

Analysis of the Thermal Stability of PTFE Nanoparticles Enriched Coating on Material Made from Al-Si Alloy

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The article focuses on technological procedures of coating of metal molds made from Al-Si alloys, especially used for making tyres. The idea is to create coating on aluminium based metal molds in order to reach a higher number of production cycles between individual cleaning operations in tyre making technology. The experiment was based on a preparation of experimental samples, which were coated with a teflon based product with the addition of nanoparticles (eg. TiO_2), in other words, particles as large as tens of nanometres, which were mixed into the teflon solution in a particular concentration. After creating the coating, the experimental samples were put under a thermal load in various thermal modes. Furthermore, roughness, coating resistance, and changes after the thermal load were subjects of the study.

Keywords: Thermal stability, PTFE coating, nanoparticles, nanocoating, nanolayers

1 Introduction

There have been more requests on the development of aluminium alloys from the manufacturers of car and aviation industries because of their low density, mechanical properties and corrosion resistance. Nowadays, the main key drivers for the increase of aluminium based manufacturing are car, aviation, and construction industries. This article deals with technological procedures of coating of metal molds made from Al-Si alloys, especially for tyre production. It is about creating coating on the aluminium based metal molds in order to reach a higher number of production cycles between individual cleaning operations in the tyre making technology. Recently, aluminium based materials are used to create metal molds for the tyre production. The metal mold consists of a certain number of segments (8-36) based on the dimensions of the produced tyre. The surface of the metal molds is not modified by any technology of the surface treatment. The selling price of the metal mold depending on the required tyre type can reach hundreds of thousands or even millions of Czech crowns. Each cleaning process causes deterioration of functional areas of the metal mold, which results in reduction of the lifespan. The maintenance of the tyre molds is money and time consuming, and it is given a high priority in order to extend its lifespan. The lifespan is considered to be autonomy of the operational mode of the mold when no maintenance is necessary. These molds are made from an aluminium based alloy of an Al-Si type. One way to extend the operational cycle is to apply protective coating. A very thin layer of the coating is

required based on the functionality of the working surface. [1].

The evaluation of the thermal stability of the PTFE nanoparticles enriched coating on a base material made from Al-Si alloy type can be found in the article. The experiment is based on preparation of the experimental samples, which were coated by a teflon based product with the addition of nanoparticles (eg. TiO_2), in other words, particles as large as tens of nanometres, which were mixed into the teflon solution in a particular concentration. After creating the coating, the experimental samples were put under a thermal load in various thermal modes. Furthermore, roughness, coating resistance, and changes after the thermal load were subjects of the study.

2 Preparation and marking of the experimental samples

The same base material was used for all the samples as a part of the research with the only difference being the technology of material coating. Overall, 140 samples were coated. The samples with PTFE+ TiO_2 are marked with index A. The samples with PTFE coating without the addition of the nanoparticles are marked with index B. Tab. There were 10 samples made for each group to objectively evaluate the results of each of the performed analysis. The samples were subject to thermal loading at different temperatures after the coating was created on all the experimental samples of the A and B type. In total, 7 modes of thermal loading were selected with the order of 1-7. The marking of the experimental samples given the used coatings and thermal loading is shown in Tab. 1.

Tab. 1 Identification of experimental samples

	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7
	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	500 °C
PTFE + TiO ₂	1A (1 ÷ 10)	2A (1 ÷ 10)	3A (1 ÷ 10)	4A (1 ÷ 10)	5A (1 ÷ 10)	6A (1 ÷ 10)	7A (1 ÷ 10)
PTFE	1B (1 ÷ 10)	2B (1 ÷ 10)	3B (1 ÷ 10)	4B (1 ÷ 10)	5B (1 ÷ 10)	6B (1 ÷ 10)	7B (1 ÷ 10)

2.1 Coating technology of the experimental samples

One way to extend the working cycle of the molds (eg. for tyre pressing) is to apply protective coating on the surface of the mold. A very thin layer is necessary about the functionality of the working space. PTFE coating is one of the appropriate types of coating as it extends the lifespan in the matter of hundreds of per cent (by 200-400 % as it was already verified by research done at FSI UJEP). There is an effort within this work to further improve the coating by adding particles of titanium dioxide (TiO₂), in the 'nano' particles scale. Grinding of the powder was done by using

a ball-mill Retsch PM 100.

