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Nanoindentation measurements of PVD coated multilayer constructions

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ABSTRACT

Purpose: Carbon fibre reinforced thermoplastics (CFRP) are intensively used in lightweight applications due to their high strength to weight ratio. In addition they offer good crash, damping and recycling properties. On the basis of their morphology they are suitable for large scale manufacturing processes. A major disadvantage consists of its poor hardness properties, which is again an important requirement to realize a good erosion and wear behaviour.

Design/methodology/approach: In this work the application of orthotropic carbon fibre reinforced polymers (PA6), with protective TiAlN coatings, produced by physical vapor deposition (PVD), is investigated. The characterization of the coating is performed by nanoindentation tests, roughness measurements and scanning electron microscopy. Furthermore micro hardness tests on selected well prepared cross sections are conducted, to compare the coating quality with established coating systems.

Findings: By applying TiAlN coating, the hardness of the CFRP samples can be increased substantially up to 15 GPa, in comparison to the basic substrate. In addition the quality of the coating surface can be improved significantly by plasma etching pre-treatment.

Research limitations/implications: The presented findings are preliminary results to prove the application of a standard processed ceramic coating on new composite types for mass production. The PVD coating process as well as the utilized testing methods are suitable to realize hard coatings on thermoplastic CFRP. This effect can be exploited for several lightweight applications to increase the erosion and wear resistance of composite materials.

Originality/value: The presented results show, that ceramic coatings can be deposited on standard thermoplastic CFRP with polyamide 6 matrix. Therewith it can be expected, that the PVD coating process can make a essential contribution to increase the range of applications.

Keywords: TiAlN-coating; Thermoplastic composites; Nanoindentation; SEM

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MATERIALS

1. Introduction

In the last years the application of carbon fibre reinforced plastics (CFRP) steadily increased in transportation industries. The BMW MegaCity Vehicle Project with a growing amount of CFRP as well as the Airbus A350 with a CFRP ratio of 52% are just some examples [1]. In aerospace industry polymer coatings are used to enhance the erosion resistance of composite materials [2]. As shown in [3] the life time of such coatings is limited and consequently alternative solutions needed. In this work the feasibility of the application of TiAlN coatings is investigated. TiAlN is one of the most studied hard coating systems. It is used due to its excellent properties such as high hardness, good wear behaviour and chemical stability [4-6]. A lot of former studies examined the deposition of TiAlN on metallic and ceramic substrates [7-10]. Other studies have demonstrated the feasibility of the deposition of Ti and TiN layers on CFRP [11, 12]. In a previous work the authors investigated the wear behaviour of TiAlN coatings on thermoplastic polyamide 6 matrix reinforced with carbon fibres [13]. The present study focuses on the hardness measurement of TiAlN coatings on thermoplastic composites. Therefore, three different coating thicknesses (s1 = 3 µm, s2 = 6 µm, s3 = 20 µm) are prepared. The surface roughness before and after the coating process is analysed. Load-displacements curves have been obtained using nanoindentation tests, hardness and Young's modulus values were determined by analysing these curves. Scanning electron microscopy (SEM) is used to evaluate the coated surfaces.

2. Experimental setup

2.1. Sample preparation

CFRP samples with a Polyamide 6 matrix and orthotropic reinforced continuous carbon fibres (Table 1) with a diameter of 30 mm are prepared using a mechanical grinding process with SiC wet sandpapers up to 2500 grit. After the grinding process the samples are cleaned with ethanol. For the coating process the CC 800/9 HPPMs PVD coating machine from CemeCon (Würselen, Germany) is used. The detailed coating process is described in [14]. Figure 1 shows the working chamber with specimen holder, Figure 2 depicts the clamping of the sample and Figure 3 the sample positioned directly in front of the TiAl - target. The nitrogen is added in the gaseous state.

Fig. 1. Working chamber CC 800/9 HPPMs

Fig. 2. Specimen holder with PA6 sample

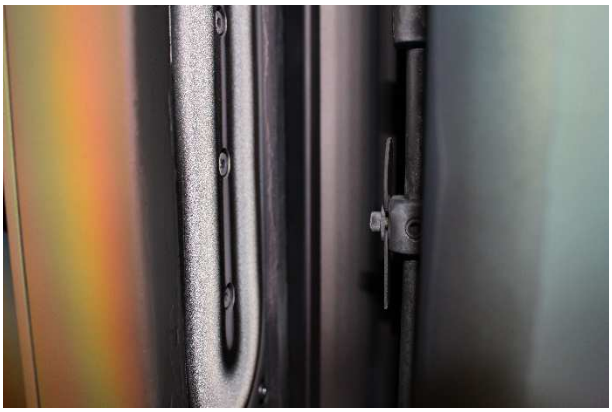

Fig. 3. Samples in front of TiAl-Target

Three different coating thicknesses are produced, a 3µm coating, a 6µm coating and a 20 µm coating. From the 20µm coating an additional sample is prepared using the plasma etching pre-treatment prior to the coating deposition to increase the adhesion between the TiAlN coating and the CFRP surface [15]. The process parameters are given in Table 2.

