Graphene coatings to enhance tribological performance of steel

GRAPHENE COATINGS TO ENHANCE TRIBOLOGICAL PERFORMANCE OF STEEL

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Abstract

Friction and wear affect machine reliability, efficiency and safety, increasing the maintenance and operating costs. A reduction of the coefficient of friction (CoF) of sliding parts would increase the machine efficiency, while a reduction of wear damage would allow higher reliability and safety. The aim of this work is to investigate the application of graphene to reduce the CoF and wear damage in mechanical components made of steel. In this work, graphene has been applied on C40 steel samples using two coating procedures based on chemical vapour deposition technique: direct growth graphene (DG) and transferred graphene coating (TGC). Tribological performance has been evaluated, by means of ball on disk tests, in terms of CoF and worn volume. Results obtained with no coated samples with have been compared to those obtained with coated ones. Results show that the proposed graphene coatings enhance tribological performance of C40 steel, in particular results show that DG sample has better wear strength, while TGC sampled are better to reduces CoF.

Keywords: graphene; coefficient of friction; steel; efficiency; wear; coating

List of acronyms and symbols

APCVD: ambient pressure chemical vapor deposition;

CoF: coefficient of friction;

CVD: chemical vapor deposition;

DG: direct growth graphene;

ESP: electrodynamic spraying process;

EVA: ethylene vinyl acetate;

GONS: fabricated graphene oxide nanosheet;

GNP: graphene nanoplatelets;

IPA: isopropyl alcohol;

LPCVD: low pressure chemical vapor deposition;

SPG: solution-processed graphene;

TGC: transferred graphene coating;

k: specific wear rate;

N: is the applied load;

r: is the wear track radius;

R: is the ball radius;

s: is the total sliding distance;

V: is the sample worn volume;

w: is the average wear race width.

1. Introduction

Mitigation of friction and wear is crucial to obtain high performance on sliding systems. The improvement of components tribological behavior is becoming an important goal for many researchers. Indeed, high friction and wear lead to less efficiency, minor reliability and to a shorter life of components. It is well known that a way to reduce friction and wear is to apply lubricants, both liquid and solid, on contact interfaces. The use of solid lubricants, such as graphite, molybdenite and polymeric composite coatings [1-3], is required in all cases in which liquid lubricants cannot be applied as automotive components, aerospace systems and ultra-high vacuum technologies. The most important problems concerning the use of solid lubricants concern their durability and sensibility to environmental conditions, such as the presence of humidity and oxygen [4-6], but also a series of limitations in its application related to the specific deposition techniques [7]. For this purpose, the study of new generation coating materials and deposition techniques is becoming of increasing importance. Recent works have been focused on the use of graphene as an additive for oil and grease lubricants or as a solid lubricant [8, 9]. Discovered in 2004 [10], graphene is a two dimensional carbon material mainly known for its exceptional mechanical and electrical properties. In addition, its tribological properties have been examined in several studies, demonstrating its big potential also in this field [11]. The effectiveness of graphene as lubricant oil additive has been proved by several researches: adding a little weight percentage of graphene leads to an improvement of the oil performances allowing a reduction of friction and wear [12-14]. Other works have been related to the use of graphene as grease additive: it was found that the presence of Graphene Nanoplatelets (GNP) into grease enhances its tribological performances bringing to a reduction of both coefficient of friction and wear up to about 50% [15-17]. On the other hand, some researches have been focused on the use of graphene as coating of substrates to improve their tribological

performances. Graphene coatings can be applied using different methods including mechanical exfoliation [18], chemical vapor deposition (CVD) [19, 20, 21], epitaxial growth [22], rod coating technique [23] and inkjet printing method [24]. In 2009, Filleter et al. [25] analyzed the effect of epitaxial graphene films on tribological properties of SiC substrates. The results show that the presence of bilayer graphene reducs the friction by a factor of 2. Kim et al. [26] fabricated Graphene Oxide Nanosheet (GONS) coatings using electrodynamic spraying process (ESP) demonstrating the feasibility of the coating method and its potentiality in reducing friction. Berman et al. [8, 27] investigated the friction behavior of self-mated steel tribo-pairs in humid air and dry nitrogen with solution-processed graphene (SPG) finding a reduction of friction and wear up to 3-4 and 6 order of magnitude respectively. The potentiality to use CVD-grown graphene films has been first studied by Kim et al. in 2011 [28]. They used graphene grown on copper and nickel observing a reduced adhesion and friction during micro-and nanoscale contact.

