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Chapter

Infrared Characterization and Electrochemical Study of Silanes Grafted into Surface of Copper

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Abstract

The formation of a protective layer of tow silane coupling agents: γ -methacryloxypropyltrimethoxysilane (γ -MPS) or γ -aminopropyltriethoxysilane (γ -APS) on copper is studied by diffuse reflectance infrared spectroscopy (DRIFT), electrochemical (Potentiodynamic polarization) and gravimetric chemical (Weight loss) measurements. Dried in ambient conditions, the silane adsorbed on the copper subtract physically, however its protective action is not reliable. Thiolate and siloxane band formation ameliorate the protective action of the silanic layer on the surface of copper especially after curing process. Potentiodynamic polarization and Weight loss experiments show that the performances protective action of cured treatment (cured/Cu-silane) is higher than that of aging process (aged/Cu-silane).

Keywords: hybrid coating, copper, corrosion, silanic compounds, infrared spectra

1. Introduction

The corrosion behavior of copper and its alloys has been extensively studied for a wide range of experimental conditions. For example, there are the dominant materials for sea water systems in many countries. In chloride-rich media, the naturally oxide formed layer is insufficient to improve the anticorrosion propriety and coating is required for providing a higher protection level. Surface treatment based on the use of chromate conversion layer is efficient for corrosive protection of metal [1]. However, toxic and carcinogenic characteristics of chromate and similar hexavalent chromium compounds resulted in legally limited use.

Organic coating adhesion to metal substrates is one of the most important physical properties for corrosion resistance. Recently, the corrosion protective performance of coupling agent attracts the attention of several researchers. In fact, silane surface treatment is can be considered as an environmentally friendly alternative to chromatation [2].

Silane coupling agents are commonly used for the pre-treatment of metal surfaces to increase adhesion between polymeric (i.e., the paint) and inorganic materials (i.e., the metal). This twofold function of the coupling agent is due to their chemical structure, corresponding to general formula R–Si–(OR')₃, where R is an organo-functional group (amine, mercapto, epoxy, methacrylic, vinyl, etc.) whose role is to establish a chemical band with the organic coating and R'stands for an alkyl group (generally Et or Me) [3].

The principle of the adhesion of silane coupling agents on inorganic specimens is based on the siloxane function (Si–OR') reactivity. Th later is hydrolysed to Si–OH. Two reactions (hydrolysis: Eq. (1) and condensation: Eqs. (2) and (3)) take place [4]:

$$RSi(OR')_3 + 3H_2O \rightarrow RSi(OH)_3 + 3R'OH$$
(1)

$$RSi(OH)_3 + (OH)_3SiR \rightarrow RSi(OH)_2 - O - (OH)_2SiR + H_2O$$
 (2)

$$RSi(OH)_3 + (R'O)(OH)_2SiR \rightarrow RSi(OH)_2 - O - (OH)_2SiR + R'OH$$
(3)

These three reactions display the importance of hydrated environment in the condensation reactions taking place between the coupling agent and the metallic surface, and which will take place on the copper surface according to the following reactions (Eqs. (4) and (5)):

$$RSi-OH + OH-Cu(surface) \rightarrow RSi-O-Cu + H_2O$$
(4)

$$RSi-OR' + OH-Cu(surface) \rightarrow RSi-O-Cu + R'OH$$
 (5)

The object of the present study is to investigate the adsorption of γ -MPS and γ -APS onto pure copper at different dried conditions and to study the possibility of using these two-coupling agent's treatment on copper in order to enhance its corrosion protective performance.

2. Experimental

For all experiments, we made use of copper sample of purity 99.99%. The copper electrodes were masked by epoxy resin, leaving 28.3 mm² as the working surface. Before each test, the exposed surface of copper was polished by SiC paper to # 1200 and rinsed with distilled water, degreased with acetone, hot air flux dried and instantly plunged in the silanic solution. The objective of all these cleaning steps is to remove of contamination and to introduce the hydroxyl group into a copper surface. The silane coupling agent solution was obtained by dissolving γ -MPS or γ -APS (5% vol./vol.) in ethanol (90% vol./vol.) and distilled water (5% vol./vol.) at ambient temperature for 10 min.