2.2. Surface roughness

The physical vapour deposition of the metallic-ceramic TiAlN coatings produces a smooth coating surface, if the process parameters are correctly adjusted. Therefore, a more intensive surface roughness is an indication for an incorrect coating process. The roughness in the recent study is measured using a Surftest 501 series 178 from Mitutoyo (Illinois, USA) and optical microscopy. The surface roughness value R_a is determined parallel as well as perpendicular to the fibres of the top layer. Multiple measurements are taken for each direction to generate suitable statistics. An average value (R_a) is calculated.

2.3. Nanoindentation

The hardness and Young's modulus measurements are performed by using a nanoindenter from ASMEC GmbH and the Software InspectorX Version 2.7.6 (Radeberg, Germany). The Quasicontinuous Stiffness Method (QCSM) is applied with a Berkovich indenter using a load of 10mN. Samples from the coatings are cut and then glued with a special wax onto the sample holder. To exclude the influence of the substrate material it is necessary for the indenter not to penetrate more than 10% of the coating thickness [16]. In preliminary investigations different loads were examined. The load of 10mN generated a penetration depth of 0.293 ± 0.009 µm on the 3 µm coating, which suites the above described requirement with respect to the maximum penetration depth. Therefore, this load is selected for the investigations. In order to compare the measurements of the different coating thicknesses the same load is applied to all coatings. The Load - displacement curves are analysed in order to obtain the hardness and Young's modulus values of the various coatings.

2.4. Microscopic investigation

Microscopic investigation are performed by means of a scanning electron microscope from Tescan (Brno, Czech Republic). Small samples are prepared from the specimen and a CRESSINGTON sputter coater 108 auto (Watford, UK) is used to deposit a thin gold coating on the samples to increase the conductivity. Electrically conductive adhesive tape is then used to fasten the specimen onto the sample holder to ensure that no electric charging of the samples occurs. All shown SEM figures in this work are of the same magnification.

3. Results and discussion

3.1. Surface roughness

In Figure 4 the results of the roughness determination tests is presented parallel to the uppermost fibre layer and perpendicular to the top layer fibres. This difference in the angles of the measurement direction is very important due to the great influence on the results. All measurements are an conducted on uncoated and coated specimen with a TiAlN coating thickness of 3 µm, 6 µm and 20 µm as well as a 20 µm coating with plasma etching pre-treatment.

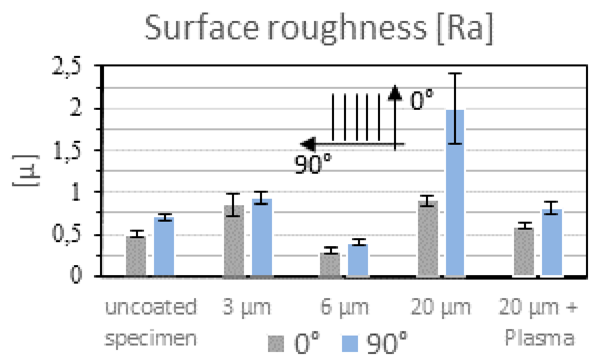

Fig. 4. Surface roughness [Ra] measured in direction of top fiber layer (0°) and perpendicularly to the top fiber layer (90°)

The presented results show that measurements perpendicular to the fibers alsways result in higher surface roughness values compared to parallel measurement direction. The specimen with a 3µm coating has a surface slightly rougher than the substrate material. The specimen with the 6µm coating shows a surprisingly small surface roughness. Whereas the 20 µm coating without the plasma etching pre-treatment has the highest surface roughness values. The 20 µm TiAlN coating with the plasma etching pre-treatment has comparable surface roughness values to the uncoated specimen.

3.2. SEM

All coatings show grooves on the surface, as available from Figures 6-9. The grooves are aligned parallel to the top fibre layer and thus are presumed to be the results of the exposed fibres through the polishing process. In Figure 5 the polished surface of an uncoated specimen is shown. The substrate material and the exposed fibres are marked.

