Deposition and characteristics of hard amorphous films on biomedical polyethylene and metallic substrates

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Abstract

The wear rate of Ultra High Molecular Weight Polyethylene (UHMWPE) particulate commonly used in hip joints as material for acetabular cup was lately decreased by a factor 30-600 by coating metallic substrates with a hard DLC film. But these particles are considered to be the main origin inducing osteolysis. Previous attempts to cover UHMWPE with hard wear resistant thin films by CVD method and also in combination with different PVD methods had not been succeeded. First in recent work [1] the authors have shown a possibility of hard DLC thin film deposition on polyethylene substrates by pulsed arc discharge (PVD) . These films are amorphous and possess high hardness, elastic modulus and low friction coefficient .
Auger and Valence bands of X-ray photoelectron spectra (XPS) indicate clearly the presence of C-H bonds in our carbon films deposited on polyethylene . Considering the incorporation of hydrogen from polyethylene into the carbon film and the low thermal conductivity of polyethylene some different deposition parameters than that in [1] have been developed with a view to diminish the temperature and destruction of polyethylene substrate surface during deposition . Preliminary experimental results show that the values of the hardness, elastic modulus and dry friction coeficient obtained using Nanoindentation technique and Tribometer with reciprocal sliding depend noticeably on C-H bonds content into the carbon film obtained with the help of the modified deposition process .

***Keywords**: PVD deposition, Diamond-like carbon, Biomaterials, Physical and Tribological Properties*

1. Introduction

Advanced materials applications in artificial prosthetics received considerable recent attention of the scientific community, aiming to minimize biomechanical complications, wear and corrosion processes of implants, in particular in total hip replacements in accordance with Lappalainen *et al.* (1998), Tiainen (2001),Amstutz *et al.* (1992), Harris (1995), Allen *et al.* (2001), Franks (1989) and Donnelly *et al.*(1999) . The wear rate of UHMWPE particulate (0.15–0.2 mm/year) commonly used in hip joints as material for acetabular cup in long-term tests was decreased by a factor 30–600 by coating with a hard DLC film by Lappalainen *et al.* (1998) and Tiainen (2001) . But, these particles are considered to be the main origin inducing osteolysis in accordance with Amstutz *et al.* (1992) and Harris (1995) . Therefore, there is considerable interest in using various forms of DLC on polyethylene since even lower limit improvement can be crucial at a solution of this problem cited by Allen *et al.* (2001) .

It is necessary to note, that the experimental attempts to cover UHMWPE with hard, wear resistant DLC thin films by CVD method and also in combination with different PVD methods had not been succeeded in references by Evans *et al.* (1991) and Donnelly *et al.* (1999). At present, a very promising candidate to protect polyethylene orthopaedic substrates from wear is ta-C films, that are usually deposited at room temperature: ($T_{\text{melt.p.}}$ of UHMWPE approx. 134 ºC) they are wear resistant and confer high hardness and adhesion, low friction, chemical stability to the orthopaedic substrates by Pharr *et al.*(1996) , Poliakov *et al.* (2002), Robertson (2002), Yamamoto *et al.* (2002) and Inkin *et al.* (2000) . In recent works the analysis of literary data about the deposition and properties of ta-C prepared on UHMWPE by PVD methods (filtered cathodic vacuum arc, pulsed arc discharge and the others) are absent.

It this article the experimental data on deposition and physical mechanical and tribological properties of hard DLC thin films on UHMWPE and for comparison on other biomaterials such as Co–Cr–Mo, Ti and stainless steel are reported.

2. Materials and methods

2.1. Sample preparation

The following materials were tested:
– UHMWPE, commonly utilized for acetabular cup.
– Metals and alloys [Ti (ASM), Co–Cr–Mo (ASM), stainless steel 138F], applicable as materials for head in hip joints.

The metallic and UHMWPE cylindrical samples (diameter: 8 mm, height: 5 mm) and UHMWPE plates (50 x 27 mm) were mechanically grounded and subsequently polished, presenting surface arithmetic average roughness (*Ra*) and root-mean-square roughness (*Rq*) value in interval 109–158 nm (*Ra*), 164–206 nm (*Rq*) for metallic substrate , and 220 nm *(Ra)* and 288 nm *(Rq)* for polyethylene ones (scan length : 200 µm; tip speed : 4 µm/s) .