The coating on the surface of the experimental samples was created by the following process:

Chemical products were used during coating of the prepared samples in a form of plates. The specific names and chemical composition of these products are kept confidential with this phase of the research. The individual parameters (temperature, time, pH of the solution) of the technology are listed in Tab. 2- 4. The pH values were checked by a pH meter in the preparation phase of the coating bath.

Tab. 2 Coating parameters and description of P1 – alkaline degreasing

Operational parameters	Alkaline degreasing (product marking.: P1) Two-component degreasing bath	Product description
Amount of product P1	component 1: about 1.4 g/l; component 2: about 1.0 g/l	Alcaline degreasing containing two-component pickling and degreasing agent for aluminium and its alloys
Temperature	55 °C	
Degreasing	5 min.	
Duration of adjustment	submersion	

Tab. 3 Coating parameters and description of P2 – zirconium nanopassivation

Operational parameters	Zirconium nanopassivation (product marking.: P2)	Product description
Amount of product P2	20 – 40 g/l P2 in demineralised water	A Liquid product based on hexafluoro-zirconic acid that is used for creating nanomolecular surfaces Sol – gel of technologies for steel and aluminium surfaces protection
Temperature of application	Room temperature	
Duration of adjustment	2 min	
Application	submersion	
pH value	5.2	
Drying conditions	150 °C	
Time	15 min	

Tab. 4 Coating parameters and description of P3 - PTFE

Operational parameters	PTFE coating (product marking.: P3)	Product description
Amount of product P3	8 – 10 g/l P3 in demineralised water	A Liquid straight component product based on PTFE to treat aluminium surface
Temperature of application	60 °C	
Duration of adjustment	10 - 15 min	
Application	submersion	
pH value	7.8 – 8.5	
Drying conditions	150 °C	

The degreasing bath consisted of a two-component product marked as P1, which was stirred in demineralised water in a prescribed amount. The concentrations of chemicals of the particular product were always used with the recommendation of the manufacturer of these products. The passivation bath consists of P2 product and demineralised water. The pH factor can be in case of a passivation bath regulated by adding the established product. This step of nanopassivation of the surface of the experimental

samples serves as a surface treatment of the base material after degreasing, and at the same time after preparation of the surface before application of the final PTFE coating. The final coating is created on the surface of the base material by using a product marked as P3 and demineralised water, in which it is applied in a prescribed amount.

A formation scheme of the PTFE coating on the surface of the experimental samples with the description of specific technological parameters of the coating can be seen in Fig. 1.

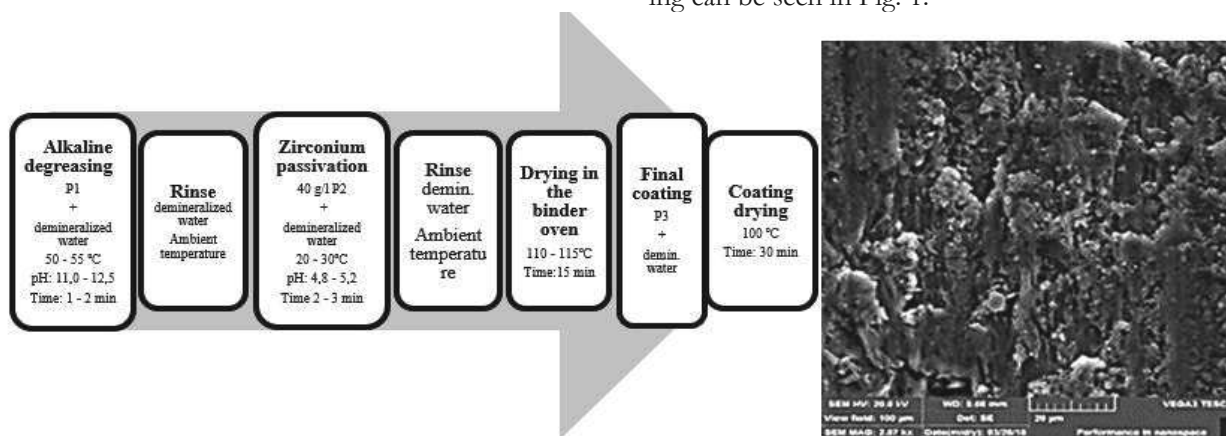


Fig. 1 PTFE coating formation scheme

In the second phase of the coating TiO_2 nanoparticles were added into P3 in a percentage ratio of 0,01 % against the overall capacity of the coating bath. In the previous research which was done at FSI UJEP, it was found out that 0,01 % ratio appears to be the best concentration of TiO_2 in the PTFE solution. Other concentrations were tested as well, however, this was the best ratio with consideration to the final coating

and anchoring of TiO_2 in this coating. That is why this TiO_2 concentration was used for the purpose of the experiment in my diploma thesis. [2].