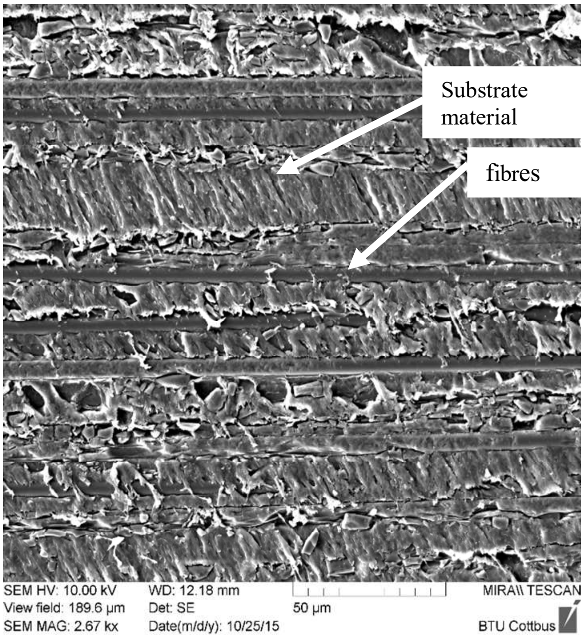

Fig. 5. Scanning electron micrograph of the surface and uncoated PA6 sample

The sample with the 3µm TiAlN coating is shown in Figure 6. The surface shows almost no grooves. The direction of the uppermost fibre layer is marked with an arrow. Figure 7 shows the sample with the 6 µm TiAlN coating. Here, the direction of the uppermost fibre layer can be clearly seen. Figure 8 represents the 20 µm coating, where the surface is much rougher and even cracks occur. With increasing coating thickness, the residual stresses inside the coating increase and lead to cracks and grooves, which leads to a poorer surface roughness (Figure 4). The coating growth can be influenced by the process parameters (process temperature, pressure and the Argon and Nitrogen flow) and the surface preparation.

