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Performance of sub-micron diamond films coated on mould inserts for plastic injection moulding

V. F. Neto · R. Vaz · N. Ali · M. S. A. Oliveira · J. Grácio

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Abstract In this article, results obtained from an investigation focusing on the application of diamond coatings on inserts for thermoplastic injection moulding applications are reported. The injection moulding industry can potentially benefit significantly from the use of diamond coatings on moulds typically employed in the injection moulding systems. Diamond films were coated on steel and onto silicon inserts and subsequently tested in real operating conditions. The moulded objects were analysed and the results were compared between bare steel and silicon inserts. The as-grown diamond coatings were characterised prior to and post the routine injection cycles using a number of techniques, such as Raman spectroscopy and SEM. Furthermore, the polymer finishing quality was assessed by optical microscopy for each material and coating used, and the results are presented and discussed in this article.

Introduction

The plastic injection moulding industry is currently developing new composite polymer based materials that present more aggressive environment for mould tools. The latter, present in polymer-carbon nanotubes composite melts, for instance, is believed to directly affect the wear mechanisms of micro-features moulds, such as code prints [1–3].

Chemical vapour deposition (CVD) diamond coatings for their well established characteristics in what concerns their high hardness, low friction coefficient and inertness [4], can potentially play an important role in the plastic injection moulding industry, thus enabling the coating of specific micro-features on mould tools and significantly contribute to reduce mould tool intervention due to service and maintenance. Furthermore, moulding release could also be enhanced due to the low friction coefficient inferred by diamond coatings.

Steel, the most commonly used mould tool material, is not a good material for diamond to deposit onto, due to the mutual diffusion of carbon into the steel matrix and the iron diffusion to the coated film, which stimulates the deposition of graphite instead of sp^3 diamond crystallites. Nevertheless, suitable interlayer systems combined with recent diamond deposition techniques, can enable the growth of good and adherent diamond coatings on steel-based substrates [5].

Diamond coatings have been obtained via a recently developed time-modulated CVD technique, where suitable modulation of the precursor gas enables to control the diamond film microstructure, such as film morphology (i.e. crystallinity, grain size and orientation, etc) [6, 7]. It is known that longer deposition times lead to thicker films and, hence, larger grain sizes. Also, due to the columnar growth mode of the crystals, thicker films induce greater internal stresses, promoting film deformation or, in extreme cases, cracking may even occur. Moreover, as the deposition time increases the incorporation of non-diamond components decrease due to the etching effect of atomic hydrogen.

A solution to overcome the above includes the deposition of a multi-layered type diamond film structure, promoting secondary nucleation during the film growth,

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V. F. Neto (✉) · R. Vaz · N. Ali · M. S. A. Oliveira · J. Grácio
Department of Mechanical Engineering, TEMA – Centre for Mechanical Technology and Automation, University of Aveiro, Aveiro 3810-193, Portugal
e-mail: vneto@ua.pt

with the modulation of the precursor gas concentration during the deposition stage. High concentration of methane in the deposition chamber promotes higher diamond crystallites nucleation density and the appearance of secondary nucleation during diamond thin film growth. Nevertheless, it should also be referred that deposition at a high methane concentration tends to promote greater incorporation of amorphous and graphite components in the film, reducing drastically the diamond quality.

Due to this, it can be then stated that the nucleation stage should be carried out at high methane concentration and the growth stage should be conducted under low methane concentration. Theoretically, the solution should be the conjugation of this two attributes, that is, pulsing the hydrocarbon gas, at different flow rates for varying time durations into the vacuum reactor during the CVD process, promoting the secondary or the required further nucleation process, in order to accomplish fine control of the film properties.

Table 1 Diamond deposition conditions

Parameter	Value
Pressure	3.9 kPa
Substrate temperature	800 °C
Filament temperature	2,100 °C
Filament-substrate distance	8 mm

Polymer injection of micro-featured objects has been highlighted as an emergent technology, when addressing issues such as Microelectromechanical systems (MEMS). The injection of micro-featured objects has been reported to be accomplished through the assistance of a microstructured plate, inserted in a mould tool. For the latter, the literature reports the usage of several types of materials, where silicon assumes a preferential role due to the vast knowledge acquired during its application on structuring silicon wafers by the semiconductor industry [8].

