

ANALYSIS OF CHEMICAL PRE-TREATMENT EXCLUDED WITH USE OF SOL-GEL TECHNOLOGY ON POLISHED SURFACE OF AL SUBSTRATE

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Abstract. The article deals with preparation and description of thin transparent nanolayers. The phase composition of the nanoparticle we use in the experiment is based on ZrF_4 and SiO_2 (different modifications). We are interested in the way how this nanoparticle after its exclusion affects the surface roughness of the basic material and the way of exclusion and morphology of the thin nanolayers on the surface of the polished aluminium material. These nanolayers are created by sol-gel technology on the material surface. Besides the thin zirconium nanolayer we tested the next product based on PTFE (polytetrafluoroethylene - teflon). This product is used for increasing of the wear resistance. The aim of the experiment is to find the suitable technology of chemical pre-treatment, which will increase the corrosion protection of the material and give to it better properties, respectively better wear resistance, better adhesion for anchoring of the final powder coating etc. For evaluation of the experimental samples we used SEM and EDS analysis and surface roughness measurements.

Keywords: chemical pre-treatment, aluminium alloy, nanolayer, sol-gel, SEM, EDS, surface roughness.

Introduction

High-quality surface preparation is an essential precondition for achieving the desired corrosion resistance and adhesion of final coating (for example, powder coating). Metals are the backbone of all engineering applications (construction, automotive, aerospace) and if we want to use them for engineering applications it is necessary to extract them from their oxide form. This extraction process results in thermodynamically unstable state to metals when metals try to revert to oxide form by chemical or electrochemical reactions. With this process the metals want to attain stability, i.e. they tend to corrode [1; 2]. Corrosion is a natural process, which converts a refined metal to a more stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical reaction with their environment. For protection of metals we use technologies of surface pre-treatments which help protect metals against corrosion and give to the basic material some useful properties like better adhesion of organic coatings. Metals are commercially pre-treated with conversion coatings – chromate, phosphate or oxidation. These conversion coatings are usually used before the application of organic coatings. Sometimes it is possible to use them also like the free-standing coatings [3-5].

At present there are on the rise alternative technologies opposite the classical surface pre-treatments (conversion coatings). The technology is based on creation of the nanolayers on the surface of the material and is excluded 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 application resulting in -Si-O-Si- bond. The relative rates and the extent of hydrolysis and condensation reactions are influenced by many factors like temperatures, concentrations, solution pH, the way of application etc. The first step involves hydrolysis of silane precursor with water, generating silanol groups. Commercially for coating applications mineral acids have been used like sulphuric, hydrochloric or nitric acids. In view of application of silane films on metallic substrate, hydrolysis of alkoxy-silanes has a significant effect on the final properties of the sol-gel film. Usually, the dipping or spraying method has been used for application of the hydrolysed silane solution. The formation of strong covalent metallo-siloxane bonds takes place during subsequent drying and curing. The application properties of the hybrid material mainly depend on the strength and durability of interfacial bonds between organic and inorganic phases, which, in turn, depend on the structure of silane and the silanization process. These organosilane coatings can offer good corrosion protection to a number of substrates like aluminium, copper, steel etc. and it has become an effective and environment friendly surface protective system [1; 4-7].

Sol-gel processing except many advantages also suffers from several drawbacks. Sol-gel coating is highly porous with low mechanical integrity. Therefore, after this technology phosphate like the

final coating technology is used before powder coating in the companies. Annealing or sintering at high temperatures is required to achieve a dense microstructure. 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 inter-face. The problem is also limitation of sol-gel coating application due to the temperatures which are used during the sintering process [7-9].

Materials and methods

Basic material chemical composition is shown in Table 1. The experimental samples were before application of the coating polished and after that pre-treated with different variations of chemical pre-treatment. Basic material is aluminium alloy EN AW 6023 – AlMgSiSnBi.

Table 1

Basic material chemical composition

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

The reason for polishing of the basic material is that we want to observe the right character of the excluded layers of chemical pre-treatment unaffected with higher roughness of the material.