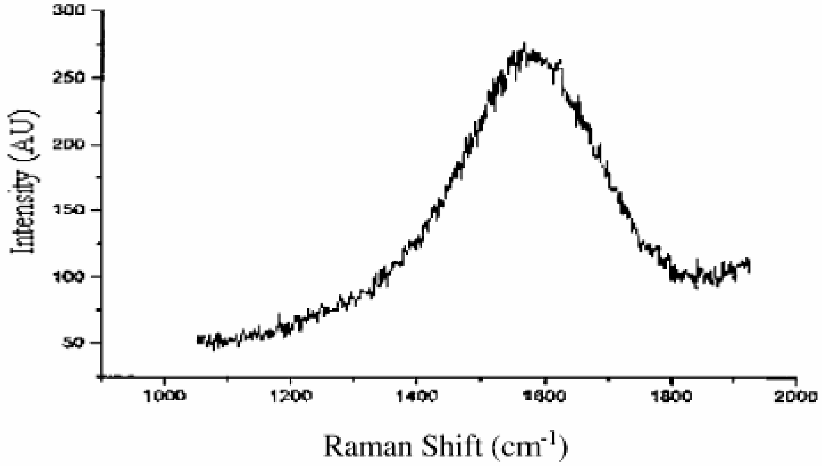

Fig. 1. MW Raman of carbon film deposited on Co–Cr–Mo alloy substrate

Pulsed arc plasma PVD was used for DLC films deposition in accordance with Inkin *et al.* (2000) . Before introduction into the vacuum chamber, substrates were cleaned in carbon tetrachloride (CCl_4) and dried in inert atmosphere. After placing it in the vacuum chamber, samples surface was sequentially treated by argon and titanium ions bombardment. The last treatment was followed by a small titanium implantation in the upper sample layers. In the sequence, fine Ti and DLC films were deposited at 20 nm/min. The temperature of UHMWPE and metallic substrates in the beginning and at the close of the deposition was in the range 25–50 ºC and 50–150 ºC, respectively. Film thickness was approximately 250 nm in all samples.

2.2. Methods of film characterization

The composition of DLC films was analyzed using a Perkin Elmer PHI-660 AES (Auger electron spectroscopy). Carbon was identified using an Auger spectrum atlas (Handbook of Auger Electron

Spectroscopy) and carbon peaks data for graphite, diamond and a few carbides by Ramaker (1985) . Raman spectroscopy analysis was performed using a JOBIN YVON S 3000 unit. Density and proportion of sp^3 bonding were obtained from EELS and XPS measurements. Hardness and elastic modulus of DLC films (approx. 250 nm) deposited on UHMWPE and metallic substrates were measured by nanoindentation (Nanoindenter XP MTS System) described on Oliver *et al.* (1992) with a Berkovich indenter.

The adhesion of 2.3-μm thick DLC films on steel ($100Cr_6$) substrates was determined by scratch test and Rockwell indentation.

To measure the dry friction coefficient *f*, 2.0-μm thick DLC films were deposited on the flat end surface of steel (62 HRc) cylinders . The average Ra of the cylinder (outer diameter: 20 mm; inner diameter: 16 mm) flat surface and of the DLC film, were, respectively, 0.12 μm and less than 0.25 μm. Tests were made using a Suzuki unit with an active cylinder rotating at 82 rev./min and sliding against the end plane surface of a passive cylinder (sliding force 98 N). Rubbing cylinders test was done in ambient atmosphere (approx. 20% humidity) at room temperature.

The friction pair steel ball ($100Cr_6$) against DLC / UHMWPE was prepared to measure the dry *f* of DLC film using Tribometer with reciprocal sliding (CSEM, Swiss).

3. Results and discussion

3.1. Microstructure and morphology of DLC films

All DLC films deposited on metallic substrates using pure graphite cathode were homogeneous in depth and consisted only of carbon. The shape of the carbon Auger peak remained the same inside the film and did not differ from that obtained from a graphite rod. TEM investigation at a resolution of 0.3 nm confirmed that the films are smooth and uniform with absence of crystalline structure. Microdiffraction did not significantly differ from that of thermally deposited carbon films by Inkin *et al.* (2000) .