It is also believed that when considering the application of silicon inserts to assist polymer injection of micro-featured objects, diamond coatings could also be applied

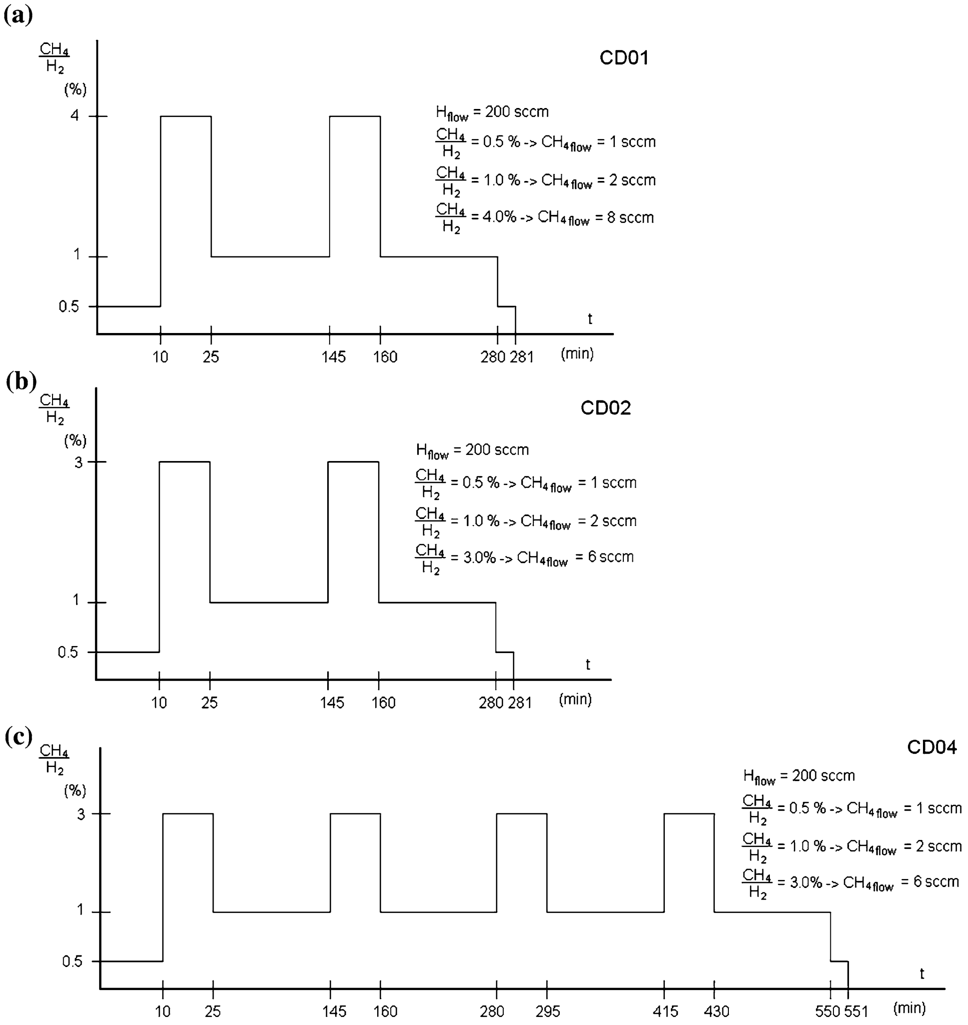

Fig. 1 Diamond deposition conditions: CD01 (**a**), CD02 (**b**) and CD04 (**c**)

inferring to the insert the above highlighted characteristics of these type of surface treatments, contributing both to improve final part quality and part-tool dimensional stability.

This article reports on the advancements accomplished in the above mentioned area of research, presenting and discussing results concerning the behaviour of diamond films with different morphological characteristics, coated on steel substrates and on silicon substrates, when subjected to polymer injection moulding cyclic routines.

Experimental details

Sets of steel (Impax Supreme™) and silicon samples of (5 × 5 × 0.5 mm) dimensions were used in this investigation. The steel samples were pre-coated with commercial grade PVD chromium nitrate (CrN) ~2 µm thick film, in order to block the mutual diffusion between the ferrous substrate and the diamond growth atmosphere [5]. All the silicon plates had the moulding surface originally mirror polished and the steel plates had the moulding surface polished with Silicon Carbide paper till grit #2000.

Prior to the diamond deposition, silicon wafers were scratched with diamond powder (2–4 µm grain size) for approximately 2 min, in order to enhance the subsequent diamond nucleation density, and then cleaned for 5 min in an ultrasonic bath with isopropanol. The steel samples coated with CrN were ultrasonic abraded with diamond solution (1/4 µm grain size) for 2.5 h and then cleaned for 5 min in an ultrasonic bath with isopropanol.

Diamond deposition was conducted in a hot-filament CVD reactor, described elsewhere [6]. The deposition parameters employed in this investigation are presented in Table 1 and Fig. 1.

