Increasing the wear resistance of molds for injection of glass fiber reinforced plastics

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A B S T R A C T

Abrasion by glass fibers during injection molding of fiber reinforced plastics raises new challenges to the wear performance of the molds. In the last few decades, a large number of PVD and CVD coatings have been developed with the aim of minimizing abrasion problems. In this work, two different coatings were tested in order to increase the wear resistance of the surface of a mold used for glass fiber reinforced plastics: TiAlSiN and CrN/CrCN/DLC. TiAlSiN was deposited as a graded monolayer coating while CrN/CrCN/DLC was a nanostructured coating consisting of three distinct layers. Both coatings were produced by PVD unbalanced magnetron sputtering and were characterized using scanning electron microscopy (SEM) provided with energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), micro hardness (MH) and scratch test analysis. Coating morphology, thickness, roughness, chemical composition and structure, hardness and adhesion to the substrate were investigated. Wear resistance was characterized through industrial tests with coated samples and an uncoated reference sample inserted in a feed channel of a plastic injection mold working with 30 wt.% glass fiber reinforced polypropylene. Results after 45,000 injection cycles indicate that the wear resistance of the mold was increased by a factor of 25 and 58, by the TiAlSiN and CrN/CrCN/DLC coatings, respectively, over the uncoated mold steel.

Keywords:
TiAlSiN coatings
Multilayered coatings
Abrasion
Plastic injection molds

1. Introduction

Automotive parts industry produces many car components by plastic injection of glass fiber reinforced plastics. These materials are extremely abrasive for mold cavities, which is one of the main problems occurring in plastics injection industry: the molds and dies lifetime is short, due to the molding surfaces wear. Glass fibers movement during the injection process leads to scratches on the mold surface caused by their tips, making them rough enough to decrease the surface brightness of the injected products. This problem leads to extra costs for reconditioning operations and non-productive time with a consequent lack of productivity. To solve this inconvenience, some solutions have been adopted, such as coatings and surface treatments, ranging from chromium plating to high velocity oxy-fuel (HVOF) WC/Co [1] and metallic coatings, like hard chromium or nickel–phosphorus produced by electro deposition or electroless [2]. Also titanium, aluminum and other carbide or nitride layers produced by physical vapor deposition (PVD) or chemical vapor deposition (CVD) [3] have been used with the same purpose.

The aim of this work is to characterize TiAlSiN and CrN/CrCN/DLC PVD sputtered coatings, to determine the one with better wear resistance for plastic injection processes using glass fibers as reinforcement. TiAlSiN coating was tested previously by micro-abrasion, showing promising results [4]. This is a single layered coating that was produced with TiAlSi targets in nitrogen atmosphere. CrN/CrCN/DLC coating is a multilayered coating that combines the high adhesion of the CrN to steel substrates with the known improved wear resistance of the DLC top layer.

2. Experimental details

2.1. Substrate material and sample geometry

In order to carry out this work, AISI P20 tool steel substrates with 380HBW 2.5/187.5/5 hardness were used. Industrial samples were

Table 1
Mass spectroscopy analysis (wt.%) of AISI P20 steel samples.

C	Si	Cr	Mn	Mo	Ni	S	Fe
0.35	0.29	1.95	1.39	0.19	1.00	0.01	Balance

Table 2
PVD deposition parameters.

Parameter	Value
Technique	Unbalanced magnetron sputtering
Samples temperature	$500 \pm 10\,^{\circ}C$
Inlet pressure	500 mPa
Target power density	$16\,A\,cm^{-2}$
Bias	−120 V
Total deposition time	4 h[a]
Rotation speed	1 rpm
N flow rate	$120–180\,ml\,min^{-1}$
Ar^{+} flow rate	$60–120\,ml\,min^{-1}$
C_2H_2 flow rate	$240–280\,ml\,min^{-1}$
Target material (TiAlSiN)	TiAlSi
Targets material (CrN/CrCN/DLC)	Cr and graphite
Target dimensions	500 mm × 88 mm × 10 mm

[a] CrN/CrCN/DLC coating: 150 min (CrN) + 30 min (CrCN) + 60 min (DLC).

