Advances in Science and Technology Research Journal
Volume 10, No. 32, Dec. 2016, pages 17–23
DOI: 10.12913/22998624/65112

Research Article

APPLICATION OF CHEMICAL PRE-TREATMENT ON THE POLISHED SURFACE OF ALUMINIUM ALLOYS

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Received: 2016.08.30
Accepted: 2016.10.08
Published: 2016.12.01

ABSTRACT

This paper reports the preparation and characterization of thin transparent nanolayers with phase composition ZrF_4 and different modification of SiO_2 with special focus on affecting the surface roughness of the material and the way of exclusion of the thin nanolayer on the surface of the polished aluminium material. The thin nanolayer was prepared by the sol-gel method. The final treatment based on PTFE was applied on the surface of some samples. This treatment is suitable for increasing wear resistance. The films were characterized with help of SEM microscopy and EDS analysis. The surface roughness was measured with classical surface roughness tester. The results on this theme have already published but not on the polished surface of the aluminium material. The results from the experiment show the problems with application of these nanolayers because a cracks were found on the surface of the material and deformations of the layer after application of the PTFE final layer. The surface layer formation is discussed.

Keywords: sol-gel technology, nanolayers, aluminium alloys, surface roughness, SEM.

INTRODUCTION

Metals, are the backbone of all engineering applications like automotive, construction, containers, aerospace, etc. due to a combination of their useful properties. They are extracted from their ores (oxide form) if we want to use them for engineering applications. This extraction process results in thermodynamically unstable state to the metals when metals try to revert to the oxide form by chemical or electrochemical reactions. With this process metals want to attain stability i.e., they tend to corrode [1, 2]. Corrosion is the process by which metals lose their useful properties. The way to protect them is to use some technology of surface pre-treatments which protect metals from corrosion and also improve the adhesion of the subsequent organic coatings. Commercially, metals are pre-treated with conversion coatings (phosphate, chromate, oxidation). These conversion coatings can be used as a base before the application of the final organic coatings or can be used as free-standing coatings [3, 4, 5]. At present alternative technologies opposite the classical surface pre-treatments (phosphate, chromate, oxidation) are on the rise. These technologies are based on nanotechnology, when occurs to the creation of the nanolayer on the material surface. In this paper we deal with the chemical surface pre-treatment nanotechnology based and created with the sol-gel process.

Sol is a colloidal suspension of nanoparticles (mainly silica) in a solvent, finally transformed into a gel after complete condensation and subsequent solvent evaporation. Alcohol formed as a by-product during hydrolysis as well as alcoholic condensation reactions, evaporates on the application resulting in –Si-O-Si- bond. The relative rates

Table 1. Chemical composition of the basic material EN AW 6023

Element	Al	Si	Fe	Cu	Mn	Mg	Cr	Bi	Zn	Pb	Sn	Ti
Content wt. %	96.05	0.838	0.212	0.278	0.566	0.627	0.024	0.509	0.019	0.017	0.758	0.047

and the extent of hydrolysis and condensation reactions are influenced by many factors like temperature, concentrations, solution pH the way of application etc. The first step involves the hydrolysis of silane precursor with water, generating silanol groups. Commercially, mineral acids like sulphuric, hydrochloric, nitric acids have been used for coating applications. In a view of application of silane films on metallic substrate, the hydrolysis of alkoxy-silanes has a significant effect on final properties of the sol-gel film. Usually, dipping or spraying method has been used for the application of hydrolysed silane solution. The formation of strong covalent metallo-siloxane bonds take place during subsequent drying and curing. The application properties of hybrid material mainly depend on strength and durability of interfacial bonds between organic and inorganic phases which, in turn, depends on the structure of silane and silanization process. These organosilanes coatings can offer good corrosion protection to a number of substrates, like aluminium, copper, steel etc. and has become and effective and environment friendly surface protective system [1, 4, 5, 6].

