The Influence of the Curing Temperature on the Properties of Some Silane Films

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This paper discusses the importance of the temperature drying process on some silane films in order to obtain a coating with specific properties (stability in time, resistance to corrosion attack and compactness) that would make them appropriate to be used as anticorrosive protection layers. Electrochemical techniques such as open circuit potential and electrochemical impedance spectroscopy were employed in order to characterize the investigated deposited silane films on aluminium substrate. The validation of the experimental electrochemical impedance spectroscopy data was carried out using the comparison of the validation coefficient versus the Pearson coefficient computed for a α=0.05.

Keywords: silane films properties, curing temperature, EIS, SEM

A special interest is given recently to the improvement of the process of silane films deposition, by characterizing the deposition solutions or by applying several deposition methods, like deep-coating, spin-coating or electro-deposition, but a closer look should be taken to the influence of the curing temperature of the deposited films [1-4].

The properties of some silane films deposited on metallic substrates are directly related to the whole deposition process, which consists in two major steps, namely physical deposition by immersion into a solution, followed by a drying process at a fixed temperature, currently named curing treatment [5].

In order to obtain a successful deposition, a thorough characterization of the solution from which the deposition is made is necessary, this step being already presented in details in [1], where the role of the optimum deposition time is properly discussed and determined.

The final properties of the silane films are related not only to the deposition itself, but also to the curing temperature of the films. The drying process strongly influences the final properties of the films such as barrier protection, compactness or structure of silane coatings. For example, applying a low temperature does not necessarily lead always to a certain compactness degree of the silane coating, and hence a small resistance at attacks or a gellified structure are achieved; a high temperature could lead in exchange to an increased density of pores and cracks into these coatings, leading to an increase number of preferential corrosion initiation spots.

Electrochemical techniques, such as open circuit potential and electrochemical impedance spectroscopy are a very useful tool in establishing whether the deposited coatings have a high enough resistance and a good compactness degree to be used as anticorrosive protection [5-15].

From the EIS tests performed on the silane coatings, the indicators of the films properties are high polarisation resistance and low capacitance, the correlation between them being presented in equation (1):

$$C_{dl} = \frac{1}{R_p \cdot \omega_{max}} \quad (1)$$

where C_{dl} is the double layer capacitance, R_p is the polarisation resistance and ω_{max} is the angular frequency [16].

The values of capacitance are an indicator of the coatings compactness, the correlation between them, given by the relative permittivity of a coating, is described by equation (2):

$$C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{l}{S} \quad (2)$$

where ε_r is the relative permittivity of a coating, ε_0 is vacuum permittivity, $F \cdot m^{-1}$, S is the films surface, m^2 and l is the thickness, m.

This may be used in conjunction with the EIS data, where the value of C is readily available [14-16].

The purpose of this paper is to establish the influence of the curing treatment on the final properties of the silane films, namely film stability given by open circuit potential, polarisation resistance and compactness by electro-chemical impedance spectroscopy.

Experimental part

The metallic substrate consists in $1cm^2$ aluminium alloy sheets whose composition was determined by scanning electron microscopy using CARL ZEISS Merlin Gemini II equipment, with OXFORD INSTRUMENTS X-Max EDS detector. The sample was cleaned in ultrasonic bath with distilled water and ethanol for 3 min. The sample is not covered with coating materials. Parameters used to analyze the sample on SEM were: the energy of the electron beam (EHT) 15kV, current on sample, I_{probe}, 1nA, and the working distance between the sample and column was 8.4mm. The process time was 2 min.

Bis-1,2-(triethoxysilyl)ethane (BTSE), bis(3-triethoxy-silylpropyl)tetrasulfide silane (BTESPT), and tetraethyl orthosilicate (TEOS), purchased from Fluorochem Ltd, Hadfield, U.K are the silanes used for obtaining the protective films.

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The deposition solutions consist in 2% and 5% silane solutions prepared as follows: BTSEPT solutions were prepared in a mixture of methanol and distilled water in silane/distilled water/methanol = 2:2:96, respectively 5:5:9 volumetric ratios; TEOS solutions were prepared similar to BTSEPT, the only difference being the solvent one used, in this case ethanol; BTSE solutions were prepared in a 50:50 (v:v) distilled water and ethanol mixture.

