

Corrosion Behaviour of Room Temperature Cured Polysilazane-Derived Silica Coatings on Al 5086

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Abstract— Silica coatings from polysilazane precursors were prepared to protect aluminium substrates from corrosion. Polysilazane can be converted to silica by simple exposition to air or basic vapours and the properties of the synthesized film make this precursor a valuable choice to obtain solid, crack-free, highly adhesive and protective coatings. The optimal deposition, obtained at 15 cm min^{-1} of dip-coating withdrawal speed, 20% PHPS precursor in *n*-butyl ether, 24 hours of exposition to 10% ammonia vapours and 6 days of ageing in air, manages to slow down the corrosion process by three orders of magnitude, therefore providing a longer lasting commodity. Specimens have been characterized by IR and XPS spectroscopy, AFM imaging and electrochemical studies.

Keywords— PHPS, Silica, Coating, Corrosion, Aluminium.

I. INTRODUCTION

Aluminium is a widely used material, due to its relatively low density and good mechanical properties [1]. However, its resistance to corrosion is low at extreme values of pH and in presence of chloride ions, which can cause pitting phenomena [2]. Aluminium is therefore usually protected by anodization in acid environments (chromic acid, sulfuric acid, phosphoric acid, etc), but this process presents serious health issues and environmental hazards. Furthermore, the aluminium oxide surface is porous and Cl^- ions can slowly penetrate it, preventing the application of the anodic oxidation technology in chloride rich environments (i.e. seawater) [3, 4]. Classic organic coatings based on paints and lacquers offer a poor environmental barrier, and suffer of many problems such as blistering and filiform corrosion [5]. Blistering can happen by volume expansion of the coating, inclusion of gas or due to build-up of osmotic pressure that can reach 3000 kPa (30 Atm.) [6]. Filiform corrosion happens at defective sites of the coating in conditions of high humidity, and it develops at the film-metal interface when water can permeate through. Protective inorganic coatings that act as environmental barrier are promising candidates for improving the corrosion resistance of many metals, and many deposition methods, like thermal spraying [7], CVD [8] or PVD [9] processes and Sol-Gel techniques [10], have been used. These methods have many drawbacks, such as the high technology required for the vapour deposition methods, which greatly increase the cost of the final product, and the porosity of the final coatings, typical of thermal spraying or Sol-Gel processing. For instance, SiO_2 and ZrO_2 coatings on aluminium, obtained from Sol-Gel precursor, proved to be an interesting alternative to the traditional chromate based surface treatment [11], but pitting corrosion and degradation products were observed on the surface after 2 days of immersion in dilute Harrison's solution (3.5% ammonium sulphate, 0.5% NaCl). Aluminium has also been protected with hybrid organic/silica films enriched with corrosion inhibitors to improve the coatings' performance and provide self-healing properties [12]. The way of adding inhibitors is simple and easy to achieve, but it is difficult to control the release of inhibitors to the surface, thus resulting in a degradation of the performances of such films over time. Sol-Gel and organic-based coatings suffer of many problems, such as the need of thermal annealing of the former to reduce porosity, which results in poor adhesion to the aluminium substrate and cracking, and high water and oxygen permeability of the latter, which leads to blistering and filiform corrosion. An alternative way to these methods is the use of organoelemental precursors that can be converted to low permeation glass or ceramic-like coatings by chemical reactions [13] at room temperature. The majority of inorganic films for corrosion protection is obtained by pyrolysis at high temperatures of appropriate precursors [14], either in inert atmosphere like argon [15] or nitrogen [16, 17], or in oxygen containing atmosphere [18] to ensure full conversion to the oxide. However, silica-based coatings can be obtained from polysilazane precursors at room temperature [19]: this method is cost effective and advantageous in terms of film stability and adhesion, since no thermal stresses (due to the difference in expansion coefficients) are introduced at the substrate-coating interface. In this work, the preparation of a stable environmental barrier coating is performed using perhydropolysilazane (PHPS) as precursor (having a theoretical Si:N ratio of 1:1). It can be easily polymerized and converted to silica either by simple exposition to air or to basic vapours [13] and it has a better adhesion to the substrate than films obtained via Sol-Gel processing due to the absence of thermal annealing. Furthermore, the film showed excellent resistance to hot water environment, thus confirming the formation of an impermeable environmental barrier. The authors had demonstrated that thin films synthesized from PHPS can be used to coat

painted glass, and that the obtained films are homogeneous with reduced ion migration [20]: the present paper focuses on the deposition of such films on aluminium substrates, with a study of deposition conditions to ensure maximal protection by AFM imaging and XPS spectroscopy, a kinetic study by IR spectroscopy and electrochemical corrosion investigation that demonstrates the effective protection offered by these PHPS-SiO₂ films.

