Micro-abrasion wear behaviour of TiAlCrSiN nanostructured coatings

R.P. Martinho[a], M.F.C. Andrade, F.J.G. Silva, R.J.D. Alexandre, A.P.M. Baptista

ABSTRACT

The injection process of glass fibres reinforced plastics promotes the moulds surface degradation by erosion. In order to improve its wear resistance, several kinds of PVD thin hard coatings were used. It is well-known that nanostructures present a better compromise between hardness and toughness. Indeed, when the coating is constituted by a large number of ultra-thin different layers, cracks and interface troubles tend to decrease. However, it is not clear that these nanostructures present a better wear behaviour in erosion processes. In order to study its wear behaviour, a sputtered PVD nanos- tructured TiAlCrSiN coating was used. The substrate and film surfaces topography were analyzed by profilometry and atomic force microscopy techniques. Film adhesion to the substrate was evaluated by scratch tests. The surface hardness was measured with a Vickers micro-hardness tester. The wear resistance was evaluated by micro-abrasion with a rotating ball tribometer tests. Slurry of SiC parti- cles in distilled water was used in order to provoke the surface abrasion. Different duration tests were performed in order to analyze the wear evolution. After these tests, the wear mechanisms developed were analyzed by scanning electron microscopy. Wear craters were measured and the wear rate was calculated and discussed. With the same purpose, coated inserts were mounted in an injection mould working with a 30% glass fibres reinforced polypropylene. After 45 000 cycles no relevant wear was registered.

Keywords: Micro-abrasion, Hard coatings, Wear, Thin films

1. Introduction

The increase of productivity requires the development of new materials in all branches of industry as the plastic industry [1]. In order to improve the mechanical properties, reinforced materials are added to plastics [2]. The use of glass-reinforced polymers is well-known to generate wear damage in the moldings [3,4] and a number of coatings and surface treatments have been used to prolong component life [4–6]. One of the most used materials, in industrial applications, are the thermoplastics provided with glass fibre reinforcement [7], in spite of present lower tensile strength than that reinforced with Kevlar and lower stiffness than carbon-reinforced materials. This limitation is due to the relatively low modulus [8].

The friction and wear mechanisms of materials, such as adhesion, abrasion or oxidation, have been studied for decades [9–11]. The adhesion of the hard thin films onto a substrate is usually verified by a scratch test [12], where it is possible to verify the cohesive or adhesive failures between the film and the substrate. Despite several wear mechanisms act in the moulds during the glass fibres plastic injection moulding process, the surface suffers a severe wear mainly by glass fibres tips micro-abrasion. Indeed, if a coated surface resists better when submitted to micro-abrasion wear tests, it is a first sign that a very good improvement can be achieved when this coating is applied in the surface mould for injection of glass fibre-reinforced plastics.

The aim of this work is to characterize the TiAlCrSiN film's nanostructure and morphology and to study the wear behaviour of the film in two different situations: laboratorial tests (ball-cratering micro-abrasion) and practical tests (injection with glass fibre-reinforced plastics). The TiAlCrSiN micro-abrasion results were compared with the same tests carried out over an uncoated AISI P20 sample. Another TiAlCrSiN-coated sample was mounted on a plastic injection machine, in order to observe the wear behaviour of the surface after 45 000 injection cycles with 30% glass fibre-reinforced polypropylene.

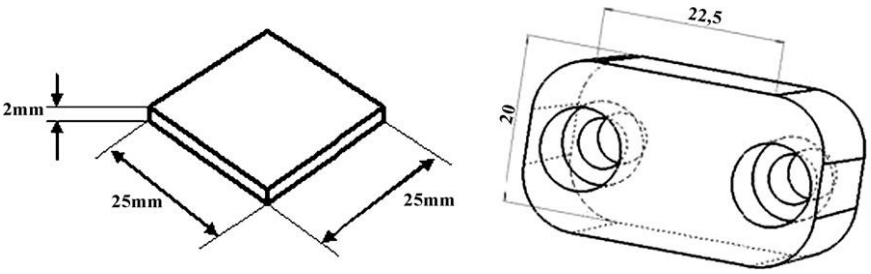

Fig. 1. (a) Laboratorial sample geometry; (b) industrial sample geometry.