In order to obtain homogeneous coatings with an average crystal size of about 1 µm, cycles of 15 min were employed for high methane pulses, followed by a low methane stage of 120 min. Diamond deposition under conditions CD01, CD02 and CD04, as shown in Fig. 1, was carried out using 2 and 4 cycles, which corresponds to a total deposition time of 4.5 and 9 h, respectively. Conditions CD01 and CD02 differ from one another on the high-pulse methane concentration. Higher methane concentration promotes the increase of diamond nucleation density [6] and consequently changes in the diamond film morphology, namely crystal size can been reduced, but at the expense of diamond quality. In order to illustrate the latter conditions, CD01 and CD02 were used to observe the effect of those morphology changes.

Table 2 Description of tested inserts

Inserts	
Ref.	Description
FD1	Steel plate diamond coated (CD01)
FD2	Steel plate diamond coated (CD02)
FD3	Steel plate diamond coated (CD04)
F1	Steel plate
SD1	Silicon plate diamond coated (CD01)
SD2	Silicon plate diamond coated (CD02)
SD3	Silicon plate diamond coated (CD04)
S1	Silicon plate

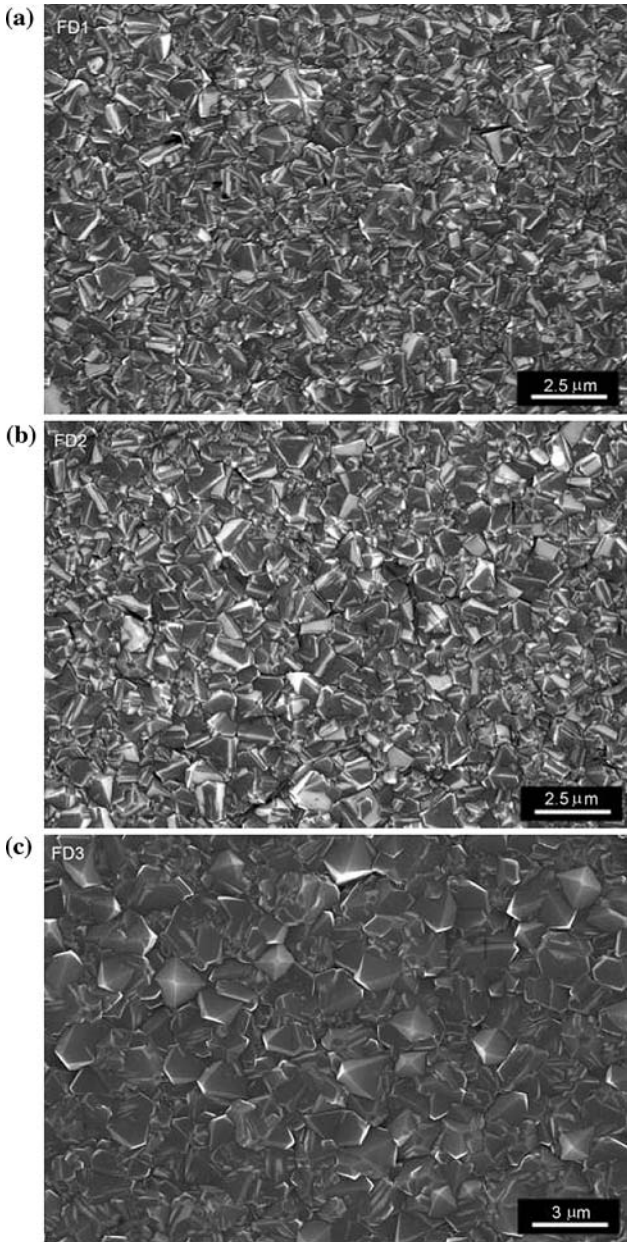

Fig. 2 Electronic microscopic images of diamond coatings on steel substrates deposited under conditions: CD01 (**a**), CD02 (**b**) and CD04 (**c**)

After the deposition of diamond coatings on all samples, the morphology of the as grown films was characterized using scanning electron microscopy (SEM) system (Hitachi S-4100) and the intrinsic stress state and quality of the diamond coatings was characterised using Raman spectroscopy (ISA JOBIN YVON-SPEX T6400 system with a 514.5 nm Ar^+ ion laser).

The eight inserts, described in Table 2, were tested for polymer injection moulding, using a mould tool specially designed to accommodate the inserts and mounted in an injection moulding machine to perform a cycle of 80 high-density polyethylene (HDPE) sample components.