II. EXPERIMENTAL PROCEDURES

2.1 General Procedures

Commercially available PHPS polysilazane is produced by ammonolysis of dichlorosilane [21] and is available as 20 wt% solution in dibutyl ether (PHPS NN120-20, formerly Clariant, Switzerland, now AZ Electronics Materials, Luxembourg). Aluminium 5086 (S.A.V. S.p.a., Italy) and silicon wafer samples were cleaned in acetone by ultrasonic treatment and dried under a N₂ stream [17]. The samples were dip-coated using an endless screw hoisting apparatus at various withdrawal speeds (5 – 25 cm min⁻¹). The PHPS to silica conversion was catalysed by exposition to 10% ammonia solution vapours for 24 hours just after dip-coating. As comparison, samples with a Sol-Gel coating (TEOS, EtOH, HCl, H₂O - $r_w = 3$, $r_s = 3.27 \cdot 10^{-2}$, $r_i = 9.72$, 1 week aging) were prepared using the same apparatus. The coatings were examined by optical microscopy (Zeiss Axiotech 100, Carl Zeiss AG, Germany) and X-ray photoelectron spectroscopy (Φ5600ci, Perkin Elmer, USA). Evolution of morphology and chemical structure has been analysed by AFM Imaging (Autoprobe CP, PSI, USA) and IR Spectroscopy (Nexus 470, Nicolet Instruments, USA). Layer thickness was estimated by XPS sputtering (Ar⁺ ions, 4 keV, 2 mm²), with a sputtering rate of ≈ 1 nm min⁻¹. The corrosion behaviour of coated and uncoated samples was analysed by determining the weight change, optical microscopy and polarisation experiments (Model 273A, EG & G, USA).

2.2 Electrochemical analysis

Electrochemical analysis has been conducted using a potentiostat operating in the range -1.3 V / -0.2 V, with a scan rate of 0.1 V s⁻¹ and a pass of 0.01 V. Pt, saturated calomel (SCE) and PHPS-coated aluminium sample were used as reference, auxiliary and working electrodes respectively. The three electrodes were immersed in a Na₂SO₄ 0.1 M (as electrolyte) and HCl 1·10⁻³ M solution (to simulate the chloride concentration of a typical industrial environment). The electrochemical tests were conducted exposing a sample total area of 2 cm². To assure the reproducibility of the analysis, the borders of the sample were previously masked with a polymeric film.

2.3 IR Analysis

IR Spectra were collected in the range 400 - 4000 cm⁻¹ using a Nicolet Nexus operating in the MIR region at a spectral resolution of 2 cm⁻¹ on films previously deposited on silicon wafers, to avoid interferences. Peaks of interest for the kinetic study: 3370 cm⁻¹ (s; ν_s (NH)), 2170-2260 cm⁻¹ (s; ν_s (SiH)) and 1100 cm⁻¹ (s; ν_{as} (SiOSi)).

2.4 XPS Analysis

Spectra collected using a Perkin Elmer Φ5600ci equipped with a double anode X-ray source (Mg/Al) and a monochromatic Al X-ray source. Anodes work with AlKα (1486.6 eV) and MgKα (1253.6 eV) sources at 20 mA and 14 kV. A CHA (Concentric Hemisphere Analyser) has been used to collect the output signals. Analysed areas are circles 0.8 mm in diameter. Scan range is 0-1350 eV (AlKα source) or 0-1150 eV (MgKα source), according to the source adopted. A charge neutraliser has been used to avoid spectral shift in samples and all spectra have been corrected according to the charging effect, assigning to C1s peak 248.8 eV binding energy. Sputtering operates with Ar⁺ ions at 4 keV on an area of 2 mm².