For evaluation of the experimental samples we observed adhesion of the excluded layers to this material and the way how each variant of pre-treatment affects the roughness. The average surface roughness of the source material is R_a 0.030 μm , R_z 0.239 μm , R_t 0.365 μm . For the evaluation of the roughness we used the classical surface roughness tester.

The character and morphology of the excluded coatings were studied using scanning electron microscope TESCAN VEGA 3 (SEM and EDS analysis).

The experimental samples were prepared in 6 variants. For chemical pre-treatment we used nanoparticle in the form of clear liquid. This product was analysed with the X-ray diffraction. The chemical was dried and after analyses it was found that the phase composition of the residue is zirconium tetrafluoride – ZrF₄ and various modifications of silico-n oxide – SiO₂ equivalent to tetraoxysilan bath for the sol-gel method [7].

Degreasing was the first step for preparation of the experimental samples, which removed all possible impurities from the material surface. The next step was application of the nanoparticle. We had for this purpose two types of nanoparticles, 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 nanoparticle can be used also instead of the classical degreasing process. We observed the influence of this step on the behaviour of the final layer. For some samples there was in the experiment also the other type of chemical pre-treatment used based on PTFE (polytetrafluoroethylene). This pre-treatment was used like the final coating and is suitable for increasing of the wear resistance. Experimental samples preparation and their marking are shown in Table 2.

Table 2

Basic material chemical composition

Sample	Chemical pre-treatment			
	Degreasing	Nano 1	Nano 2	PTFE
A	yes	yes	no	no
B	yes	yes	no	yes
C	yes	yes	yes	no
D	no	yes	yes	no
E	no	yes	yes	yes
F	yes	yes	yes	yes

Figure below shows the technological process of the experimental samples preparation.

Technology	Degreasing	Dip	Nano 2 (cleaning operation)	Dip	Nano 1	Dip	Drying	Nano 2	Dip	Drying	PTFE	Drying
Conditions	Temperature: 50 °C Time: 5 minutes	Demineralized water 2x	Temperature: 50 °C Time: 5 minutes	Demineralized water 2x	Temperature: 20 °C Time: 2 minutes pH:	Demineralized water	Temperature: 130 °C Time: 15 minutes	Temperature: 20 °C Time: 5 minutes	Demineralized water	Temperature: 130 °C Time: 15 minutes	Temperature: 60 °C Time: 15 minutes pH: 7.5	Temperature: 100 °C Time: 30 minutes
Sample												
A												
B												
C												
D												
E												
F												

Fig. 1. Preparation of experimental samples

Chemical pre-treatment Nano 2 can be used like the cleaning operation instead of degreasing or like the final protecting coating.

Results and discussion

We evaluated our experimental samples using surface roughness analysis and SEM and EDS analysis.

Surface roughness analysis

For evaluation of the influence of the chemical pre-treatment on the basic material surface roughness were used the R_a , R_z (Fig. 2) and R_t (Fig. 3) parameters.