Assumed that graphene coats may improve tribological performance, it would be interesting to evaluate the tribological performance of coated materials (in particular steel as it is the most used material to produce mechanical components) produced with different coating techniques in order to verify their capability in view of industrial application.

For this reason, in this work, the tribological performance of C40 steel samples uncoated and coated with graphene produced by two different methods has been evaluated and compared. C40 steel was selected as a base material because it is widely used to produce mechanical components in many industrial fields. The first coating method used in this work, consists in CVD grown graphene on copper and then transferred on steel samples (TGC). In the second method graphene is directly grown on steel by CVD technique (DG), this method has been applied with two growing times, respectively 5 and 10 minutes. A series of ball-on-disc tests have been made in order to evaluate the tribological performances of the different graphene coated samples, and therefore to find out which of the proposed

coating methods gives the best performance in terms of CoF reduction and wear damage reduction when applied on C40 steel.

2. Materials and Methods

The samples used for the tests are made of C40 steel, with the following dimensions: 10x10x4mm.

Before coating the surfaces, the samples have been grinded (the average Ra roughness of the samples after grinding was 0.4μm) and cleaned by sonication in acetone, then washed with water and finally sonicated in IPA (Isopropyl Alcohol) to remove any impurities and dirt.

2.1. Coating processes

In this work, DG and TGC coating techniques have been used to coat the steel samples.

The tribological performance of the two different coatings has been analyzed and compared in order to define the best coating solution.

2.1.1. Direct growth

The DG process uses the CVD technique [19, 20] to synthesize large-area graphene directly on the sample surface. In particular, in this work, the Ambient Pressure Chemical Vapor Deposition (APCVD) method has been used [21]. The sample is first inserted into the CVD furnace and the temperature increased up to 1000°C in 30min within hydrogen environment (10 sccm of H_2). A pre-annealing process is then conducted by maintaining 1000 °C for 30min. The graphene synthesis starts when methane/hydrogen mix (10 sccm of methane and 100 sccm hydrogen) is introduced into the APCVD system. In this work, samples have been directly grown for respectively 5 minutes (DG-5min) and for 10 minutes (DG-10min). After growth, the samples were quickly cooled to room temperature. Growing time in this coating process may affect the quality and quantity (in terms of coated surface) of graphene

layer [20], [21]. For this reason samples have been coated with two growing times (5 and 10 minutes) in order to evaluate the influence of this parameter on the tribological performance of coated samples.

2.1.2. Transferred graphene coating

In the TGC process the monolayer graphene film is grown on copper foil substrate following a standard Low Pressure Chemical Vapor Deposition (LPCVD) procedure [21]. Due to the rough surface of C40 steel samples, conventional PMMA based transfer failed in our experiment. Thus, EVA (Ethylene Vinyl Acetate) was used as transfer supporting layer [29]. EVA solution (Aldrich, vinyl acetate 40 wt %, 10 wt % dissolved in xylene) is firstly spin-coated on the graphene/copper foil and then baked in the oven at 80 °C. Then, the copper foil is removed using the copper etchant (Copper Etchant TFB, Transense). EVA/graphene/EVA stack is then rinsed in a deionized water bath and subsequently transferred on the sample surface. After blowing with N_2 gas, the samples were baked at 80 °C for one hour. Finally, the EVA is removed using Xylene at 90 °C. This procedure is schematically resumed in Figure 1. The graphene coating obtained by this method is only 1 atomic layer in thickness [29].