2. **Experimental**

2.1. Substrate material and sample geometry

In this wok, AISI P20 tool steel with 380HBW 2.5/187.5/5 hardness was used as substrate. The laboratorial samples, with a quadrangular shape of 25 mm × 25 mm and 2 mm thickness, were milled and grinded to a mean surface roughness R_a of 0.060 μm in the work surfaces. The industrial samples were machined following the necessary shape and the work surface was also grinded until a same surface roughness had been obtained. Both samples shape are shown in Fig. 1. The chemical composition of this substrate material was confirmed by mass spectroscopy and is given in Table 1.

2.2. Coating process

In this work an industrial CemeCon CC800/9ML PVD Magnetron Sputtering reactor was used. Four different targets (Ti, Al, Cr and Si) were used in order to obtain a nanostructured TiAlCrSiN coating, about 4.5-μm thickness. The deposition parameters were as follows: gas pressure 500 mPa, temperature 500 °C, target power density 16 A cm^{-2}, bias in the range of −120 V to −50 V, and deposition time 4 h. The sample holder was animated of circular motion (1 rpm), in order to expose all the samples at all the targets and to obtain better homogeneity in the film composition.

2.3. Surface and thickness analysis

In order to measure the film thickness and to observe the sample surface, a FEI Quanta 400FEG scanning electron microscope (SEM), provided with an EDAX genesis X-ray spectroscope (EDS), was used. The mean surface roughness was measured with a VEECO multimode atomic force microscope (AFM) equipment (7 nm tip radius) provided with the NanoScope 6.13 software.

2.4. Adhesion analysis

The adhesion between TiAlCrSiN film and substrate was verified by scratch tests. These tests were developed by a CSM REVETEST scratch tester. This kind of test allows the quantification of the normal adhesion load between the film and the steel substrate. A posterior optical microscopy analysis allows the identification of the local and corresponding normal load that provoked cohesive (Lc_1) and adhesive (Lc_2) failures in the interface. To carry out these tests, the following parameters were used: normal and progressive load of 0–80 N, sliding speed of 10 mm min^{-1} and 100 N min^{-1} as load per time, as recommended in EN 1071-3:2005. Three tests were carried out in two orthogonal directions, in order to identify possible different behaviours caused by grinding texture.

Table 1
AISI P20 mass spectroscopy analysis (wt%).

C	0.35%
Si	0.29%
Cr	1.95%
Mn	1.39%
Mo	0.19%
NI	1.00%
S	0.01%

2.5. Micro-abrasion tests

In order to quantify the abrasive wear resistance of the TiAlCrSiN film, when compared with the uncoated sample, micro-abrasion tests were performed in a ball-cratering tribometer. A polished ball of AISI 52100 steel of 25 mm diameter was etched in a 10% NITAL solution during 20 s, in order to increase its superficial roughness. In these tests abrasive slurry composed by 35.4 g of SiC F1200 (according to FEPA — Standard 42-2:2006) in 100 ml distilled water was used. The ball rotation speed was 80 rpm (corresponding to 0.105 m s^{-1}) and the normal load, 0.25 N. A schematic diagram of the ball-cratering tribometer used in the laboratorial work is presented in Fig. 2. In order to guarantee the consistence of the results, all tests were made three times with the duration of 200, 500 and 700 cycles (corresponding to 15.71, 39.27 and 54.98 m, respectively), each. At the end of the tests, the micro-abrasion craters were measured and observed by SEM and by optical microscopy (OM) using OLYMPUS BX51M microscope provided with ANALYSIS DOC software and 12.5Mpixel OLYMPUS digital camera.

