

# Zr-DLC coatings - analysis of the friction and wear mechanisms

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## Introduction

In the last few decades, the amorphous or nanostructured carbon structures prepared by several deposition techniques are a subject of considerable research interest due to their excellent properties, such as high hardness and chemical inertness, wear resistance or low friction [1,2]. There have been also attempts to improve the mechanical, chemical or tribological properties of carbon coatings by addition of other elements. Generally, specific chemical composition of the modified films strongly affects the surface energy, and may modify various physical properties and decrease compressive stress, making some metal-doped carbon films suitable for large variety of practical applications [3].

Our work was focused on the structural, chemical and tribological properties of Zr-doped DLC coatings with controlled composition. The main attention was paid to the determination of the wear mechanisms, characterization of the worn surfaces and wear debris and formation of a tribolayer affecting the tribological process. The as-deposited coatings and worn surfaces were studied using 3D optical profilometry, Raman spectroscopy, X-Ray diffraction (XRD) and Scanning electron microscopy (SEM).

## Experimental Details

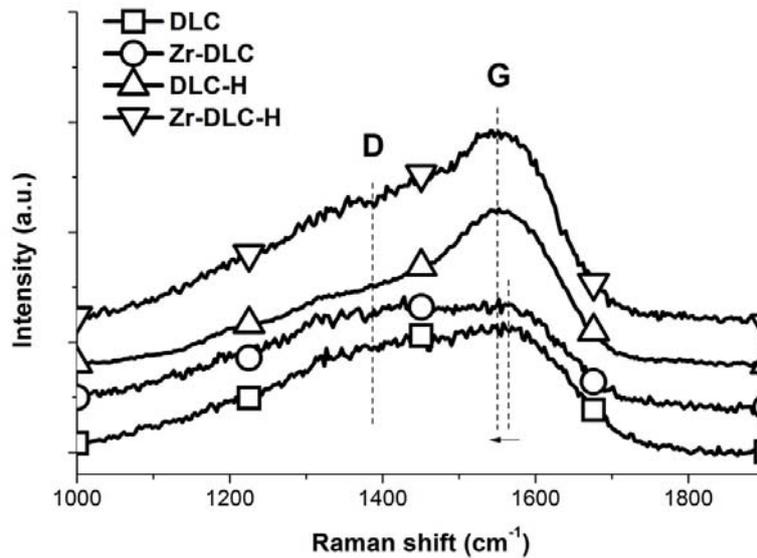
Two d.c. magnetron sputtering deposition configurations were used to obtain both non-hydrogenated (Ar atmosphere) and hydrogenated DLC structure (reactive CH<sub>4</sub>/Ar atmosphere). The coating structures were deposited using four targets - two of them were of pure carbon, one target was composite carbon with pellets of zirconium located in the erosion zone, fourth target was of Ti due to the adhesion interlayer deposition. The composite Zr/C target power was changed in order to obtain the structures with different zirconium content.

The coatings were studied from the structural, morphological and chemical point of view. The coatings composition was studied by Electron probe micro-analysis (EPMA). The XRD enabled to comprehend the coatings structure, Raman spectroscopy ( $\lambda = 532$  nm) was used for detailed analysis of as-deposited, as well as worn areas and testing counter-parts. The tribological tests were performed by pin-on-disc Tribometer CSM at room temperature against 100Cr6 bearing balls with a diameter of 6 mm. The wear rates were observed using

3D non-contacting profilometer.

## Results and discussion

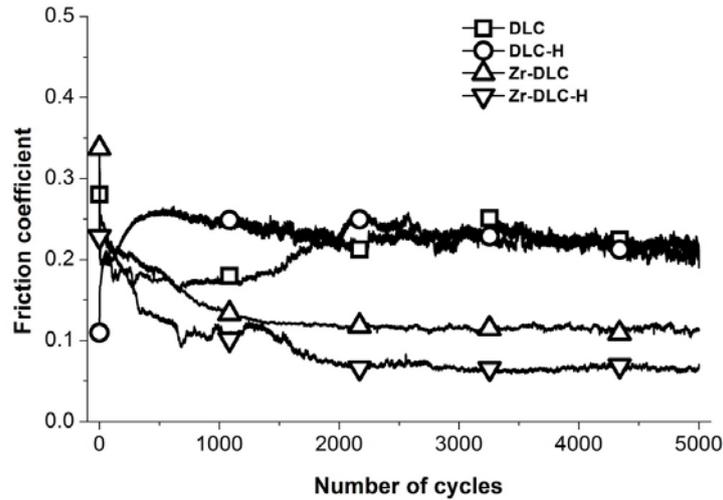
The Zr-DLC(-H) coatings composition obtained by EPMA clearly proved that introducing of Zr/C composite target power led to the increasing zirconium content from 0 to 4.5 at.% approx. The Raman spectra of as-deposited Zr-DLC(-H) coatings are shown in Fig. 1.