Prior to coating treatment, the coupling agent solutions were stirred for 120 min to allow the hydrolysis of the Si-OC₂H₅ groups. The organosilanes employed in this work were γ -methacryloxypropyltrimethoxysilane, (γ -MPS) and γ -aminopropyl-triethoxysilane, (γ -APS), with a high purity (98%). The chemical structures of these compounds are schematically represented in **Figure 1**.



Figure 1. *The molecular structure of* γ *-MPS (a) and* γ *-APS (b).*

All experiments were executed only on dipped substrate and dried at room temperature for 1440 min (aged/Cu-silane) and cured at 100°C for 60 min (cured/Cusilane). After silanization step, all specimens were washed with ethanol for 5 min.

The Fourier transformed infrared (FT-IR) analysis was carried out using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Therefore, in order to analyze the chemical groups presented on the surface, we used the diffuse reflectance mode (DRIFT). The obtained spectra of the modified substrate were obtained by means of the diffuse reflectance accessory. The spectrum was recorded with a resolution of 2 cm⁻¹, with a total of 20 scans. The spectra were treated using BOMEM GRAMS software for the deconvolution of different region of the spectrum.

Potentiodynamic polarization curves were plotted from -400 to 600 mV/SCE at a polarization scan rate of 0.5 mV/second. Before all experiments, the potential was stabilized at free potential during 30 min. To guarantee the reproducibility, at least four replicates were run for each experiment. Electrochemical measurements were taken using an electronic potentiostat galvanostat radiometer controlled using the Volta Lab software. While, the electrochemical analyses were conducted under computer control.

For all tests, electrochemical experiments were performed using a standard three-electrode cell configuration. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum sheet with 2 cm² totals surface area was used as counter electrode. All potentials values given in this work were referred on the SCE electrode. Electrochemical measurements were performed in aerated NaCl 3 wt % solution, at 298 \pm 1 K.

The gravimetric measurements were performed under ambient conditions using an analytical balance (precision ± 0.1 mg). The dimension of the rectangular copper coupons was $31 \times 8 \times 8$ mm. After weighing, the treated coupons were suspended in our saline solution for different exposure periods (3 – 12 days). Then, the surface of the specimens was carefully washing and degreased with ethanol and acetone, dried at room temperature and then weighted. Triplicate experiments were carried out in each case and the mean weight losses were reported.

3. Results and discussion

3.1 Characterization of silane film formed on copper

In order to demonstrate the interaction mechanisms between silane coupling agents and substrate, the treated surface is submitted to: (i) only dipped specimens and dried at room temperature for 1440 min followed by washing with ethanol for 10 min (aged/Cu-silane) and (ii) heat treated at 100°C for 60 min followed by washing with ethanol for 10 min (cured/Cu-silane).

Figure 2 shows the FT-IR spectra of a pure γ -MPS (a) and the DRIFT of aged/Cu-MPS (b) and cured/Cu-MPS (c) in the region 4000-400 cm⁻¹. The band assignments for the pure γ -MPS are presented in **Table 1** [5].

It can clearly see that the spectrum of pure γ -MPS is different to the modified specimens (Cu-MPS) spectra.

In the spectra of aged/Cu-MPS and cured/Cu-MPS, the band around 2841 cm⁻¹ corresponds to C-H stretching vibrations of the methoxy groups decrease and move to higher frequencies (2890 cm⁻¹). This designates a performs hydrolysis in the Si-OCH₃ linkages of the γ -methacryloxypropyltrimethoxysilane molecules attached on the substrate. These two spectra reveal an extensive band about 3427 cm⁻¹ corresponded to OH stretching of Si-OH groups (hydrolysed Si-OCH₃) but only a decrease is detected in this band after cured treatment. The similar phenomenon is observed for Si-OH



Figure 2.

