66 days of immersion. Regarding the low frequency area, the decrease of the impedance at 10^{-3} Hz with the immersion time can be a consequence of the decreasing of the slope in this section, from -0.84 to -0.75 , is also attributed to the permeation of electrolyte. Nevertheless, the impedance values after two months of immersion are three

orders of magnitude higher than that of the bare substrate during the first day and after 28 days of immersion. These results confirm that this coating provides a good corrosion protection of AISI 304 stainless steel in NaCl solutions. The 60MTES/40DMEDES coating presents a different behavior, although the slope of the impedance modulus at high frequencies (-0.96) during the first day of immersion is similar than that

Fig. 9. Variation of impedance modulus at 1 mHz versus immersion time of the coated stainless steel substrates in 3.5 wt.% NaCl solution.

observed for the 70MTES/30DMDES coating, showing only two time constants. However, after only three days of immersion a drop in the phase angle plot is observed than can be attributed to the presence of some paths in the coating for the electrolyte permeation, and the presence of a charge transfer process at the metal-coating interface at low frequencies. The subsequent increase in the immersion time does not lead to changes in the shape of the curves, although a shift of the time constant at intermediate frequencies is observed. This displacement is the result of the reduction of the coating resistance to the passage of the ions through the defects. The two remaining compositions (75MTES/25DMDES and 65MTES/35DMDES) exhibit an intermediate behavior, although during the first day of immersion, high impedance values and only two time constants are obtained. At longer immersion times, the three processes associated with coating properties, oxide film and charge transfer process at the interface can be observed.

4. Conclusions

Homogeneous and crack-free hybrid glass coatings (thickness up to 10 μm) obtained by consolidation of diluted melting gels based on methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES) were obtained on AISI 304 stainless steel. After evaluation of different MTES/DMDES ratios, the 70MTES/30DMDES coating presents improved behavior for corrosion protection of this steel in NaCl solutions. It seems that this composition combines the right mix of properties: 1) a highly cross-linked inorganic structure that provides a good barrier against the electrolyte penetration; 2) an appropriate amount of methyl groups attached to the silicon atom that affords plasticity, facilitating stress release without producing defects in the coatings; and 3) a good adhesion of the coating to the substrate based on bonds at the interface through hydroxyl groups and coating flexibility that allows the deformation of the coating without a premature detachment.

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