Multi-wavelength Raman (MW Raman) studies of DLC films deposited on metallic substrates showed a Raman shift of 1560 cm^{-1} , (G peak; λ=325 nm), corresponding to amorphous carbon structure into ta-C on Fig. 1 [Ferrari ,(2002) , p. 1055, Fig. 1a].

Based on our EELS and XPS results, the DLC film deposited on metallic substrate included 76% of sp^3 bonds and the density was 2.94 $g.cm^{-3}$ (carbon plasmons energy was 31 eV). Similar results were obtained in Ref. Yamamoto *et al.* (2002).

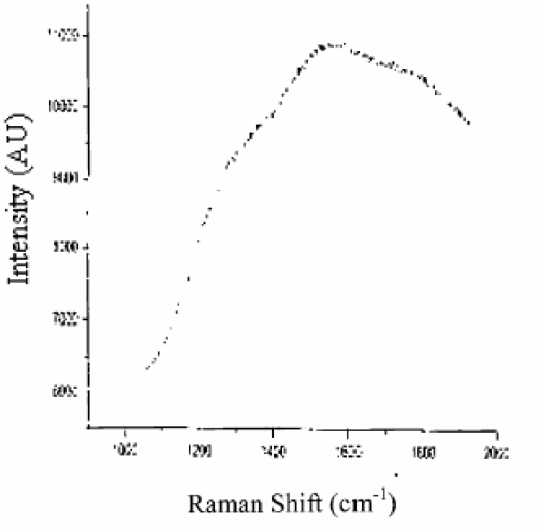

Fig. 2. MW Raman of carbon film deposited on polyethylene substrate.

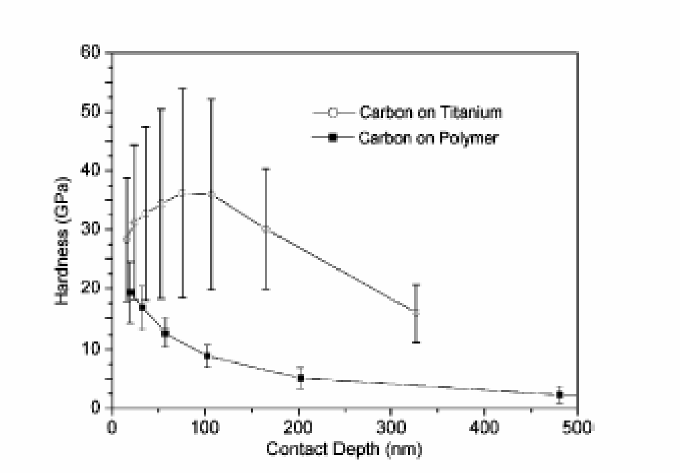

Fig. 3. Hardness as a function of depth for DLC films deposited on polyethylene and titanium.

Comparing these results with Ferrari (2002) (88% sp^3 ; density is equal to 3.26 $g.cm^{-3}$), one can conclude that the DLC films density increases results from the increase in its sp^3 bond fraction .

DLC film deposited on polyethylene substrate contained 65% sp^3 bonds (EELS) and also hydrogen (SIMS). Multi-wavelength Raman (MW Raman) of carbon films deposited on polyethylene substrate at the same parameters as on metallic ones is shown in Fig. 2. The curve of Fig. 2 is different from that for ta-C and almost resembles the MW Raman in [Ferrari (2002), p. 1055, Fig.1b,c] for ta-C:H or sputtered a-C:H. Presence of hydrogen in carbon films deposited on polyethylene may be originated by the destruction of the polyethylene surface, due to carbon ions bombardment during film deposition in Robertson (2002) . Hydrogen atoms possess high diffusibility and can penetrate into the amorphous carbon film in accordance with Keudell *et al.* (2001).

3.2. Mechanical properties of DLC Films

3.2.1. Measurements of nano-hardness and elastic modulus

Hardness of the DLC films deposited on metallic substrates is larger than the hardness of those deposited on UHMWPE (Fig. 3). Different DLC films nanohardness dependencies on penetration depth (Fig. 3) probably are caused by surface irregularities. This large dispersion, also observed in elastic modulus values of DLC films deposited on metallic and polyethylene substrates, apparently result from their noticeable superficial roughness, occurring when indenter penetration is less than approximately 200 nm, in the limits of roughness values measured.