2.5 Optical Microscopy

Optical Microscope images were obtained with a Zeiss Axiotech 100, working in reflected light operating in the 5x-100x magnifying range and acquired with a Nikon D90 Digital Camera.

2.6 AFM Analysis

Images collected using a Park Scientific Instruments (PSI) Autoprobe CP, working in contact mode in air, equipped with a silicon nitride cantilever and a silicon monocrystal tip. The investigated area is 25 x 25 μm. A setpoint of 25 nN has been used throughout the experiments.

2.7 Qualitative corrosion test

Weight changes were measured before and after a corrosion test on a 2 cm² exposed area of coated sample immersed in a 2.5 M HCl solution. An uncoated sample is immersed in the corrosive solution at the same conditions as reference. Samples were thoroughly washed with acetone and dried under a stream of nitrogen before each weighing.

III. RESULTS AND DISCUSSION

Silica films were obtained from PHPS precursor using three different dilutions of the commercial solution (20 % in dibutyl ether) and the corrosion resistance performances were assessed by qualitative corrosion test (immersion in 2.5 M HCl solution for 1 h and weigh change measurement). Silica thin films on Al 5086 samples were prepared by dip coating with a withdrawal speed of 10 cm min⁻¹ and the conversion to silica was obtained either by simple ageing in air for one week or by 24h of treatment with NH₃ vapours and ageing in air for further 6 days. Results are reported in **Table 1**.

TABLE 1

QUALITATIVE CORROSION TEST ON AL 5086 PROTECTED BY DIP COATING (10 cm min⁻¹ WITHDRAWAL SPEED) IN A PHPS SOLUTION IN DIBUTYL ETHER. 2 cm² AREA EXPOSED TO CORROSIVE ENVIRONMENT, 1 HOUR TOTAL CORROSION TIME. WEIGHT LOSS ARE AN AVERAGE ACROSS THREE DIFFERENT CORROSION TESTS PERFORMED ON DIFFERENT SAMPLES. ERROR GIVEN AS STANDARD DEVIATION FROM MEAN VALUE.

| | 20 % PHPS | 20 % PHPS NH ₃ 24h | 10 % PHPS | 10 % PHPS NH ₃ 24h | 5 % PHPS | 5 % PHPS NH ₃ 24h | Classic Sol-Gel | Uncoated |
|------------------|-------------|-------------------------------|-------------|-------------------------------|------------|------------------------------|-----------------|------------|
| Weight loss (mg) | 1.92 ± 0.11 | 1.13 ± 0.15 | 5.86 ± 0.24 | 1.54 ± 0.18 | 19.6 ± 0.2 | 12.9 ± 0.2 | 25.3 ± 0.6 | 41.7 ± 0.8 |

Optical microscopy analysis (**Figure 1**) of samples after corrosion showed extensive pitting and intergranular corrosion on the uncoated sample (panel A) and the Sol-Gel coated one showed extensive cracking (panel B), but only a few pits and signs of film degradation on the coated samples that did not receive NH₃ treatment. The samples treated with ammonia for 24 hours before the corrosion test performed generally better than the non-treated ones, but only the NH₃-treated samples obtained from the 20 % and 10% PHPS solution showed no signs of corrosion on the metal surface and degradation of the protective film (panel D). A longer test, with corrosion in 2.5 M HCl for 100 hours, showed that the 10 % PHPS sample is less resistant to extended periods of time in harsh environments, with a total weight loss of 99.2 ± 5.3 mg and widespread blistering (panel E) and fissuring in the SiO₂ coating. The 20 % PHPS sample lost only 2.62 ± 0.21 mg while the uncoated sample was completely corroded. The poor performances of the Sol-Gel coated samples can be ascribed to poor adhesion of the film to the aluminium substrate: during the ageing of the coating, and the corresponding shrinking of the film, cracks and fissures are formed, thus reducing the overall resistance to corrosion.

An important parameter that determines the thickness of the polysilazane layer and, therefore, the protection offered by the final environmental barrier is the withdrawal speed used during dip-coating. A set of samples obtained by dip-coating at different withdrawal speeds in 20 % PHPS in dibutyl ether has been tested using the procedure described previously. Results are reported in **Table 2** and plotted in **Figure 2**.

