



Microstructural and Electrochemical Analysis of Inorganic and Hybrid Sol Gel Silica Coatings on Al 7075 Alloy: Effect of Additives

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Inorganic and organic hybrid coatings were deposited on Al 7075 substrate by dip coating in a sol prepared from tetraethoxysilane with and without addition of both boric acid and ormosil. The samples were heat treated at two different temperatures of 120 and 220 °C. In case of using ormosil coated samples it was necessary to be heat treated at 120 °C to obtain full coverage of coatings. For this composition a film thickness of 2-3 micron could be reached by repeatedly coating and heat treatment for 5 times, whereas by other compositions a thickness of only about 1 micron could be reached. Microstructures of the films were characterized by SEM and energy dispersive X-ray analyses (EDX). The crystallization behaviour and thermal analysis of the films as well as gels were studied by XRD and DTA. According to electrochemical results the coated samples from the composition with ormosil repeatedly coated and heat treated for five times at 120 °C showed the best corrosion resistance. However increasing the temperature resulted in occurrence of micro holes defects and in island forms broken of coatings, which caused weakness of corrosion effect. These findings were confirmed with the SEM micrographs of the same samples. On the other hand boron additives exhibited better adherence of the solution to the substrate compared to tetraethoxysilane solution.

Key Words: Sol-gel, Tetraethoxysilane, Microstructure, Electrochemical corrosion.

INTRODUCTION

Light metal alloys such as of aluminium and magnesium have excellent physical and mechanical properties, in particular to their high strength: weight ratio make them an attractive material for automotive and aircraft applications¹⁻³. Unfortunately, these alloys are highly susceptible to corrosion and thus has limited their useful applications^{4,5}. There are a number of surface treatment methods to improve the corrosion resistance of these alloys.

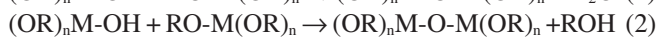
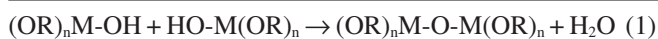
The films made by chromate solutions have excellent corrosion resistance and adhesion ability, but this process causes serious health problems to humans and is not an environmentally friendly surface treatment method^{1,2,4,6}.

Sol gel technology is one of the most promising alternative methods for chromium coatings for the corrosion protection of light metals. It is economic, environmentally friendly and coatings can be easily deposited on the surfaces. However there are some handicap in this method as of adherence weaknesses of the coatings to the substrate, micro cracks occurring during the heat treatment and limitation in coating thickness. By increasing of coating thickness some defects as micro cracks and pores occur on the surface and these defects cause

decreasing the corrosion resistance⁷⁻¹⁰. These problems need to be overcome and it is necessary that the sol gel coating method proves itself to be a reliable coating technique.

In the literature several different surface pretreatments¹¹⁻¹³ are made and chemicals as of chemically etching materials and/or organically modified silanes are added in to the sol gel solutions in order to increase their adherence ability to the substrate and to prevent coating defects during firing as well as to obtain thicker coatings^{2,4,9,12,14-16}.

The sol consists of a colloidal suspension of solid particles in a liquid. Precursors used to prepare a colloidal sol consist of metal organics, metals, or inorganic salts dissolved in an organic liquid. The chemistry of the sol-gel process is based on hydroxylation and condensation of molecular precursors. The use of metal alkoxide $M(OR)_n$ precursor is the most popular in sol-gel processing. Hydrolysis takes place when alkoxides react with water as described by the following reaction and a hydroxyl part becomes attached to the metal atom. Surfaces bearing hydroxyl groups are a prerequisite to obtain amorphous film growth using the surface sol-gel process. Condensation takes place when two partially hydrolyzed molecules or a partially hydrolyzed molecules with an -OR group come together as follows:



where, M represents the metal and R the alkyl group.

When the reaction completes and the molecular network extends throughout the solution, the substance transforms to a gel. This reaction can proceed until all of the hydroxide groups have been used up resulting in a network of ceramic type bonds.

In this work, it is aimed to develop multilayer sol gel coatings with sufficient film thickness in order to avoid this corrosion problem. Special attention is given to improve the adherence ability of sol gel solutions to the underlying substrate and to determine the properties of sol gel solutions for each coating process. For these purposes two kinds of additives as of boric acid and glymo are used. It was anticipated that boric acid acts as a chemical etching material and glymo play a role as binding material in the sol gel solutions prepared with tetraethoxysilane silicon alkoxide precursor.

EXPERIMENTAL

The specimens of aluminum 7075 alloy, in the form of 60 × 30 mm taken from a sheet 3 mm thick, were abraded to 800 finish with SiC grit papers, degreased in acetone, washed with distilled water and dried in dry air. The nominal composition was as follows (wt. %): 5.6 Zn-2.5 Mg-1.6 Cu-0.23 Cr-bal Al.