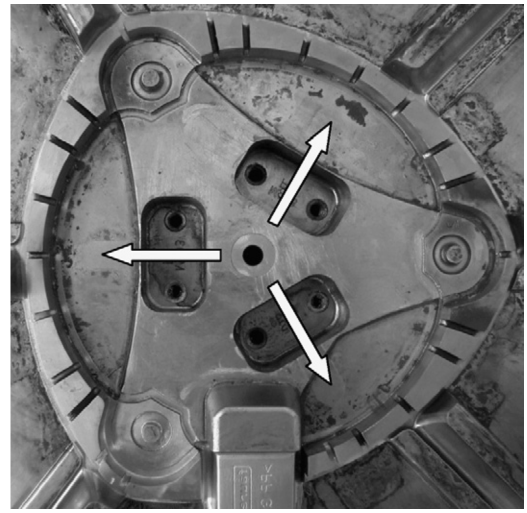

Fig. 1. Industrial mold cavity used for industrial wear tests.

specifically produced to allow its assembly in the plastic feed channel, inside the mold. Lateral surface has a slight slope to promote a better sample adjustment on the special cavities produced in the mold. The top surface remains coincident with the feed channels surface, allowing a normal flow of the mixture (plastic plus fiber) during the injection process.

Sample work surfaces (top) were milled and ground to an average surface roughness $R_a = 0.060\,\mu m$. The chemical composition of the substrate material was determined by mass spectroscopy and shown in Table 1.

2.2. Coating process

TiAlSiN and CrN/CrCN/DLC coatings were produced in an industrial CemeCon CC800/9ML PVD Magnetron Sputtering system. TiAlSiN coating was produced on four industrial targets of TiAlSi alloy. CrN/CrCN/DLC multilayered coating was obtained as following: the CrN bottom and intermediate layer layers were generated from two Cr targets using N and Ar^{+} feed gas, when for the last one C_2H_2 was added to N and Ar^{+}. For the top layer, the Cr targets were hidden behind the shutters and two graphite targets were exposed.

Deposition parameters can be observed in Table 2. This reactor allows sample rotation during the deposition process providing better homogeneity in the film composition. Prior to PVD deposition, samples were ultrasonically cleaned in an ethanol bath during 20 min. After this operation, with the samples assembled in the PVD chamber holder and under vacuum, they were sputtered cleaned to remove native oxides. The substrates were connected to the negative of the DC power supply and the targets, connected to the positive, were covered by shutters. Gas projected during 10 min against the substrates, remove undesirable surface particles. After this, shutters were removed and the polarity was reversed.

2.3. Coating characterization

A FEI Quanta 400FEG scanning electron microscope (SEM) provided with an EDAX Genesis X-ray spectroscope (EDS) was used in order to observe the sample surface morphology and measure the coating film thickness.

Attending to different expected tribological properties, two dissimilar techniques were used to evaluate the micro-hardness of the TiAlSiN and CrN/CrCN/DLC coatings. For the TiAlSiN coating, measurements were carried out in a micro-hardness Fischerscope® H100 equipment, using a Vickers indenter. Selected normal load was 50 mN that was kept constant during 30 s (avoiding creep phenomena). This equipment produces 'load–depth' curves, which permit the hardness (H) and Young's modulus (E) to be computed. The DLC top layer hardness of the CrN/CrCN/DLC multilayered coating was determined from force–displacement curves obtained by nanoindentation tests, with a 1.5 mN load and 5 s loading time. This lower value was selected to minimize the influence of the other two layers. These tests were performed in a Micro MaterialsTM NanoTest system equipped with a diamond Vickers indenter. These values, also allowed the H/E and H^3/E_r^2 ratios determination. According to Leyland and Matthews [5], it was recognized by several authors that the materials ranking according to the H/E ratio can provide extremely close agreement to their ranking in terms of wear.

2.4. Adhesion analysis

Adhesion between coatings and substrate was verified by scratch test and Rockwell indentation. Scratch tests were carried out in a CSM REVETEST scratch equipment, according to the BS EN 1071-3 (2005) standard. The normal load was increased from 0 to 80 N, at $100\,N\,min^{-1}$ rate, and the indenter sliding speed was $10\,mm\,min^{-1}$. Considering that sample surface showed some texture effect due to grinding process, two orthogonal measurements were made to understand the texture effect on the adhesion failure mechanisms. So as to maximize the results accuracy, three different tests were done in each direction. Then, grooves were carefully examined by optical microscopy, relating the location in the groove with the load acting in each point. The grooves observation allows identifying when cohesive and adhesive failures occur and determine the corresponding critical loads. Rockwell indentation with coating fracture observation allowed confirming qualitative results.