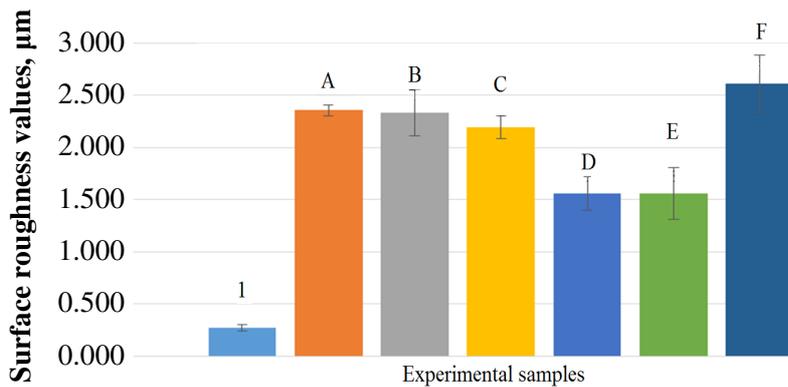


Fig. 2. Surface roughness analysis – R_z parameter

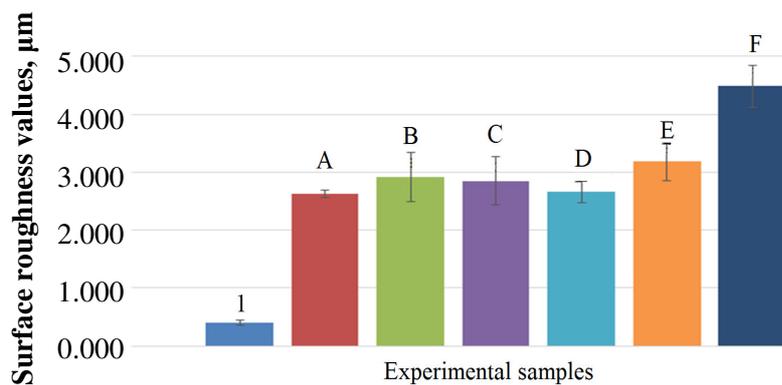


Fig. 3. Surface roughness analysis – R_t parameter

30 measurements were performed on the surface of each sample. The average R_z 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 and the average R_t values are: sample without any pre-treatment 1 – 0.392 μm , A – 2.618 μm , B – 2.917 μm , C – 2.844 μm , D – 2.664 μm , E – 3.177 μm , F – 4.481 μm .

From the surface analysis we can conclude that:

- degreasing causes increasing of the surface roughness.
- All samples pre-treated with this technology have higher roughness – A, B, C and F. It is due the etching of the substrate surface during this technology. Degreasing of the product etches away impurities from the material sample and also the surface layers of the material and due to this process increasing of the roughness occurs.
- PTFE pre-treatment causes decreasing of the roughness.
- It is because of the way how this pre-treatment is excluded. This pre-treatment is excluded in the form of very small spheroidal particle which fills in the cracks and other inequality of the surface.
- zirconium nanopassivation nano 1 caused additional increasing of the roughness. This effect is suitable for the application of the final powder coating. This technology creates good profile for anchoring of the coating.
- zirconium nanopassivation nano 2 product has the 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.

SEM and EDS analysis

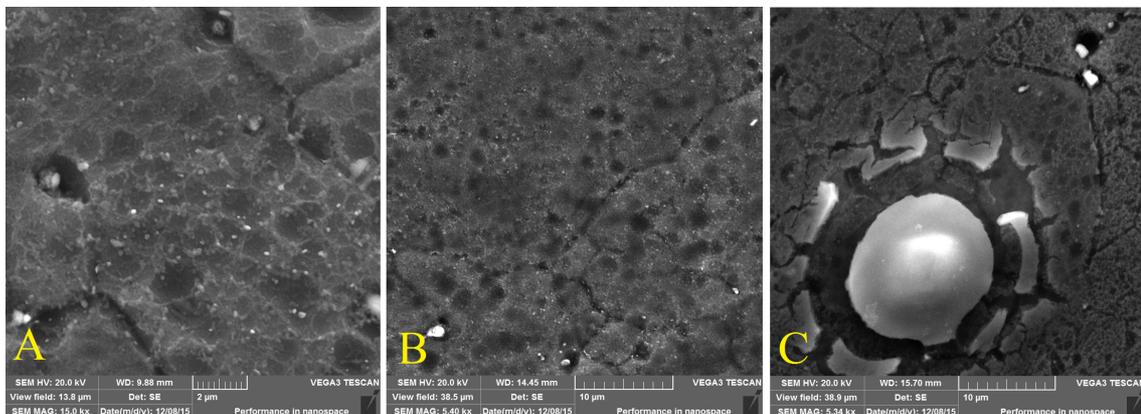


Fig. 4. SEM analysis of the sample surface A, B, C

After surface roughness measurements and discussion of the results we performed SEM and EDS analysis. The SEM image showed the sample surface with appreciable delamination or cracking of the coating. Behaviour of the nanolayers is by each chemical pre-treatment different. Fig. 4 shows the SEM images of the A, B and C experimental samples. These samples were pre-treated by the same sol-gel film and on the surface of the sample B there 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 the small particles of spherical shape. These particles cover the whole surface of the sample and fill in the cracks. Variant C has a little bit different appearance. Formations of spherical shape appeared on the surface of the samples. Fig. 4 C suggests a possibly 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 cracks of the nanolayer occurred but the mechanism of this change is a little bit different probably due to the use of degreasing as the first step in the experimental sample preparation.