**Fig. 1** Raman spectra of as-deposited Zr-DLC(-H) coatings

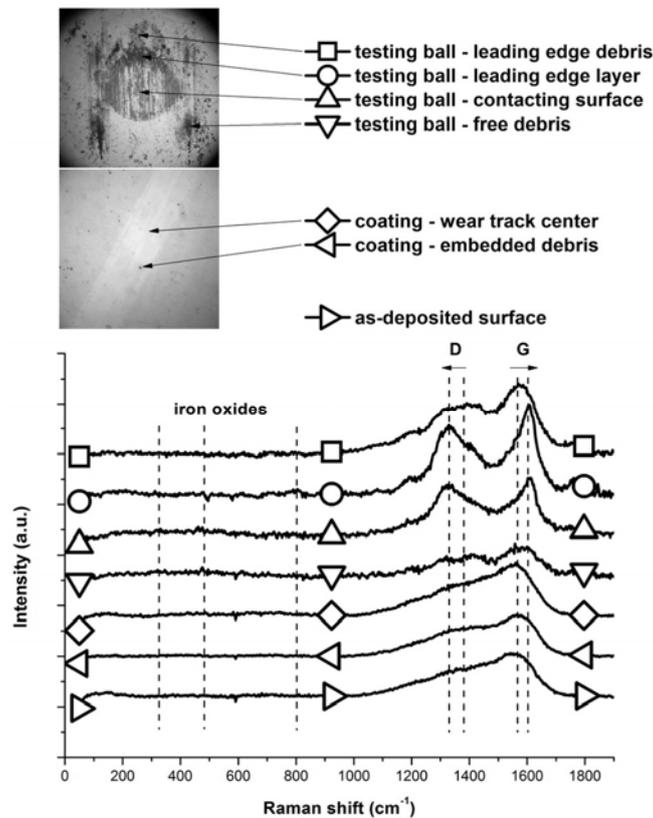
All Raman spectra clearly showed main carbon D and G peaks. With the incorporation of the Zr into the films, the G peak position shifted slightly towards lower wavenumbers. This G peak shift was associated with carbon bonds disordering and fragmentation [4]. Generally, the G peak position was slightly lower for hydrogenated coatings regarding on the Zr content in the film. Moreover, both the D and G peak appeared more pronounced compared to the corresponding hydrogen-free samples.

The hydrogenated films exhibited slight background photoluminescence effect. The  $I_D/I_G$  ratio determined from peak areas clearly supported the conclusions given by the G peak analyses. First, the incorporation of Zr dopants caused significant  $I_D/I_G$  ratio growth for both the hydrogen-free and hydrogenated coatings. Second, the hydrogenation of the DLC and Zr-DLC films resulted in the lower  $I_D/I_G$  ratio. More pronounced D peaks corresponded to the higher degree of C-C bonds fragmentation and decreasing of the specific size of carbon clusters. Lower  $I_D/I_G$  ratio could be also an indirect proof of the increasing  $sp^3/sp^2$  fracture [5]. The friction curves of the Zr-DLC(-H) coatings were relatively stable with significant running-in stage (Fig. 2). The average friction coefficient varied from about 0.07 (hydrogenated Zr-DLC) to 0.24 (non-doped coatings).



**Fig. 2** Typical friction curves of Zr-DLC(-H) coatings at room temperature

The contacting area on the steel ball contained a mixture of iron oxides and graphitized carbon structure (Fig. 3). Although the free unworn surface of the 100Cr6 steel ball could not prove any vibration spectra, the contacting surface showed several driving effects - presence of iron oxides, slight photoluminescence effect and the G peak position shift towards higher wave numbers compared to as-deposited coating.



**Fig. 3** Raman analysis of the ball vs. Zr-DLC-H contact

The tribolayer on the ball surface was formed from a mixture of iron oxides and reordered C-C structure. Moreover, the thin layer formed at the leading edge exhibited Raman spectra similar to the pure graphite. This could be explained by strong graphitization of the outer coating surface during the friction process. The graphitic interlayer formation, as well as iron oxides presence was significantly dependent on coating composition.

### **Conclusions**

It was showed that the wear processes taking place at the contact interface were significantly dependent on the coatings composition. Fundamental relations between as-deposited coating properties, wear track surface properties, tribolayer properties, and tribological tests conditions has been described.

### **Acknowledgement**

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### **References**

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