2.5. Industrial wear tests

As previously referred, the objective of this work is to study the wear resistance of TiAlSiN and CrN/CrCN/DLC coatings when applied in injection mold cavities used to produce glass fiber reinforced plastic automotive parts. Thus, an industrial mold used in radiator plastic fans production was selected and three symmetrical cavities were made with the work surface centered in each plastic feed channel. Fig. 1 depicts the cavity of the mold. In service, glass fiber reinforced plastic flows by the main feed channel at the

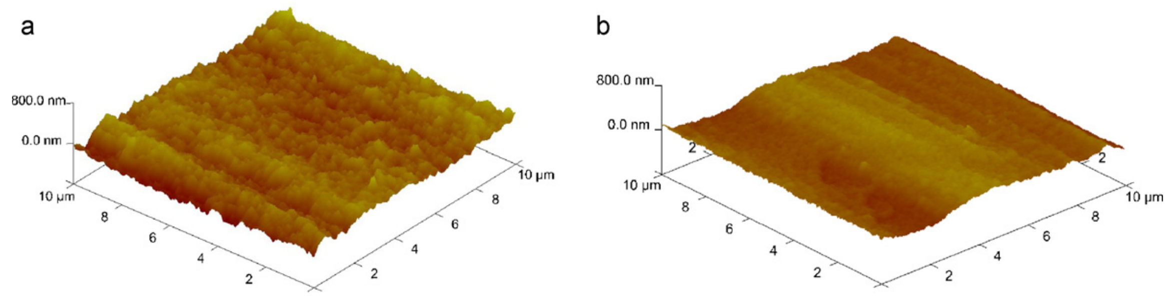

Fig. 2. 3D surface plot of (a) TiAlSiN and (b) CrN/CrCN/DLC coatings, obtained by AFM analysis, according to DIN 4768 standard.

Table 3
Samples roughness.

Samples	R_a (μm)	R_t (μm)
Uncoated sample	0.060	0.365
TiAlSiN	0.061	0.635
CrN/CrCN/DLC	0.054	0.385

Table 4
Critical loads L_{c1} and L_{c2} in both longitudinal (L) and transversal (T) directions, related to the grinding direction, for both coatings.

Samples	L_{c1} (N)		L_{c2} (N)	
	L	T	L	T
TiAlSiN	25	23	29	23
CrN/CrCN/DLC	No failure	No failure	11	10

center, being then divided in three different ways. Arrows included in this figure show the three plastic flux directions, corresponding to secondary plastic feed channels. These arrows were drawn over the sample cavities, specially produced in the mold in order to assemble three different samples. These samples fit in the cavities, due to its geometry. Inserts were located in a turbulent zone, to maximize the abrasive effect of the glass fibers due to a previous quick flow direction shift. The composite used in the process is polypropylene reinforced with 30 wt.% glass fibers. To study the wear behavior of both coatings, 90,000 injections were made. It is well-known that after this number of injection cycles, AISI P20 tool steel presents eye-visible severe wear marks all over the exposed areas. With this surface degradation, mold needs a complex and expensive maintenance process, implying production breaks, accurate production plans and smart stock management or delivery delays. For this propose, a KRAUSS MAFFEI injection machine was used, with 5000 kN clamp force and inner initial mold pressure of 140 bar. The injection speed used was 50 m/s and injection temperature was about 250 °C.

After these tests, all the surfaces were carefully examined by SEM to identify wear failure mechanisms and new surface morphology.

3. Results and discussion

Samples surface preparation was made by milling and grinding processes to reach similar surface finishing of mold cavities for glass fiber reinforced plastic injection. Polished surface finishing is not common in this kind of automotive glass fiber reinforced plastic parts because the components surface is affected by the injected material heterogeneity. The uncoated sample surface presents R_a = 0.060 μm (mean arithmetic roughness) and R_t = 0.365 μm (maximum roughness height). Similar AFM analysis was done for both coatings (see Fig. 2), and the results presented in Table 3, are comparable to the ones usually measured in mold cavities for glass fiber reinforced plastic injection.