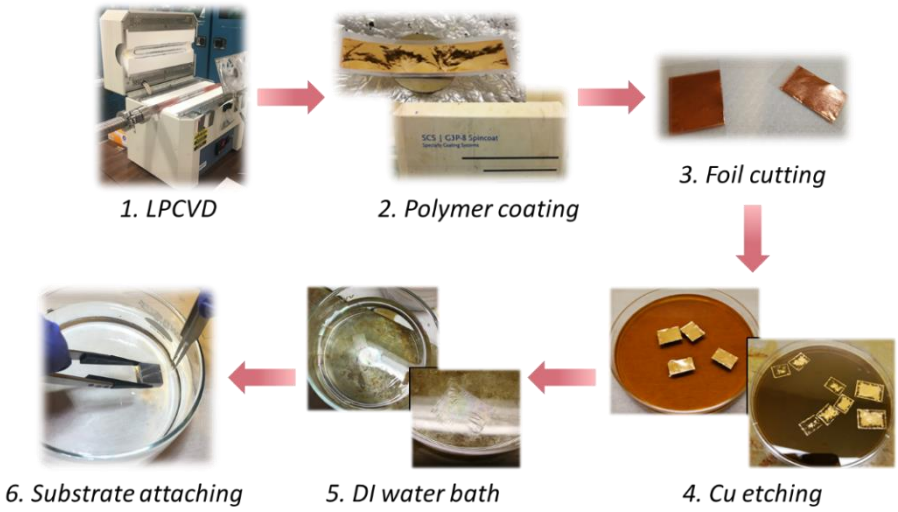

Figure 1: Transferred graphene coating process.

3. Tests description

Tribological tests have been performed using a “TRB Anton Paar” ball-on-disc tribometer (Figure 2). The machine measures the instantaneous friction force of the tribometer system and calculates the CoF, given the normal load applied on the disk. During the ball-on-disc tests a load of 5N has been applied on the sample and then put in rotation with a linear speed of 50 mm/s, this speed has been kept constant in all the performed tests. The total sliding distance of each test has been set at 100 m. The sampling frequency during the tests was 100Hz. As a counterpart, a 100Cr6 steel ball, 6 mm diameter, has been used.

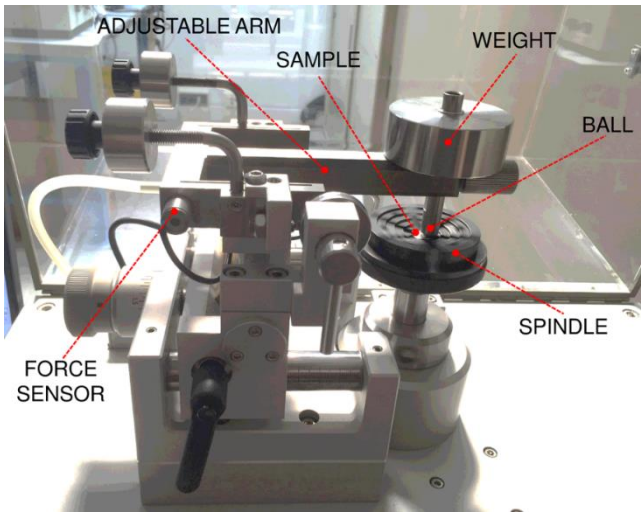

Figure 2: Anton Paar Tribometer.

The maximum and average Hertzian contact pressure between ball and sample, calculated considering 210GPa as Young’s modulus, 0.3 as Poisson’s ratio and neglecting the effect of graphene layer, were respectively 710MPa and 470MPa. The temperature and humidity of the air were respectively 23°C and 39%. In order to have statistical strength of the results, three tests for each sample have been carried out.

The material worn volume V has been calculated according to ASTM G99 standard [30], by the following equation:

$$V = \frac{\pi \cdot w^3 \cdot r}{6 \cdot R}, \qquad (1)$$

where w is the average wear race width (measured at three different locations of the sample surface at about 120° distance one from the other); r is the wear track radius; R is the ball radius. The wear race width has been measured by means of a profilometer (SM Metrology Systems PGS200).