2.6. Industrial wear tests

The main objective of this work is to guarantee a longer moulding surface life, when it is submitted to glass fibre-reinforced plastics. Hence, three cavities were made in an industrial mould

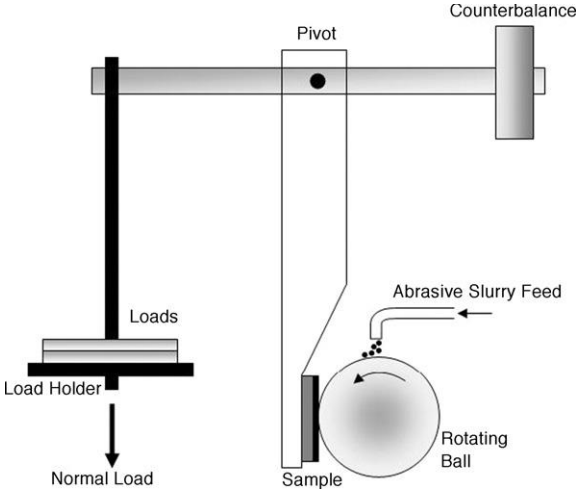

Fig. 2. Schematic diagram of the ball-cratering tribometer used in this work.

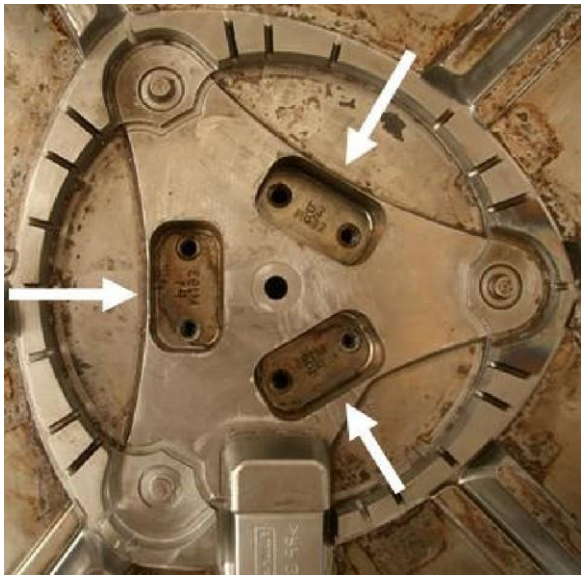

Fig. 3. Mould aspect and insert cavities.

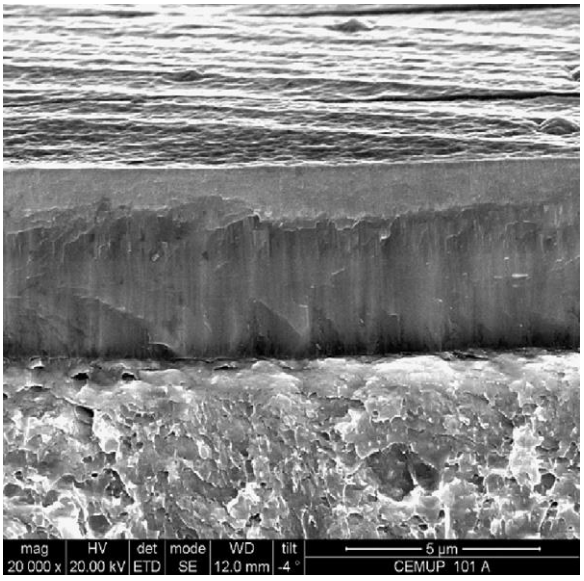

Fig. 4. TiAlCrSiN coating morphological characterization.

dedicated to produce automotive radiator fans in 30% glass fibre-reinforced polypropylene. This mould, with its cavities, can be observed in Fig. 3. The mould allows obtaining two fans per each injection, in order to increase the productivity. Three inserts were manufactured in order to fit inside the cavities, previously made in the mould. The reinforced polypropylene is injected in the centre of the mould and flow by each feed channel. The local of the inserts was selected in order to obtain the same turbulence conditions of the plastic moisture in the surface, after a quick flow direction shift. 45 000 injections were made, in order to analyze the TiAlCrSiN-coated surface behaviour. In these conditions, it is well-known that AISI P20 tool steel presents an eye-visible abrasive wear, needing a complex maintenance process. Results were carefully analyzed by SEM, in order to identify possible changes and respective wear mechanism compared with the original TiAlCrSiN surface.