Film morphology, cross-section structure and thickness were analyzed by SEM, as can be seen in Fig. 3. Fig. 3a shows some surface texture, resulting from the sample grinding process. Both sputtered coatings show that the surface morphology of the sample is followed by the films, despite its thickness. Surface morphology of TiAlSiN film is similar to the ones obtained by industrial sputtering processes, but it is very smooth for CrN/CrCN/DLC coating. Some aggregates can be seen randomly distributed on the TiAlSiN film surface, which is the result of the high deposition rates and usual characteristics of the industrial equipment. A careful analysis of these aggregates shows that its formation starts on or near the substrate surface and ends on the top of the film surface. When its height above the surface is sizeable, some tribological problems can occur. These large particles are, usually, the first ones to run off the coating, because counter face acts mainly on them. These aggregates leave the coating, running in the contact as a third – body particle with large dimensions, usually inducing serious damage on the surface, as pronounced grooves. The film is also affected because the gap created on the surface works as a weak point, accelerating the abrasive process. These aggregates are much less common on CrN/CrCN/DLC coatings.

Fig. 3b shows that the mechanical cross-sectional break exposed a homogeneous columnar structure, which corresponds to zone 1 pointed by Thornton [6], related to medium reactor pressure and low "Deposition temperature/Coating melting point" ratio. A polished metallurgical sample cross-section allows an accurate thickness measurement of 4.52 μm for TiAlSiN film (Fig. 3a) and 3.60 μm for CrN/CrCN/DLC nanostructured coating (Fig. 3c).

Good adhesion between coatings and substrate is an important goal for tribological applications. If adhesion is poor, coating tends to detach and this aspect deserves particular attention in this study. Scratch tests were done to quantify the normal load that corresponds to the initial failure. Attending to surface texture six tests were performed in each sample, using two orthogonal directions. Considering cohesive and adhesive failures as L_{c1} and L_{c2}, respectively, the values obtained are shown in Table 4.

Then, critical load values are a little bit higher in the direction of the grooves (L), confirming our expectations. Effectively, when

Table 5
Data related to micro-hardness tests in TiAlSiN and CrN/CrCN/DLC coatings.

Coating	Thickness (μm)	Maximum load (mN)	Indentation depth (μm)	Hardness (GPa)
TiAlSiN	4.52	50	0.317	21.8
CrN/CrCN/DLC	3.60	1.5	0.158	19.2