FT-IR spectrum of pure γ -MPS (a) and DRIFT spectra of aged/Cu-MPS (b) and cured/Cu-MPS (c) (4000–400 cm⁻¹ region).

Band position (cm^{-1})	Assignments	
2945	CH ₃	$\nu_{as}(C-H)$
2841	O-CH ₃	ν _s (C-H)
1720 ²	methacrylic	ν(C=O)
1638	methacrylic	ν(C=C)
1454	CH ₂	δ(C-H)
1404	Si-CH ₂	δ(Si-C)
1320	C-O-C	$\nu_{as}(C-O)$
1296	C-O-C	ν _s (C-O)
1191	O-CH ₃	ρ(O-C)
1167	CH ₃	δ(C-H)
1089	Si-O-C	$\nu_{\rm as}(C-O)$
1012	Si-O-Si	δ_{as} (Si-O)
980	Si-O-Si	δ_{s} (Si-O)
940	C=C-C=O	$\delta_{s}(C=C)$
818	C=C-C=O	$\delta_{as}(C=C)$

Table 1.

The FT-IR vibration band positions and their assignments of γ -MPS.

bond at 905 cm⁻¹. These evolutions prove the beginning of the silane condensation step. Moreover, the relatively higher Si-OH bands of uncured specimens, maybe due to the entrapped of water in the γ -MPS xerogel. A simulation of the spectrum region between 1770 and 1650 cm⁻¹ (**Figure 3**) shows that after curing treatment, a decrease in C=O—HO bonding, giving a peak at around 1700 cm⁻¹, compared with the band at 1720 cm⁻¹ assigned to $\nu_{C=O-free}$ [6]. This characterizes the interaction between –OH group (silanol and/or water) and C=O group.



Figure 3. C=O band deconvolution of Aged/Cu-MPS (a) and cured/Cu-MPS (b) (1770–1650 cm⁻¹ region).



Si-O band deconvolution of Aged/Cu-MPS (a) and cured/Cu-MPS (b) (1250–950 cm⁻¹ region).

The bands characteristic of the different Si-O forms are observed in the region from 1250 cm⁻¹ to 950 cm⁻¹ in DRIFT spectral. A deconvolution of this region spectrum is used to elucidate the evolution of different Si-O forms (**Figure 4**). The

presence of the peaks at around 1183 and 978 cm⁻¹ indicates that the hydrolysis process remains unaffected (Si–OCH₃ remaining) [7]. The decreases of these bands, after heat curing (**Figure 4b**), recommend the auto-condensation of the methoxy groups and/or the grafting of coupling agent onto copper surface. As described in a previous research [8], the curing process can accelerate the condensation. The increase in the Si–O–Si bond, at around 1138 cm⁻¹ and 1206 cm⁻¹, signify an intermolecular condensation between adjacent adsorbed –Si–OH groups. These results are in good agreements with those of other studies dealing with glass surfaces coated with the tow similar silanes [9]. Finally, **Figure 2b** and **c** also shows.

Finally, it can also be seen from **Figure 2b** and **c** the existence of several peaks in the region of the infrared spectrum from 850 cm⁻¹ to 400 cm⁻¹, particularly after curing. This is may be caused by the Cu–O band [8, 10].

In the case of γ -APS modified copper, DRIFT spectra of the aged/Cu-APS (a) and cured/Cu-APS (b) are exhibited in **Figure 5**. For the reference, the FT-IR spectrum of modified substrate has been superposed in this figure. Significant changes in the intensity of the bands can be clearly seen in the range from 1250 to 850 cm⁻¹ [11]. For the FT-IR spectrum of γ -APS (**Figure 5c**), the absorption bands at 1167, 1104, 1080 and 957 cm⁻¹ related to Si-O-C₂H₅ group disappeared after silanization in an aqueous solution. The major IR absorption peaks and tentative assignments band for pure γ -APS are cited in our previously work [8].