The Coating formation scheme of PTFE + TiO_2 on the surface of the experimental samples with a description of technological parameters is mentioned in Fig. 2.

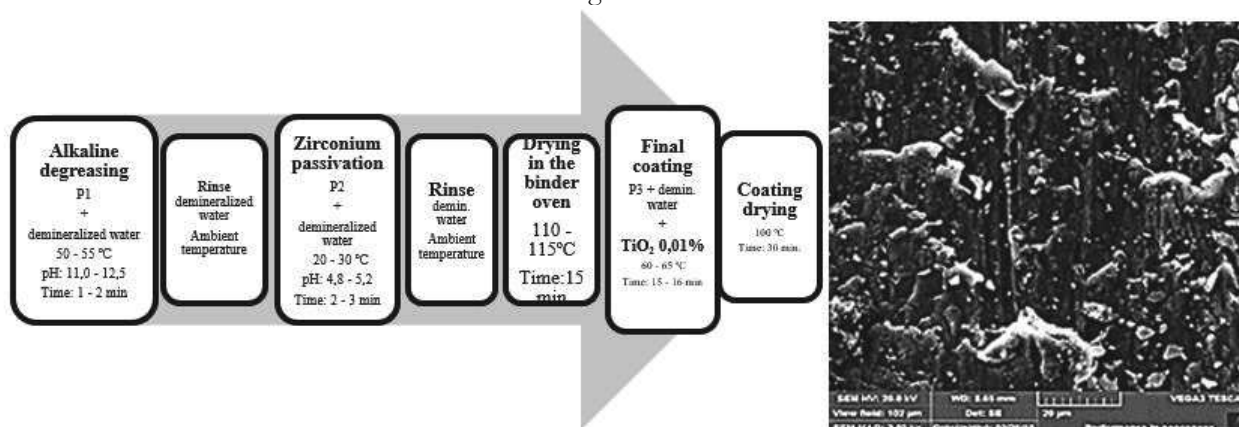


Fig. 2 Coating formation scheme PTFE + TiO_2

2.2 Thermal loading

140 samples with the coating (PTFE, PTFE + TiO_2) were used for the thermal loading. The purpose of this work is to study the thermal stability and identification of potential changes on the surface of the experimental samples post coating. In total, there were seven groups created based on the temperature of the

load. Each of these groups was put under the load for 30 and 60 minutes. Tab. 5 shows the marking of all the experimental samples which were used for the testing of the thermal stability according to set conditions and parameters [3].

The temperature of the loading was chosen with respect to the operating temperature of the mold for

tyre pressing. Considering the purpose of improving the properties of the PTFE coating by adding nanoparticles, I wanted to find out with this experiment,

whether there is degradation of the coating with respect to temperature or time. The temperature of 500 °C is selected as the maximum since the base material itself could be affected by exceeding it.

Tab. 5 Thermal loading according to specified conditions

Coating	Duration of loading	Gr. 1	Gr. 2	Gr. 3	Gr. 4	Gr. 5	Gr. 6	Gr. 7
		150 °C	200 °C	250 °C	300 °C	350 °C	400 °C	500 °C
PTFE + TiO ₂	30 min	1A1	2A1	3A1	4A1	5A1	6A1	7A1
		1A2	2A2	3A2	4A2	5A2	6A2	7A2
		1A5	2A5	3A5	4A5	5A5	6A5	7A5
		1A6	2A6	3A6	4A6	5A6	6A6	7A6
		1A7	2A7	3A7	4A7	5A7	6A7	7A7
	60 min	1A3	2A3	3A3	4A3	5A3	6A3	7A3
		1A4	2A4	3A4	4A4	5A4	6A4	7A4
		1A8	2A8	3A8	4A8	5A8	6A8	7A8
		1A9	2A9	3A9	4A9	5A9	6A9	7A9
		1A10	2A10	3A10	4A10	5A10	6A10	7A10
PTFE	30 min	1B1	2B1	3B1	4B1	5B1	6B1	7B1
		1B2	2B2	3B2	4B2	5B2	6B2	7B2
		1B5	2B5	3B5	4B5	5B5	6B5	7B5
		1B6	2B6	3B6	4B6	5B6	6B6	7B6
		1B7	2B7	3B7	4B7	5B7	6B7	7B7
	60 min	1B3	2B3	3B3	4B3	5B3	6B3	7B3
		1B4	2B4	3B4	4B4	5B4	6B4	7B4
		1B8	2B8	3B8	4B8	5B8	6B8	7B8
		1B9	2B9	3B9	4B9	5B9	6B9	7B9
		1B10	2B10	3B10	4B10	5B10	6B10	7B10