The surface EDS analysis was performed on the surface of each sample and the 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.

- Sample C (wt. %): aluminium 43.25, oxygen 23.82, zirconium 18.90, phosphorus 7.98, fluorine 3.23 and magnesium 2.82.

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

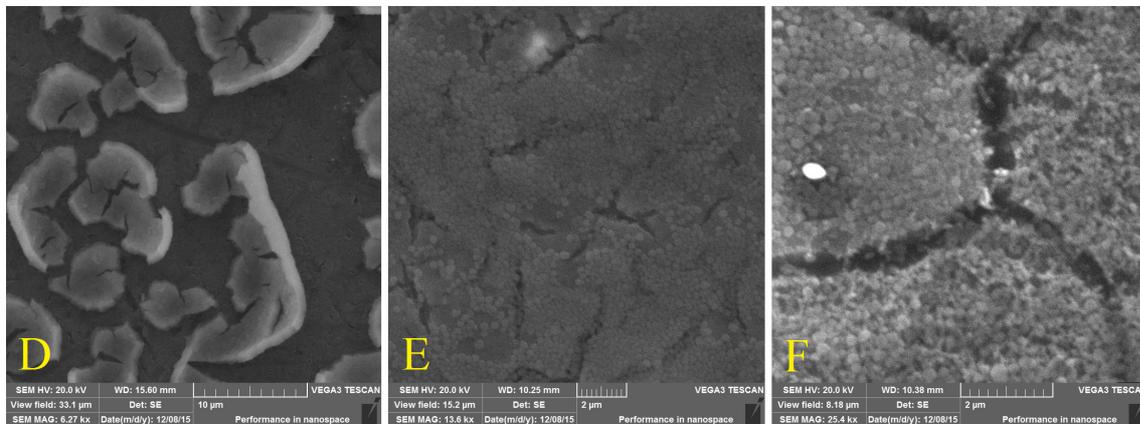


Fig. 5. SEM analysis of the sample surface D, E, F

Different is the exclusion of the layer on the sample surface D and E, Fig. 5. These samples were not pre-treated with degreasing and by omitting of this step extensive delamination on the surface of the sample occurs. This delamination is caused probably by localized electrochemical reaction at the interface resulted in debonding, delamination and lifting of the sol-gel coating from the substrate due to 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. Variant F has a different appearance. Formations of spherical shape appeared on the surface of the samples.

The surface EDS analysis was performed on each experimental sample surface and the 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.
- Sample F (wt. %): aluminium 75.06, oxygen 7.19, zirconium 1.65, phosphorus 0.52, fluorine 3.11, carbon 11.83 and magnesium 0.63.

The presence of calcium is due to omitting of degreasing. Thanks to it there may exist on the material surface some impurities after the previous polishing. The higher content of zirconium and fluorine are due to the use of two nanoparticle during the chemical pre-treatment. Both of these pre-treatments are zirconium nanoparticle. Nano 2 is 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 the sample E is because this sample has the final coating PTFE like it is in the case of the sample B.

Conclusions

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 can be accepted like environmentally friendly surface pre-treatment methods. The three dimensional networks 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 with dipping application. The experiment was based on preparation of 6 variants and using of two nanoparticle 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 prepare the material surface before application of the final coating. Application of PTFE is used for increasing of the wear resistance of the 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. The other variants C, D, E and F have problems with delamination of the nanolayer and this fact is caused probably due to the higher thickness of the nanolayer, when extensive cracking and delamination during the drying process occur.
- 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-treatment before the nanoparticle application.

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