TABLE 2

QUALITATIVE CORROSION TEST ON AL 5086 PROTECTED BY DIP COATING IN A 20% PHPS SOLUTION IN DIBUTYL ETHER. 2 cm² AREA EXPOSED TO CORROSIVE ENVIRONMENT, 1 HOUR TOTAL CORROSION TIME. WEIGHT LOSS ARE AN AVERAGE ACROSS THREE DIFFERENT CORROSION TESTS PERFORMED ON DIFFERENT SAMPLES. ERROR GIVEN AS STANDARD DEVIATION FROM MEAN VALUE.

| | 2 cm min ⁻¹ | 5 cm min ⁻¹ | 8 cm min ⁻¹ | 10 cm min ⁻¹ | 12 cm min ⁻¹ | 15 cm min ⁻¹ | 18 cm min ⁻¹ | 20 cm min ⁻¹ | 25 cm min ⁻¹ |
|---|------------------------|------------------------|------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| Weight loss (mg) (Aged in Air) | 1.84 ± 0.12 | 1.51 ± 0.16 | 1.78 ± 0.18 | 1.92 ± 0.11 | 1.23 ± 0.14 | 0.45 ± 0.04 | 0.62 ± 0.06 | 1.29 ± 0.19 | 2.01 ± 0.32 |
| Weight loss (mg) (NH ₃ 24 hours) | 0.81 ± 0.11 | 0.72 ± 0.10 | 0.91 ± 0.14 | 1.13 ± 0.15 | 0.69 ± 0.09 | 0.18 ± 0.03 | 0.32 ± 0.06 | 0.90 ± 0.18 | 1.53 ± 0.24 |