In spite of all the advantages of sol-gel processing, sol-gel oxide coatings suffer from several drawbacks. In general, sol-gel coating are highly porous with low mechanical integrity. Annealing or sintering at high temperatures is required to achieve a dense microstructure. Therefore, sintering at high temperatures might introduce cracks and delamination of sol-gel coatings due to a large mismatch of thermal expansion coefficients and possible chemical reactions at the interface. Sintering at high temperatures also limits application of sol-gel coatings on temperature sensitive substrates. When appropriate chemical composition and processing conditions are applied, relatively dense organic-inorganic hybrid coatings can be developed for application including wear resistance and corrosion protection [7, 8, 9].

EXPERIMENTAL SAMPLES PREPARATION

Our samples were prepared in some variations on the aluminium material polished surface. The chemical composition of the experimental material is shown in table 1. This is an aluminium alloy with the designation EN AW 6023. Experimental samples were polished before the application of chemical pre-treatment. The reason is that we want to observe the right character of excluded layers of chemical pre-treatment unaffected with the higher roughness of the material and after that we observed adhesion of the excluded layers to this material and the way how each variant of pretreatment affect the roughness. The average surface roughness of the source material is Ra 0,030 µm, Rz 0,239 µm, Rt 0,365 µm. For evaluation of character and morphology of excluded layers we used SEM and EDS analysis and for the evaluation of the roughness we used the classical surface roughness tester.

The experimental samples were prepared in 6 variants. For the chemical pre-treatment we used nanoproduct in a form of clear liquid. This product was analysed with the X-ray diffraction. The chemical was dried and after the analysis it was found that the phase composition of the residue is zirconium tetrafluoride – ZrF_4 and various modifications of silicon oxide – SiO_2 equivalent to tetraetoxysilan bath for the sol-gel method.

The first step for preparation of experimental samples was degreasing, which removed all possible impurities from the material surface. The next step was application of the nanoproduct. We had two types of nanoproducts for this purpose: one especially for aluminium alloys (nano 1) and the second type (nano 2) for aluminium alloys and other materials especially for steels and galvanized steels. The second type of nanoproduct can be used also instead of the classical degreasing process. We observed the influence of this

Table 2. Experimental samples preparation

Sample	Chemical pre-treatment			
	Degreasing	Nano 1	Nano 2	PTFE
A	*	*	-	-
B	*	*	-	*
C	*	*	*	-
D	-	*	*	-
E	-	*	*	*
F	*	*	*	*

step on the behaviour of the final layer. For some samples the other type of chemical pre-treatment based on PTFE (polytetrafluorethylene) was also used in the experiment. This pre-treatment was used as the final coating and is suitable for the increasing of the wear resistance. Experimental samples preparation and their marking is shown in Table 2.

The first technology – degreasing – was used for samples A, B, C and F. The degreasing bath is composed with 2 agents and mixed with demineralized water, conditions for this step were temperature 50°C, application by dipping for 5 minutes. After this step follows the dip in the water. The next step was application of zirconium nanoproduct with designation no. 1 created on the material surface by sol-gel technology. The chemical was mixed with demineralized water. The conditions for this step was room temperature 20°C, pH of the solution 4.8, application time is 2 minutes by dipping and slow removing from the solution and dip in demineralized water. The samples with designation A finish with this operation and after that they were dried in the dryer for 15 minutes at temperature 130°C. The samples with designation B were also dried for 15 minutes at temperature 130°C and with this step were prepared for the next operation (application of PTFE coating). The next operation for the samples C, D, E, and F was the application of the nanoproduct no. 2. Solution for this step was two component and mixed with demi water. The conditions for application are temperature of the bath: room temperature 20°C in the case when is used like the protective coating (samples C, F) and 50°C when was used as the first step (when we use it like the first cleaning step; samples D, E), application time 5 minutes, slow removing from the solution and dipping in the water. After application of this pre-treatment the samples are dried 15 minutes at temperature 130°C. The samples C and D finish with this step. When the samples B, E and F are dried the last final coating application with PTFE follows. This coating is also in a form of solution and mixed with demi water. The conditions for application are temperature 60°C, pH of solution 7,5 and time of application 15 minutes. The samples are dipped into the solution and after removing from the bath are dried at temperature 100°C for 30 minutes.