A new broad band at around $1010-1140 \text{ cm}^{-1}$, characteristic of siloxane bonds, appeared instead in the DRIFT Spectra, signifying that most ethoxy groups were hydrolyzed and Si–O–Si linkages were formed on the surface by condensation and lateral polymerization of γ -APS. These absorption bands become clearer after curing treatment. This means that there is an evolution toward better interconnected



Figure 5.

Infrared spectra for fresh/Cu-APS (a), aged/Cu-APS (b), cured/Cu-APS (c) and aged-cured/Cu-APS (d) $(850-400 \text{ cm}^{-1} \text{ region})$.

networks [12, 13]. Contrary to the aging process, after curing this coupling agent adsorption via both physical and chemical interactions, so that chemisorption has been suggested to be the dominant adsorption mechanism. As previously reported [8, 11], the Si–O–Si stretching band at higher frequencies is due to cyclic siloxane units, and the lower one is assigned to the long Si–O–Si chains. After curing treatment, the proportion of the Si–O–Si chains peak (close to 1012 cm⁻¹) increases. This indicates that the higher temperature of treatment has a significant effect on the structure of γ -APS films. More Si–O–Si chains will be formed on the film and may contain fewer defects. Moreover, **Figure 5a** reveals the presence of a weak absorption band at around 920 cm⁻¹ corresponding to the Si-O stretching of residual Si-OH groups. The intensity of this absorption band decreases sharply after heat treatment (**Figure 5b**), indicating additional polymerization of the adsorption γ -APS. Finally, the increase of Si-CH₂(CH₂CH₂) band at 1193 cm⁻¹, after heat treatment process, implies an increase in the silane quantity at the metal surface.

Finally, it can be concluded from infrared results, that the greater temperature of curing may favor both the surface condensation process (formation of Cu-O-Si bands in the interfacial layer through the reaction between Si–OH groups, and the hydroxylated copper surface) and the Si–O–Si linkages formation.

3.2 Corrosion protection

3.2.1 Potentiodynamic polarization

The polarization curves of pure copper (i.e., the blank) (a), aged/Cu-MPS (b), cured/Cu-MPS (c), aged/Cu-APS (b) and cured/Cu-APS (e) in aerated NaCl 3 wt % aqueous solution are shown in the **Figure 6**. It is well known that the cathodic part of the polarization curves can be divided into three regions of potential: Region I corresponds to the weak polarization region near OCP; Region II is associated to the reduction of dissolved oxygen (Eq. (6)); and Region III (below - 320 mV) is attributed to the hydrogen evolution rection given in Eq. (7) [14, 15]:



$2H_2O + 2e^- \to 2OH^- + H_2$ (6)

Figure 6.

Potentiodynamic polarization curves of Cu (a) aged/Cu-MPS (b), cured/Cu-MPS (c), aged/Cu-APS (d) and cured/Cu-APS (e), in NaCl 3 wt % solution.

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$$O_2 + 2H_2O + 4e^- \to 4OH^-$$
 (7)

It could be observed that the pH value of the solution after the electrochemical experiments is a little higher than that before the experiment.

The anodic part of the curve copper shows three main regions to [15, 16]:

In the first region, an apparent Tafel behavior is observed and the current density increases up to a critical passivation value (J_{cp}) , due to the oxidation of Cu (0) to Cu(I) (Eq. (8))

 $Cu \rightarrow Cu^+ + e^-$

In the second region, The current density decease from J_{cp} to full passivation current density (J_{pas}). Cu(I) is rapidly transformed to an insoluble CuCl film (Eq. (9)) [17].

$$Cu^+ + Cl^- \to CuCl \tag{9}$$

(8)

In aqueous solution, CuCl would be unstable. It is immediately converted to the soluble cuprous complex $CuCl_2^-$ (Eq. (10)) [18]. The current density suddenly increases again from J_{pas} to elevated anodic potential. We detected a small full passivation field (7 mV) in the case of the untreated copper. Thus, the dissolution of substrate is happening step by step.

$$CuCl + Cl^{-} \rightarrow CuCl_{2(surface)}^{-}$$
(10)

In the third region, the potential increases again before to stabilize when it reaches a limiting current density. $CuCl_2^-$ is oxidized to Cu^{2+} ions according to the following reactions (Eqs. (11) and (12)):

$$CuCl_{2(surface)}^{-} \rightarrow CuCl_{2(solution)}^{-}$$
 (11)

$$CuCl_{2 (solution)}^{-} \rightarrow Cu^{2+} + 2Cl^{-} + 2e^{-}$$
(12)

However, according to some authors, other corrosion products could be also formed, such as Cu_2O , CuO, $Cu(OH)_2$ [14, 19–22].