3. **Results**

3.1. Morphological characterization

After PVD deposition, the film surface was characterized by SEM and AFM. In Fig. 4 it is possible to observe the film morphology with its columnar structure. In the same picture it is possible to observe two distinct layers: a bottom layer with a columnar structure well-defined and a top layer with a compact structure, corresponding to different PVD deposition phases. These differences are well depicted also in Fig. 5a, obtained in a cross-section view by SEM, after metallographic preparation. Different layers, labelled Z1 and Z2 in Fig. 5a, present small composition differences: the area Z1 is constituted by nano-layers of Al, Ti and Si, when the area Z2 presents only Cr. Chromium nitride is the first layer to deposit. After this, all targets participate in the deposition process. Due to the holder circular motion, samples are exposed to each target in each rotation. Controlling the holder rotation and deposition rate, we can achieve nano-layers with the desired thickness. High magnification Fig. 5b (200 000×) allows to observe a multilayered nanostructure with a period of about 65 nm.

The topography and roughness of the TiAlCrSiN film were accessed by AFM with two different analysis areas: 10 µm × 10 µm and 50 µm × 50 µm. The mean average roughness (R_a) measured on the film was 0.033 µm (0.128 µm in the substrate surface) and the maximum roughness height (R_{max}) was 0.414 µm (2.067 µm in the substrate surface) according to DIN 4768. As can be observed, the roughness parameter values decreased after PVD film deposition, which corresponds to a preferable physical deposition on the substrate valleys. Despite of this, some film peaks can be seen in the

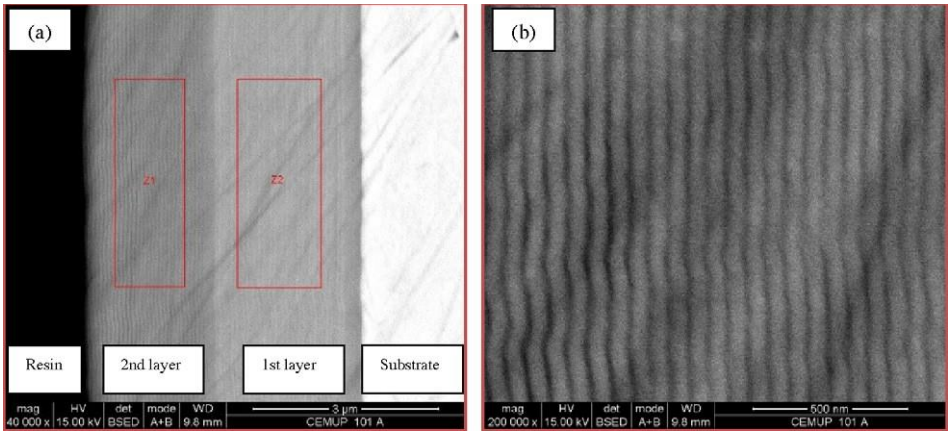

Fig. 5. (a) Cross-section TiAlCrSiN film SEM micrograph after metallographic preparation; (b) Z1 multilayered nanostructure view.

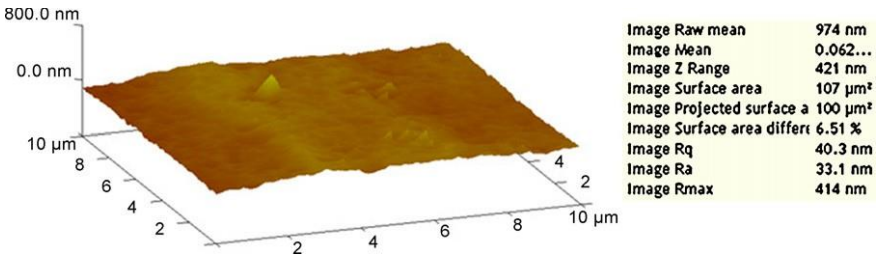

Fig. 6. TiAlCrSiN film surface AFM analysis.