Table 1 resumes the tribological tests performed on the samples with the testing parameters.

Table 1: Test parameters.

Sample Type	Number of test repetitions	Normal load [N]	Sliding speed [mm/s]
No coated	3	5	50
TGC	3	5	50
DG-5min	3	5	50
DG-10min	3	5	50

The DG process involves the sample to be exposed to high temperature and relatively quick cooling. Therefore, in order to verify if the coating process modified the steel microstructure, the surface hardness has been measured before and after coating. In particular the Vickers Hardness (HV/0.3) has been measured by means of a micro Vickers hardness tester (Rupac Innovatest Nexus 4500). For each sample, five measurements have been performed and then the average hardness values calculated.

4. Results and discussion

4.1. Hardness measurement

The results of the Vickers Hardness measurement are shown in Figure 3. The Pure Steel sample is characterized by the higher value of hardness, equal to 189 HV. For the DG samples, the hardness of the DG-5min results to be similar to the pure steel and equal to187 HV, while for the DG-10min the value decreases up to about 164 HV, this can be due to

decarburization of the steel surface and to the grain growth and microstructure changes due to the high temperature of the direct grown coating process [31].

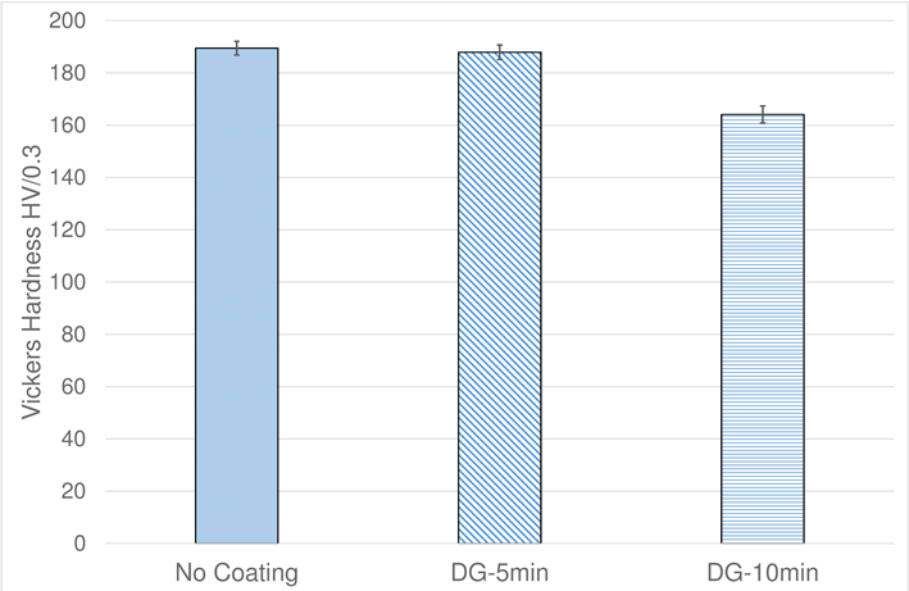

Figure 3: Vickers Hardness measurement results with standard deviation.

4.2. Friction Coefficient

The coefficient of friction values for the different samples have been obtained as the average CoF measured during each test (100m total sliding).

Figure 4 shows an example of the CoF trend vs sliding distance. It is possible to divide the test in the transient zone (where the CoF vary due to the coating wear), and the steady state zone where the CoF is almost constant. The CoF value of each test has been calculated as the average CoF of the steady state zone. Considering the obtained CoF trends, the steady state zone has been considered, for each test, starting from 40m travelled distance (Figure 4).