Figure 6 also shows that the specimen coated with silane coupling agents have a different behavior for untreated copper. In addition, both cathodic and anodic current decreased and the corresponding slopes vary, which indicated that the γ -MPS or γ -APS coating is mixed-type corrosion coating, i.e. inhibitor and barrier coating.

The electrochemical parameters such as E_{corr} , corrosion potential, J_{corr} , corrosion current density, β_c , cathodic and β_a , anodic slopes, R_p , polarization resistance, CR, corrosion rate and P_{EF} , protective efficiency are calculated according to polarization curves and summarized in **Table 2**. The values of J_{corr} and E_{corr} were obtained by the extrapolation of anodic and cathodic Tafel curves. The R_p values are calculated by the next formula (Eq. (13)) [18],

$$R_p = \frac{B}{J_{corr}} \tag{13}$$

here, *B* is a constant that is calculated by using Stern–Geary equation (Eq. (14)) [23],

$$B = \frac{\beta_c \beta_a}{2.303(\beta_c + \beta_a)} \tag{14}$$

Solution	Parameters							
	E _{corr} (mV)	J _{corr} (μA cm ⁻²)	-β _c (mV/ dec)	$egin{array}{c} eta_a \ ({ m mV}/{ m dec}) \end{array}$	R_p (k Ω cm ²)	CR (mmy)	P _{EF} %	
Cu	-220	17.78	104	58	1.07	0.207	_	
aged/Cu-MPS	-224	2.85	103	55	5.46	0.033	84.06	
cured/Cu-MPS	-195	0.63	82	30	15.14	0.007	96.62	
aged/Cu-APS	-192	3.31	270	85	8.48	0.038	81.64	
cured/Cu-APS	-180	2.14	150	70	9.68	0.025	87.86	

Electrochemical kinetics parameters and protective efficiency obtained from potentiodynamic polarization curves.

The values of corrosion rate (*CR*, millimeters per year (mmy^{-1})) are calculated using the expression (Eq. (15)) [8],

$$CR = 3.268 \times 10^3 \frac{J_{corr}}{\rho} \frac{MW}{Z}$$
(15)

where ρ is the density of Cu in g.cm⁻³ (= 8.92), MW is molecular weight of copper in g and Z is the number of electrons transferred in the corrosion reaction; Z = 2 in the case of Cu reaction.

After silane-modified copper surface, the potentiodynamic polarization curves moved toward anodic direction and toward less current density. The values of corrosion potential shift in the positive direction, denoting the beneficial effect of the two coupling agents' treatments on copper substrate corrosion. These two treatments produce best results mainly on the copper anodic oxidation reaction when the coating is the γ -APS, whose currents are reduced by about two orders of magnitude, at 0 mV/SCE. Nevertheless, the cathodic currents are reduced only by about one order of magnitude for the tow used coupling agents.

Table 2 also depicts that the values of J_{corr} and *CR* decease, after treatments, while the protective efficiency increases sharply to reach 96.62% for the cured/Cu-MPS specimen). By leaving the silane coupling agent coating in contact with the substrate for 24 h, Si–O–Si linkages formation begins to take place. This generates a more robust and adherent coating. The notable hindrance to the copper anodic oxidation process, watched from the noticeable diminution in corrosion current density and corrosion rate values and the increase in the polarization resistance and the protective efficiency, can mostly be ascribed to the strong Si–O–Si linkages [11]. The corrosive attack can be demonstrated only in the coating holes and after a period of time it causes a noticeable attack of the metal. Additionally, heat treatment helps the interconnected networks of the coupling agent on the surface through the elimination of water molecules [24]. More condensation takes place mostly in the outermost part of the silane film, leading to a polymolecular, denser, less permeable and, consequently, more corrosion resistant coating.