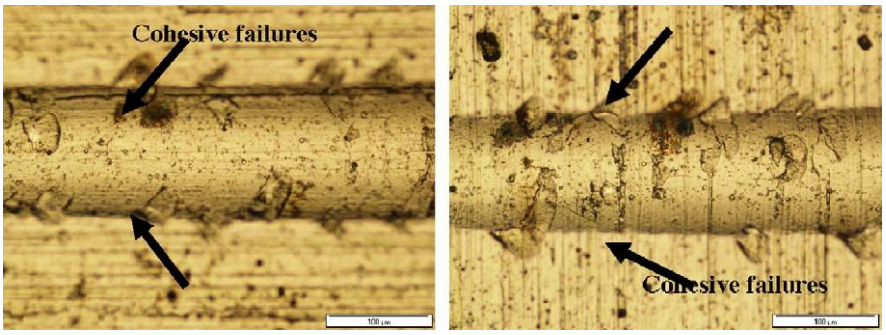

Fig. 7. TiAlCrSiN film cohesive failure in longitudinal and transversal directions.

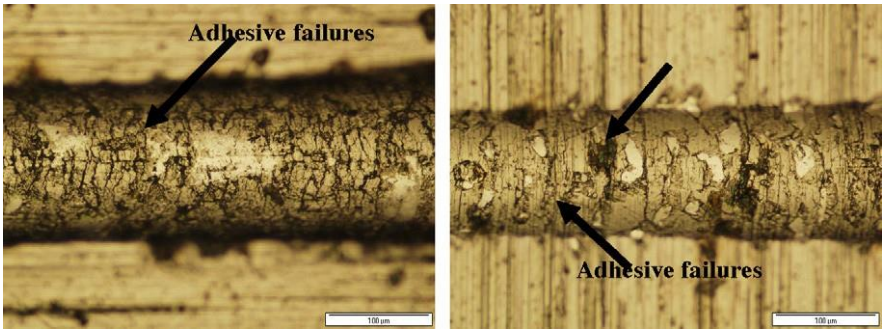

Fig. 8. TiAlCrSiN film adhesive failure in longitudinal and transversal directions.

AFM scan depicted in Fig. 6. These peaks correspond to aggregates grew in the surface during the PVD deposition process, due to thermodynamic favourable conditions. This phenomenon was already largely discussed in the literature [9,13] and it is common in PVD industrial processes.

3.2. Scratch tests

In order to evaluate the adhesion between the TiAlCrSiN film and substrate, six scratch tests were carried out, three in each orthogonal direction (parallel and perpendicular to the texture left