Tetraethylortosilicate, glymo and H₃BO₃ are used as starting compounds. Different amount of other ingredients were necessary namely distilled H₂O for hydrolysis, HCl (0.01 M) as a catalyst and C₂H₅OH as solvent. Generally as a basis all solutions was started with 50 mL tetraethoxysilane and 125 mL ethanol were used in total. The molar ratio of water (and HCl) to tetraethoxysilane varied from 2 to 3. All solutions were prepared at room temperature under continuous stirring. It is emphasized that ultrasonic agitation was essential to obtain a clear and homogeneous alkoxide solutions. Furthermore water had to be added drop by drop in order to avoid precipitation.

Before each coating procedure the viscosity and surface tension of the solutions were measured. The viscosity was measured by Stokes's falling sphere method. For measurement of viscosity a glass test tube was used filled with freshly prepared alkoxide solution and then covered by plastic foil with a small hole through which the spheres could be dropped.

The measurements of the surface tension were made by Wilhelmy plate method. A thin plate is lowered to the surface of liquid and the downward force directed to the plate is measured in newtons per meter.

Surface tension is directly the force divided by the perimeter of the plate. The plate weight and the force were measured by means of torsion balance. The surface tension 'σ' was calculated by the following formula:

$$\sigma = \frac{F - Q}{2l} \quad (3)$$

where, F-force of tearing off, Q- plate weight, l- length of the plate.

The gels and films were subjected to X-ray diffraction analysis. All samples appeared amorphous and there were no traces of crystallinity. DTA analyses (Shimadzu model) were employed to study the transformation of the gel upon heating

and to obtain information regarding the releasing temperature of organic solvents and water in the dried sample. All analyses were made in air atmosphere at 10 °C min up to 700 °C. The thickness of coatings was measured by using a profilometer (Ambios XP Series) on samples after heat treatment of the coatings. After each coating process whereby fresh coated samples dried and heat treated, the films were subjected to SEM analyses in order to investigate the microstructure of the films regarding their adherence and covering conditions to the substrate and coating defects as micro cracks and micro pores.

The electrochemical tests of coated and bare Al alloys were performed by using potentiodynamic polarization module of Gamry Reference 600 Potentiostat at room temperature in 3.5 wt. % NaCl solution, which is often known to have similar corrosive properties as seawater¹⁷. Aluminium and its alloys are susceptible to corrosion especially in chloride containing environments¹⁸ and thus using NaCl solution in electrochemical tests allowed us a better investigation of the electrochemical properties of sol-gel coatings. The electrochemical polarization tests were conducted by using a standard three electrode electrochemical cell setup with a saturated calomel electrode (SCE) as reference electrode, a graphite bar as auxiliary electrode (AE) and the test specimen as working electrode (WE). Prior to starting of the polarization tests, the rest potential of the test specimens was allowed to stabilize for 30 min, which the potential was shifted from about -0.1 V_{SCE} of the rest potential in the noble direction at a scan rate of 0.25 mV/s. Once a current density of 1 mA/cm² was reached in the external circuit between the working and auxiliary electrodes, the potential scan was stopped. All of the electrochemical tests were performed in a PVC cell as shown in Fig. 1.

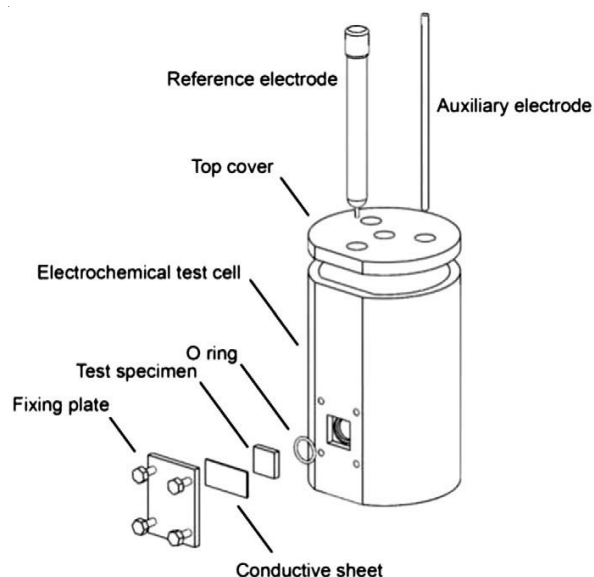


Fig. 1. Electrochemical test setup used for potentiodynamic polarization of Al alloys and sol-gel coatings

Three different sol gel solutions have been synthesized to prepare multilayer coatings on the substrates and to study the adherence ability of the coating to the substrate. The first main sol (composition 1) was prepared by mixing tetraethoxysilane, which served as the silica source and ethanol in a volumetric

ratio of 1:1. H₂O-HCl solution (20 % volume) was added drop wise into the solution, or else precipitation occurred. The solution was stirred for 3 h. Next the remaining amount of ethanol and H₂O-HCl solution were added to the solution and stirring was continued for another 1 h. A clear solution was obtained. The second and third sols were obtained by adding appropriate amount of glymo and H₃BO₃ in to the first solution, respectively and stirred further for another 2 h. To obtain the second sol (composition 2) glymo was added drop wise into the solution with a 20 % volume ratio to the existing tetraethoxysilane.

