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# Carbon-based coatings doped by copper: tribological and mechanical behavior in olive oil lubrication

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## Abstract

We deposited C-based films doped with Cu and tested their sliding properties in olive oil as environment-friendly lubricant, which can be used in many mechanical systems, particularly in agriculture engineering. The coatings were deposited in a four unbalanced magnetron sputtering device combining C and C/Cu targets; argon (hydrogen-free films) and Ar/$CH_4$ (hydrogenated films) atmospheres were used. Cu content of the films was in the range 5-14 at.%. The hardness of the films was almost constant whatever the Cu content was. On the other hand, hydrogen-free coatings were much harder (about 15 GPa) than hydrogenated ones (about 4 GPa). The coatings were oleophilic and their sliding properties were evaluated using ball-on-plate tests with 200000 cycles. The non-hydrogenated coating with 6 at.% of copper showed the best tribological performance with negligible wear for all olive oil testing temperatures (i.e. up to 120 °C).

Keywords: DLC, Cu, wettability, tribology, olive oil

## Introduction

Carbon-based films can be used as protective coatings for a wide range of tribological applications demanding high hardness, low friction coefficient, high wear resistance, chemical inertness, optical transparency, or thermal conductivity [1, 2, 3, 4]. The addition of metallic or non-metallic elements can improve the coating tribological properties [5, 6] and the adhesion, which can be related to a minimization of the residual stresses [7, 8, 9]. The addition of a soft metal which does not form hard carbides, such as Cu, can also be used for the reduction of the residual stress [10]. Furthermore, the absence of the carbides and bonds between the alloying element and the carbon matrix facilitates the grain–matrix interface sliding [11].

Carbon-based films are often used in lubricated contact; however, their tribochemical interaction with oils is not well known [12, 13]. It has been shown that the wetting of surfaces is a very important property in boundary lubrication conditions, since it determines the slip at the solid–liquid interface [14]. Wettability is based on the interfacial energies of the solid–liquid–vapour system, and it is typically measured by contact angle techniques[15-17].

Biodegradable oils are becoming an environmentally friendly alternative to conventional lubricants, and are already used in a variety of applications, in particular in the machinery used in forests, agriculture, mining, or constructions. Moreover, several biodegradable oils possess a good lubricating ability (good anti-wear properties and low friction), often much better than mineral or conventional synthetic oils [13, 18] as a result of the large amount of unsaturated and polar component; however, their main drawback is the low oxidation resistance and thermal stability [18-20].

This work deals with the deposition, characterization and tribological analysis of carbon-based film with copper deposited by magnetron sputtering. The sliding tests were performed in lubricated contact using pure olive oil as lubricant.

## Experimental

The films were deposited on Si wafers (chemical composition analysis), glass (wettability tests) and steel, 100Cr6 polished to final roughness of Ra ≤ 30 nm (mechanical and tribological evaluation), substrates. After deposition of a thin titanium interlayer (~300 nm) from a Ti target, the C-based films were prepared by magnetron sputtering in argon atmosphere or in argon and methane atmosphere from two carbon targets and one carbon target embedded with 14 pellets of copper with a diameter of 20 mm. The substrate bias voltage was set at -50 V. The discharge pressure varied between 1.4-4.0 Pa and the deposition time was in the range of 3-4 hours. The film structure was studied by X-ray diffraction (XRD—Philips diffractometer, Co Kα radiation with λ = 0.178897 nm) and the chemical composition was determined by electron probe micro-analysis (EPMA - Cameca SX 50). The hardness (*H*) and Young's modulus (*E*) of the coatings were measured by nanoindentation using a Micro Materials Nanotest platform.