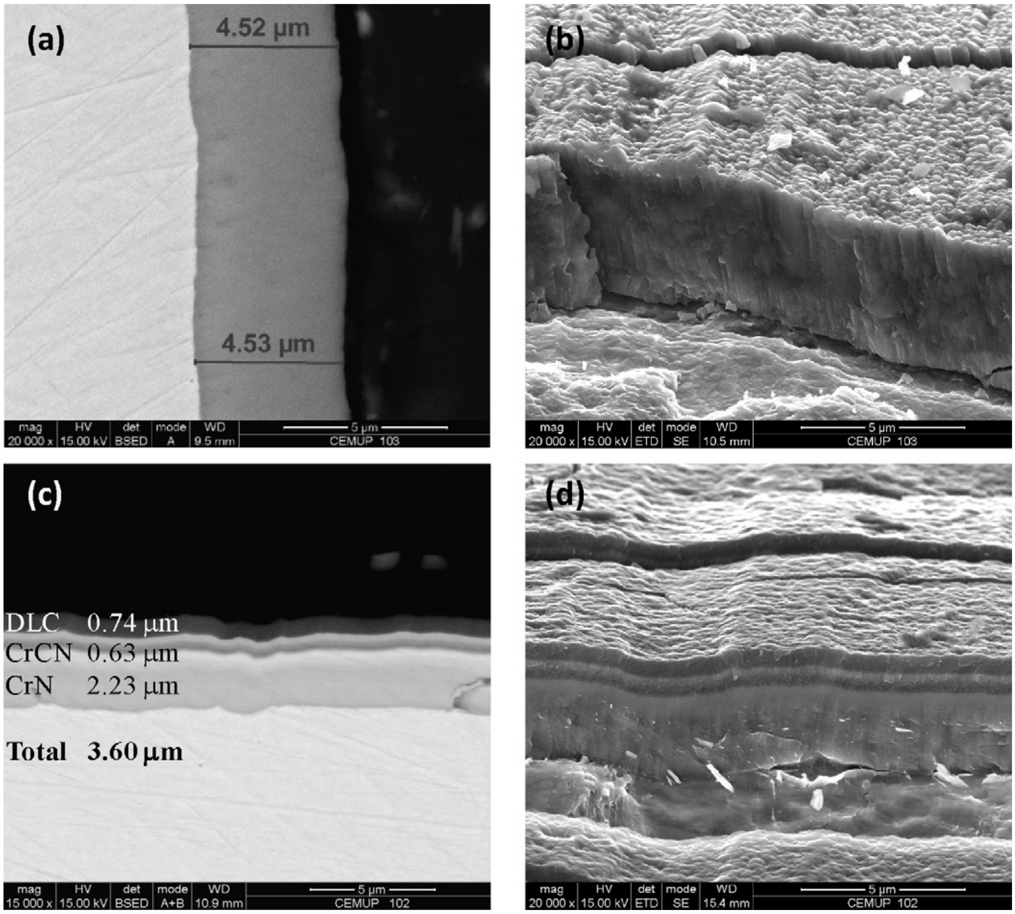

Fig. 3. SEM coating analysis of TiAlSiN: (a) thickness by cross-section view and (b) surface morphology, and of CrN/CrCN/DLC: (c) thickness by cross-section view and (d) surface morphology.

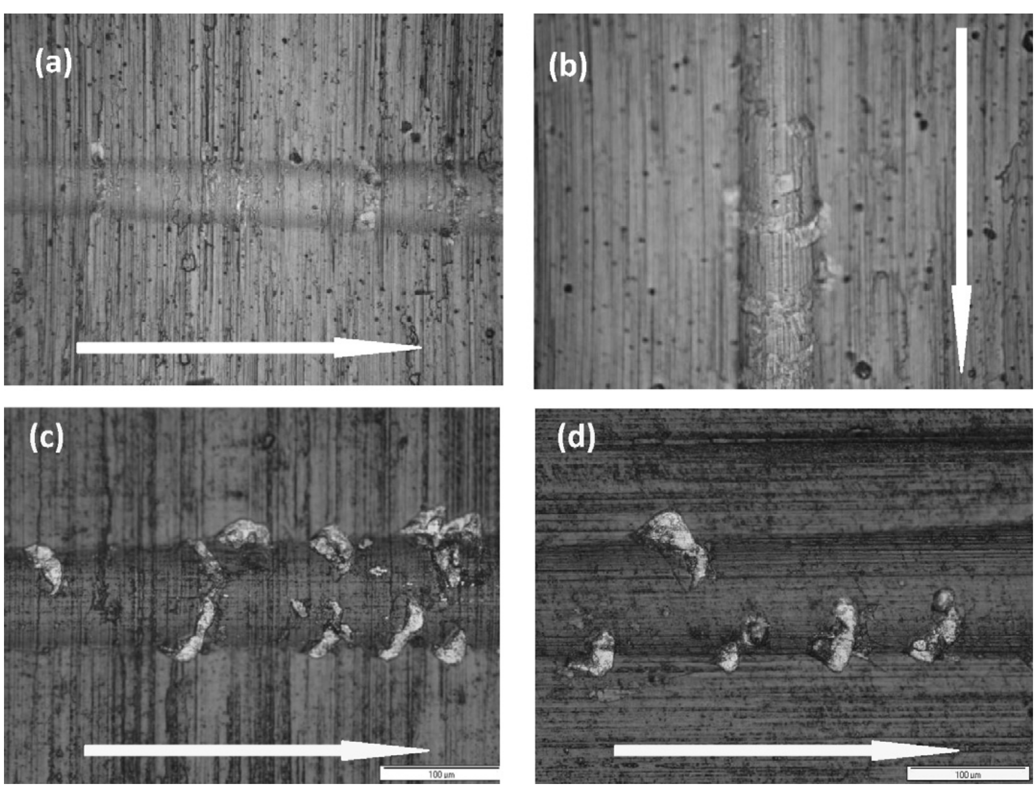

Fig. 4. Scratches made in (a and b) TiAlSiN and (c and d) CrN/CrCN/DLC coatings in orthogonal directions. White arrows indicate the sliding direction of the indenter.