Glymo ormosil is an organically modified silane that improves the bond at molecular level of both, organic and inorganic networks. The second sol with glymo called hybrid organic-inorganic sol with a higher organic content help producing thicker coatings. The third sol (composition 3) containing H₃BO₃, which served as the boron oxide source and as well as etching compound to the substrate was firstly dissolved in warm H₂O and then incorporated into the first solution. The precise weight of H₃BO₃ used was dependent upon the condition of the solution. The H₃BO₃ should be added very carefully and stopped when the solution started to become cloudy. Use of H₃BO₃ was approximately 2-3 wt %.

In order to prepare thin sol gel films on substrates, the solutions were poured into plastic beakers and kept overnight. The substrate were cleaned in two steps, firstly in an acid mixture of HNO₃ with a few drops of HF, then in acetone with ultrasonic cleaner for 10 min, followed by a dry ethanol wash. The cleaned substrates were then dipped into the solutions, kept for *ca.* 1 min and withdrawn slowly with a speed of 30 sec/cm to form thin films. The films prepared in this manner were allowed to dry slowly in air for about 3 h and then the coated samples were heat treated inside a muffle furnace at two different temperatures of 120 °C and 220 °C. The samples were coated, dried and heat treated for 3 to 5 times depending on the coated surface conditions, if major defects were detected it was stopped with further coatings.

Freshly prepared solutions were kept in plastic beakers covered with para film. Clear and homogeneous gels were formed in this manner. The solutions were gelled in 2-10 days depending upon composition. After long aging periods the bulk gels cracked into small pieces but the films retained their integrity even after long period exposure to the atmosphere.

In order to be able to prepare multilayer thin films by dip coating it was important to hold the viscosity constant over long period of time. When the viscosity of the solution started to increase it was diluted with ethanol to increase the solution volume twice to threefold. By diluting the solution it was possible to delay the reaction and to keep the low viscosity of solution because of increased separation of the reacting species. The viscosity value was kept in the region of 0.2 to 0.5 dPas.

RESULTS AND DISCUSSION

The dried and heat treated gels were subjected to XRD analyses. All compositions appeared to be amorphous up to 800 °C. The composition containing B₂O₃ showed a crystalline structure started at 900 °C. All the other compositions remained amorphous up to 1000 °C. Early crystallization of

the composition with boric acid may be indicated that boron oxide incorporate into silica structure. Fig. 2 shows XRD patterns of boron containing composition heat treated at different temperatures of 800 and 1000 °C.

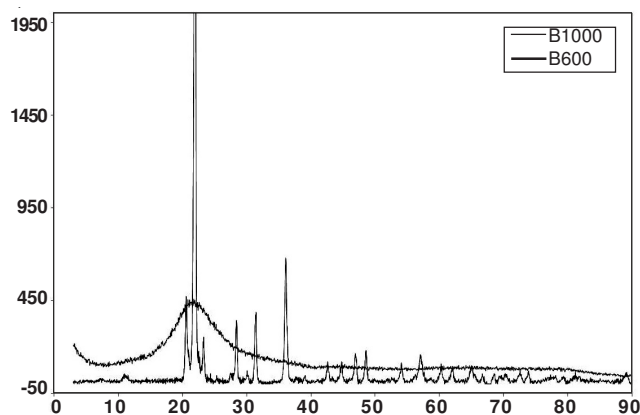


Fig. 2. XRD patterns of composition 2 in two different temperatures

DTA results of compositions 1 and 2 without and with ormosil are shown in Fig. 3. The curves exhibit low temperature endotherms at about 100 °C. These endotherms may be associated with the loss of organic solvent and water. In the 200 to 250 °C range one observes exotherms, which are attributed to the oxidation of residual organic matter of the precursor. The peak position shift to higher temperature with the composite 2 containing ormosil. These findings are in accord with Ghasemi *et al.*¹⁹ and may be interpreted as an exotherm due to combustion of high content of organics. According to DTA results two different temperatures as of 120 and 220 °C are chosen for the heat treatment of coatings, since at 120 °C organic solvent and water and at about 220 °C residual organics are supposed to be released from the samples.