The above mentioned solutions were used to depositing silane films after 400 min (BTESPT 2% and BTSE 2%), 640 min (BTESPT 5%), 180 min (BTSE 5%), 720 min (TEOS 2%), 600 min (TEOS 5%) after the preparation of the solutions, these time intervals corresponding to the optimum deposition time for the silanes used as shown in [1]. The deposition process consists in the immersion of the metallic substrate into silane solution for 10 min. Prior to deposition, the metallic substrate was immersed into ethanol, rinsed with distilled water and dried.

After the deposition, the films were cured in an oven at three different temperatures, namely 25 °C, 120±2 °C and respectively, 180±2° C.

The electrochemical tests were performed in a three-electrode electrochemical cell which consists of an Ag/AgCl reference electrode, a platinum mesh counter electrode and an aluminium sheet coated with silane films electrode. The electrolyte used was a 3.5% NaCl solution.

The open circuit potential (OCP) was registered for 10 minutes with an acquisition rate of 12 measurements/minute. The electrochemical impedance spectroscopy (EIS) measurements were carried out by applying a 10 mV sinusoidal potential perturbation and scanning a frequency range between 100 kHz and 100 mHz with a measurement rate of 10 measurements/decade.

All electrochemical tests were performed after 1, 7, and 30 days after the films were subjected to the curing treatment.

Results and discussions

SEM characterisation of the metallic substrates

Prior to depositing the silane films, the metallic substrates composition was investigated using scanning electron microscopy (SEM) (table 1). The analysis confirmed that the substrate is an aluminium and carbon alloy (fig. 1).

Open circuit potential

The variation of the open circuit potential for coated samples indicates the stability in time of the deposited silane films. One has chosen from the multitude available data the most favourable representatives and the least favourable cases, figures 2a. and 2.b., to illustrate the variation of potential in time for some of the investigated silane films, namely the variation of OCP for the samples

Element	Wt, %
Al	81.83
C	15.24
O	2.11
Fe	0.51
Ag	0.30

Table 1
THE ALUMINIUM SUBSTRATE COMPOSITION

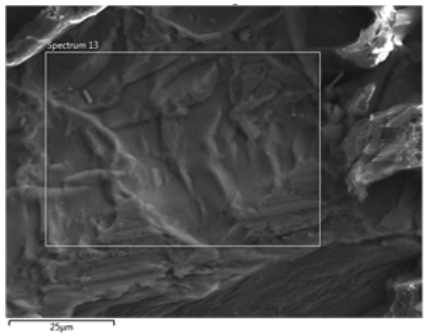

Fig 1. SEM image for the metallic substrate used for silane deposition

with very high stability in time (figure 2.a) and also for the ones with a low stability (fig. 2.b). All the remaining investigated samples fall within these two extremes, but are far too many to depict all of them here, and this is not necessary.

A high stability of a film is encountered for the ones that registered a variation of OCP in a small range of values and a small stability in time of a coating is given by a variation of the OCP in a wide range of values. In this particular case, samples from figure 2.a. behave obviously according to the expectations while the ones from figure 2.b. representing a weak stability of silane films in time.

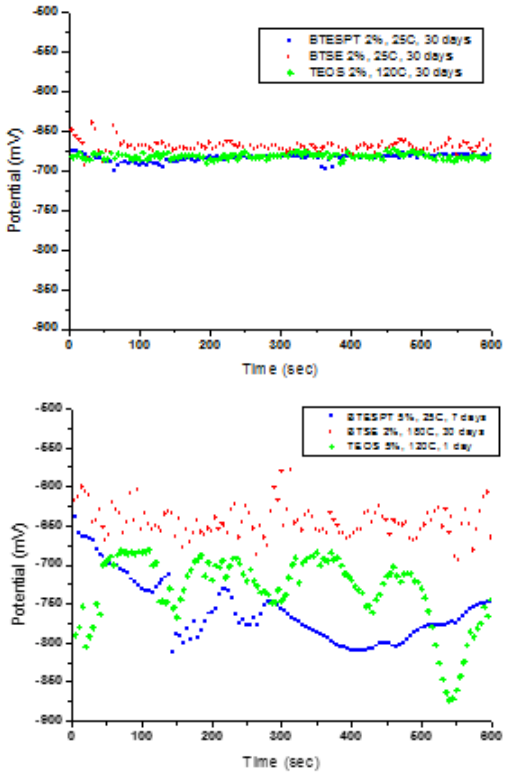

Fig 2.The variation of OCP for silane films with a). high stability in time, b). low stability in time

Electrochemical impedance spectroscopy

The EIS results of the tested samples are presented in tables 2-7 and in figure 3 is presented an example of the Nyquist plots that were used in order to establish the polarisation resistance. Further on, one shall discuss only about the polarisation resistance, since the capacitance is correlated to it as shown in equation (1).