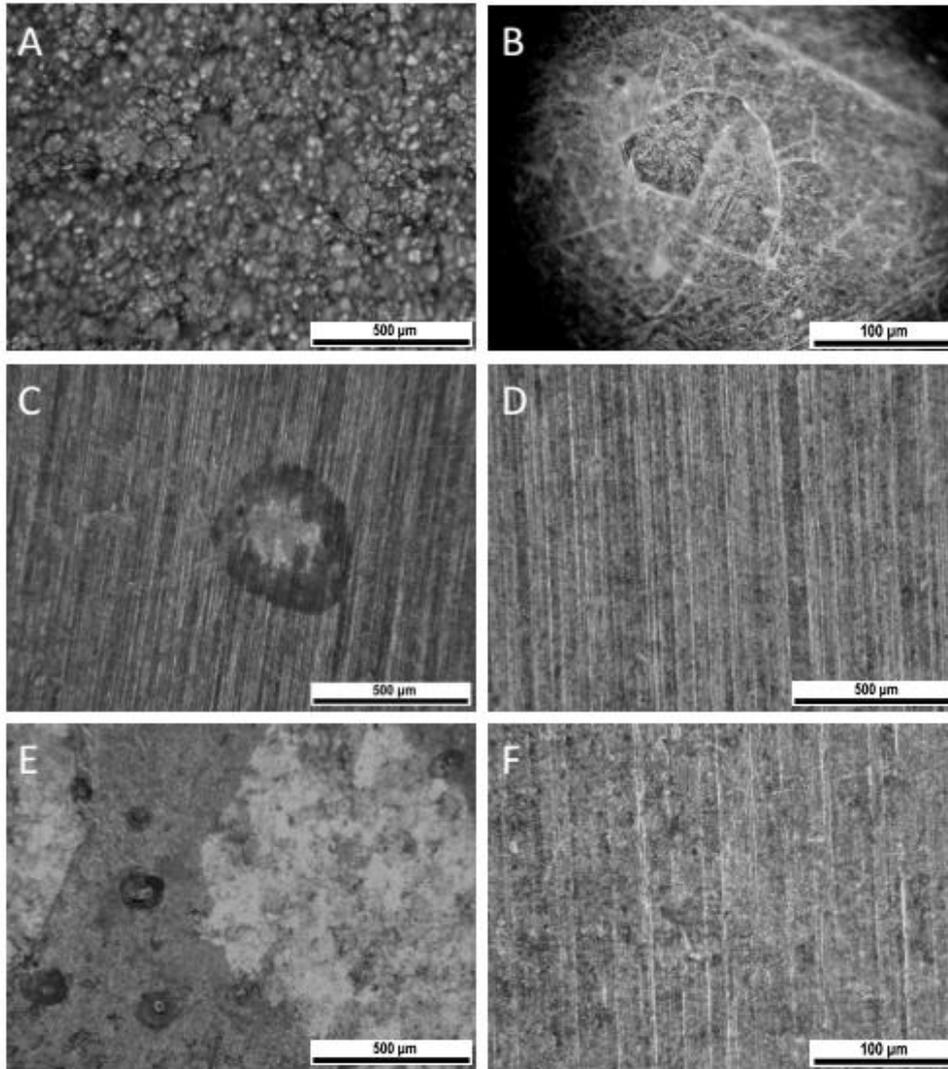


FIGURE 1: OPTICAL MICROSCOPY OF SAMPLES AFTER THE CORROSION TESTS. A) BARE AL SAMPLE, 1 HOUR CORROSION. B) SOL-GEL COATED SAMPLE, 1 HOUR CORROSION. C) 10 % PHPS SAMPLE, 1 HOUR CORROSION. D) 20% PHPS, NH₃-TREATED SAMPLE, 1 HOUR CORROSION. E) 10 % PHPS, NH₃-TREATED SAMPLE, 100 HOURS CORROSION. F) 20 % PHPS, NH₃-TREATED SAMPLE, 100 HOURS CORROSION.

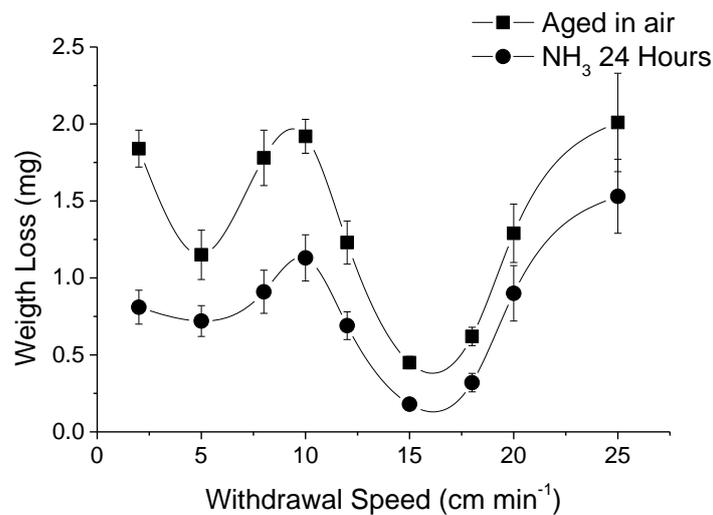


FIGURE 2: CORROSION RESISTANCE (WEIGHT LOSS) AGAINST WITHDRAWAL SPEED. SPLINE INTERPOLATION INCLUDED AS GUIDE TO THE EYE.

The optimal withdrawal speed for dip-coating Al 5086 samples has been therefore found at 15 cm min^{-1} . It is evident that to obtain maximum protection against corrosive attacks, NH_3 treatment is essential as it promotes polymerization and catalytic conversion to SiO_2 , resulting in a more effective environmental barrier. The poor protection offered by coatings obtained at withdrawal speed inferior to 15 cm min^{-1} is due to an insufficient thickness of the PHPS / SiO_2 layer, unable to homogeneously cover the substrate. On the contrary, the increase in weight loss at high withdrawal speed ($18 - 25 \text{ cm min}^{-1}$) can be ascribed to the formation of cracks and fissures during the polymerization and conversion to silica process: the film is too thick and the conversion reaction, happening at the surface in the presence of O_2 , induces strains in the coating that eventually breaks. This is confirmed by optical microscopy and XPS study (*vide infra*). It should be noted that the substrate must be thoroughly degreased before dip-coating; optimal substrate cleaning has been obtained with 30 minutes of ultrasonic bath in acetone, while treatment with surfactants resulted in poor adhesion of the film to the substrate, with fissures and cracks in the coating visible with an optical microscope.