The friction and wear tests have been performed in an Optimol SRV high frequency test device using a steel ball (100Cr6) oscillating against the test disc. The tests were carried out with a load of 50 N and a number of cycles of 200000; the following testing temperatures were used: 25, 70, 100, and 120°C. Olive oil (Gallo – Grande Escolha, Portugal) was used as lubricant. The wear rate was determined at the end of the test using optical microscopy and 3D white light profilometer (Zygo NewView 7200). The thickness of the films was evaluated by ball-cratering tests (Calotest, CSM Instruments) whereas a conventional scratch test (CSEM Revetest), load 0-50 N and Rockwell indenter, was used for assessing the adhesion / cohesion of the coatings.

To study the wettability, the coated slide glass was used. A drop (7 μL) of olive oil was placed on the coated surface for contact angle measurements. Two temperatures were used: 25 and 74° C.

## Results and discussions

The copper content in the films was controlled by the power applied to the carbon target with Cu pellets. Due to the much higher sputtering yield of copper compared to that of carbon, only a very limited power was used in the puzzled target. As expected, a linear increase of the deposition rate with the (C+Cu) target power was observed (Table 1). The difference between the deposition rates of hydrogenated and non-hydrogenated films cannot be attributed exclusively to the additional carbon originated from the methane, since the power to the copper target had to be increased on order to maintain a similar final copper content in the coating. Table 1 shows the chemical composition, the thickness, deposition rate, hardness and reduced elastic modulus of the deposited C-based films. Relatively high oxygen content, particularly in the case of hydrogenated films, was measured originated from the residual atmosphere.

The C-based films exhibited amorphous-like XRD patterns, see Figure 1. The only visible peaks belong to the titanium interlayer (ICDD card. N 44-1288 and 44-1294). When copper was added, a very broad peak appeared at the position of Cu phase (ICDD card. N 85-1326). Scherrer equation gave a rough estimate for the copper grain size of 3-5 nm. Since copper carbides peaks were not observed and the copper carbide was not formed under similar deposition conditions [**21**], the film could be considered as nanocomposite consisting of copper nanograins embedded into an amorphous carbon matrix.

The adhesion of the a-C film (i.e. non-hydrogenated film), evaluated through the measurement of the critical load by scratch testing, was approximately 45 N. When Cu was added, the critical load decreased to 35 N, which can be still considered as a sufficient value for further mechanical testing. Thus, contrary to the literature[**22**], the incorporation of Cu into the films did not improve the adhesion. In the case of a-C:H coatings (i.e. hydrogenated films deposited in Ar/$CH_4$ atmosphere), with and without Cu alloying, a further decrease of the critical load (28 N) was observed which, as it will be shown later, impeded the evaluation of the tribological performance of the coatings.

The hardness and reduced elastic modulus determined by nanoindentation are summarized in Table 1. The decisive factor controlling the hardness was the presence of hydrogen, whereas copper content played only a minor role. The hardness and the reduced elastic modulus of hydrogen-free coatings, with and without Cu alloying, were about 15 and 130 GPa, respectively. On the other hand, the hydrogenated films exhibited extremely low hardness values close to 4 GPa (reduced elastic modulus 30 GPa). The hydrogen content was measured only in the case of the pure hydrogenated film (i.e. the film without copper) by elastic recoil detection analysis; the high hydrogen content, 36 at.%, could be responsible for the low hardness due to polymerization[23]. Moreover, a high amount of hydrogen can be responsible for a reduction of the residual stress with the consequent drop of the hardness.

The tribological properties in the lubricated contact depend largely on the surface characteristics, i.e., material properties, roughness, wettability and surface energy. Since olive oil is not a typical lubricant, the sessile drop wettability tests were carried out measuring the contact angles and evaluating the oleophobic and oleophilic nature of the coating surface.