Figure 6 also reveals that the untreated copper immersed in saline solution reaches passivity in a typical active-passive transition. Coupling agent modified copper in NaCl 3 wt % aqueouse solution features much wider potential range of full passivation, which offers further protection at elevated values of positive potential. The electrochemical parameters such as J_{cp} , critical current density of passivation, E_{cp} , critical passivation potential, J_{pas} , full passivation current density, E_{pas} , full passivation potential, E_{tp} , trans-passivation potential and ΔE , passivation range are listed in **Table 3**. Compared with the untreated copper (i.e., the blank), the E_{pas} and E_{cp} values shifted toward the cathodic direction and the J_{pas} and J_{cp} values decrease abruptly. The move of E_{pas} and E_{cp} values toward cathodic potentials demonstrates higher corrosion resistance of the coupling agent modified copper. Moreover, the lower value of full passivation current density verifies a better tightness on the silane film formed on the copper surface after treatments.

The passivation ability of the substrate corresponding to the significant criterion of passivation kinetics is verified through the drop of J_{cp} value. Indeed, the area delimited by the peak of activity, identified by J_{cp} , corresponds to the amount of electricity required for the passivation of the material. The weak dissolution of the material is, on its side, verified by the decrease of this surface which is easily passive. These phenomena become more pronounced when the used silane is γ -APS.

In the fully passive range, the current density is independent of the potential. When the potential of full passivation finishes, E_{tp} is reached. After this, the passive film continuity is damaged and the metal gets trans-passivated.

The passivation of silane-modified copper becomes more rapid and the passivation range, characterized by the difference between E_{tp} and E_{pas} ($\Delta E = E_{tp} - E_{pas}$), is more extensive than that of pure copper. This confirms the relatively high corrosion resistance of silane modified copper.

At the end of the passivation, an unexpected increase in the current density has been detected, along with the evolution of molecular oxygen as well as the return of the active area, where copper dissolution takes place.

3.2.2 Gravimetric measurements

To investigate the effect of the treatments on the corrosion inhibition of copper in aerated NaCl 3 wt % aqueous solution at ambient temperature, gravimetric measurements were carried out. **Figure** 7 shows the plot of the weight losses versus time curves of specimen blank (a) aged/Cu-MPS (b), cured/Cu-MPS (c), aged/Cu-APS (d) and cured/Cu-APS (e). The weight loss (Δm , mg cm⁻²) and the corrosion rate (*CR*, mg cm⁻¹ h⁻¹) were calculated as follows (Eqs. (16) and (17)) [25]:

$$\Delta m = \frac{W_1 - W_2}{A} \tag{16}$$

$$CR = \frac{\Delta m}{t} \tag{17}$$

Where, W_1 and W_2 are the weight before and after exposure to saline solution, respectively, A is the total surface area and t is the immersion period.

According to **Figure 7**, the weight losses of untreated copper in NaCl 3 wt % solution increases with the increase in the immersion period as a result of the

Solution	Parameters							
	$\overline{E_{cp}}$ (mV)	J_{cp} (µA cm ⁻²)	E_{pas} (mV)	J_{pas} (μ A/cm ²)	E_{tp} (mV)	$\Delta E (mV)$		
Cu	7	7586	40	1288	47	7		
aged/Cu-MPS	-41	2690	-25	1170	40	15		
cured/Cu-MPS	-43	2570	-30	1410	46	16		
aged/Cu-APS	-57	138	-46	126	-3	43		
cured/Cu-APS	-55	105	-47	112	-2	45		

Table 3.

Characteristic passivation parameters obtained from potentiodynamic polarization curves.



Figure 7.