From these results, one can draw three different directions to interpreting them: the films behaviour in time, the role of concentration on the films properties and the influence of the curing temperature on the silane film properties.

Firstly, one shall discuss the films behaviour in time, namely the variation of the resistance to corrosion attack,

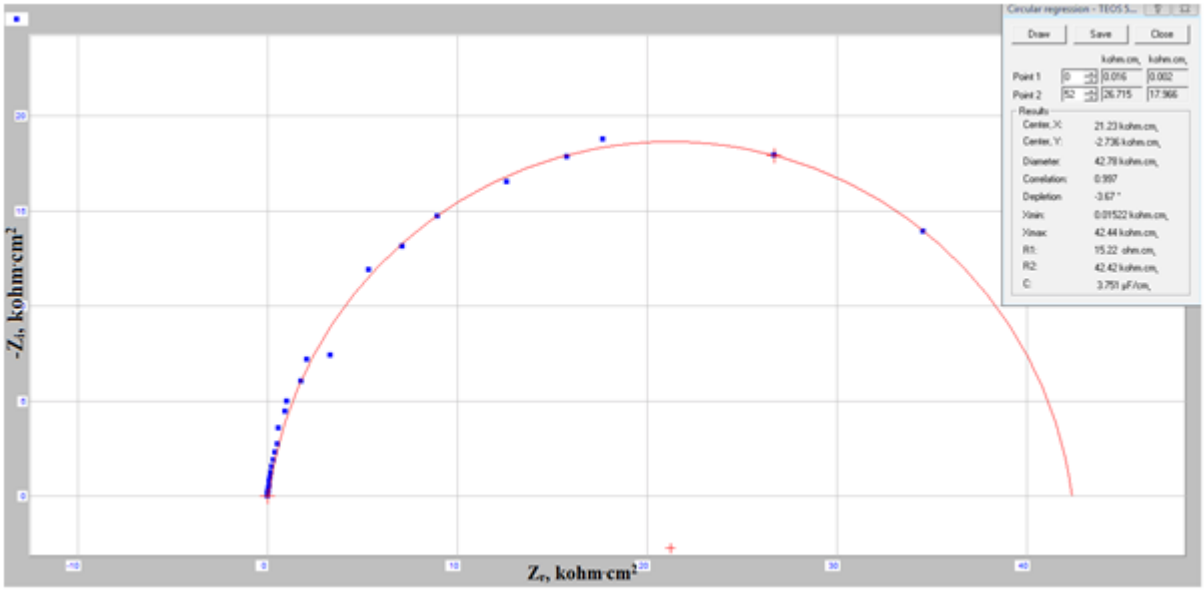

Fig 3. Screen capture of a circular regression procedure applied to a TEOS film deposited from a 5% silane solution, cured at 120°C and analyzed after 1 day in 3.5% NaCl solution

by taking into account the values of the polarisation resistance given by the Nyquist plots.

TEOS films deposited from 2 and 5% concentration solutions and dried at 25 °C and 180°C have similar behaviours, characterized by an increase in time of the polarisation resistance, this being explained by the possible presence of a *self-healing* process of the films. The same behaviour is seen in 2% TEOS films cured at 120°C, while for 5% TEOS cured also at 120°C, the variation of the polarisation resistance decreases in time, effect associated to the apparition of some cracks or the enlargement of already existing pores in the film, that inevitably lead to a smaller resistance.

For all BTSE films, except 2% BTSE film cured at 120°C, the highest value for the polarisation resistance was registered after 7 days from the films deposition. This variation could be explained similarly to TEOS films, by a *self-healing* process of the films during the first week from deposition. After 30 days, one can see a decrease of the values of the polarisation resistance compared to the one registered at 7 days age, but similar to the one obtained for the 1 day films. In the case of 2% BTSE film cured at 120°C, the resistance polarisation increases in time. The BTESPT films cured at120°C have similar behaviour with the BTSE films.