EVALUATION OF THE EXPERIMENTAL SAMPLES STATE

SEM and EDS analysis

The samples were closely analysed by SEM. The SEM image showed sample surface with appreciable delamination or cracking of the coating. Behaviour of the nanolayers is by each chemical pre-treatment different. Figure 1 shows SEM images of the A and B experimental samples. These samples were pre-treated by the same sol-gel film and on the surface of the sample B was as a final coating applied the PTFE coating. We can see a lot of cracks on the surface caused during the drying process. The application of PTFE caused the exclusion of small particles of spherical shape. These particles cover the whole surface of the sample and fill in the cracks. The EDS analysis

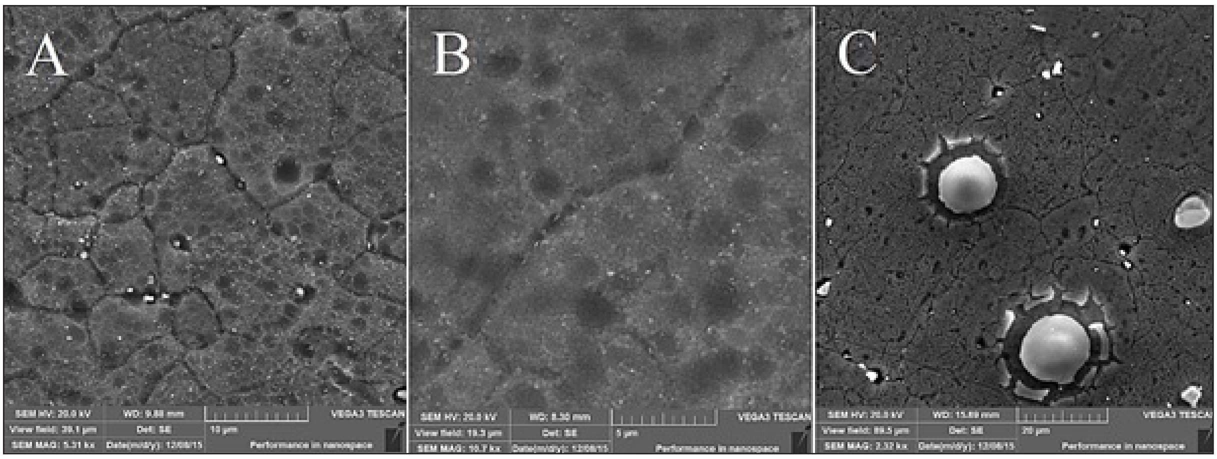

Fig. 1. SEM analysis of the sample surface A, B, C

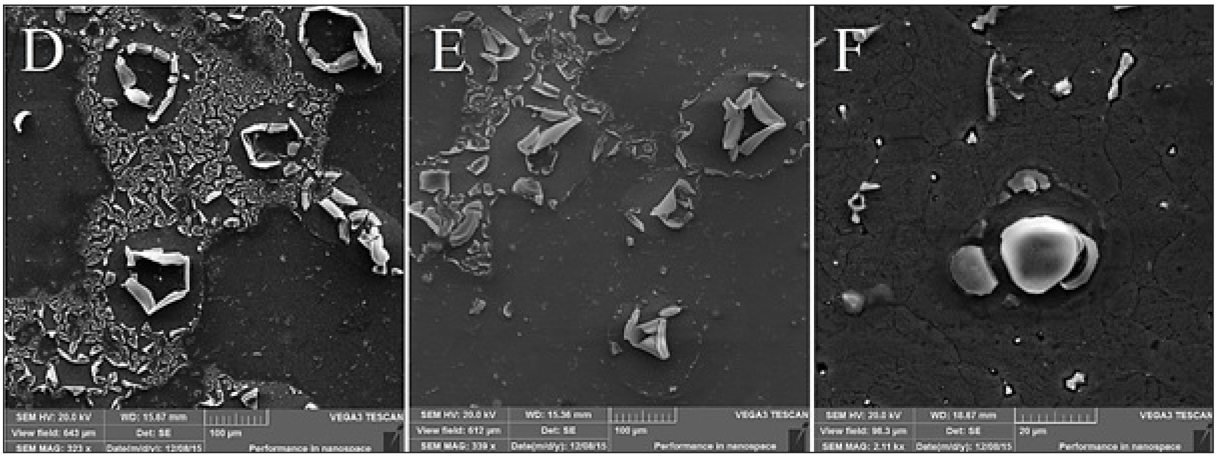

Fig. 2. SEM analysis of the sample surface D, E, F

for these samples is shown in the Figure 3 and chemical elements found on the surface of the samples are:

- Sample A [wt. %]: aluminium 85.66, oxygen 9.84, silicon 1.08, zirconium 1.94, magnesium 0.91 and manganese 0.57.
- Sample B [wt. %]: aluminium 81.99, oxygen 3.99, silicon 0.41, magnesium 0.60, manganese 0.68, fluorine 1.90 and carbon 10.43.

Zirconium and fluorine are the basic compounds of the nanoproduct with designation nano 1. The presence of carbon on the sample B is because this sample have the final coating PTFE.

Different is the exclusion of the layer on the sample surface D and E, Figure 2. These samples were not pre-treated with degreasing and by omitting of this step occurs the extensive delamination on the surface of the sample. This delamination was probably caused in localized electrochemical reaction at the interface resulted in debonding, delamination and lifting of the sol-gel coating from the substrate due to a volume expansion as a result of metal oxidation. Delamination between the sol-gel coating and the substrate could be attributed, at least partly, to hydrolysis reactions at the interface. The EDS analysis for these samples is shown in the Fig. 4 and chemical elements found on the surface of the samples are:

- Sample D [wt. %]: aluminium 59.77, oxygen 21.23, zirconium 9.03, phosphorus 4.92, fluorine 3.12, magnesium 1.00 and calcium 0.93.
- Sample E [wt. %]: aluminium 14.01, oxygen 23.00, zirconium 11.90, phosphorus 6.63, fluorine 26.13, calcium 1.46 and carbon 16.87.

The presence of calcium is due to the omitting the degreasing. Thanks to this some impurities after the previous polishing may exist on the material surface. Higher content of zirconium and fluorine are due to the use of two nanoproducts during the chemical pre-treatment. Both of these pre-treatments are zirconium nanopassivation.