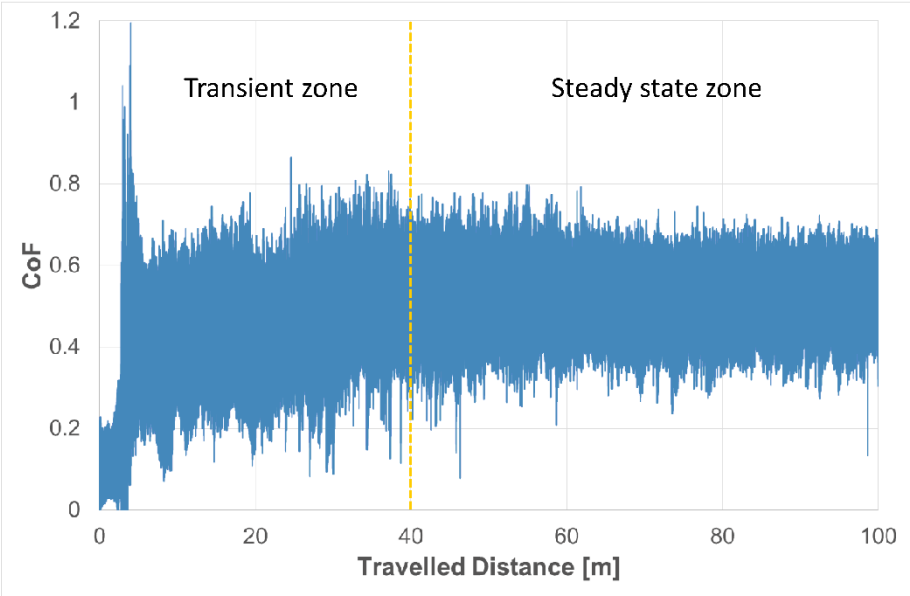

Figure 4: CoF trend vs sliding distance (Test 1, DG-10min sample).

Figure 5 resumes the average CoF results obtained from the ball-on disk tests. Each value represents the average the three tests performed for each kind of sample.

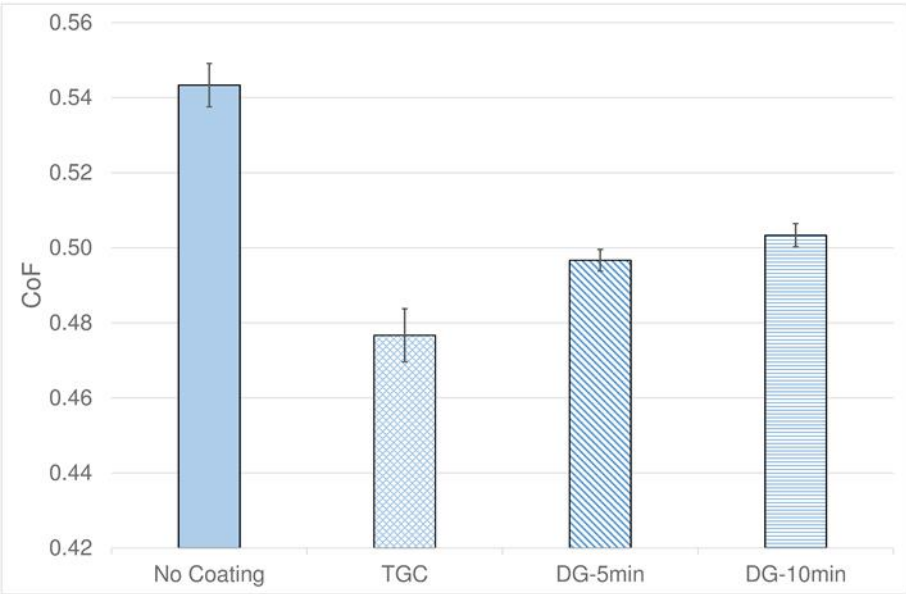

Figure 5: Coefficient of friction with standard deviation.