The injection moulding machine used for the experiments was an EURO INJ D065, by Lien Yu Machinery Co LTD. The amplification (intensification) factor of the hydraulic pressure at the nozzle was 12.7. Other characteristics of the machine include: a screw diameter of 32 mm, maximum injection rate of 65 g/s, maximum injection pressure of 1777 bar, maximum injection stroke of 160 mm and maximum locking force of 65 ton.

The mould tool that accommodates the coated inserts was a multi-cavity tool, where one of the cavities houses a 46 × 46 × 6 mm steel sheet in which eight (5 × 5 × 0.5 mm) holes were open to accommodate the testing samples. This cavity allows the testing of all the samples being evaluated in each injection cycle and thus at the same processing conditions.

The injection material selected for the experiments was HDPE "Politeno HDPE IA-59 U3" (Braskem, Brasil). It offers high stiffness and impact strength, combined with good processability and low warpage. The characteristics were a density of 0.96 g/cm^3 (ASTM D-792), Melt Mass-Flow Rate (MFR) (190 °C/5 kg) at 7.3 g/10 min (ASTM D1238), a tensile strength at break of 25 MPa (ASTM D-638), a tensile strength at yield of 28 MPa (ASTM D-638), a izod impact resistance of 73 J/m (ASTM D 256) and a heat deflection temperature (HDT) of 81 °C at 0.45 MPa (ASTM D-648).

The HDPE injection temperature and pressure through the entire study were kept at 200 °C and 50 bar, respectively. A holding pressure was used for 5 s followed by a cooling time of 22 s, before the samples were extracted.

After carrying out the injection moulding cycles, the inserts morphology was assessed using SEM and a number

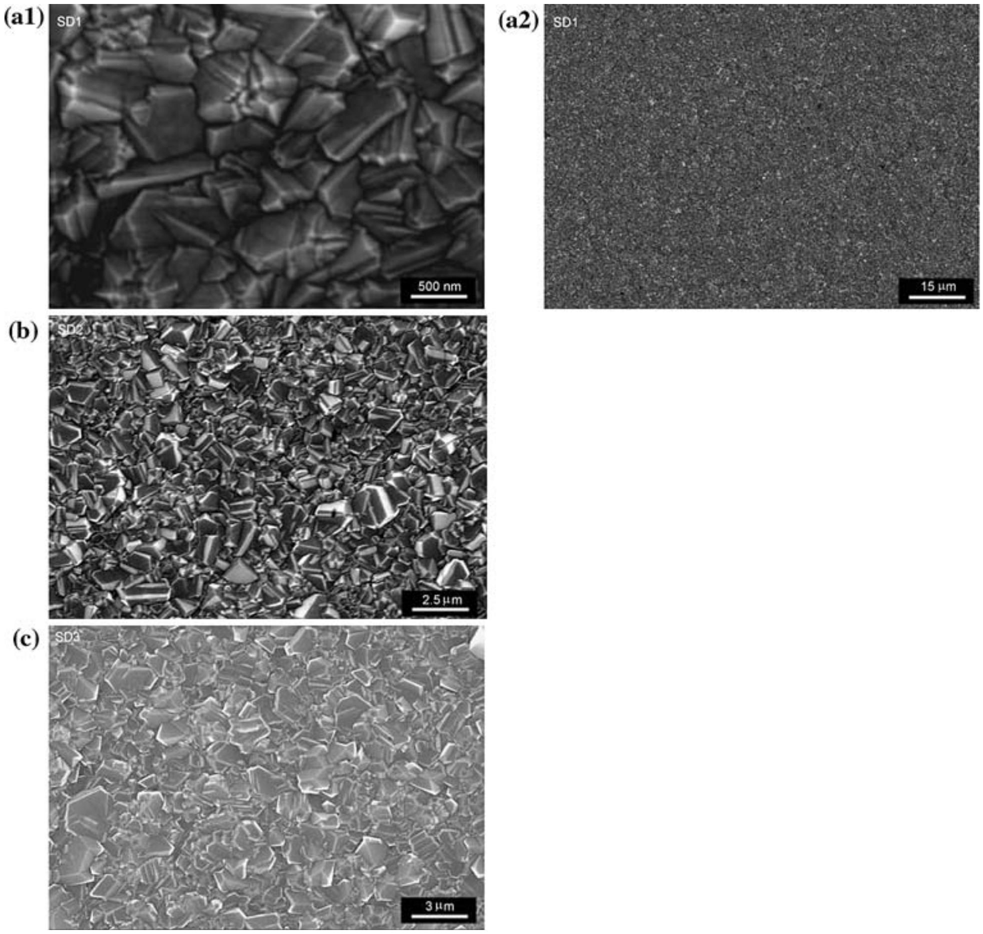

Fig. 3 Electronic microscopic images of diamond coatings on silicon deposited under conditions: SD01 (**a1** and **a2**), SD02 (**b**) and SD04 (**c**)

of the moulded objects with the inserts were analysed using an optical microscope (Nikon Eclipse LV150).