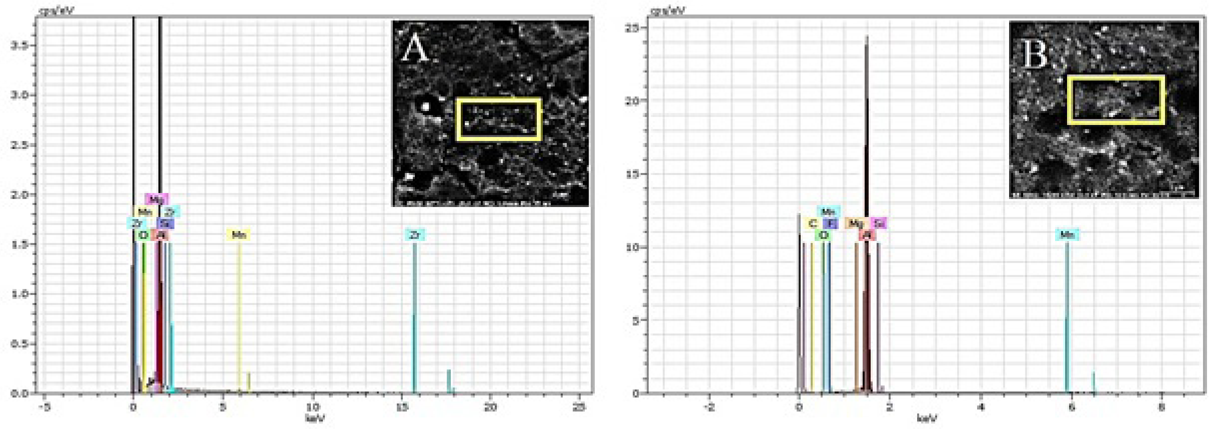

Fig. 3. EDS analysis of the samples A and B

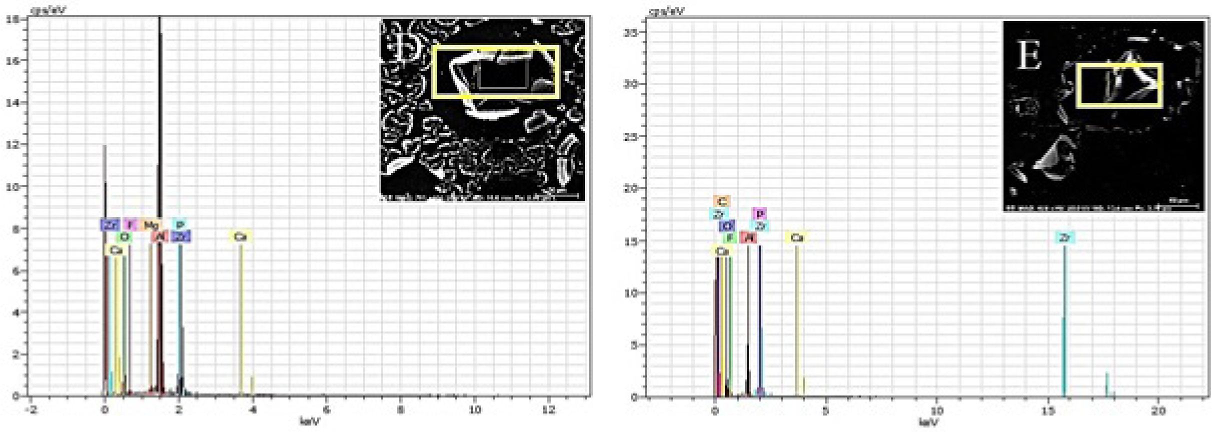

Fig. 4. EDS analysis of the samples D and E

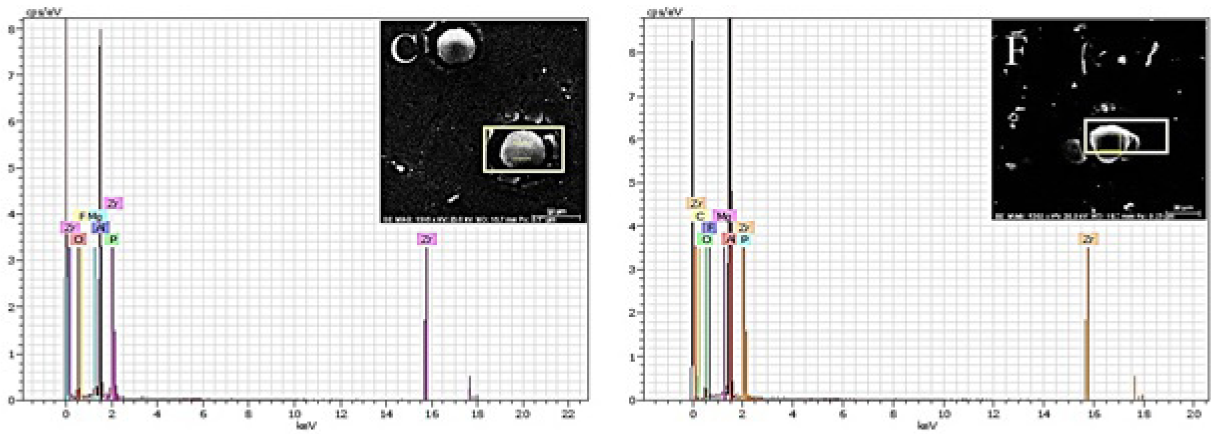

Fig. 5. EDS analysis of the samples C and F

Nano 2 is to it composed with two chemicals and one of them contains phosphorus. That is why, we found this element on the material surface. The presence of carbon on sample E is because this sample had the final coating PTFE, like it is in the case of sample B.

The last two variants of pre-treatments have a little bit different appearance. Formations of spherical shape appeared on the surface of the samples. Figure 1 C and Figure 2 F suggest a possibly of a different mechanism at the interface between the sol-gel coating and Al substrate. It is also possible that these formations occurred due to the presence of some dust particles or impurities on the material surface. But like in the previous case occurred to delamination of the nanolayer from the substrate but the mechanism of this change is slightly different, probably due to the use of degreasing as the first step in experimental sample preparation. The difference between each sample and the influence of each chemical pre-treatment variant can be seen after surface roughness analysis. The EDS analysis of the samples C and F is shown in the Figure 5 and chemical elements found on the surface of the samples are:

- Sample C [wt. %]: aluminium 43.25, oxygen 23.82, zirconium 18.90, phosphorus 7.98, fluorine 3.23 and magnesium 2.82.
- Sample D [wt. %]: aluminium 75.06, oxygen 7.19, zirconium 1.65, phosphorus 0.52, fluorine 3.11, carbon 11.83 and magnesium 0.63.