The contact angles of olive oil on coatings are shown in Figure 2. The roughness of the films deposited on glass substrates was identical and the sessile drops tests were carried out under temperatures of 25 and 74 °C. When the wettability tests were carried out at 25 °C, the value of the contact angle increased with the copper content whatever the hydrogen content. Such a result would be expected, since Cu decomposes oils catalytically leading to compounds with low affinity to the coatings. As a consequence, the increase of contact angles should occur with the increase of the content of this metal [24, 25]. For high temperature, generally the contact angle of hydrogenated coatings was lower than for hydrogen-free ones. However, it is not clear whether the decrease of the contact angle is exclusively related to hydrogen. In fact, the hydrogenated coatings with Cu showed higher content of oxygen which, due to its high electronegativity, can easily establish bonds with oil contributing to the decrease of wettability. Obviously, the viscosity of the oil and thus the contact angle was lower at 74 °C. Since the values of contact angles are lower than 60°, the coatings can be considered oleophilic [26].

Fig. 3 shows the friction coefficient of the a-C, a-C:Cu and uncoated steel substrates in the presence of olive oil as lubricant. At the highest temperatures, the analysis of the wear track revealed the total coating penetration and thus the friction of these films was not presented. Hydrogenated films were worn through after the tests clearly due to the low adhesion to the steel substrate; therefore, the friction coefficient and the wear rate are not presented.

The friction coefficient for steel/steel contact was lower compared to a-C or a-C:Cu films. It was surprising, since metals typically decompose carbohydrates of oil producing polar species such as carboxylic acid, which are absorbed at the surface and forms metallic compounds [24, 25]. These compounds should increase the friction coefficient. Nevertheless, the friction coefficient in the range 0.09 - 0.11 was relatively low [27] demonstrating the potential of this bio-lubricant.

Table 2 shows the worn volume of the a-C and a-C:Cu coatings together with the uncoated substrate. At room temperature, the worn volume was very small in the case of the a:C film and negligible (i.e. the wear track is not distinguishable from surface roughness) for a-C:Cu films. The worn volume increased with the oil temperature and all films were worn out at 100 °C except for a-C:Cu-6, which did not show any measurable wear even at 120 °C. The ball wear rate was very limited at room temperature and significantly increased when the oil was heated. Fig. 4 shows the optical micrographs of the ball and the wear track coupled with 3D profile of the wear track and its cross-section in the centre perpendicular to the sliding direction. At room temperature, the scratches from the original ball polishing are still visible in the ball scar (Fig. 4 a), whereas a much higher wear, with deep scratches parallel to the sliding movement, can be observed after the test at 75ºC (Fig. 4 e). The images for all the other a-C and a-C:Cu films are similar to those presented in Fig. 4; the only exception is the a-C:Cu film with 6 at.% of copper which shows 3D profiles almost identical to that of Fig. 4a whatever the testing temperature used.

## Conclusions

Carbon-based coatings containing copper were deposited by magnetron sputtering from composite carbon-copper and carbon targets in argon or argon/methane atmosphere. Moreover, pure carbon films prepared under the same conditions, using exclusively the carbon targets, were deposited as reference. The power of composite target was varied in order to obtain three copper contents in the range 5-14 at.%. The hydrogen-free coatings showed a hardness of about 15 GPa, while those with hydrogen were significantly softer. The low hardness together with the limited adhesion caused the failure of the hydrogenated films during tribological testing. a-C:Cu films showed a slightly higher friction coefficient compared to steel-to-steel contact; however, their wear was negligible at room temperature. We could conclude that the a-C:Cu coating with 6 at.% of copper was the best candidate for further investigation, since the coating wear was negligible whatever the testing temperature was. The synergy between the a-C:Cu films and the olive oil seems to be an interesting ecological approach for sliding contacts.