Results

Figures 2 and 3 show microscopic images of diamond coatings on steel and silicon samples, respectively. All the as-grown films exhibited sub-micron diamond crystallite size, mainly displaying (111) crystal orientation, but (100) crystal orientation was also observed. These growth directions are typical for the processing temperatures employed in this investigation. The average diamond crystallite sizes of the deposited films are shown in Table 3.

Figures 4 and 5 display Raman spectra of the as-deposited samples. It is known that CVD diamond typically exhibits a Raman peak centred at approximately 1,333 cm^{-1}, although this scattering centre may shift to the right or to the left of the spectrum depending on the residual stress imposed by the difference in thermal expansion coefficients of the substrate and the film, or to the intrinsic stress due the columnar growth of the crystals [7].

Ralchenko et al. [9] reported a theoretical value of ~7.2 GPa for the residual stress of a diamond film grown on steel at 800 °C. An experimental estimation of the residual stresses can be achieved from the Raman spectrum shift (Δv), by $\sigma = -0.567\ \Delta v$ [9, 10]. Calculated residual stress values for the diamond coatings are presented in Table 4. The Raman spectra of the samples, shown in Figs. 2 and 3, were used to assess the quality of the film samples, in terms of diamond carbon-phase purity and/or sp^3 to sp^2 bonding. A semi-quantitative measure of the quality of the diamond film can be calculated from $Q = I_d (I_{glc} + I_d)^{-1}$, [11], where Q is the 'Quality factor' of the diamond film, I_d is the intensity of the diamond peak and I_{glc} is the intensity of the graphite-like carbon peak. It is worth noting that pure diamond has a quality factor, Q, value of 1. Calculated quality factor values for the diamond coatings are shown in Table 4

Table 3 Average diamond crystallite sizes

Diamond film	Diamond crystal size (μm)
FD1	0.61
FD2	0.71
FD3	0.83
SD1	0.62
SD2	0.68
SD3	0.85

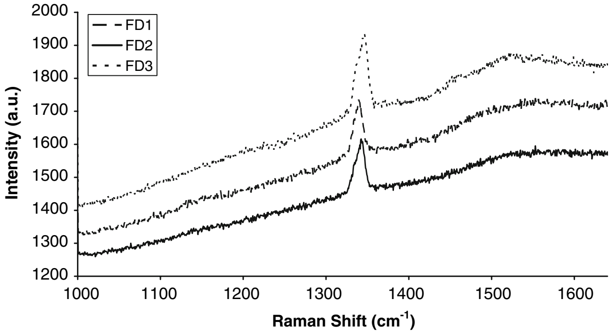

Fig. 4 Raman spectrum of the diamond-coated steel plate

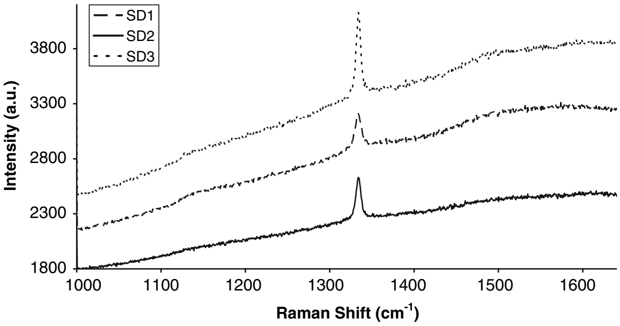

Fig. 5 Raman spectrum of the diamond-coated silicon plate

Figure 6 displays optical microscopic images of a 10 times magnified enclosed surface of the 80th injected HDPE moulded piece.

Finally, Figs. 7 and 8 show SEM micrographs of diamond-coated steel and silicon samples, respectively, after the injection routine cycles were carried out.

Discussion

Polycrystalline sub-micron diamond films were obtained both on steel and silicon substrates, using the pre-treatments described in the experimental section and the conditions described in Table 1 and Fig. 1.