The problem with delamination can also be caused by the thickness of the layer. This is the problem of variants C, D, E and F where two nanoproducts were applied together. When applying only the nano 1 product the layer is uniform without delamination, even if a crack appeared during the drying process.

Surface roughness analysis

For evaluation of the influence of the chemical pre-treatment the Ra, Rz (Fig. 6) and Rt parameters were used. The best predicative value

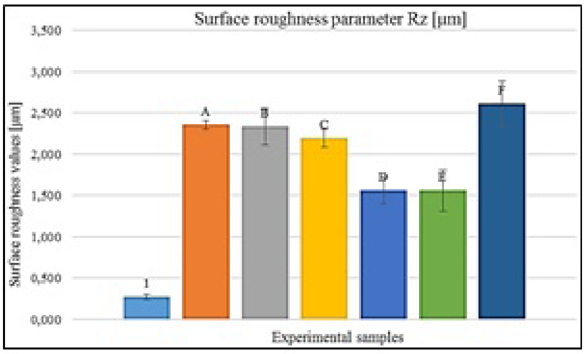

Fig. 6. Surface roughness analysis – Rz parameter

in our case has parameter Rz (roughness of the profile determined from 10 points).

30 measurements were performed on the surface of each sample. The average Rz values are: sample without any pre-treatment 1 – 0.271 µm, A – 2.356 µm, B – 2.335 µm, C – 2.211 µm, D – 1.560 µm, E – 1.558 µm, F – 2.611 µm.

From the surface analysis we can see that degreasing causes increasing of the surface roughness. All pre-treated samples with this technology have higher roughness – A, B, C and F. It is due the etching of the substrate surface during this technology. The degreasing product etch away impurities from the material sample and also the surface layers of the material and due to this process occurs to the increasing of the roughness. The PTFE pre-treatment causes the decreasing of the roughness. It is because of the way how this pre-treatment is excluded. This pre-treatment is excluded in a form of very small spheroidal particle which fill in the cracks and other inequality of the surface. Application of the nano 1 caused additional increasing of roughness. This effect is suitable for the application of the final powder coating. This technology creates good profile for anchoring of the coating. The nano 2 product have opposite effect. Connection of two nanoproducts nano 1 and nano 2 causes delamination of the layer. We see this technology as unsuitable like from the viewpoint of corrosion resistance increasing and also application of the final coating.

CONCLUSION

The sol-gel based coatings can be an efficient tool to replace the classical pre-treatments, like for example highly toxic and hazardous chromate based pre-treatments, on metals and their alloys. These pre-treatments nanotechnology based can be accepted as environmentally friendly surface pre-treatments methods. The three dimensional network of cured sol-gel coatings can provide good corrosion resistance, oxidation and wear resistance and good anchor profile before application of the final organic coating. The thin surface nanolayers in this experiment were prepared by sol-gel method. Experiment was based on application of 6 variants of two nanoproducts with different chemical composition and the final PTFE coating. The nanolayers are used for increasing of the corrosion resistance of the basic material and also as the product which helps to prepare the material surface before the application of the final coating. Application of PTFE is used for increasing the wear resistance thus pre-treated material. We can conclude from the results of SEM, EDS and surface roughness analysis that the best result for practical use have variants A and B. Other variants: C, D, E and F have problems with delamination of the nanolayer and this fact is caused probably due to higher thickness of the nanolayer when occurs to the extensive cracking and delamination during drying process. We can conclude that this technology has some limitations like the temperature of drying, the thickness of the excluded layer and the technology of application. Some limitations of this process can be overcome by optimizing the silane treatment process, the technology of application and pre-tretment before the nanoproduct application.

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