## Acknowledgments

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Table I – Chemical composition, thicknesses and deposition rate of the coatings.

| **Coating** | **at. %** | | | Thickness (μm) | Deposition rate (nm/min) | Hardness (GPa) | Reduced elastic modulus (GPa) |
|---|---|---|---|---|---|---|---|
| | **C** | **Cu** | **O** | | | | |
| a-C | 94 | 0 | 6 | 0.7 | 4.2 | 13.0 ± 1.6 | 137 ± 9 |
| a-C:H | 91 | 0 | 9 | 2.6 | 10.8 | 4.0 ± 0.1 | 17.0 ± 0.3 |
| a-C:Cu-6 | 90 | 6 | 4 | 1.1 | 4.6 | 15.7 ± 1.0 | 129 ± 4 |
| a-C:Cu-11 | 83 | 11 | 6 | 1.1 | 6.0 | 14.6 ± 0.9 | 134 ± 5 |
| a-C:Cu-13 | 83 | 13 | 4 | 1.5 | 6.3 | 14.1 ± 1.1 | 130 ± 8 |
| a-C:H:Cu-5 | 81 | 5 | 14 | 1.8 | 10.8 | 3.8 ± 0.2 | 37.9 ± 0.8 |
| a-C:H:Cu-10 | 76 | 10 | 14 | 2.1 | 12.6 | 3.6 ± 0.9 | 33.4 ± 4.6 |
| a-C:H:Cu-14 | 80 | 14 | 6 | 2.3 | 12.8 | 2.9 ± 0.1 | 27.4 ± 0.7 |

Table II – Worn volumes of DLC and DLC-Cu films compared with uncoated sample.

| Coating | Olive oil temperature (ºC) | | | |
|---|---|---|---|---|
| | 25 | 70 | 100 | 120 |
| a-C | 2.6 μm$^3$ | 5.8 μm$^3$ | worn out | worn out |
| a-C:Cu-6 | very low | very low | very low | very low |
| a-C:Cu-11 | very low | 22 μm$^3$ | worn out | not realized |
| a-C:Cu-13 | very low | 8.3 μm$^3$ | worn out | not realized |
| uncoated | 5.6 μm$^3$ | 419 μm$^3$ | 539 μm$^3$ | 869 μm$^3$ |

Figure captions

Figure 1 –XRD patterns of the deposited coatings.

Fig. 2 – Contact angle of the coatings measured at 25ºC and 70ºC.

Fig. 3 – Friction coefficient of steel, a-C and a-C:Cu coatings sliding against 100Cr6 ball with olive oil lubrication (* - coating worn through).

Fig. 4 – Optical micrographs of the a-C:Cu-11 coating wear tracks, a) and e). and ball wear scars, b) and f), 3D profile of the wear track, c) and g), and the wear track cross-section, d) and h), after SRV tests in olive oil for two tested temperatures: a-d 25°C, e-h 70°C.