XPS analysis has been carried out to evaluate the quality of the coating by measuring the intensity of peaks relative to the film ($\text{Si}2s$, $\text{Si}2p$, $\text{N}1s$) and to the sample ($\text{Al}2s$, $\text{Al}2p$). Relative intensity of the $\text{O}1s$ peak has been also used to qualitatively assess the composition of the surface. Both aluminium peaks ($\text{Al}2s$ and $\text{Al}2p$) are present in XPS spectra of samples coated with PHPS 5 %, confirming that the surface is not homogeneous and some regions of the substrate are not fully protected: the resulting film is too thin to adequately cover the rough metallic surface. No traces of aluminium are present in spectra collected from the sample dip-coated in PHPS 20 % solutions, and the composition is homogeneous in all the spots analyzed. Moreover, a comparison between aged samples and freshly deposited ones (24 hours of ammonia treatment) has been performed. In freshly deposited samples, XPS spectra evidence the $\text{N}1s$ peak deriving from a non-complete conversion mechanism, and from a Si/N/O composition a ratio of $\approx 1.2:1$ SiO_2 : PHPS can be calculated. On the other side, samples aged in air after the 24 hours of ammonia treatment show no traces of nitrogen, confirming that the conversion is complete at the surface (**Table 3**), while Ar^+ sputtering reveals the presence of unreacted polysilazane in the bulk of the film (**Figure 3**). The Si/O ratio on the surface is consistent with the suggested conversion to SiO_2 . Using a sputtering rate of $\approx 1 \text{ nm min}^{-1}$ it is possible to estimate the thickness of the coating (until the detection of Al peaks in the XPS spectra) in 85-100 nm. This value is considerably lower than the theoretical value calculated using the Landau-Levich equation [22] (300 nm) and the experimental value measured on glass samples (150 nm) [20], but this difference can be ascribed to the roughness of the Al substrate (114 nm) as measured by AFM microscopy (*vide infra*), and to the possible catalytic effect of aluminium, that can help polymerization [23] acting as a Lewis acid causing shrinkage of the film.

TABLE 3
XPS QUANTITATIVE ANALYSIS PERFORMED ON PHPS COATED SAMPLES (AS ATOMIC PERCENTAGES)

| | N1s | Si2p | O1s | Al2p |
|---|------------|-------------|------------|-------------|
| 20 % PHPS + 24 hours NH_3 – 15 cm min^{-1} | 7.2 % | 44.7 % | 48.1 % | 0 % |
| 20 % PHPS + 24 hours NH_3 + 6 days ageing in air – 15 cm min^{-1} | 0 % | 32.2 % | 67.8 % | 0 % |
| 5 % PHPS + 24 hours NH_3 – 15 cm min^{-1} | 3.7 % | 35.2 % | 59.7 % | 1.4 % |

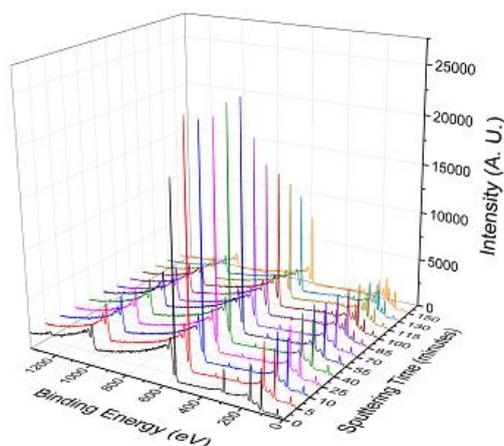


FIGURE 3: XPS DEPTH PROFILE OF THE COATING OBTAINED BY Ar^+ SPUTTERING ON A SAMPLE OBTAINED BY DIP-COATING AL IN PHPS 20%, 24 HOURS OF AMMONIA TREATMENT AND FURTHER 6 DAYS OF AGEING IN AIR. THE SPUTTERING RATE IS NOT HOMOGENEOUS, BUT CAN BE APPROXIMATELY ESTIMATED IN 1 nm min^{-1}

Furthermore, as can be inferred from the XPS sputtering, while on the surface there is no N1s signal (402 eV), it appears after only five minutes of Ar^+ sputtering. The conversion to SiO_2 is therefore complete only at the very surface of the coating, in the range 0 – 5 nm. The kinetics of the reactions happening during the aging of the sample has been monitored by IR spectroscopy. The analysis shows that the rate of polymerization, derived from a swift decay over time of the Si-H stretching signal ($2170\text{--}2260\text{ cm}^{-1}$), is faster than the rate of conversion (growth of the Si-O-Si asymmetric stretching signal (1100 cm^{-1})). Therefore, a few days of aging of the sample is needed for quasi-completion of conversion reactions (**Figure 4**).