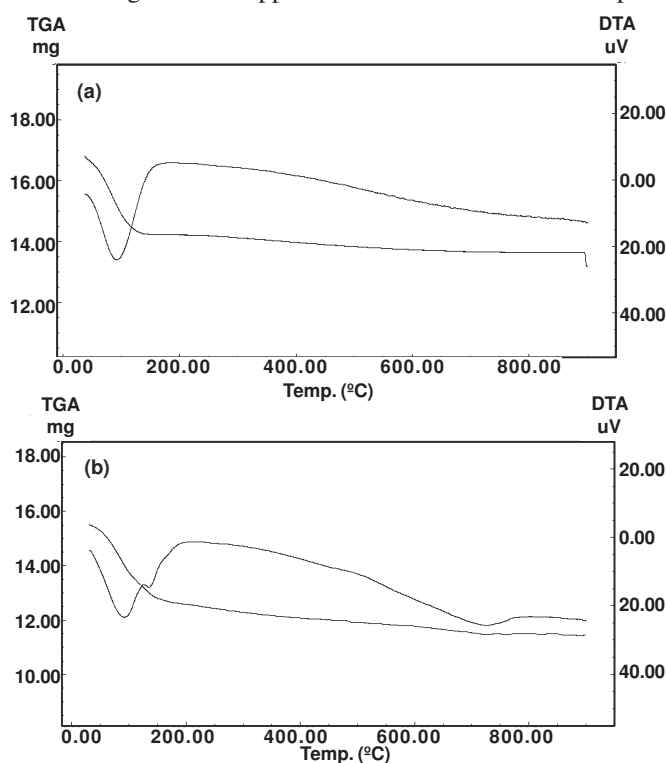


Fig. 3. DTA analysis of coatings (a) composition 1, (b) composition 2

SEM micrographs of single and multilayer coatings on Alumina 7075, heat treated at two different temperatures are shown in Figs. 4-6. Morphologies observed in these Figures are quite different from each other.

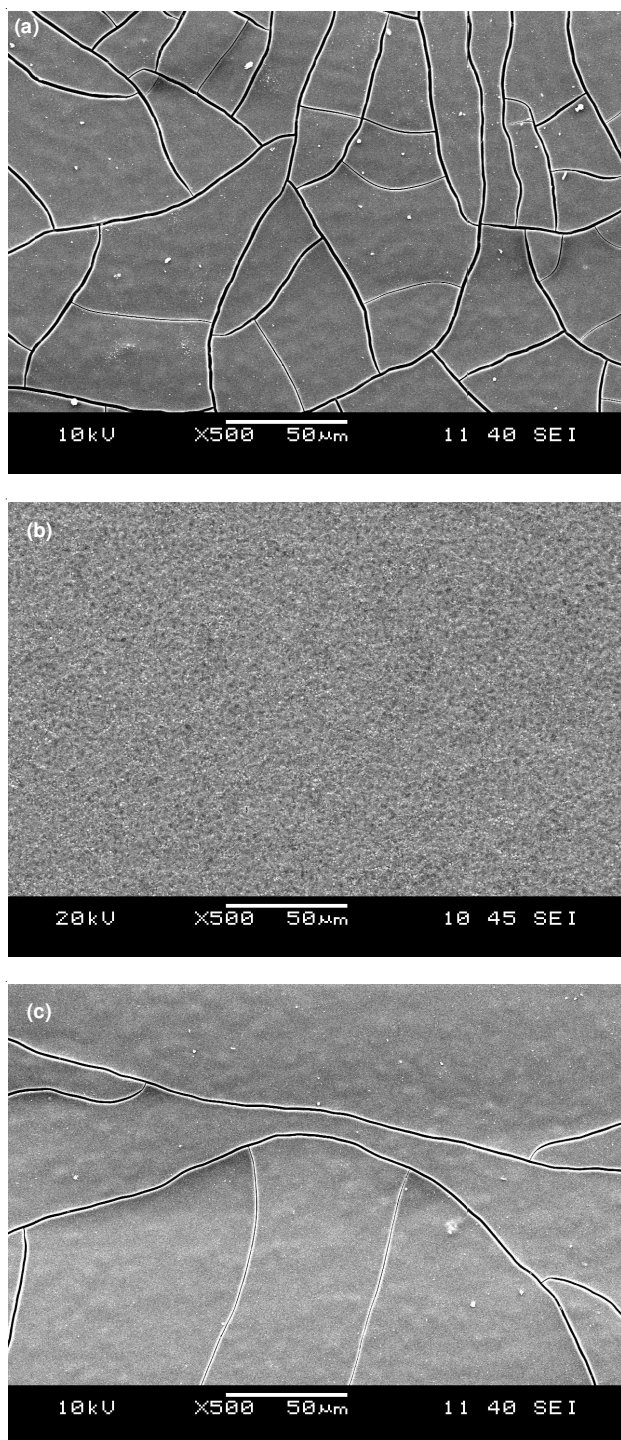


Fig. 4. SEM images of Sol-gel coatings prepared with a) composition 1, b) composition 2, c) composition 3

Fig. 4 shows the single layered surface morphologies of the coatings heat treated at 120 °C. Comparing their surface morphologies, it is realized that their adherence ability to the substrate. Fig. 4a represents composition 1, which prepared with only tetraethoxysilane shows a separated island forms of coatings instead of a full coverage, whereby Fig. 4b shows a

full covered coating without any serious defects. Fig. 4b represents the composition 2 containing ormosil additive. The morphology of the coatings of the composition 3 shown by Fig. 4c indicates a better covering capability compared to the morphology of Fig. 4a. These findings explain the effects of boric acid and ormosil on the adherence ability of coatings to the substrate, whereby boric acid play a roll of chemical etching and ormosil a binding effect to the substrate.