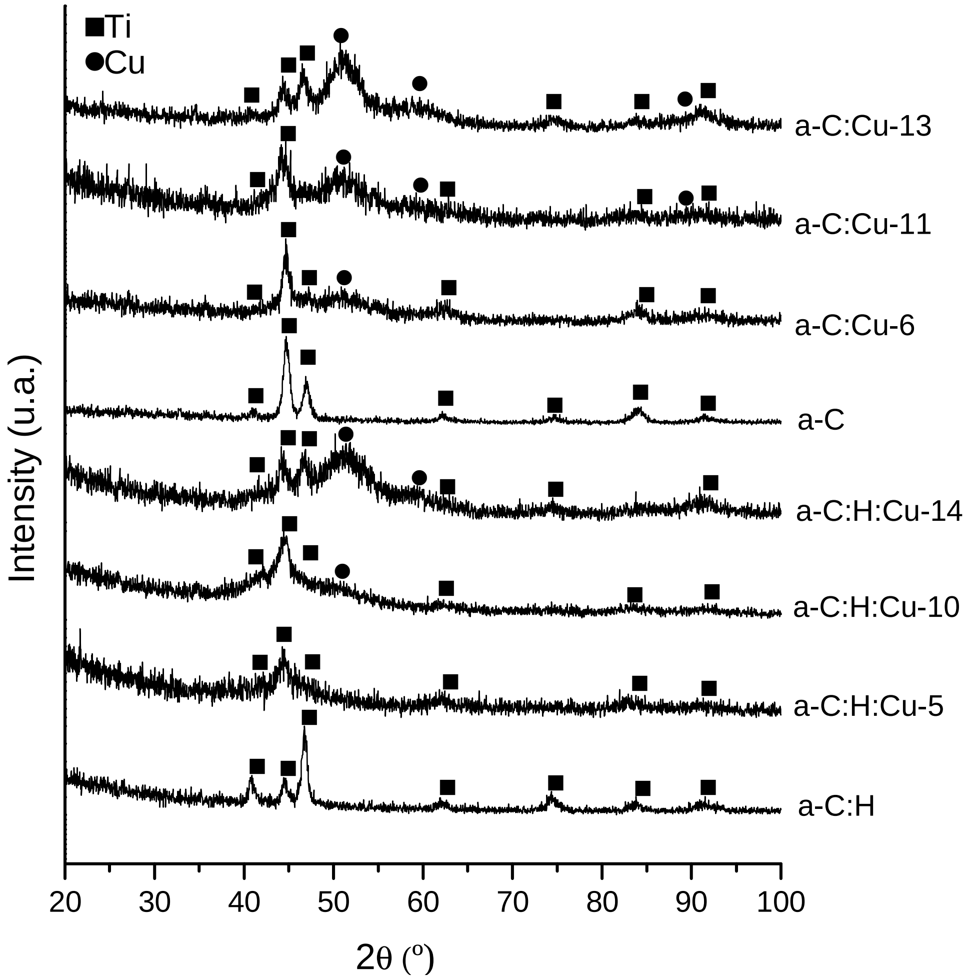
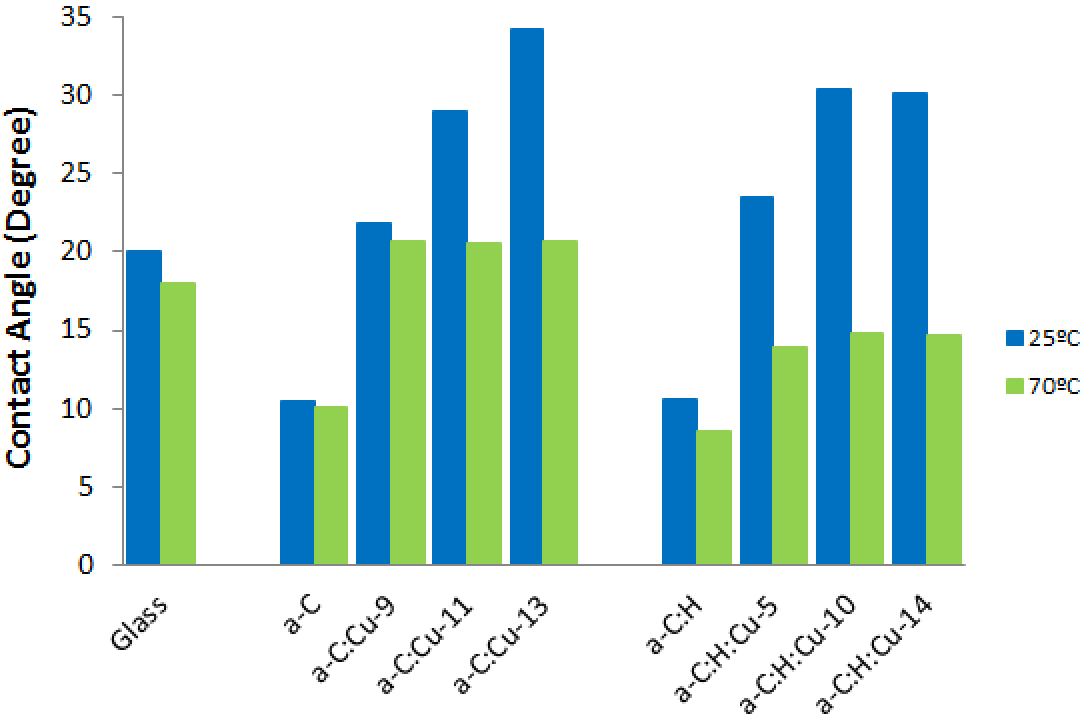