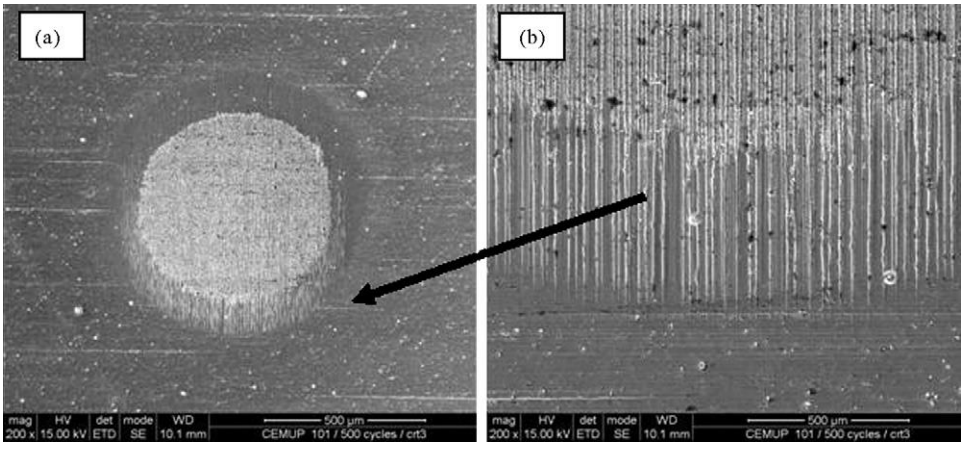

Fig. 9. (a) SEM micrograph of micro-abrasion crater after 500 cycles; (b) abrasion grooves.

by the grinding process), following the test parameters described in Section 2. At the end of the tests, the scratch grooves were carefully observed by optical microscopy. Cohesive failures result of film internal failure mechanisms and the substrate was not visible. In this case, no interface troubles are usually observed. Adhesive failures acting in the film/substrate interface provoke film detachment. The critical load Lc_1, corresponding to cohesive failure, measured in longitudinal and transversal directions were 18 and 16 N, respectively, and the critical load Lc_2, corresponding to adhesive failure, measured in the same directions were 39 and 25 N, respectively. The difference between Lc_1 and Lc_2 values must be due to the grinding marks. Cohesive and adhesive failures can be observed in Figs. 7 and 8, respectively. These values are in line with other analysis made in similar films, but are lower than the expectations. This can be due by the high hardness of the film, thin thickness and/or surface roughness. Nevertheless, micro-abrasion crater borders showed a very good adhesion between the film and substrate because no spallation was observed in the crater exit border grooves.

3.3. Micro-abrasion tests

Micro-abrasion tests were carried out according to the conditions mentioned in Section 2. All the craters present well-defined circular shape. After 200 cycles (corresponding to 15.71 m), no film perforation was observed. Nevertheless, tests with 500 cycles show coating perforation as can be seen in Fig. 9a.

Summary results of micro-abrasion tests can be observed in Table 2. Each crater diameter was measured in two orthogonal directions, in order to minimize error measurements due to crater circular distortion. The results presented correspond to three tests average, made according each test conditions. Observing Fig. 9b, regular-spaced parallel grooves, corresponding to the

Table 2
Micro-abrasion wear tests summary results.

Cycles	Sliding distance (m)	Normal load (N)	Uncoated sample crater diameter (mm)	TiAlCrSiN-coated sample crater diameter (mm)	Uncoated sample removed volume (mm^3)	TiAlCrSiN-coated sample removed volume (mm^3)	Uncoated sample wear coefficient (mm^3/N m)	TiAlCrSiN coating wear coefficient (mm^3/N m)	TiAlCrSiN-coated sample wear coefficient (mm^3/N m)
200	15.71	0.25	1.11	0.5750	0.0060	0.0004	0.0015	0.000517	0.0001
500	39.27	0.25	1.39	1.0100	0.0123	0.0041	0.0013	0.000364	0.0004
700	54.98	0.25	1.51	1.2150	0.0204	0.0086	0.0015	0.000312	0.0006