The difference in rate between the two reactions can induce stress in the evolving coating, as the film is contracting at different rates in the bulk and at the surface. This supports the data obtained from film with different thickness (**Table 2**): for thicker films (obtained at higher withdrawal speed) the evolution of the coating results in cracks and fissures due to surface strain.

The evolution of surface morphology over time has been monitored by AFM imaging: a smoother surface (lower RMS roughness) can better resist to corrosive attacks thanks to the absence of high energy spots such as crests and ridges. The purpose of the analysis was to rationalize the differences in morphology evolution of samples obtained from 5% and 20% PHPS in n-Butyl Ether. The surface roughness lowers after deposition for both samples, but after having reached a minimum it starts to increase in the 5% PHPS specimen, while in the case of the 20% solution the average roughness continuously decreases until it reaches a plateau (**Figure 5**). This phenomenon can be ascribed to the fact that the 5% solution is less viscous than the 20% one, and the resulting coating is thinner: polymerization, conversion to SiO_2 and solvent evaporation will decrease its thickness, causing the resurfacing of crests and ridges, where the film will not be able to provide adequate protection.

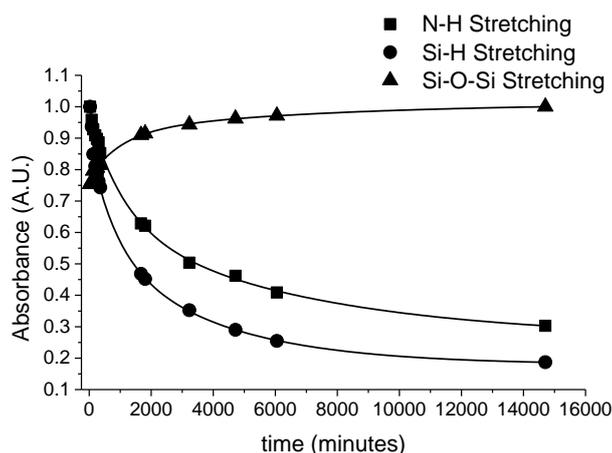


FIGURE 4: IR KINETIC STUDY ON A Si WAFER SAMPLE COATED WITH 20 % PHPS AT 15 cm min^{-1} . PEAK INTENSITY HAS BEEN NORMALISED, USING THE STARTING Si-H STRETCHING AS REFERENCE.

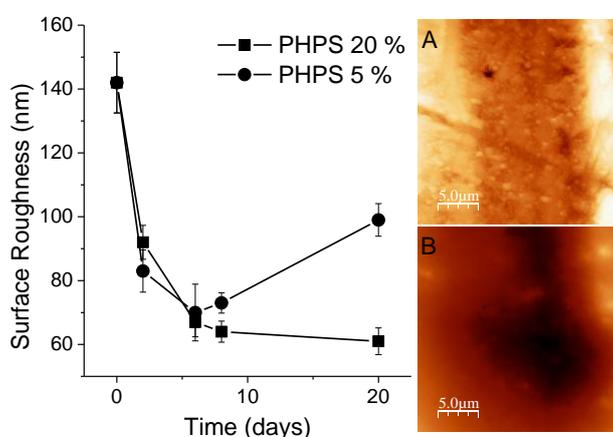


FIGURE 5: FILM MORPHOLOGY EVOLUTION DETERMINED FROM AFM IMAGING. ROUGHNESS VALUES ARE THE AVERAGE ACROSS 5 DIFFERENT ACQUISITIONS AND THE ERROR IS THE STANDARD DEVIATION OF DATA. A) AFM MICROGRAPH OF Al SURFACE WITHOUT PHPS COATING. B) AFM MICROGRAPH OF A SAMPLE COATED WITH 20% PHPS AFTER 24 HOURS OF NH_3 TREATMENT AND 7 DAYS OF AGING IN AIR. AFM MICROGRAPHS SCALE IS 0 (BLACK) TO 700 (WHITE) nm.