Variations of the weight losses with time for Cu (a) aged/Cu-MPS (b), cured/Cu-MPS (c), aged/Cu-APS (d) and cured/Cu-APS (e), in NaCl 3 wt % solution.



Figure 8.

Variations of the corrosion rate with time the different treatments.

continuous dissolution of copper ions, due to the severe aggressiveness of the chloride ions.

aged/Cu-MPS decreases the weight loss of specimen, especially after 3 and 6 immersion days. Above this period, the weight loss value increases significantly to reach the value obtained for blank specimen after 12 immersion days. A further decrease in the loss of weight took place after curing and/or when the coating is γ -APS. The advantageous effect endures until 9 days of immersion, which indicates an improvement in coupling agent film durability. In fact, curing treatment catalyzes the formation of both chemisorbed and polymerized product forming more robust coupling agent layer. Nevertheless, after 12 immersion days this layer cannot resist whatever the silane coating used. This is also illustrated by the **Figure 8**, from which it can be seen that, after this period, there is no notable difference of the corrosion rate obtained for the untreated or silane coated copper.

4. Conclusions

The main conclusions of this study are summarized below:

• Room temperature aging allows a certain condensation between the loosely adsorbed silane molecules, which relatively improves the performances of the silanic layer.

- Curing treatment may favor both the surface condensation process (formation of Cu-O-Si bands in the interfacial layer through the reaction between silanol groups and the hydroxylated copper surface) and the siloxane band formation.
- $\gamma\text{-MPS}$ and $\gamma\text{-APS}$ act as mixed corrosion inhibitor for copper in NaCl 3 wt % solution.
- The corrosion protection offered by coupling agent coating is due to both the blocking of copper surface parts with the reduction of oxygen and the metal dissolution occurring in the pores of the coating layers.
- A relatively high corrosion resistance of γ -MPS modified copper, especially after curing treatment, was remarked. Therefore, the passivation zone is more extensive when the coating is γ -APS.
- Gravimetric results show that the curing process leads to lower weight loss for the silane film, chemisorbed at the copper surface, after 3 and 6 immersion days. However, after 12 days of immersion this film cannot resist whatever the silane used.

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References

[1] Van Ooij WJ, Zhu D, Stacy M,
Seth A, Mugada T, Gandhi J, Puomi P.
Corrosion Protection Properties of
Organofunctional Silanes-An Overview.
Tsinghua Science & Technology. 2005;
10:639-664.

[2] Subramanian V, Van Ooij WJ. Silane based metal pretreatments as alternatives to chromating:Shortlisted. Surface Engineering. 1999;15:168-172.

[3] Cecchetto L, Denoyelle A, Delabouglise D, Petit JP. A silane pretreatment for improving corrosion resistance performances of emeraldine base-coated aluminium samples in neutral environment. Applied Surface Science. 2008;254:1736-1743.

[4] Arkles B, Steinmetz JR, Zazyczny J, Mehta P. Factors contributing to the stability of alkoxysilanes in aqueous solution.Journal of Adhesion Science and Technology. 1992;6:193-206.

[5] Masmoudi M, Abdelmouleh M, Abdelhedi R. Infrared characterization and electrochemical study of γmethacryloxypropyltrimethoxysilane grafted in to surface of Copper. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014; 118:643-650.

[6] Abdelmouleh M, Boufi S, Ben Salah A, Belgacem, MN Gandini. Interaction of Silane Coupling Agents with Cellulose. Langmuir. 2002;18: 3203-3208.

[7] Kozelj M, Vuk AS, Jerman I, Orel B. Corrosion protection of Sunselect, a spectrally selective solar absorber coating, by (3-mercaptopropyl) trimethoxysilane. Solar Energy Materials & Solar Cells. 2009;93:1733-1742.

[8] Masmoudi M, Rahal C, Abdelmouleh M, Abdelhedi R. Hydrolysis process of γ-APS and characterisation of silane film formed on copper in different conditions. Applied Surface Science. 2013;286:71-77.