Morphologies of the same coatings but heat treated at 220 °C were also observed. With increasing the heat treatment temperature no detectable difference appeared in the coatings except with the compositions containing ormosil (Fig. 5).

Morphologies (Fig. 5) shows some defects of micro holes and separated coated forms, which may be associated with the combustion of high residual content of organics because of employed ormosil in that composition.

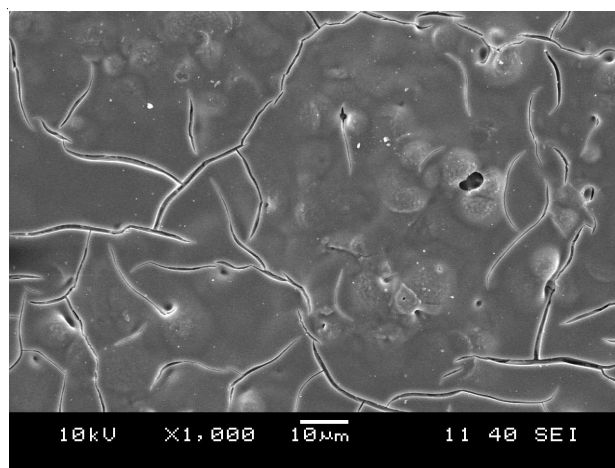
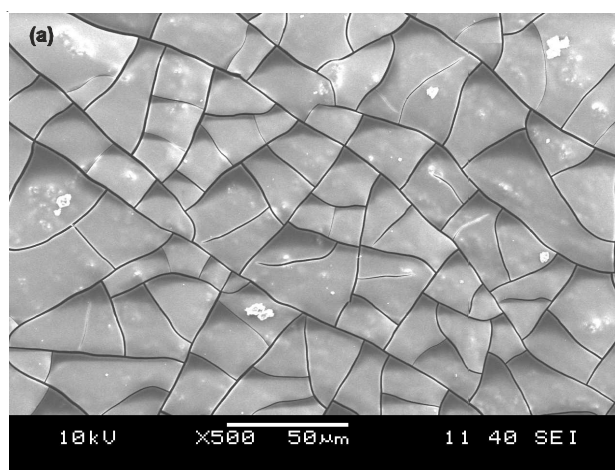


Fig. 5. SEM image of the coating after heat treatment

Fig. 6 demonstrate the morphologies of multilayer films heat treated at 120 °C and coated 3 times. Fig. 6a shows composition of 1, as can be seen on morphology separated island forms cover the underlayer and there are not a fully coverage of coatings. Fig. 6c represents the composition of 3 with boron additives. Compared to Fig. 6a, one can see a better coverage of coatings, which can be explained with the etching effect of boron additives increasing the adherence ability of sol gel solution to the under layered substrate.