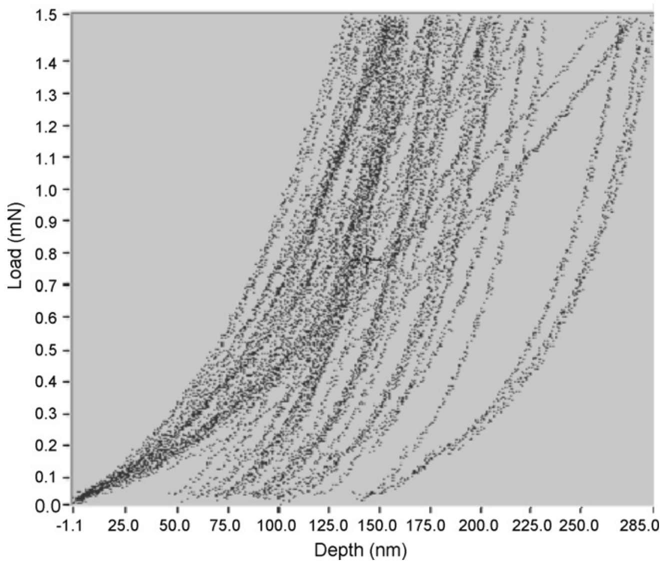

Fig. 5. "Load–displacement" curves resulting from the 50 measurements on the top of CrN/CrCN/DLC coating.

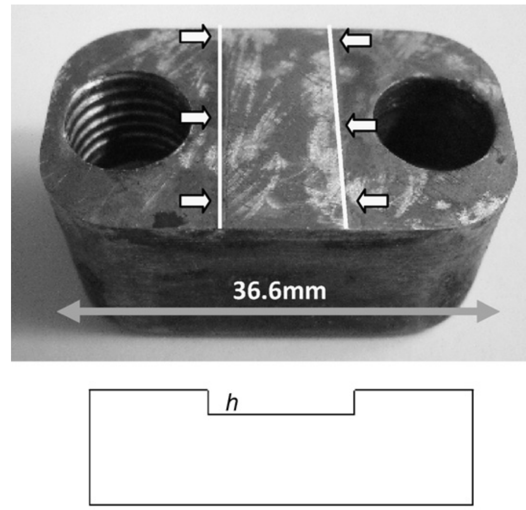

Fig. 6. Aspect of the CrN/CrCN/DLC coated sample after 90,000 cycles and schema of how profilometry measurements were made.

diamond tip moves perpendicularly to the groove border peaks, coating is under higher stress and the film tends to an earlier detachment. The failure mechanisms detected in TiAlSiN coating were conformal and lateral cracking in the first direction and internal delamination in the second one. Partial loaded paths can be observed in Fig. 4. Critical load values obtained are typical for industrial applications, being close to those found by some authors [7–9] for other PVD sputtered coatings.

One of the most important parameters for tribological applications is the hardness. Due to the reduced coating thickness, some care must be taken. It is well known [10] that, when the indentation depth is more than 10% of the film thickness, hardness measurements can be affected by the rather soft substrate. In order to overcome this problem, relatively low load (50 mN) was selected, minimizing the indenter penetration depth. Problems with elastic recovery and creep were avoided, keeping constant the maximum load during 30 s. The hardness value obtained for TiAlSiN coating, 21.8 GPa, is lower than others registered by some authors (∼40 GPa) [11]. The value obtained results from 10 different measurements in different zones of the sample, with a standard deviation of 0.76 GPa. This disparity can be attributed to Si and Al contents and the set of PVD sputtering selected parameters. The average values of micro-hardness tests are shown in Table 5. Because of the DLC top layer reduced thickness of the CrN/CrCN/DLC coating, a different technique for hardness measurement was applied. The load was decreased from 50 mN to 1.5 mN producing an indentation depth (h_c) of 0.158 μm. This value, about 20% of the DLC coating thickness (0.740 μm), allows that the measured surface hardness is not influenced by the substrate and not even probably by the other two layers. In this case, 50 measurements were completed to increase the results accuracy. "Load–displacement" curves of these tests can be seen in Fig. 5. Vickers indenters were used in all the hardness tests.