Hardness (20 GPa) and elastic modulus (100 GPa) measured for carbon films deposited on polyethylene are noticeably smaller, than those for DLC films deposited on metallic substrates. The thin hard carbon film can deflect at the loading point because polyethylene has very small hardness (0.01 GPa) and low elastic modulus by Brookes (1997) . The values of hardness of DLC film on UHMWPE are affected by experimental parameters that influence hardness values measured by nanoindentation.

The large difference on hardness and elastic modulus of film and substrate influences the values principally considering that the thickness of the film is 250 nm. In addition, the surface roughness decreases the measured values of hardness by nanoindentation since the contact depth is increased because of the tip-surface contact occurs at the asperities on the rough surface.

Under larger loads the DLC film break getting the behavior of the UHMWPE substrate. For small loads the almost linear elastic behavior of the DLC film is accompanied by high value of hardness. It should be noted that for loads larger than 30 mN (Fig. 4) the behavior of the DLC film changes, indicating the failure of hard film deposited on UHMWPE.

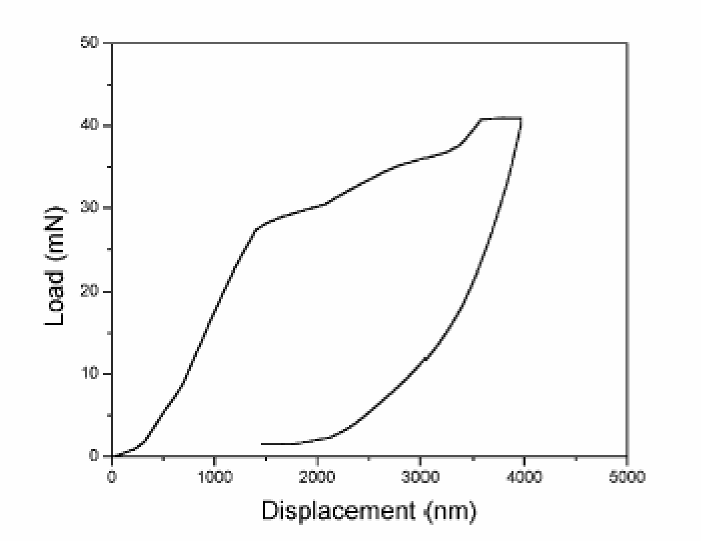

Fig. 4. Applied load as a function of depth for carbon films deposited on polyethylene, with occurrence of film failure.

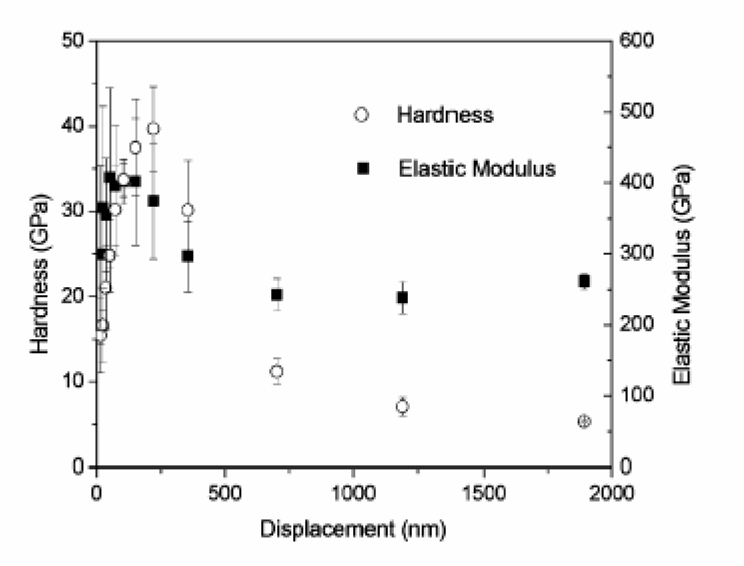

Fig. 5. Hardness and elastic modulus as a function of depth for hard DLC films deposited on Co–Cr–Mo.

The deposition of DLC films on Co–Cr–Mo substrate raises surface nano-hardness from 5 to 43 GPa (Fig.5). Similar effect is observed for Ti and stainless steel F138 substrates, where nano-hardness increases from 4 GPa to 28 and 40 GPa, respectively, after DLC coating.