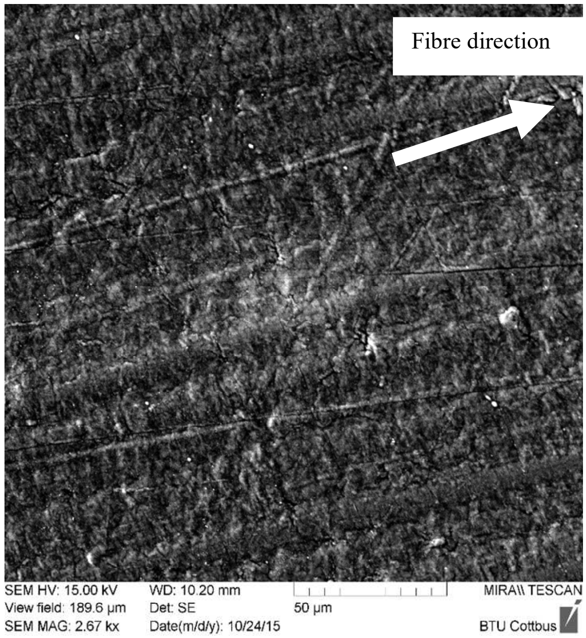

Fig. 6. Scanning electron micrograph of the surface of the 3 µm TiAlN layer

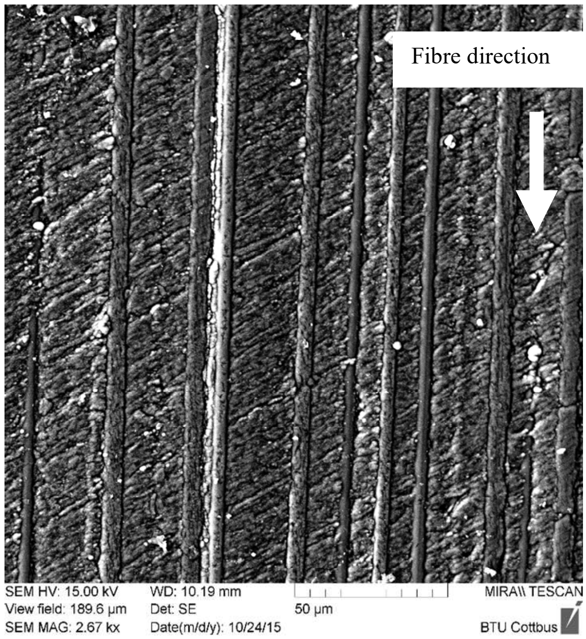

Fig. 7. Scanning electron micrograph of the surface of the 6 µm TiAlN layer

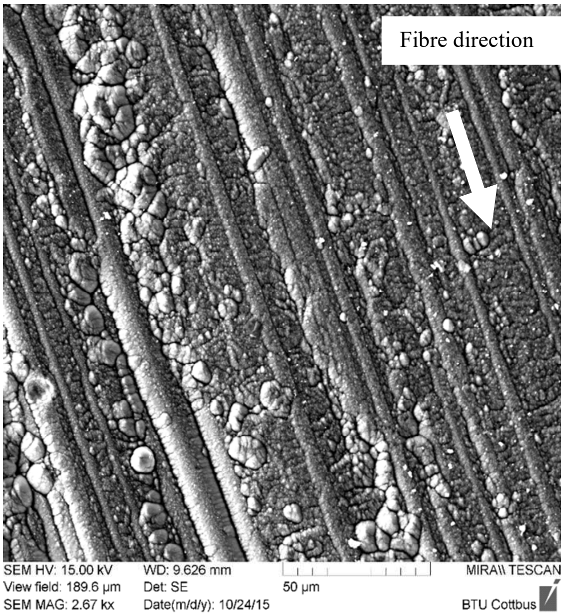

Fig. 8. Scanning electron micrograph of the surface of the 20 µm TiAlN layer

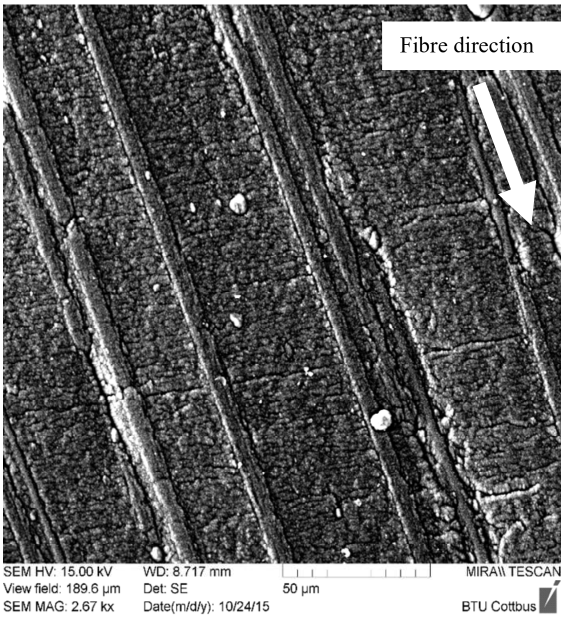

Fig. 9. Scanning electron micrograph of the surface of the 20 µm TiAlN layer with plasma etching pre-treatment

In this work a plasma etching pre-treatment was used to analyse the influence of the surface preparation. A substantial effect on the surface morphology can be observed in Figure 9 as well as in the surface roughness values in Figure 4. Apart from the grooves shown in Figure 7 and 8 no cracks are observed on the specimen.

3.3. Nanoindentation

The results of the nanoindentation tests are shown within Table 3 and Figures 10 and 11. Depicted are the penetration depth of the indenter, the Hardness value in GPa as well as in Vickers Hardness and the Young´s modulus. The number of evaluated tests is shown in Table 3. For optimal nanoindentation tests a smooth and parallel surface is necessary. The pronounced grooves on the samples, with the exception of the 3 µm coating, made the measurements difficult.

Within the margin of error, it can be seen that the hardness of the coatings of different thicknesses is approximately 13GPa. In [17] hardness values of 33-37 GPa have been found for 3 µm TiAlN coatings on WC/Co cutting inserts. In [18] TiAlN coatings were applied on AISI P20 and hardness values of 23 GPa were measured.

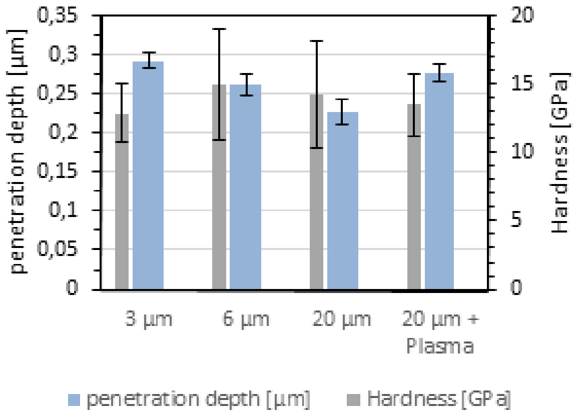

Fig. 10. Nanoindentation results, penetration depth and Hardness values for uncoated and coated specimens