As expected, diamond coatings on the silicon plates presented higher quality and comparatively lower residual stress, once diamond linear thermal expansion coefficient is similar to the one presented by silicon [12]. On the other

Table 4 Raman shift of the diamond peak, calculated residual stress and Raman quality factor

Diamond film	Raman shift (cm^{-1})	Residual stress (GPa)	Quality factor (%)
FD1	1,341	4.5	50.9
FD2	1,344	6.2	55.9
FD3	1,346	7.4	58.3
SD1	1,334	0.6	51.6
SD2	1,335	1.1	66.2
SD3	1,334	0.6	67.1

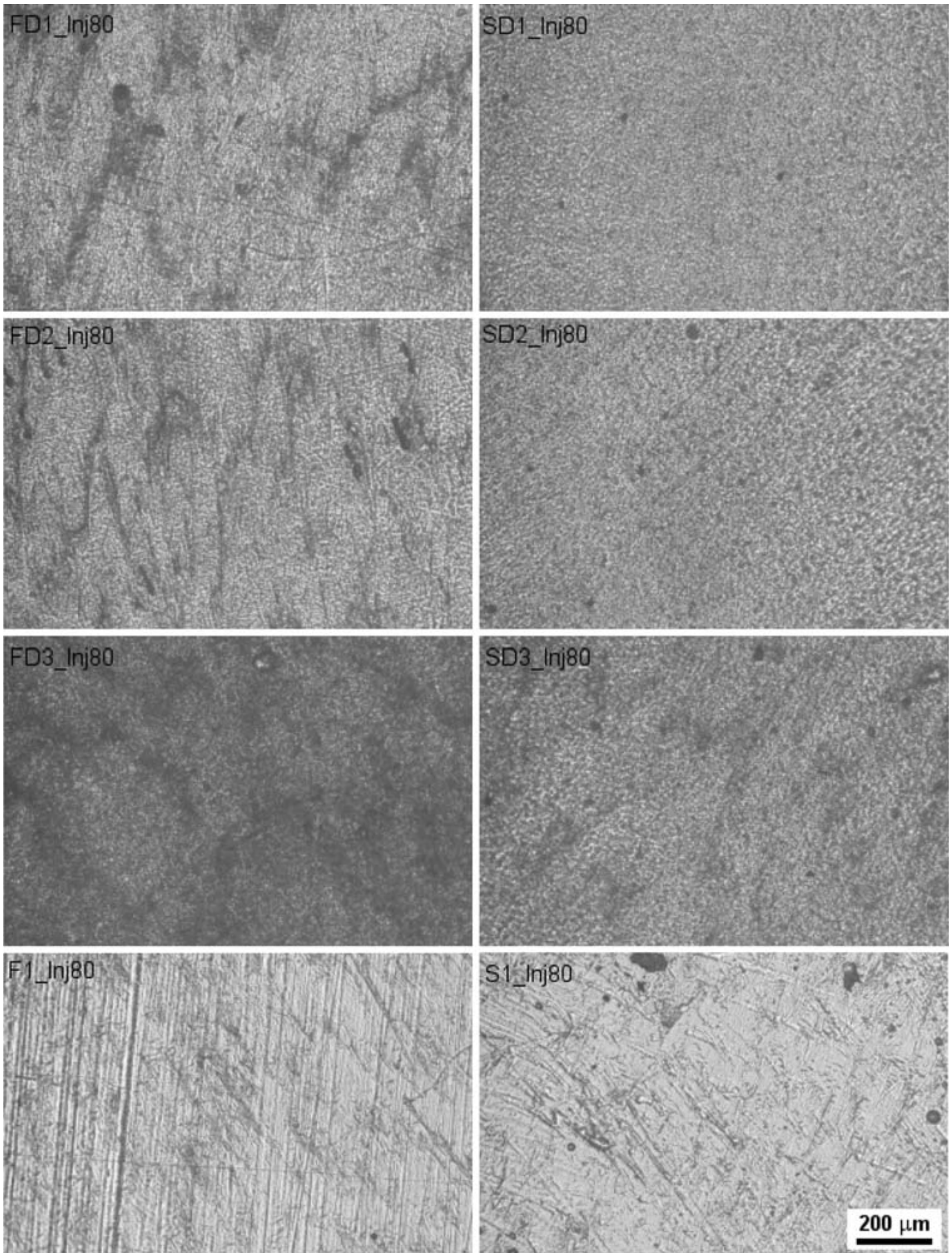

Fig. 6 Optical microscopic image of the HDPE-injected plate surface, by the different inserts, in the 80th run

hand, steel linear thermal expansion coefficient largely differs from the coefficient value displayed by chemical vapour-deposited diamond [5]. Samples FD1 and FD2 display values of 4.5 and 6.2, respectively. The longer deposition time sample, FD3, exhibited a residual stress of 7.4 GPa. Time-modulated CVD process helps to attenuate the direct time dependence of the residual stress of diamond films growth on steel substrates, but does not eliminate it. The films grown on silicon contain very low residual stress, displaying values of 0.6, 1.1 and 0.6 GPa, for samples SD1, SD2 and SD3, respectively. It can be stated that in both the samples (steel and silicon) growth under deposition condition CD01, which consists of 4% high-pulse methane concentration, exhibits lower residual stress than the samples grown for the same time but with the 3% methane concentration on the high-pulses (CD02).