2.3 Measuring of the surface roughness

By measuring the surface roughness the aim was to find out whether thermal loading affects the roughness of the surface of the experimental samples. The measurement was done before and after the loading, so that the results could be compared and evaluated afterwards. The roughness measurement was carried out on a Hommel Tester T8000 apparatus. The measurement on this apparatus is standardised according to the ČSN EN ISO 4287 norm. The measurement was carried out on the base material before and after coating (marked as sample 1-3), in a way that it would be possible to compare the influence of the coating on the surface roughness. Moreover, the roughness measurement of the thermally loaded and unloaded experimental samples was performed. Thermal loading of the samples was done with respect to the set temperatures as listed in Tab. 5 in the previous section. For the measurement, two samples were selected from each group (1A, 2A, 2B, ...). Only the measurement of the surface roughness of the base material was carried out on three samples. Each of these samples was measured ten times.

The following parameters of roughness were chosen for the evaluation of the measurement-Ra (average arithmetic deviation of the assessed surface), Rz (greatest height of the profile) and Rt (overall height of the

profile) [5].

When comparing the values of surface roughness of the base material with the values of the roughness of the already coated material, it is apparent that the values of the coated material (without thermal loading) differ. As can be seen in Fig. 3 and 4, the roughness values of the coated material (R_a , R_z i R_t) are lower than the base material. The coating helped to level out the inequalities of the surface of the studied material. The recorded values were processed in Excel. The arithmetic average was calculated from the roughness values to provide greater clarity of the results. The tables placed under the bar charts show the average values of the surface roughness of the individual experimental samples and the roughness parameters.

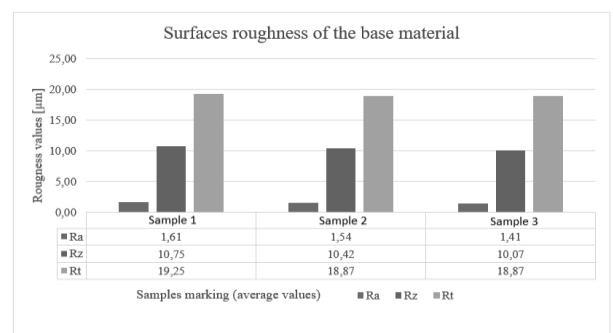


Fig. 3 Surface roughness of uncoated base material

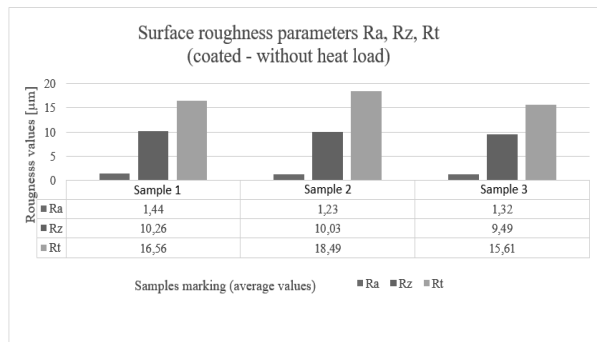


Fig. 4 Surface roughness of coated base material (without thermal loading)

The samples with the PTFE coating were put under load for 30 and 60 minutes. The experimental samples which were under load for 30 minutes displayed lower roughness values, which is apparent in Fig. 5 and 6. The lowest values of roughness with the PTFE coating was displayed by the 2B sample group, which was put under load for 30 minutes. The group 2B represents the PTFE coating which was exposed to the temperature of 200 °C. Conversely, as can be seen in Fig. 7 and 8, the highest values of roughness were shown in the 3B sample group which was put under load for 60 minutes. The 3B group represents the PTFE coating which was exposed to the temperature of 250 °C.