Secondly, the role of the concentration of deposition solution is important for the properties of the films, because a small concentration could lead to a very thin film that could not be used as a protective layer and a higher concentration of the silane solution could lead to a gelified film with a poor adhesion to the metallic substrate. From the EIS results one may see that in most cases, the films with better resistance are the ones deposited from the solution with higher concentration (5%). An exception from this was registered for the BTSE films, where the highest values for the resistance were registered for the smaller concentration of the deposition solution (2%). This trend could be explained by the fact that when the deposition is made from a higher concentration, the obtained films could have a more gellified consistence, hence poor adhesion of the films onto the metallic substrate and small resistance to corrosion attacks. Another similar trend was seen for the 2% BTESPT film dried at 180°C, because this particular film has proven to have close polarisation resistance values, with the film obtained from a 5% concentration deposition solution, hence similar properties could be noticed. While the concentration increases, one may see that the curing temperature decreases toward 25°C, this trend being observed for the TEOS and BTESPT films, but not for the BTSE 5% film with the 7 days age, where the polarisation resistance is significantly lower than the ones for the 1 day (196.1 kohm . cm²) and 30 days (333.9 kohm·cm²) age films.

One possible explanation could be the fact that while increasing the silane solutions concentration, the silanization occurs with a higher rate and the resulting film is more compact, hence better properties for the film being observed at lower temperatures.

The BTSE 5% 7 days age film exception could not be attributed to experimental errors during the electrochemical impedance spectroscopy analysis because the results obtained are reproducible and close, still one possible cause could be the insufficient pretreatment of the metallic surface that lead to a not adherent enough coating.

Thirdly, the influence of the curing temperature on the silane films properties should also be discussed here, as one could establish the best option to dry the silane films, namely at 120°C even though the values registered for the polarisation resistance are close to the ones registered at 180°C, but from economics point of view, the preferred one could be the one at the lower temperature. This case is encountered for the 2% BTESPT films, as they offer a similar corrosion protective behaviour at 120 and 180°C, so one will decide on curing them at lower temperature on economic grounds as well as the reduced probability of cracking during the curing process.

The curing temperature of the silane film is related to the structure, molecular mass and concentration of the silane. One may see that for the films obtained from 2% concentration solutions, it is not properly defined a certain curing temperature like in the case of a 5% concentration, where, to obtain a film with good properties, one should take into account both the molecular mass and structure of the silane, namely the recommended curing temperature increases with increasing the molecular mass (M_{TEOS} < M_{BTSE} < M_{BTESPT}) and increasing the length of the main organic chain.

Also, for the validation of the EIS data, one has applied the model for experimental data validation described in

Table 2

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 2% SILANE SOLUTION AND ANALYZED AFTER 1 DAY

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, µF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 2%	25	6.688	9.517	47	0.999	0.288	0.712
	120	12.530	3.175	47	0.992	0.288	0.711
	180	12.400	2.026	50	0.994	0.279	0.720
BTSE 2%	25	126.700	1.983	52	0.999	0.273	0.727
	120	22.740	1.105	44	0.992	0.304	0.695
	180	175.900	0.452	47	0.995	0.288	0.711
TEOS 2%	25	4.339	4.621	45	0.995	0.294	0.705
	120	4.996	5.032	47	0.992	0.288	0.711
	180	6.561	3.832	50	0.998	0.279	0.721

Table 3

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 2% SILANE SOLUTION AND ANALYZED AFTER 7 DAYS

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, µF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 2%	25	9.519	1.671	40	0.992	0.312	0.687
	120	17.430	1.441	47	0.997	0.288	0.712
	180	16.600	1.514	49	0.993	0.282	0.717
BTSE 2%	25	135.600	1.173	50	0.998	0.279	0.721
	120	44.820	0.561	42	0.998	0.304	0.696
	180	36.480	0.872	43	0.994	0.301	0.698
TEOS 2%	25	10.210	4.924	48	0.991	0.285	0.714
	120	6.666	4.774	47	0.992	0.288	0.711
	180	7.480	1.702	39	0.999	0.316	0.684

Table 4

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 2% SILANE SOLUTION AND ANALYZED AFTER 30 DAYS