It is possible to observe that, generally speaking, the graphene coat seems to reduce the CoF of sliding parts. In particular, the sample with TGC shows the best performance, by

reducing the CoF of 12.5%. Samples with DG graphene also show CoF reduction, but less than the TGC one, in particular DG 5 min coat allow a CoF reduction of 8.5% while DG 10 min coat a reduction of 7.5%. Better behaviour of graphene coated samples could be explained as 2D material as graphene inserted between contact surfaces allow reduction of shear stresses and therefore reduction of CoF [8, 27, 32, 33]. The three different coating processes bring to different coatings quality, in particular TGC should produce a graphene layer with less adhesion respect to DG graphene [19, 34] while, for DG coatings the adhesion should be higher, but the number of defects on graphene coating is related to the growth time [34]. As the difference in terms of CoF reduction between the three coating procedures is not so high, it can be supposed that after some sliding laps, the graphene coat is broken, but graphene patches stays attached to the sliding surfaces working as solid lubricant [35].

4.3. Wear coefficient

The effect of graphene coat on wear strength has been evaluated by calculating the specific wear rate k, according to Archard theory [36]:

$$k = \frac{V}{s \cdot N}, \tag{2}$$

where V is the sample worn volume (obtained as described in Section 3), s is the total sliding distance and N is the applied load.

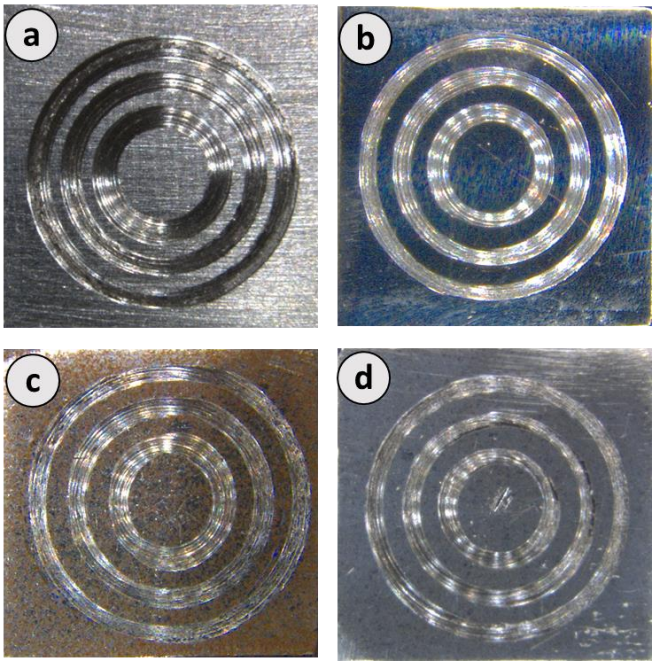

Figure 6: samples after wear tests: (a) no coated steel; (b) transferred graphene coating; (c) direct grown graphene for 5 minutes; (c) direct grown graphene for 10 minutes.

Figure 6 shows the samples after wear tests where it is possible to appreciate the circular wear traces.

The average specific wear rate results, obtained repeating three times each test, are shown in Figure 7.

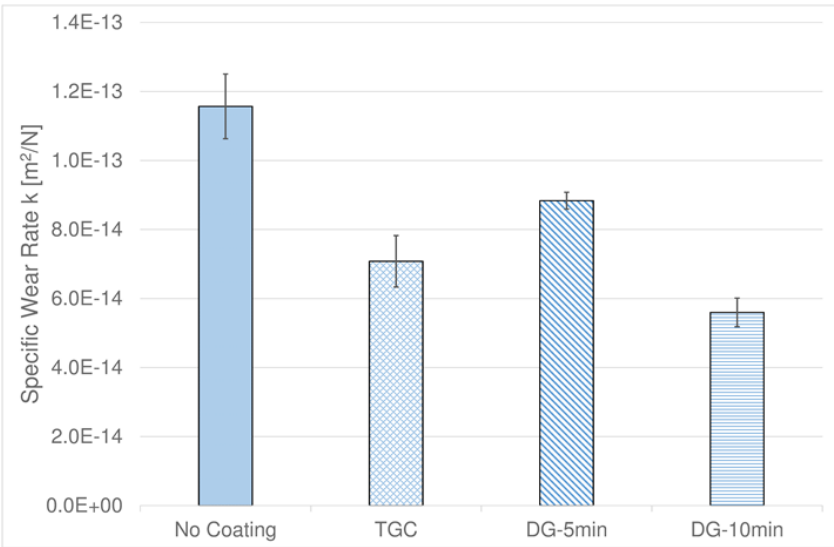

Figure 7: Specific wear rate k, calculated according to equation (2), with standard deviation.