■Ti
●Cu
Intensity (u.a.)
a-C:Cu-13
a-C:Cu-11
a-C:Cu-6
a-C
a-C:H:Cu-14
a-C:H:Cu-10
a-C:H:Cu-5
a-C:H
20
30
40
50
60
70
80
90
100
2θ (º)

Figure 1



Contact Angle (Degree)
35
30
25
20
15
10
5
0
Glass
a-C
a-C:Cu-9
a-C:Cu-11
a-C:Cu-13
a-C:H
a-C:H:Cu-5
a-C:H:Cu-10
a-C:H:Cu-14
25ºC
70ºC

Figure 2

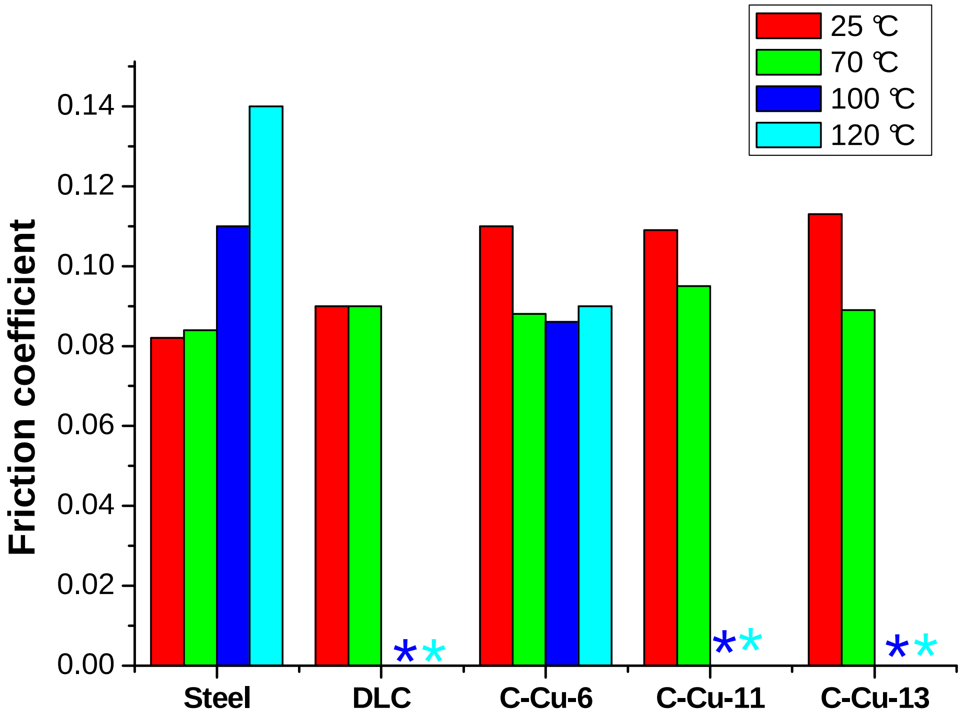

25 ℃
70 ℃
100 ℃
120 ℃
Friction coefficient
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
*
*
*
*
*
*
Steel
DLC
C-Cu-6
C-Cu-11
C-Cu-13