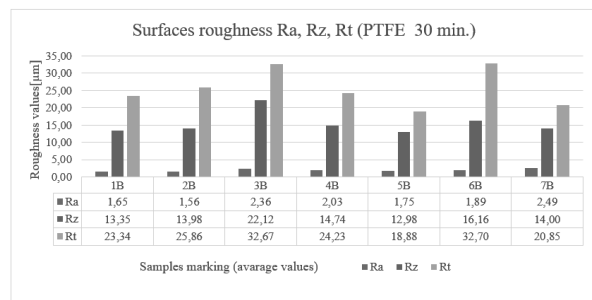


Fig. 5 Surface roughness for PTFE coating (thermal load for 30 min.)

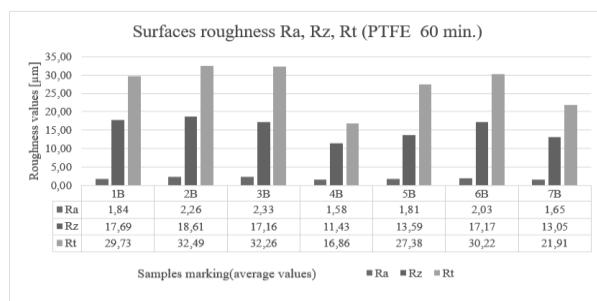


Fig. 6 Surface roughness for PTFE coating (thermal load for 60 min.)

The PTFE coating samples with the addition of TiO₂ nanoparticles were also put under load for 30 and 60 minutes. The 7B sample group showed the lowest

roughness values of PTFE+ TiO₂ coating, and it was under load for 60 minutes. The group 7B represents the PTFE + TiO₂ coating which was exposed to the temperature of

500 °C. Conversely, as can be seen in Fig. 7 and 8, the highest values of roughness were shown in the 4B sample group which was put under load for 60 minutes. The group 4B represents the PTFE + TiO₂ coating which was exposed to the temperature of 300 °C.

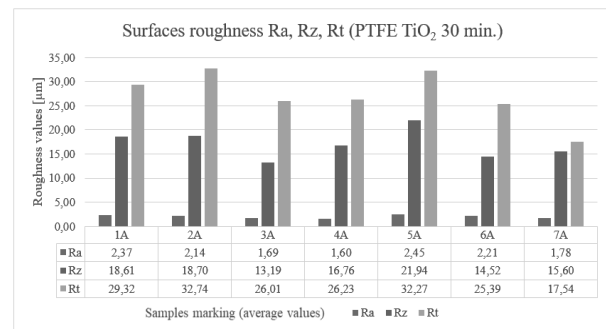


Fig. 7 Surface roughness for PTFE + TiO₂ coating (thermal load for 30 min.)

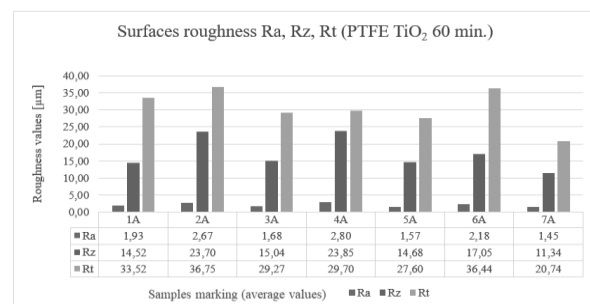


Fig. 8 Surface roughness for PTFE + TiO₂ coating (thermal load for 60 min.)

2.4 Measurement of the coefficient of friction - Tribometer

Deterioration and friction are sensitive to a change in conditions (change in temperature, load or moisture). Tribometers are machines used for this case [4]. The measurement of the coefficient of friction was carried out on a Bruker UMT TriboLab apparatus. It is a multifunctional tribometer, which represents a flexible modular system used for all common tribological tests. A ball with a diameter of 12.7 mm was used for the tribometer measurements, and it is provided straight from the manufacturer. During the measurement, the ball was being turned slightly to avoid affecting the measurement caused by the applied coating. The ball moved on a 10 mm track with 4N or 2N load. The coefficient of friction measurement was always performed on one sample of each group at a time, and each of these samples was measured five times. The average values of the coefficient of friction are listed in Tab 6, 7, 8. [6].