One of the principal points of this study is the analysis of the polymeric objects moulded by the different surface-engineered inserts.

Figure 6 displays micrographs of the polymeric moulded surface by the eight inserts, on the 80th injection run. Apart from the first set of samples, that present marks of

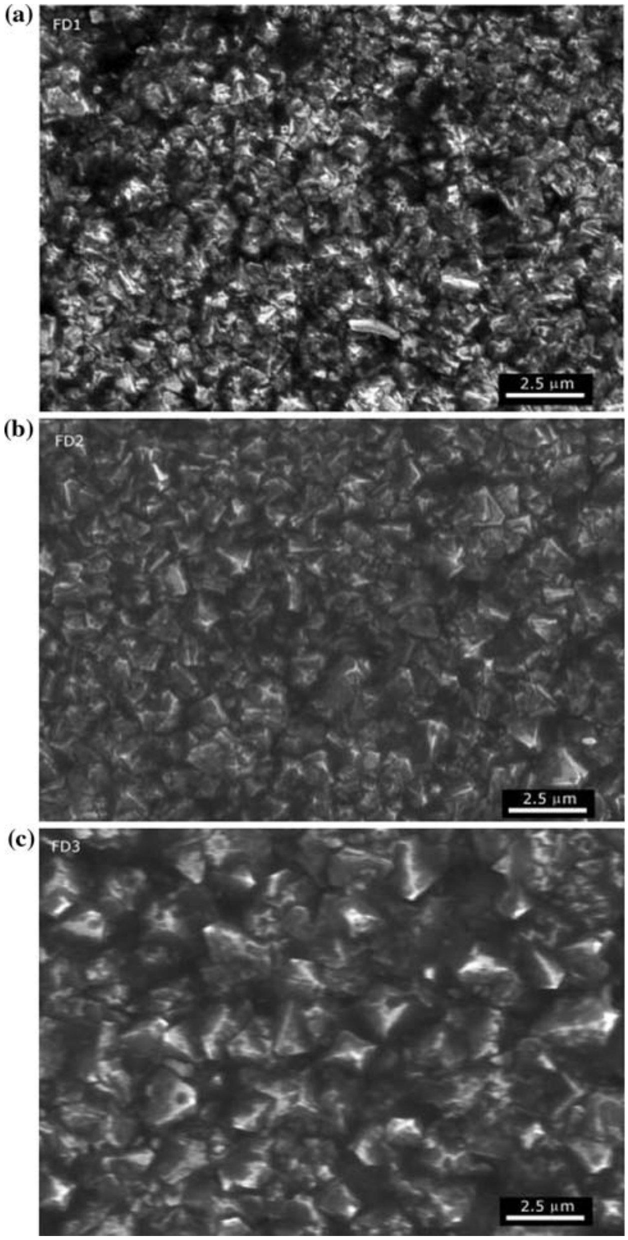

Fig. 7 Electronic microscopic images of diamond coatings on steel after HDPE moulding injection: CD01 (**a**), CD02 (**b**) and CD04 (**c**)