The nano-hardness values (28–43 GPa) obtained for DLC films (sp^3 bond fraction – 0.76) deposited on metallic substrates is noticeably larger than that for ta- C (approx. 20 GPa, 70% sp^3) determined in Ref. [24]. However, the values of above-mentioned results are essentially smaller than that (65 GPa) presented in Ref. Yamamoto *et al.* (2002) (Si – substrate, film thickness approx. 400 nm).

The elastic modulus of DLC films deposited on Co– Cr–Mo substrate are shown in Fig. 5. Note that the maximum value of elastic modulus of DLC films on Co–Cr–Mo alloy reaches 500 GPa. For DLC films deposited on Ti and stainless steel this value is larger than 400 GPa in Ref. Poliakov *et al.* (2002) .

Considering the described above, experimental results and literature data, one must note that hard (approx.43 GPa) fine (250 nm) hydrogen free amorphous DLC films (76% sp^3 bonding) deposited on metallic substrates (hardness of approx. 5 GPa) by pulsed arc discharge method cited in Inkin *et al.* (2000) can be characterized as ta-C films.

Following data of Ref. Schultrich (1998) , a Young's modulus (*E*) of approximately 450 GPa is expected for ta-C with density 2.94 $g.cm^{-3}$, which correlates with that of ta-C deposited on Ti and stainless steel substrates.

The comparison of the above-mentioned *E*-data with those of elastic modulus of hard carbon film (mass-separation ion beam deposition) deposited on Si substrate at carbon ion energy of 31 eV in Yamamoto *et al.* (2002) shows noticeable difference. Following the dependence of *E* of prepared carbon films on carbon ion energy, the value of elastic modulus of ta-C prepared at ion energy of 31 eV is equal to approximately 350 GPa in accordance with Yamamoto *et al.* (2002) , which is smaller than that of carbon film deposited on metallic substrates (>400 GPa) in Ref. Poliakov *et al.* (2002) (Fig. 5).

3.2.2. Measurements of adhesion and friction

The first crack in the scratch test appeared in the track of the needle scratching the DLC film at 25 N. In the range 50–55 N the track began to be completely worn out. The results of the Rockwell indentation test confirmed the scratch test results.

To measure steady state friction coefficient f the DLC film with the thickness 0.5 μm and roughness of 100 nm deposited on UHMWPE was used. The steady state f was monitored throughout the tests lasting 2000m. The mean value of steady state f is 0.12 for pair steel ball ($100Cr_6$) / DLC on UHMWPE. The initial f (0.16) for DLC on UHMWPE is noticeably larger that steady state f.

The values of the steady state f for DLC film on steel before and after 5000 rotations are 0.18 and 0.14, respectively. The initial f (0.44) of DLC films is noticeably larger than steady state f. In general, these results are confirmed by pin-on-disk method measurements, where the initial f for DLC films is 0.3 and the corresponding steady state value is 0.12–0.13 [15] . In Lappalainein (1998) the extreme values giving the average f are 0.10 and 0.17 for uncoated and hard hydrogen-free DLC films coated 32 mm Co–Cr–Mo balls.

The investigation of wear rate of hard DLC film on polyethylene is now in course and the results expected will be discussed in detail in a planned article. The obtained experimental values of f suggest that UHMWPE deposited by hard DLC film may be applied in artificial prosthetics.

4. Conclusions

It is experimentally demonstrated that the hard DLC thin films deposited on polyethylene by pulsed arc discharge are amorphous and possess high hardness, elastic modulus and low friction coefficient.

The discrepancy of nano-hardness and elastic modulus of carbon films deposited on polyethylene in comparison with those of DLC films deposited on metallic substrates can be explained by very low hardness and elastic modulus of polyethylene and presence of hydrogen in the bulk of carbon film.

Based on experimental and literature data, the Co–Cr–Mo alloy apparently is preferable for artificial prosthetics than Ti and stainless steel, concerning the influence of the substrate material on mechanical and tribological properties of deposited hydrogen-free hard DLC films.

The comparison of hardness and elastic modulus of DLC films deposited on metallic substrates with the literature data certifies the high level of mechanical properties of the obtained films.

The obtained results suggest that hard DLC film covered UHMWPE is suitable to improve the performance of prosthetic pairs because only carbon particles will be produced by wear instead of particulate polyethylene.

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