Tab. 6 Average values of coefficient of friction material and material without thermal loading

Sample name	Coating	Load duration [min]	Temperature [°C]	Average value of CoF	Conditions of measurement
Base material	0	0	0	0.148	1
6A10	PTFE + TiO ₂	0	0	0.101	1
6B10	PTFE	0	0	0.100	1

In Tab. 6, it can be seen that the base material reaches the highest average values of coefficient of friction without being coated and thermally loaded. Conversely, the sample 6B10 shows the lowest average values. It is the sample with the PTFE coating

which was not put under thermal loading. There is an increase of the coefficient of friction with the applied coating (PTFE or PTFE + TiO₂).

Tab. 7 Average friction coefficient values for PTFE coated samples

Sample name	Coating	Load duration [min]	Temperature [°C]	Average value of CoF	Conditions of measurement
1B5	PTFE	30	150	0.163	1
1B9	PTFE	60	150	0.102	1
2B7	PTFE	30	200	0.103	1
2B10	PTFE	60	200	0.119	1
3B7	PTFE	30	250	0.182	1
3B10	PTFE	60	250	0.184	1
4B6	PTFE	30	300	0.165	2
4B8	PTFE	60	300	0.435	2
5B6	PTFE	30	350	0.861	2
5B9	PTFE	60	350	0.838	2
6B6	PTFE	30	400	0.846	2
6B8	PTFE	60	400	1.335	2
7B6	PTFE	30	500	1.197	2
7B9	PTFE	60	500	1.118	2

The PTFE coating degraded at a temperature of 350 °C, which is reflected in a sharp increase of the friction coefficient for this temperature. The sample 1B9 shows the lowest average value of the friction coefficient. It is the sample with the PTFE coating which

was put under load at 150 °C for 60 minutes. Conversely, the sample 6B8 shows the highest values of coefficient of friction. It is the sample with the PTFE coating which was put under load at 400 °C for 60 minutes.

Tab. 8 Average friction coefficient values for PTFE coated samples PTFE + TiO₂

Sample name	Coating	Load duration [min]	Temperature [°C]	Average value of CoF	Conditions of measurement
1A5	PTFE + TiO ₂	30	150	0.165	1
1A10	PTFE + TiO ₂	60	150	0.115	1
2A7	PTFE + TiO ₂	30	200	0.113	1
2A8	PTFE + TiO ₂	60	200	0.201	1
3A6	PTFE + TiO ₂	30	250	0.106	1
3A8	PTFE + TiO ₂	60	250	0.179	1
4A8	PTFE + TiO ₂	60	300	1.297	2
4A6	PTFE + TiO ₂	30	300	1.134	2
5A7	PTFE + TiO ₂	30	350	1.182	2
5A8	PTFE + TiO ₂	60	350	0.879	2
6A5	PTFE + TiO ₂	30	400	1.110	2
6A9	PTFE + TiO ₂	60	400	1.134	2
7A8	PTFE + TiO ₂	60	500	1.182	2
7A6	PTFE + TiO ₂	30	500	0.879	2

There was a significant increase of the coefficient at the temperature of 300 °C. The sample 3.46 shows the lowest friction coefficient. It is the sample with the PTFE+TiO₂ coating which was put under load at 150 °C for 30 minutes. Conversely, the sample 4.48 shows the highest values of coefficient of friction. This sample was put under load at 300 °C for 60 min.

2.5 SEM and EDS analysis

The presence of the PTFE coating on the surface of the sample and its uniformity were proven by using the SEM and ESD analysis. The experimental samples were evaluated by using a TESCAN VEGA 3 electron microscope, which is available in the laboratories at UTM FSI UJEP. The thickness of the surface layer is measured based on the images of the surface layer taken by the electron microscope (fig. 9). The thickness ranges between 10 and 20 µm and it is a homogeneous layer, but uneven.