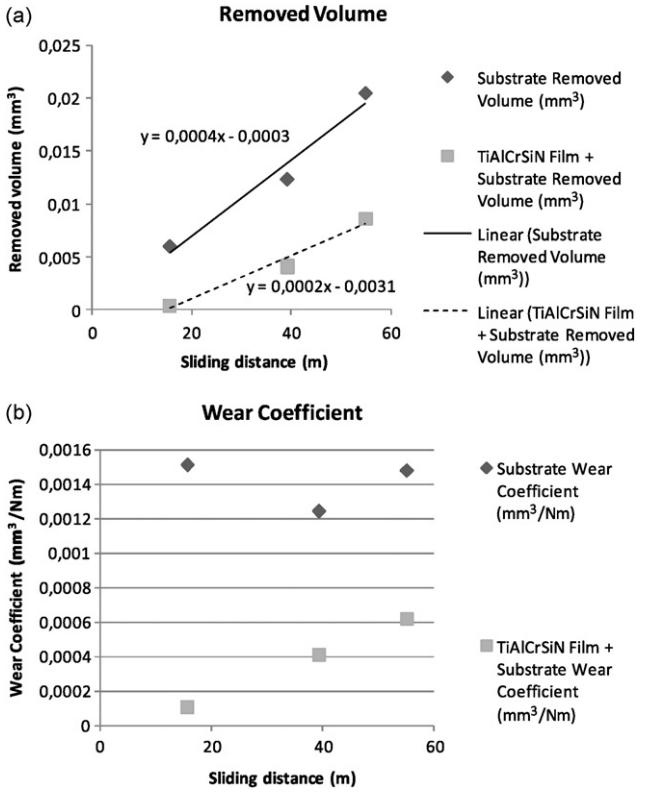

Fig. 10. (a) Volume removed by micro-abrasion; (b) wear coefficient for uncoated and TiAlCrSiN samples.

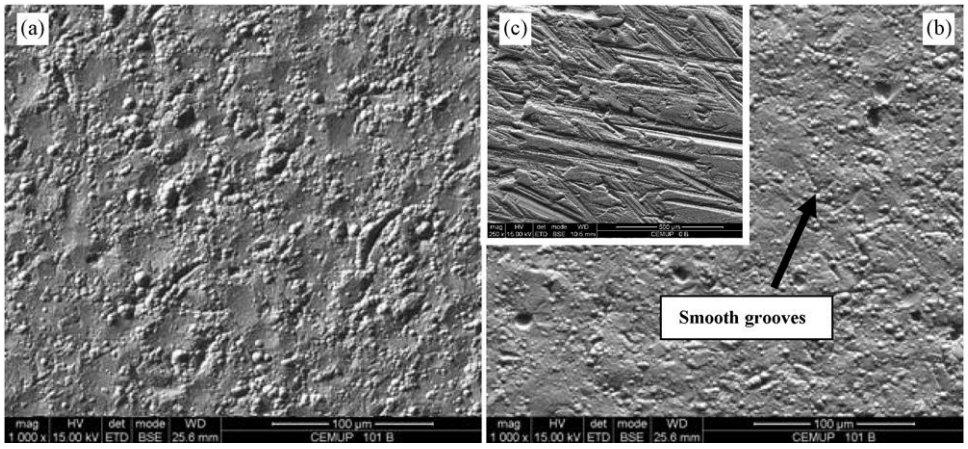

Fig. 11. (a) Original TiAlCrSiN-coated surface (1000×); (b) moulding TiAlCrSiN-coated surface after 45 000 cycles of the injection of 30% glass fibre-reinforced polypropylene (1000×); (c) uncoated steel moulding surface after 45 000 cycles of the injection of 30% glass fibre-reinforced polypropylene (250×).

crater side where abrasive slurry left the contact, denoting that a two-body wear mechanism was present can be seen. Basically, it is possible to observe that the wear resistance was drastically improved by the TiAlCrSiN coating. This can be observed attending the trend lines drew on the graphic of Fig. 10a where the line slope for TiAlCrSiN-coated substrate present a large benefit when compared with uncoated substrate. Three wear coefficients were calculated: substrate, coating and global. Calculations were made according to the integrated form [14] of an equation originally proposed by Kassman et al. [15]. The wear coefficient increases consistently for TiAlCrSiN-coated samples, due to film perforation, when remains quasi-constant for the uncoated samples (Fig. 10b).

In order to test the same coating in industrial environment, coated inserts were mounted in the mould, as described before. In Fig. 11a it is possible to compare the original coated surface (a), with the smooth worn-coated surface (b). After 45 000 injections with 30% glass fibers-reinforced polypropylene, only very small and rare scars and also random smooth grooves (ill-defined) were observed in the coated surface due to glass fibers tips during injection process. A light surface smoothness was also observed, resulting in some aggregate polishing process. No film aggregates detachment was registered. In the same Fig. 11c a steel AISI P20 worn surface subject to the same work can be observed.