[9] Li C, Yin Y, Hou H, Fan N, Yuan F, Shi Y, Meng Q. Preparation and characterisation of $Cu(OH)_2$ and CuOnanowires by the coupling route of microemulsion with homogenous precipitation. Solid State Communications. 2010;150: 585-589.

[10] Yan X, Xu G. Surface Coating Technology. Synergy effect of silane and CTAB on corrosion-resistant property of low infrared emissivity Cu/ polyurethane coating formed on tinplate. 2010;204:1514-1520.

[11] Rahal C, Masmoudi M, Abdelmouleh M, Abdelhedi R. An environmentally friendly film formed on copper: characterization and corrosion protection. Progress in Organic Coatings. 2015;78:90–95.

[12] Ishida H, Naviroj S, Tripathy SK, Fitzgerald JJ, Koenig JL, The Structure of an Aminosilane Coupling Agent in Aqueous Solutions and Partially Cured Solids. Journal of Polymer Science. 1982; 20:701-718.

[13] Song J, Van Ooij WJ. Bonding and corrosion protection mechanisms of γ -APS and BTSE silane films on aluminum substrates. Journal of Adhesion Science and Technology. 2003;16:2191-2221.

[14] Liao X, Cao F, Zheng L, Liu W, Chen A, Zhang J, Cao C. Corrosion behaviour of copper under chloridecontaining thin electrolyte layer. Corrosion Science. 2011;53:3289-3298.

[15] Masmoudi M, Rahal C, Abdelhedi R, Khitouni M, Bouaziz M. Inhibitive action of stored olive mill wastewater (OMW) on the corrosion of copper in a NaCl solution. RSC Advances. 2015;5: 101768-101775. [16] Otmacic H, Lisac ES. Copper corrosion inhibitors in near neutral media. Electrochimica Acta. 2003;48: 985-991.

[17] Refait P, Rahal C, Masmoudi M.
Corrosion inhibition of copper in 0.5 M
NaCl solutions by aqueous and
hydrolysis acid extracts of olive leaf.
Journal of Electroanalytical Chemistry.
2020;859:113834-113843.

[18] Rahal C, Masmoudi M, Abdelhedi R, Sabot R, Jeannin M, Bouaziz M, Refait P. Olive leaf extract as natural corrosion inhibitor for pure copper in 0.5 M NaCl solution: A study by voltammetry around OCP. Journal of Electroanalytical Chemistry. 2016;769: 53–61.

[19] Sherif EM, Erasmus RM, Comins JD. Corrosion of copper in aerated synthetic sea water solutions and its inhibition by 3-amino-1,2,4-triazole. J. Colloid Interface Science. 2007;309:470-477.

[20] Chu C, Lee C, Wang Y, Wan C, Chen C. The role of cuprous ion as corrosion inhibitor for copper in a chloride medium. Journal of the Chinese Institute of Chemical Engineers. 2007; 38:361-364.

[21] Scendo M. Inhibition of copper corrosion in sodium nitrate solutions with nontoxic inhibitors. Corrosion Science. 2008;50:1584-1592.

[22] Kear G, Barker BD, Walsh FC, Electrochemical corrosion of unalloyed copper in chloride media–a critical review. Corrosion Science. 2004;46: 109-135.

[23] Zhong X, Li Q, Hu J, Yang X, Luo F, Dai Y. Effect of cerium concentration on microstructure, morphology and corrosion resistance of cerium–silica hybrid coatings on magnesium alloy AZ91D. Progress in Organic Coatings. 2010;69:52-56. [24] Doidjo MRT, Belec L, Aragon E,
Joliff Y, Lanarde L, Meyer M,
Bonnaudet M, Perrin FX. Silane
Coupling Agent for Attaching FusionBonded Epoxy to Steel. Progress in
Organic Coatings. 2013;76:1765-1777.

[25] Sherif EM, Park SM. 2Amino5ethyl-1,3,4-thiadiazole as a corrosion inhibitor for copper *in* 3.0% NaCl solutions. Corrosion Science. 2006;48; 4065-4079.