Figure 3

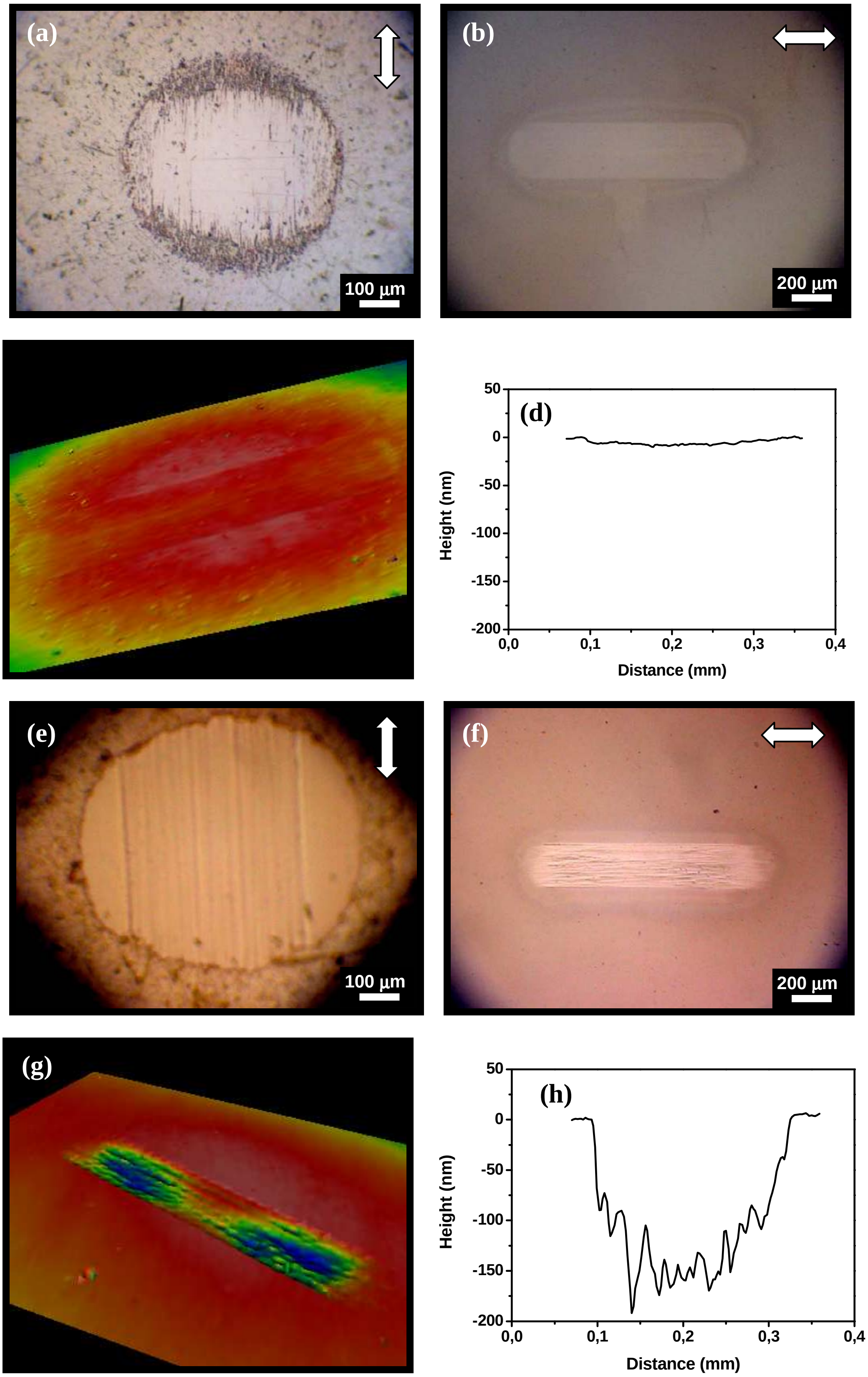

(a)
100 µm
(b)
200 µm
(d)
50
0
-50
-100
-150
-200
0,0
0,1
0,2
0,3
0,4
Height (nm)
Distance (mm)
(e)
100 µm
(f)
200 µm
(g)
(h)
50
0
-50
-100
-150
-200
0,0
0,1
0,2
0,3
0,4
Height (nm)
Distance (mm)

Figure 4