To have a quantitative measure of the extent of corrosion in the coated samples, an electrochemical study has been performed on coated samples, prepared by dip-coating Al substrates in 20 % PHPS solution with a withdrawal speed of 15 cm min^{-1} , followed by 24 hours of ammonia vapour treatment and 6 days of ageing in air. The analysis was performed to obtain the Tafel Plot, characterised by E_{CORR} and i_{CORR} , where i_{CORR} is directly proportional to the corrosion rate. The film provides protection even without the aging process, thanks to a reduction of the i_{CORR} value of 2 orders of magnitude (**Figure 6, Table 2**). Improved protection is achieved with ageing, reflecting in a reduction of the i_{CORR} value of nearly 3 orders of magnitude. In terms of corrosion resistance, an aged PHPS-coated aluminium sample has a lifetime nearly 1000 time superior to an unprotected one.

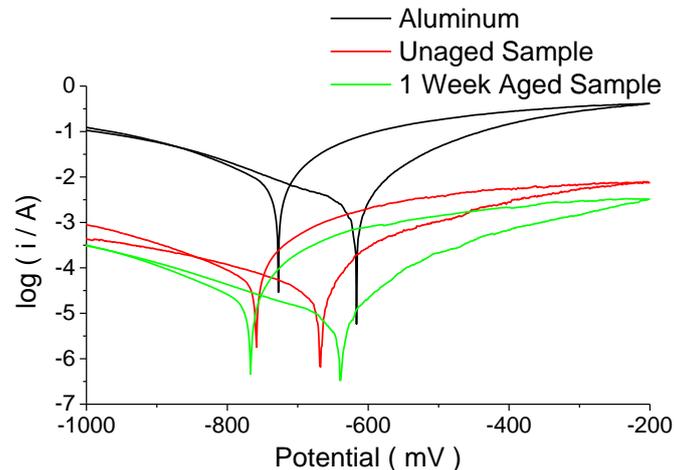


FIGURE 6: TAFEL PLOT OF UNTREATED AL SAMPLE AND SAMPLES COATED WITH 20 % PHPS AT 15 cm min^{-1} , WITH AND WITHOUT FURTHER AGEING IN AIR.

TABLE 4

E_{CORR} AND i_{CORR} VALUES OBTAINED FROM THE TAFEL PLOT. THE TWO SAMPLES WERE OBTAINED BY DIP-COATING AL SUBSTRATES IN 20% PHPS AT 15 cm min^{-1} AND TREATED FOR 24 HOURS WITH AMMONIA VAPOURS.

| | $E_{\text{CORR-1}}$ (mV) | $E_{\text{CORR-1}}$ (mV) | $i_{\text{CORR-1}}$ (logA) | $i_{\text{CORR-1}}$ (logA) |
|--------------------------------|--------------------------|--------------------------|----------------------------|----------------------------|
| Uncoated Al | -614 | -728 | -2.61 | -2.23 |
| PHPS coated sample | -668 | -759 | -4.72 | -4.42 |
| 6-days Aged PHPS coated sample | -639 | -768 | -5.11 | -4.93 |

IV. CONCLUSIONS

PHPS has been deposited on aluminium 5086 substrates to improve their resistance to corrosion. The deposition process has been optimized, to find the parameters to guarantee maximum protection (dip-coating of substrates in 20% PHPS solution at a withdrawal speed of 17 cm min^{-1} , n-butyl ether as solvent, 24 hours of exposition to ammonia vapours, 6 days of aging in air). IR and XPS analyses demonstrate that the film is a mixed structure silica/polysilazane, with the silica outer layer acting as a barrier to prevent corrosive phenomena. Films are homogenous on the surface as found by XPS investigations, and AFM imaging demonstrates that some morphological rearrangement occurs during the aging process, requiring the use of PHPS in 20% concentration to obtain a film thick enough to provide adequate protection. Electrochemical analysis confirms the corrosion protection offered by PHPS-derived silica/polysilazane films, ensuring a reduction of nearly 3 orders of magnitude of the value of i_{CORR} , which implies a 1000-times longer lifespan.

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