4. Conclusions

After the present work, the following conclusions can be drawn:

- TiAlCrSiN coatings based on two different layers (CrN + nano-structured TiAlCrSiN) present a very good adhesion to the AISI P20 steel substrate.
- The wear resistance was increased about 50% with the TiAlCrSiN coating, related with the uncoated substrate, attending to the micro-abrasion ball-cratering tests.
- Practical tests allow observing that only very small damages were provoked in the coated surface after 45 000 injection cycles of 30% glass fibre-reinforced polypropylene.

Acknowledgments

The authors would like to thank INEGI, Instituto de Engenharia Mecânica e Gestão Industrial (FE-UP) and CIDEM, Centro de Investigação e Desenvolvimento em Engenharia Mecânica (ISEP) for the financial support and facilities. The authors also wish to thank Prof. Teresa Vieira and Prof. José Manuel Castanho of FCTUC for scratch tests facilities availability and useful discussion. PLASTAZE (SIMOLDES Group) Portuguese company and Eng. Luís Carvalho plastic injection collaboration are also acknowledged.

References

[1] E.J. Bienk, N.J. Mikkelsen, Application of advanced surface treatment technologies in the modern plastic moulding industry, Wear 207 (1997) 6–9.
[2] A. Güllü, A. Özdemir, E. Özdemir, Experimental investigation of the effect of glass fibres on the mechanical properties of polypropylene (PP) and polyamide 6 (PA6) plastics, Materials & Design 27 (2006) 316–323.
[3] G. Mennig (Ed.), Wear in Plastic Processing, Hanser/Gardner, Munich, 1995.
[4] P. Boey, W. Ho, S.J. Bull, The effect of temperature on the abrasive wear of coatings and hybrid surface, Wear 258 (1–4) (2005) 149–156.
[5] G. Paller, B. Matthes, W. Herr, E. Broszeit, Tribological properties of R.F. sputtered titanium based hard coatings and their behaviour under plastic-processing conditions, Materials Science Engineering A 140 (1991) 647–654.
[6] M. Heinze, G. Mennig, G. Paller, Wear resistance of PVD coatings in plastic processing, Surface and Coatings Technology 74/75 (1995) 658–663.
[7] P. Wambua, J. Ivens, I. Verpoeste, Natural fibres: can they replace glass in fibre reinforced plastics? Composites Science and Technology 63 (2003) 1259–1264.
[8] M. Ashby, K. Johnson, Materials and Design—The Art and Science of Materials Selection in Product Design, Elsevier, Butterworth, Heinemann, Oxford, 2002, p. 214.
[9] B. Bhushan, B.K. Gupta, Handbook of Tribology: Materials, Coatings and Surface Treatments, McGraw-Hill, New York, 1991.
[10] E. Rabinowicz (Ed.), Friction and Wear of Materials, 2nd ed., Wiley/Interscience, New York, 1995.
[11] B. Bhushan (Ed.), Modern Tribology Handbook Volume One Principles of Tribology, CRC Press, Boca Raton, 2001.
[12] A. Rodrigo, H. Ichimura, Analytical correlation of hardness and scratch adhesion for hard films, Surface and Coatings Technology 148 (2001) 8–17.
[13] K. Holmberg, A. Matthews, Coatings tribology, in: D. Dowson (Ed.), Tribology Series, vol. 28, Elsevier, Amsterdam, 1994.
[14] Y. Kusano, K. Van Acker, I.M. Hutchings, Methods of data analysis for the micro-scale abrasion test on coated substrates, Surface and Coatings Technology 183 (2004) 312–327.
[15] A. Kassman, S. Jacobson, L. Erickson, P. Hedenqvist, M. Olsson, A new test method for the intrinsic abrasion resistance of thin coatings, Surface and Coatings Technology 50 (1991) 75–84.