Graphene coats seem to have a big impact on specific wear rate k. In particular the DG 10 minutes coat shows the best performance by reducing k of about 52%, followed by TGC with a reduction of about 39% and then DG 5 minutes with a reduction of 24%. This behavior could be explained considering that for DG samples, the most is the deposition time and less defects appear on the coating [34]. Therefore, DG-10 min sample shows better performance than DG 5 minutes sample; moreover, the coating adhesion of DG 10 min coat should be the best between the considered samples (better adhesion brings to better tribological performance [19]). TGC has performance between the two direct grown coatings.

4.4. Wear Mechanisms

Figure 8 reports SEM images of the worn surface of each kind of sample. The evident differences between the tracks of each sample (Figure 8 (a), (b), (c) and (d)) indicates a different wear rate produced by ball-on-disc test. In particular, the wear scar width of the uncoated steel is larger than those obtained with coated samples. The track magnification (Figure 8 (a')) reveals a much worn surface of uncoated steel, characterized by many craters that is typical of heavy adhesive wear.

The wear track of the TGC sample (Figure 8 (b)) appears to be quite clear and outlined. In the whole wear scar width, several scratch lines along the sliding direction are present denoting an abrasive wear form. The presence of abrasive wear instead of adhesive wear may explain the better results in terms of CoF compared to the other samples. Moreover, at greater magnifications (Figure 8 (b')) the worn surface appears to be smoother than that of the samples coated using the DG process (Figure 8 (c'), (d')), confirming the better results in terms of the CoF.

Analyzing the wear track of the DG-5min, it results to be the less defined (Figure 8 (c)). The evident presence of furrows and spalling are typical of an adhesive wear mechanisms; this would explain the results in terms of poor friction reduction of the DG-5min coating. Moreover, the magnification on the center of the wear scar (Figure 8 (c')) reveals the presence of a crack, demonstrating the fatigue wear is also affecting the DG-5min sample.

For the DG-10 min (Figure 8 (d)) the degree of scuffing and plowing increases, but some furrow is still presents (highlighted by the magnification in Figure 8 (d')), indicating the coexistence of adhesive wear and abrasive wear.

The magnifications of the coated samples (Figure 8 (b'), (c') and (d') reveal different black zones, that are missing on the uncoated steel, representative of the possible presence of particles of graphene inside the track at the end of the test.