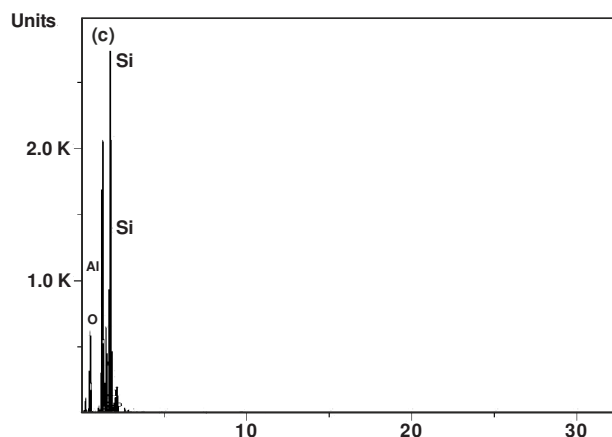
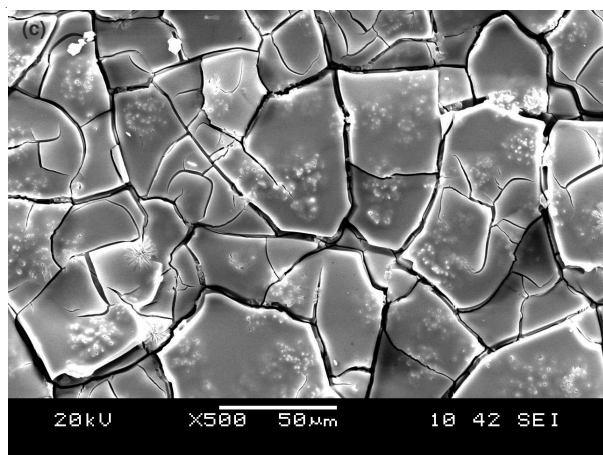
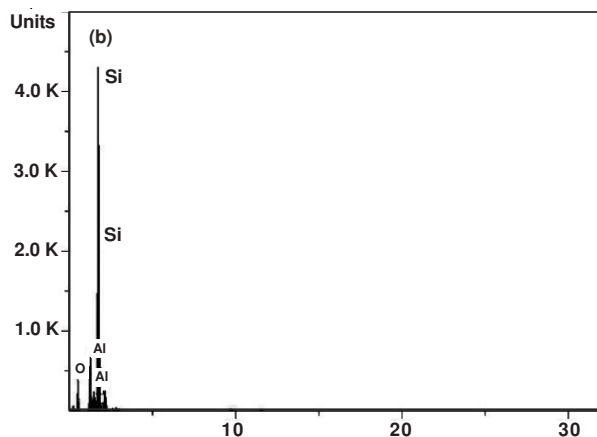
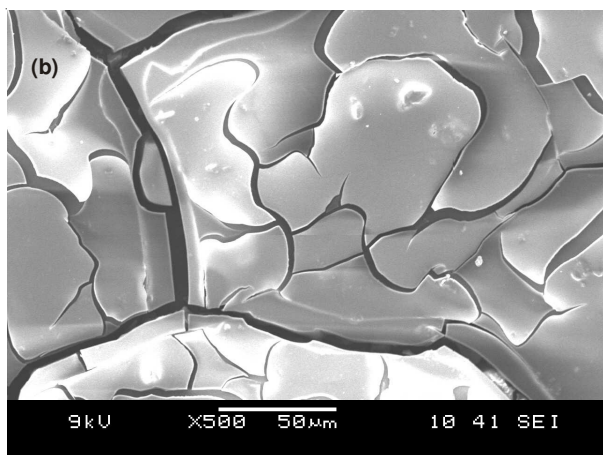
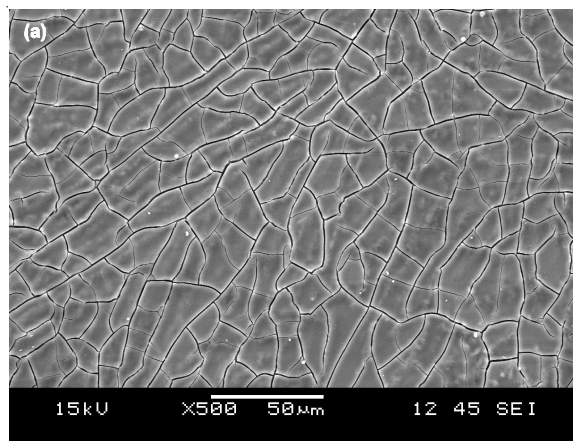
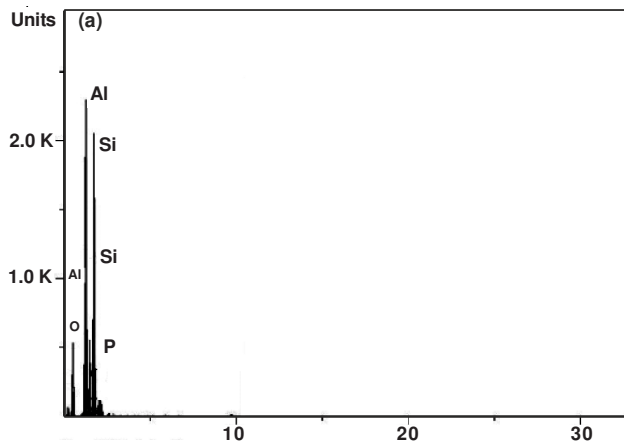


Fig. 7. EDX analysis of the coatings a) composition 1, b) composition 2, c) composition 3

Fig. 6. SEM images of the coatings after heat treatment with multi layer coating prepared in a) composition 1, b) composition 2, c) composition 3

Fig. 6b shows the morphology of composition 2 with glymo additives. Compared to Fig. 6a and 6c, one can see much better coverage of coatings, which can be explained with binding effects of ormosil causing a better adherence of solution to the substrate and prior coatings. The results of corresponding EDX analysis of the coated samples are shown in Fig. 7. The peaks of Si are a clue of the presence of SiO_2 in the coating. EDX analysis from the coatings explain and conform the quality of the coatings, where composition 2 shows high contents of Si, the other compositions show lower content of Si and high content of Al, which comes from the substrate.

When the multilayer coatings of the compositions 1 and 3 heat treated at 220°C we obtained similar morphology results as of 120°C , but the composition of 2 with ormosil showed microhole defects, which may be associated with the combustion of high residual content of organics as explained before. Therefore further coatings for this composition underwent to heat treatment only at 120°C . Fig. 8 show multilayer thin films coated for 5 times. Fig. 8b shows the morphology of the composition 2. As seen from the figure a full covered coatings could be obtained without any serious surface defects, while on the coated samples of the composition 1 (Fig. 8a) and 3 (Fig. 8c) one see clearly the defects of micro cracks occurred after 5 times coating, which might be interpreted due to the stress occurring upon certain thickness of coatings.