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, µF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 2%	25	9.085	2.207	50	0.986	0.279	0.719
	120	12.630	2.518	50	0.990	0.279	0.720
	180	22.760	11.040	52	0.991	0.273	0.726
BTSE 2%	25	77.370	0.514	45	0.918	0.294	0,693
	120	103.600	1.934	51	0.994	0.276	0.723
	180	67.700	0.470	43	0.970	0.301	0,694
TEOS 2%	25	13.270	1.893	42	0.999	0.304	0.696
	120	12.700	7.916	50	0.998	0.279	0.721
	180	9.600	2.619	46	0.986	0.291	0.707

Table 5

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 5% SILANE SOLUTION AND ANALYZED AFTER 1 DAY

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, µF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 5%	25	47.050	0.676	43	0.996	0.301	0.698
	120	24.790	0.809	41	0.994	0.308	0.691
	180	123.700	1.028	49	0.993	0.282	0.717
BTSE 5%	25	196.100	1.282	52	0.996	0.273	0.726
	120	56.970	0.223	39	0.991	0.316	0.683
	180	62.430	2.039	50	0.992	0.279	0.720
TEOS 5%	25	21.040	9.527	52	0.999	0.273	0.727
	120	42.420	3.751	52	0.997	0.273	0.727
	180	18.780	5.354	50	0.994	0.279	0.720

Table 6

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 2% SILANE SOLUTION AND ANALYZED AFTER 7 DAYS

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, μF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 5%	25	160.900	1.562	52	0.998	0.273	0.727
	120	166.100	1.915	53	0.955	0.271	0.723
	180	41.290	1.217	46	0.996	0.291	0.708
BTSE 5%	25	15.710	2.531	50	0.997	0.279	0.721
	120	370.100	1.358	55	0.992	0.266	0.733
	180	90.350	1.761	50	0.995	0.279	0.720
TEOS 5%	25	30.430	2.614	47	0.998	0.288	0.712
	120	28.150	1.130	43	0.993	0.301	0.698
	180	22.120	3.597	47	0.995	0.288	0.711

Table 7

THE VALUES OF R_2, C, R^2, R_{CRITIC}, K_{VD} FOR THE SILANE FILMS DEPOSITED FROM A 2% SILANE SOLUTION AND ANALYZED AFTER 30 DAYS

Silane	Curing temperature, °C	R_2, kohm·cm^2	C, μF/cm^2	No of points	R^2	r_{critic}	k_{VD}
BTESPT 5%	25	1086	1.465	60	0.961	0.254	0.741
	120	96.620	1.316	49	0.994	0.282	0.717
	180	18.050	2.204	48	0.996	0.285	0.714
BTSE 5%	25	333.900	0.753	52	0.999	0.273	0.727
	120	54.260	0.927	47	0.998	0.288	0.712
	180	64.970	2.449	50	0.994	0.279	0.720
TEOS 5%	25	56.500	2.253	50	0.997	0.279	0.721
	120	17.630	3.610	46	0.997	0.291	0.709
	180	36.270	2.194	47	0.981	0.288	0.709

[17]. The validation coefficient was calculated using the Pearson coefficient computed for $\alpha=0.05$.

From tables 2-7, one may see that the values of the determination coefficient (R^2) associated to the regression equations for each Nyquist plot are close to the unit ($0.918<R^2<0.999$), all these values being obtained for more than 40 experimental points. The values of the validation coefficient calculated taking into account the Pearson coefficient are between 0.683 and 0.733, values that satisfy the *sine qua non* condition, explained in equation (3) and that validate the high level of credibility for the experimental determinations.

Conclusions

This paper showed the importance of the appropriate curing temperature that should be applied to some silane films, by pointing out the differences that appear into the final properties of these films, such as resistance to corrosion attacks, compactness and film structure. When deciding the value of the drying temperature, one should take into account parameters such as silane type and concentration of the deposition solution, and decide on the appropriate temperature that should satisfy all economical, technical and practical criteria.

Failing to comply with the appropriate recommended curing temperature, the drying of the films could lead either to unwanted pores and cracks determined by the inadequate high temperature or to a gellified structure of the film and poor adhesion, when the temperature is lower than the recommended one.

Another important aspect to consider is the economical criterion. Although similar film properties are obtained during the curing process for the same films dried at different temperatures, it is obvious that the lower temperature will be preferred on the basis of economic grounds (lower costs dictated by lower energy consumption) as well as an easier manipulation of the processed samples.

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