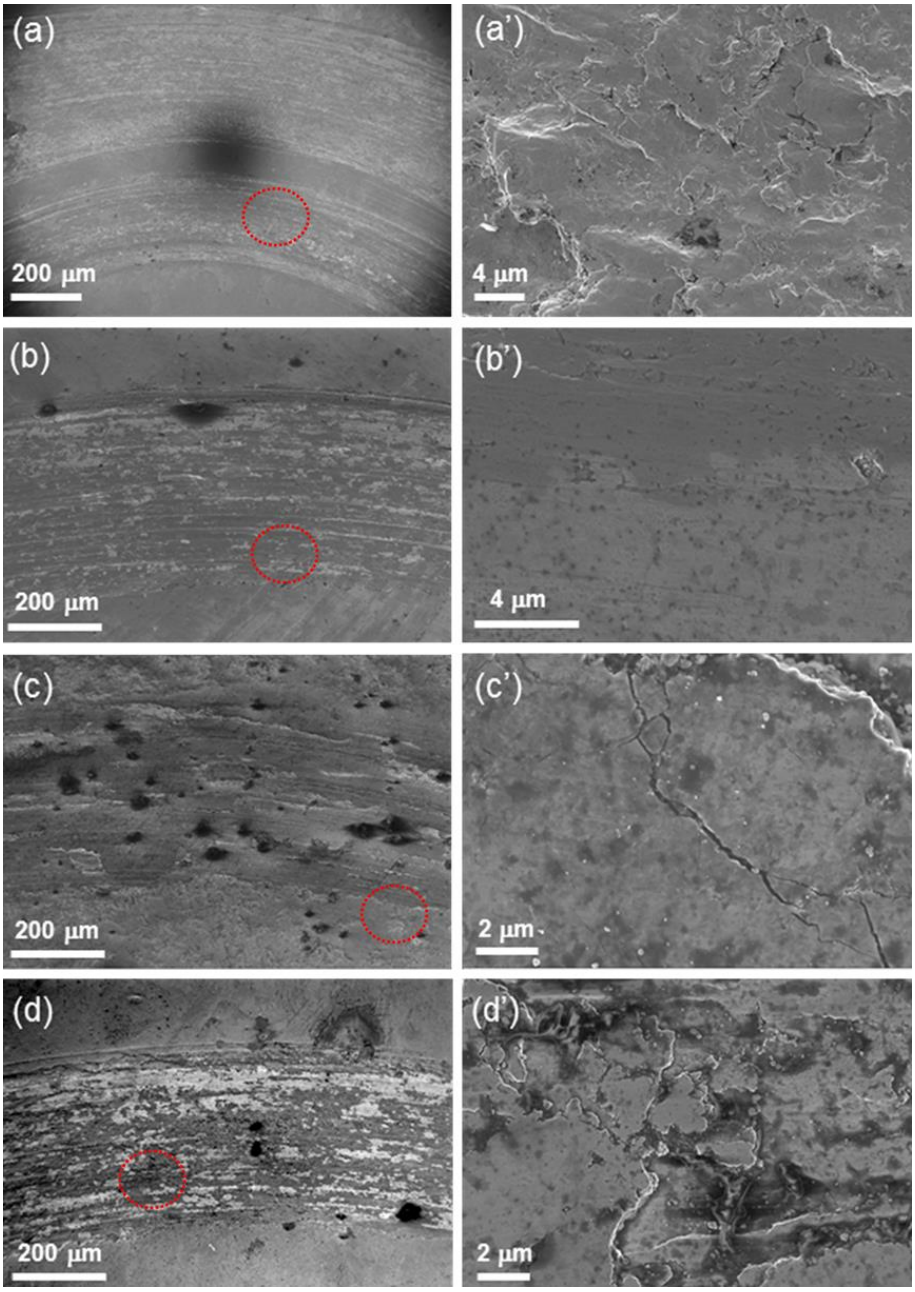

Figure 8: SEM images of the worn surface of the samples after the ball-on-disc test; (a) steel; (b) TGC; (c) DG-5min; (d) DG-10min; images marked with apex (') are the relative magnifications.

5. Conclusions

In this work, the tribological performance of C40 steel coated with graphene by two techniques is studied. The two methods used to coat the samples are: directly grow the graphene on steel sample (DG) and transferring the graphene previously grown on

copper substrate (TGC). DG samples have been coated letting the samples in the furnace for respectively 5 and 10 minutes, in order to evaluate how the coating time would affect tribological performance. Results show that DG 10 minutes coating gives the best performance in terms of wear reduction, while TGC gives the best reduction of CoF.

Surface wear analysis shows that uncoated steel is mainly affected by adhesive wear while TGC sample abrasive wear is dominant. Concerning DG samples both adhesive and abrasive wear appear.

The sample heating during the DG process causes a reduction of samples hardness, probably due to decarburization and grain growth.

It may be concluded that the two coating methods are suitable to improve tribological performance of C40 steel. Concerning industrial application DG method should be more scalable respect to TGC method and therefore less expensive for mass production. Generally speaking the coatings tested in this work could be suitable to replace lubricants in order to reduce both the environmental impact and the weight of machines.

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