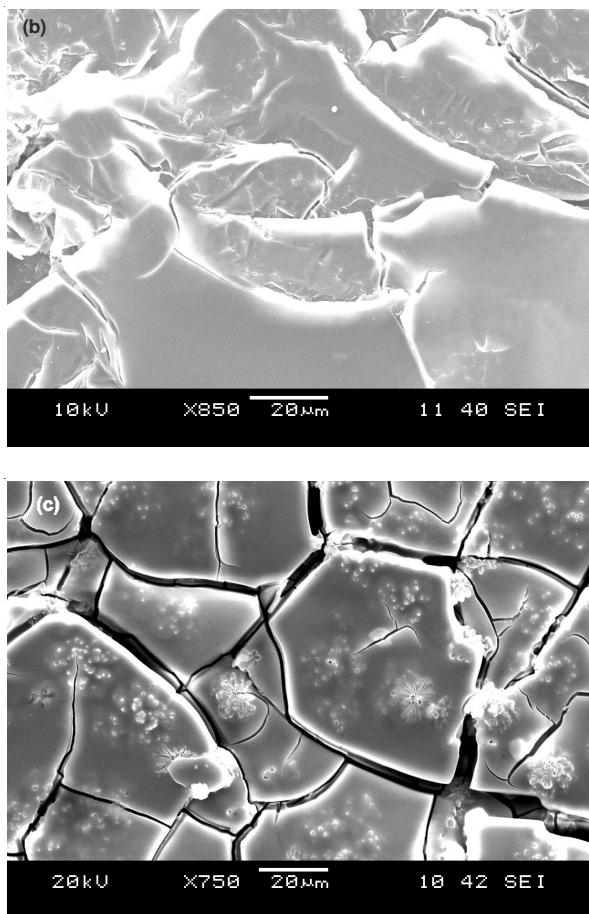


Fig. 8. SEM images of coatings after heat treatment a) composition 1, b) composition 2, c) composition 3.

Composition 2 with additives of glymo, heat treated at 120 °C and coated for 5 times, enabled us to obtain a film thickness of 3-4 micron without any surface coating defects, while with the other compositions we could obtain thickness of max. 1-2 micron only, heattreated at 220 °C and coated 3 times.

Surface tensions of the prepared sol-gel solution are summarized in Fig. 9.

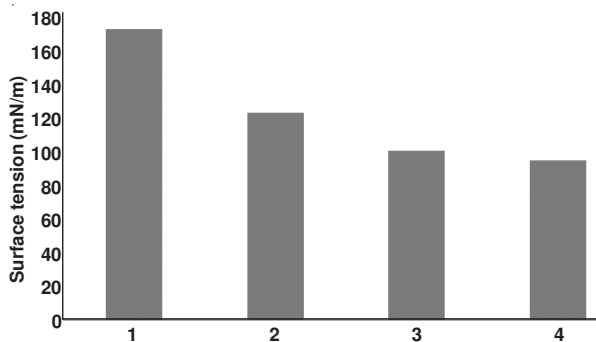


Fig. 9. Surface tension of the solutions

As can be seen from the table that both boric acid and ormosil addition lower the surface tension. These finding might be an indication for the explanation of better adherence ability of solutions with boric acid and ormosil additions. It is known that surface tension is a phenomenon caused by the cohesive forces between liquid molecules and it is an effect within the surface film of a liquid that causes the film to behave like an elastic sheet. The knowledge of surface tension of solutions is useful for many applications and processes, as it governs the chemical and physical behaviour of liquids.

The electrochemical behaviour of sol-gel coatings is influenced by many factors including surface roughness, coating thickness and porosity level.

The potentiodynamic polarization curves of uncoated 7075 Al alloy and sol-gel coatings is given in Fig. 10.

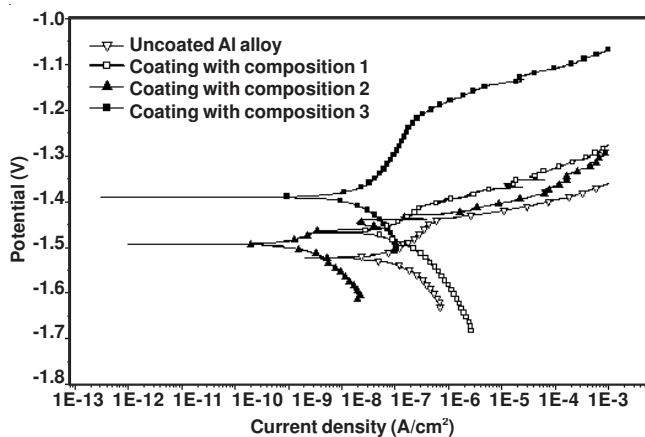


Fig. 10. Potentiodynamic polarization curves of uncoated and coated Al alloy

Uncoated Al alloy corroded at 3.5 % NaCl solution during the test potential reach to steady state at stabilization period. Moreover, several active pitting site on the surface were seen prior to starting of the polarization tests. In the anodic branch of potentiodynamic polarization curve of bare Al alloy, slightly pseudo passive zone was observed due to an active corrosion first and a subsequent coverage of the working electrode surface with the corrosion products. This is related to the high reactivity of Al alloys in Cl⁻ containing environments. As potential increased from open circuit potential in the noble direction rapid dissolution of bare metal took place.