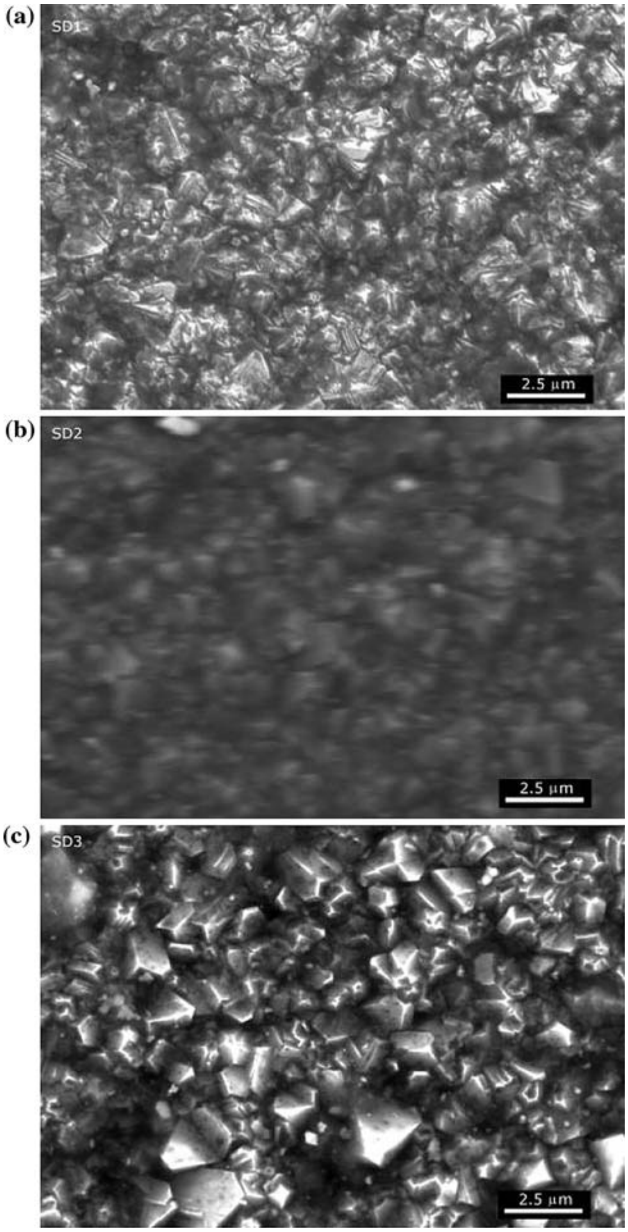

Fig. 8 Electronic microscopic images of diamond coatings on silicon after HDPE moulding injection: SD01 (**a**), SD02 (**b**) and SD04 (**c**)

the demoulding spray used in the beginning of the processing work, the injected part is very identical.

From the images presented in Fig. 6, the first evidence that can be taken is that the moulded objects with the diamond-coated inserts, present more homogeneous surfaces than the ones moulded by inserts without coating. It should be noted that inserts F1 and S1, described in Table 2, have the same or better surface finish than the samples that were used to deposit diamond coatings, because their surface was not diamond abraded similar to the ones pre-treated for diamond coating. The initial steel samples were not surface polished to achieve a mirror surface, in order to obtain optical smooth surfaces and, hence, good quality plastic components/parts. Therefore, the results indicate that polishing time may be saved when using diamond-coated surfaces, nevertheless this statement must be refined with further work, in order to establish the need for mould tool intervention on a long-term service basis.

When comparing the moulded objects by diamond films grown at the same conditions on steel and on silicon, it is clear that the silicon coated inserts present an even more homogeneous surface. Evaluating the moulded injected surfaces by the different diamond deposition conditions, no significant changes are observed. These parameters may be more critical when the number of injection cycles is increased.

Although in this work a reduced number of moulding cycles were carried out, it is also important to assess the characteristics of the diamond films after the injection period. Therefore, by comparing SEM images (see Figs. 2 and 3) prior to injection with post-injection (see Figs. 7 and 8) it can be stated that no degradation is observed.

Conclusions

The work presented in this article is part of an investigation into the application of diamond coatings to moulds inserts used in plastic injection moulding, which may enhance wear resistance of the inserts and improve the moulding release. Six diamond-coated inserts were prepared, three of them on silicon substrates and the other three on steel substrates. One bare silicon insert and one bare steel insert were used without surface modification, in order to establish comparison standards to the engineered surfaces.

Recently developed diamond deposition process, time-modulated CVD, was employed to better control the growing diamond film microstructure. Moreover, the deposition of diamond films on steel substrates was assisted with the use of a commercial CrN interlayer material.

The resulting diamond coating presented an average crystal size ranging from 610 nm (on steel, with deposition condition CD01) to 850 nm (on silicon, with deposition condition CD04), a residual stress ranging from 0.6 GPa (on silicon, with deposition condition CD01 and CD04) to 7.4 GPa (on steel, with deposition condition CD04) and a Raman quality factor ranging from 50.9% (on steel, with deposition condition CD01) to 67.1% (on silicon, with deposition condition CD04).

Moulded objects with the diamond-coated inserts seem to present more homogeneous surfaces than the ones moulded by inserts without coating, indicating that overall mould-tool intervention may be reduced when using diamond-coated surfaces. Silicon-coated inserts, compared with the steel-coated inserts, present even better surface quality. The different diamond deposition conditions did not present great difference from one another, nevertheless they may become more critical when degradation of the tool is established with an increased number of injection cycles.

Finally, although a reduced number of moulding cycles were performed, comparing the diamond coating before and after the plastic injection procedure, no degradation was observed.

Furthermore, it is fundamental, in order to establish the relative influence of the coating on the remaining injection parameters, to broaden the scope and the number of injection cycles.

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