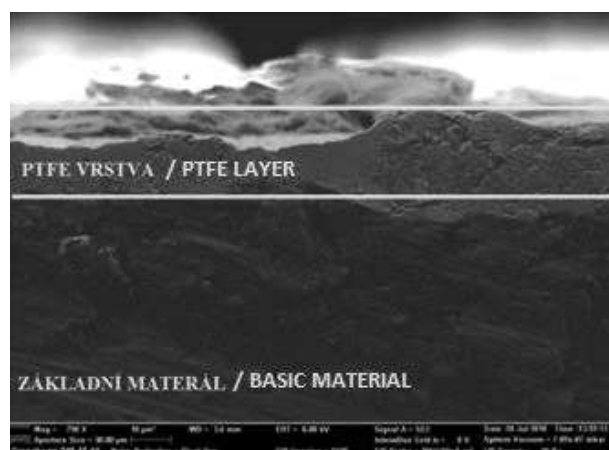


Fig. 9 Coating thickness PTFE

SEM proves expulsion of the PTFE coating on the surface (fig. 10 and 11). The coating covers the whole surface of the sample, but it is not compact. It is expelled in a form of scale fragments. The EDS analysis complements the SEM (fig. 12, Tab. 9) and with those elements typical for PTFE were identified, namely C and F. Zirconium nanopassivation is a substrate under the PTFE coating and that is why Zr is also present. The other elements are closely linked with the base material (Al, Si, Mg).

Tab. 9 EDS result of analysis of the PTFE coating

Element	Norm. C [%]	Norm. C [%]
Al	70.16	58.29
O	6.19	8.67
C	11.90	22.21
F	4.04	4.76
Si	6.44	5.14
Zr	0.36	0.09
Mg	0.91	0.84