The polarization resistance (R_p) and corrosion rate values of bare and sol-gel coated Al alloy were calculated by using the following Eqs. (1.4) and (1.5) respectively²⁰,

$$R_p = (b_a \cdot b_c) / 2.303 \cdot I_{corr} \cdot (b_a + b_c) \tag{4}$$

$$Corr_{Rate} = K \cdot I_{corr} \cdot E_w \tag{5}$$

where, E_w is equivalent weight of alloy (g/equivalent), K is a constant with a value of 0.0895 that defines the unit for the corrosion rate (mg/cm²/year). The calculated values were listed in Table-1.

TABLE-1 ELECTROCHEMICAL PARAMETERS OF SOL-GEL COATED AND BARE ALUMINIUM ALLOY						
Material	E_{corr} (V)	I_{corr} (A/cm ²)	β_a (V)	β_c (V)	Corrosion rate (mg/cm ² year)	Polarization resistance (Ω cm ²)
Uncoated aluminium alloy	-1.621	$0.620 \cdot 10^{-5}$	0.071	0.094	24.304	2831
Coating with composition 1	-1.553	$1.152 \cdot 10^{-7}$	0.299	0.151	0.508	337007
Coating with composition 2	-1,398	$3.542 \cdot 10^{-7}$	0.345	0.125	0.585	228236
Coating with composition 3	-1.514	$2.12 \cdot 10^{-7}$	0.315	0.138	0.401	428389

Low corrosion current density and more noble free corrosion potential values generally indicate enhanced corrosion resistance. The free corrosion potential values increases in the case of coated alloys as compared to bare alloys. All of the coated specimens reveal lower corrosion current density, which decreases by approximately two orders of magnitude as compared to bare Al alloy.

Conclusion

A multi-layer inorganic or hybrid inorganic-organic sol-gel coatings on Aluminium 7075 alloy were obtained using tetraethoxysilane, tetraethoxysilane/ormosil, or tetraethoxysilane/boric acid with the aim of obtaining coatings with complementary properties and improving the corrosion resistance of 7075 alloy. Coatings were made by using dip coating method and low temperature heat treatments repeated after each coating.

It is found that the addition of boric acid or ormosil to sol gel solution of increased the adherence ability of coating promoting the corrosion protection of aluminium 7075 alloy.

Present results demonstrated that the best corrosion resistance coating can be obtained with the hybrid sol gel coatings using tetraethoxysilane/ormosil.

XRD patterns revealed a completely amorphous structure of the samples heat treated up to 800 °C. The composition containing B₂O₃ started to crystallize at 800 °C, whereby the other compositions remained amorphous up to 1000 °C. The crystallization product is determined as trydymite phase of SiO₂.

The thermal degradation process of gel powder was characterized by TGA/DTA. The results showed that organic solvent and water are released at about 100 °C and residual organic compounds in the film decomposed in the temperature range from 200 °C to 250 °C. Based on the DTA and SEM results, two different temperatures as of 120 and 220 °C are chosen for the optimum heat treatment of coatings. For the composition 2 containing ormosil, optimum heat treatment temperature for depositing a dense, porous-free and high optical quality hybrid inorganic organic sol-gel film is chosen at 120 °C, whereas for the other compositions at 220 °C.

For the composition 2 containing ormosil a film thickness of 2-3 micron were obtained without any formation of cracks on the coating layer, heat treated at 120 °C and repeatedly coated for 5 times, while for other compositions a maximum film thickness of 1 micron could be obtained heat treated at 220 °C and coated for 3 times, further coatings of that compositions induced the formation of cracks leading to reducing the corrosion resistance.

In order to be able to prepare multilayer coatings it was important to keep the viscosity constant over long periods of time during dip coatings.

Surface morphologies of single and multilayer coatings on Aluminium 7075 are demonstrated by SEM micrographs. Composition containing ormosil additives and heat treated at

120 °C demonstrate full coverage of coatings with good adherence of solution to the substrate and prior coatings. With increasing heat treatment it occurs some defects as of micro holes and separated forms of coating, which are attributed to combustion of high residual content of organics. The morphologies consist of only tetraethoxysilane solutions show a weak adherence to the substrate separated island forms of coating covering the underlayer and there are not one times fully bulk coverage of coatings, whereas SEM micrographs of composition with boron or ormosil additives to tetraethoxysilane solution represent a better coverage of coatings. These findings might be explained with the etching and binding effect of additives increasing the adherence ability of coatings to the underlayered substrate. The low surface tensions of the solutions with additives were also related to better adherence of solutions to the substrate.

The effectiveness of good corrosion protection of the composition containing ormosil is confirmed by potentiodynamic corrosion tests. Similar results even though with less effectiveness are also obtained for the composition with boron additives.

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