Industrial wear tests with glass fiber reinforced plastic were carried out using manufacturing plastic injection equipment, provided with a previously prepared mold with three samples located at the feed channels. In these tests, wear was measured by profilometry relatively to unworn surfaces (lateral buttress). Height loss (h) measured after 90,000 cycles was 0.049 μm for TiAlSiN and 0.017 μm for CrN/CrCN/DLC coating. After 45,000 injections, values obtained were 0.021 μm and 0.009 μm, respectively. These average values were based on 10 measurements carried out by profilometry, after ultrasonic cleaning operation in ethanol bath during 30 min. Fig. 6 schematically shows how measurements were

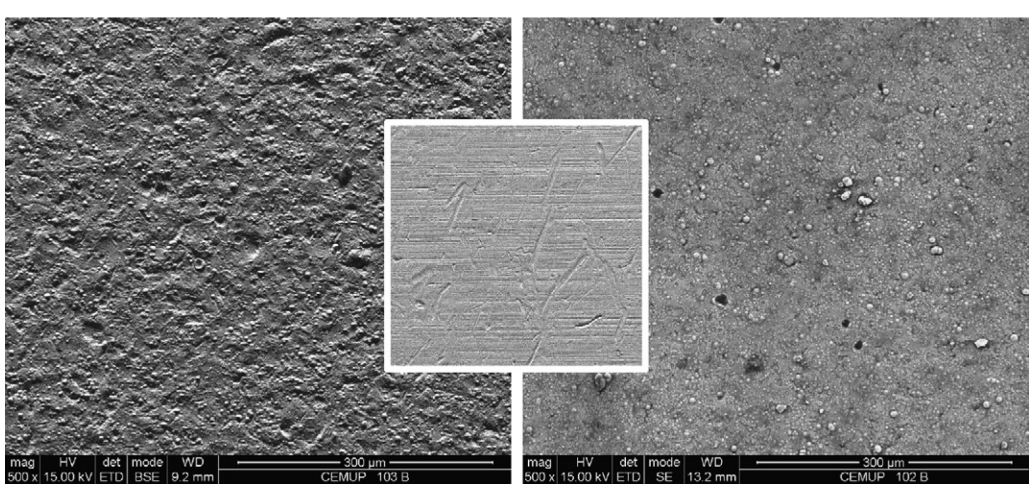

Fig. 7. Coating surface morphology (top view) of (a) TiAlSiN and (b) CrN/CrCN/DLC coatings after 90,000 injection cycles of PP reinforced with 30 wt.% of glass fiber. Central picture (c), with identical magnification, shows AISI P20 steel after 45,000 injection cycles with the same composite.

made. Compared to the reference uncoated surface, which presents a height loss of 0.524 μm after 45,000 cycles, coated ones present 25 and 58.2 times higher wear resistance, respectively. The surface of the TiAlSiN coating, shown in Fig. 7a, did not present obvious abrasive wear marks, while the substrate shown in Fig. 7c presents clear wear grooves even after only half number of cycles. Otherwise, CrN/CrCN/DLC coating, after 90,000 injection cycles (Fig. 7b) presents some wear marks, resulting from the DLC partial removal. SEM studies with image treatment software allow concluding that only about 0.13% and 0.03% of the coated surface was removed after 90,000 cycles, for TiAlSiN and CrN/CrCN/DLC, respectively, corresponding to peaks detachment. Close observation of the coating damages shows that some aggregates disappeared from the surface, leaving various spots where substrate becomes visible to back-scattered electrons.

4. Conclusions

After this work, the following conclusion can be drawn:

- When tested in an industrial environment consisting of a production injection molding die, the monolayer TiAlSiN coating was found to be 25 times more wear resistant than the uncoated substrate, and the three-layer CrN/CrCN/DLC coating was found to be 58 times more wear resistant.

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