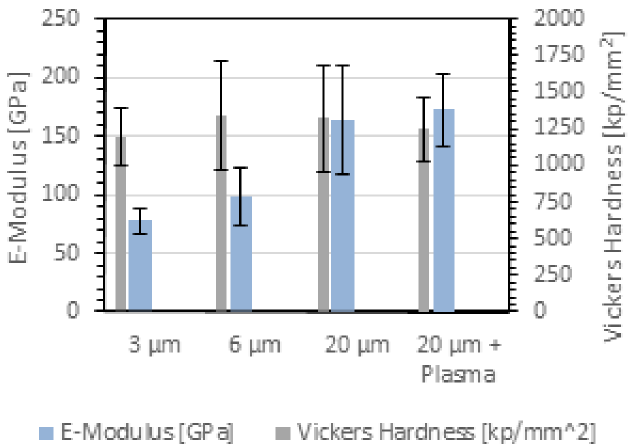

Fig. 11. Nanoindentation results, E-Modulus and Hardness values for uncoated and coated specimens

Table 1.
Properties of the utilised CFRP

FRP type	Prepreg	Lay up	Young´s modulus $E_1 = E_2$	Tensile strength $\sigma1 = \sigma2$	Fiber volume ratio	Thickness	Glass transition temperature
CFRP	UD carbon fibre/PA 6 (Ticona)	$[(0/90)_3]_s$	49.5 GPa	860 MPa	0.6	1.8 mm	220°C

Table 2.
Process parameters for CC 800/9 HPPMs

Coating process			Unit
Test Chamber	Process temperature	150 ± 5	°C
	Working pressure	< 8.0	mPa
	Argon	200	mln
	Nitrogen	20	mln
Cathode	TiAl Target	2000	W
	Voltage	90	V
	Frequency	280	kHz
Plasma etching pre-treatment			
Argon		160	mln
Table Voltage		650	V
Frequency		240	kHz
Time		300	s

Table 3.
Results of the conducted nanoindentation tests

Coating thickness [µm]	penetration depth [µm]	Hardness [GPa]	E-Modulus [GPa]	Vickers Hardness [kp/mm^2]	Measurements
3 µm	0.293 ± 0.009	12.863 ± 2.135	77.38 ± 11.25	1191.5 ± 197.8	24
6 µm	0.262 ± 0.014	14.992 ± 4.042	98.24 ± 23.86	1388.7 ± 374.4	32
20 µm	0.227 ± 0.017	14.240 ± 3.945	164.15 ± 46.80	1319.1 ± 365.4	35
20 µm+Plasma etching	0.227 ± 0.011	13.486 ± 2.330	172.22 ± 31.21	1249.2 ± 215.9	24

The Vickers Hardness values correspond to preliminary micro hardness measurements on polished cross-section of the 6µm and 20µm coatings. With a load of 5 g indentations were made and the resulting indentations were analyzed using a scanning electron microscope (Tescan). The sample with a coating thickness of 6 µm shows a hardness value of 1212HV 0.05±62, whereas the samples with a coating thickness of 20 µm without plasma pre-treatment offer a hardness value of 1422HV 0.05±132. With a growing coating thickness, the Young´s modulus shows a steady increase, from 77 GPa on the 3 µm TiAlN coating up to 172GPa on the 2 0µm TiAlN coating with plasma etching pre-treatment.

This could be explained by higher residual stresses in thicker coatings. But this is in contrast to the lower surface roughness for the 20 µm coating with plasma etching pre-treatment, which was explained with lower residual stresses. Therefore, a different mechanism must explain the lower surface roughness for the sample with plasma etching.

4. Conclusions

The present investigations show that TiAlN coatings can be deposited on thermoplastic Composites with a polyamide 6 matrix and carbon fibre reinforcement. Therewith the new approach can make a contribution to increase the further range of applications.

To evaluate the hardness nanoindentation tests can be used to for the TiAlN coated composite materials. Further improvement regarding the nanoindentation test method are necessary to reduce the standard error and maximize the reproducibility of the measurements.

Especially the parallel positioning of the composite samples on the sample holder of the nanoindenter is difficult to realize, since the sample surfaces are not exactly parallel aligned. Regarding to this it is planned to measure the hardness on polished cross sections of the coatings that have already been prepared.

Acknowledgements

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME’2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering

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