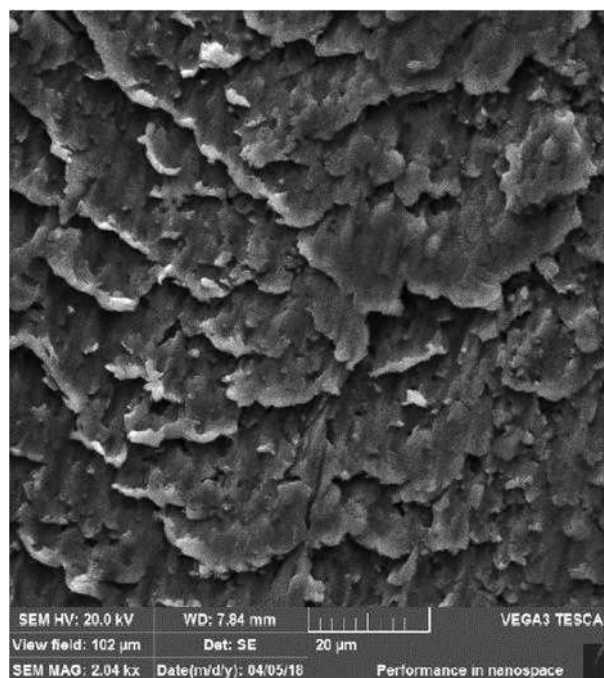


Fig. 10 Sample surface with PTFE coating

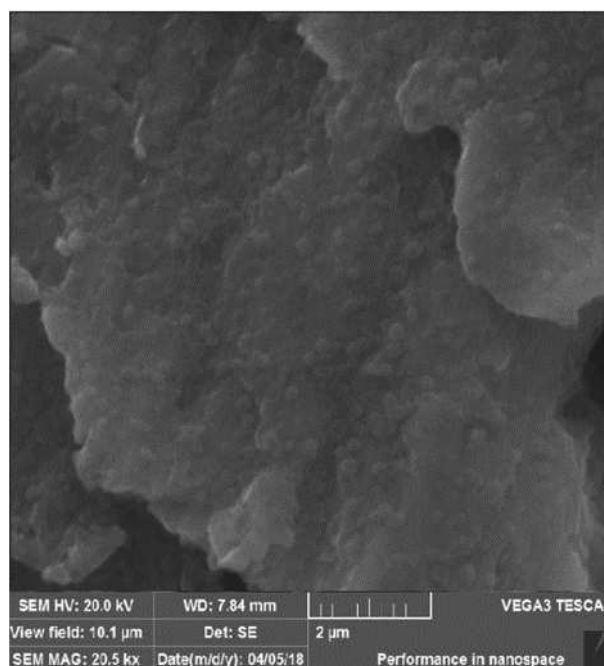


Fig. 11 PTFE coating on the sample surface

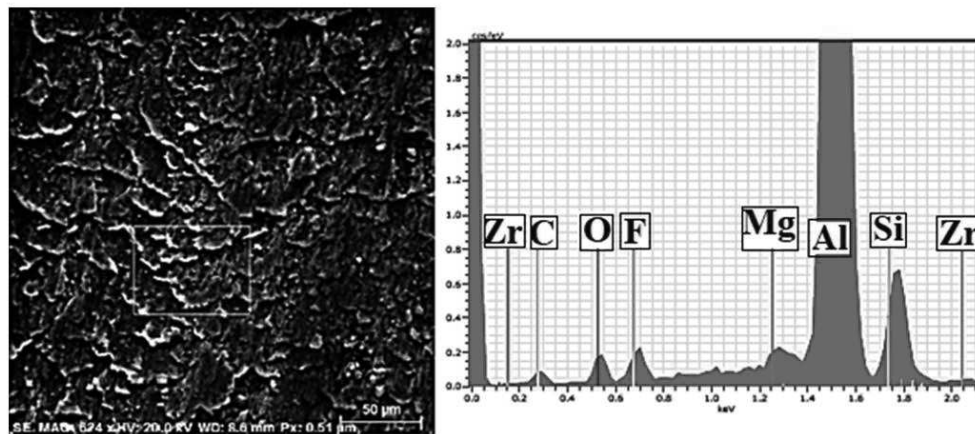


Fig. 12 PTFE coating on the sample surface EDS

3 Discussion of results

The findings of the influence of temperature and load duration of the experimental samples on the surface roughness were the first performed analysis. The measurement was carried out on the base material (before coating) and after coating in a way that it would be possible to compare the effect of the coating on the surface roughness. Furthermore, the roughness measurement was performed on both the thermally loaded and not thermally loaded samples. The values of the roughness of the coated material (R_a , R_z i R_t) are lower than the values of the base material. Using the coating helped to level out any surface inequalities of the tested material. The samples with the PTFE coating were put under loading for 30 and 60 minutes. The samples which were put under loading for 30 minutes show lower roughness values. The 2B sample group displays the lowest values of the coating roughness, and it was put under loading for 30 minutes. The 2B group represents the PTFE coating which was exposed to the temperature of 200 °C. The 7B sample group displays the lowest values of the PTFE + TiO₂ coating roughness, and it was put under loading for 60 minutes. The 7B group represents the PTFE + TiO₂ coating which was exposed to the temperature of 500 °C. This measurement verified that neither temperature nor time affects the roughness significantly. The roughness values do not display significant discrepancies, and thus it was not possible to draw a clear conclusion.

The measurement of the friction coefficient was performed on a Bruker UMT TriboLab apparatus. The comparison of the friction coefficient of the base material with the coated materials proved that there is an increase of the friction coefficient with the coating (PTFE or PTFE + TiO₂). The friction coefficient increases sharply when the temperature rises. The PTFE coating degraded at 350 °C which manifests through a sharp increase of the friction coefficient starting at this

temperature. The 1B9 sample shows the lowest average value of the friction coefficient. It is the sample with the PTFE coating which was put under loading at 150 °C for 60 minutes. The coefficient of friction increases sharply with the rising temperature as it was the case with the PTFE coating. There was a significant increase in the coefficient of friction from the temperature of 300 °C and up. The 3/46 sample shows the lowest average value of the friction coefficient. It is the sample with the PTFE + TiO₂ coating which was put under loading at 150 °C for 30 minutes. The friction coefficient increases significantly with the rising temperature with the PTFE coating as well as the PTFE + TiO₂ coating.

4 Conclusion

This research aimed to evaluate the thermal stability of the PTFE coating with the addition of nanoparticles on the base material made from Al-Si alloy. For the experiment purposes, there were samples with the PTFE and PTFE + TiO₂ coating. Each coating was put under loading for 30 and 60 minutes with set temperatures in the range between 150 and 500 °C. It is possible to draw the following conclusions based on the performed measurements. When measuring the surface roughness, the aim was to measure the surface roughness of the experimental samples and evaluate the effect of the thermal loading and the loading duration of the samples with the PTFE coating and PTFE coating with the addition of TiO₂. The values of the R_a , R_z and R_t parameters were used for the analysis. It can be stated that the temperature and time do not affect the surface roughness significantly. When comparing the friction coefficient of the base material with the coated materials, it is apparent that with the rising temperature the friction coefficient increases. The sample 1B9 shows the lowest average value of the friction coefficient. It is the sample with the PTFE coating which was put under loading at 150 °C for 60 minutes. The coefficient of friction increases