Pulsed laser deposition (PLD) of diamond-like carbon (DLC) thin film on Polymethylmethacrylate (PMMA) and tool steels

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ABSTRACT

Pulsed laser deposition with KrF-excimer laser radiation (λ= 248 nm; t = 25 ns) is used to grow diamond like carbon (DLC) thin films on PMMA and tool steel substrates. The investigations are focused on the adherence of the DLC thin films. The pre-treatment of the metallic samples was a corrosion process to passivate the surfaces and of the PMMA samples the deposition of a titanium buffer layer as well as a mechanical surface modification. The analytical techniques used to determine the structural and chemical characteristics of the films are Raman spectroscopy, X-ray photoelectron spectroscopy, optical and electron microscopy. The hardness and the elastic modulus of the films are measured by nano-indentation. The adherence characteristics of the DLC thin films are compared with the films of ZrO_2 and Al_2O_3 deposited by PLD on PMMA.

Keywords: *Pulsed Laser Deposition, DLC, tool steel, PMMA.*

1. INTRODUCTION

Thin films of DLC can be produced by pulsed laser deposition (PLD) with a variety of thickness on different substrates. DLC thin films have wide applications in technology and science owing to its unique properties like extreme hardness, chemical inertness, optical transparency, high dielectric constant and electrical resistivity. DLC thin films deposited on hard metals is of industrial interest for protection in applications like cutting tools (drills and mills), medical prosthesis and surgical instruments with excellent bio-compatibility [1,2]. Polymethylmethacrylate (PMMA) has been used in the biomedical industry for manufacturing various implants. The long-term failure of the PMMA prostheses is now believed to the directly or indirectly due to its lower hardness, its wear resistance, and its vulnerability to biomedical degradation. Therefore, a DLC coating on PMMA should reduce these problems and extend prostheses life [3].

PLD is an alternative growth technique of DLC thin films and the purpose of this investigation is to determine whether PLD can be utilised to grow DLC thin films and to improve the adhesion of hard DLC thin films on tool steels and PMMA with different pre-treatments. The nucleation phenomena play a key role in the determination of the growing morphology and the film quality during deposition of DLC. The nucleation mode strongly depends upon the pre-treatment technique used for the substrate as well as upon the deposition procedure[4]. In the case of tool steel a corrosion process (passivation) is employed and in the case of the PMMA a titanium buffer layer and also a mechanical dressing process are used. The application of buffer layers or the mechanical modification of the polymers surfaces are promising techniques for the deposition of more adherent DLC films on PMMA.

The morphology of the DLC thin films is characterised by optical microscopy and scanning electron microscopy (SEM), the presence of sp^3 and sp^2 bonds is analysed by micro-Raman spectroscopy. Analytical technique used to determine the structural and chemical characteristics of the films is X-ray photoelectron spectroscopy (XPS). The hardness and the elastic modulus of the films are measured by nanoindentation.

2. THEORETICAL BACKGROUND

2.1 Pulsed Laser Deposition

In PLD, the laser radiation is directed on a target located in a vacuum chamber. The impact of the laser radiation on the target surface results in various complicated processes including removal, melting, evaporation of material and/ or plasma generation due to excitation and ionisation of the species ejected from the target by the laser photons. All these processes are triggered by a conversion into thermal, chemical, and mechanical energy. The material ejected from the target is deposited on a substrate generally positioned opposite the target [5].

2.2 Passivation

A number of reactive metals that come in contact with corrosive environments can abruptly turn into an extremely corrosion resistant state due to a phenomenon called "passivation" [6]. In passivating, a metal reacts to form a layer of corrosion products so thin that it is invisible and so complete a barrier that it slows corrosion by several orders of magnitude. This thin passivation layer is largely composed of amorphous oxides and hydroxides of the metal [6].

Apparently during the H_2SO_4/H_2O_2 treatment of Co containing tool steels a thin $CoO/CoSO_4$ film forms [7], which prior to the diamond deposition by chemical vapor deposition (CVD) would be reduced to Co/CoS, controlling the diamond growth [7]. Previous work reported that the Co in the hard metals binder phase could however detrimentally influence the chemical vapor deposition of diamond. Also the Co vapour pressure, surface migration and carbon solubility are main parameters influencing diamond nucleation and growth and coating adhesion [7].

3. EXPERIMENTAL DETAILS

3.1 Set-up

A KrF excimer laser (λ_L=248 nm,L τ_L= 25 ns) is used for pulsed laser deposition in a UHV chamber which was evacuated by a turbo molecular pump to a base pressure of typically 10^{-6} mbar before deposition. The pulsed laser radiation was focused on a high purity (99.999%) graphite target with an angle of incidence of 45°. The laser typically runs at a repetition rate of 1 Hz for the production of an initial coating for 1000 pulses that helps the nucleation of DLC on the pre-treated surfaces and for the deposition of the main coating a repetition rate of 10 Hz is used for 5000 pulses. The target substrate distance is 4 cm. The deposition is carried out using argon as processing gas with pressures of 10^{-5} - 10^{-4} mbar, and fluence εe_L = 3,3 J/cm^2.
The substrates are cleaned before the deposition of DLC using a r.f system by Ar^+ bombardment for 5 min, employing a processing gas pressure of 10^{-2} mbar, to reduce the contamination by oxygen and OH^- arising from residual water vapour.

3.2 Pretreatment of tool steels

Distinct improvement of the adhesion of diamond-like carbon coatings on the tool steel substrates is achieved by substrate surface pre-treatment: The samples are polished with a diamond solution and washed in ultra-sonic with ethanol for 5 min before the corrosion treatment. For the tool steel substrates two different passivation processes are used: the first is to grow Cr_2O_3 coating from the Cr into the tool steels using a 50% HNO_3 solution [6], the second is to form an amorphous $CoO/CoSO_4$ film from the cobalt content in the tool steels using a H_2SO_4/H_2O_2 solution (8% H_2SO_4 in 54% H_2O_2) [7]. For the both cases the solution temperature was 80°C, and the time was about 5 min. The reaction of the samples during the corrosion process is higher and the gas bubbles sweep across the surface, after that the samples were washed in ultra-sonic with ethanol for 5 min. The chemical composition of the tool steels before the pre-treatment is shown in the table 1.

3.3 Pre-treatment of PMMA

Two different processes are used to increase the adhesion of DLC coating on virgin PMMA. The first pre-treatment is to deposit a Ti buffer layer on PMMA by DC sputtering, the second is a mechanical grinding of the PMMA with a grinding paper 1200. The surface shows a homogeneous distribution of scratches and this new morphology is used to improve the adherence and to prevent the delamination of the DLC coatings.

3.4 Surface analysis

The morphology of the DLC films is analysed by optical and scaning electron microscopy (SEM). The amount of sp^2 and sp^3 bonds are determined by micro-Raman spectroscopy (the spectra were excited with Ar ion laser radiation, λ= 488nm). Analytical technique used to determine the structural and chemical characteristics of the films was X-ray photoelectron spectroscopy (XPS) using non-monochromatised MgKα radiation (hν = 1253.6 eV). The hardness and the elastic modulus of the films are measured by nanoidentation using an nanoindenter XP with a target depth of 50 nm.

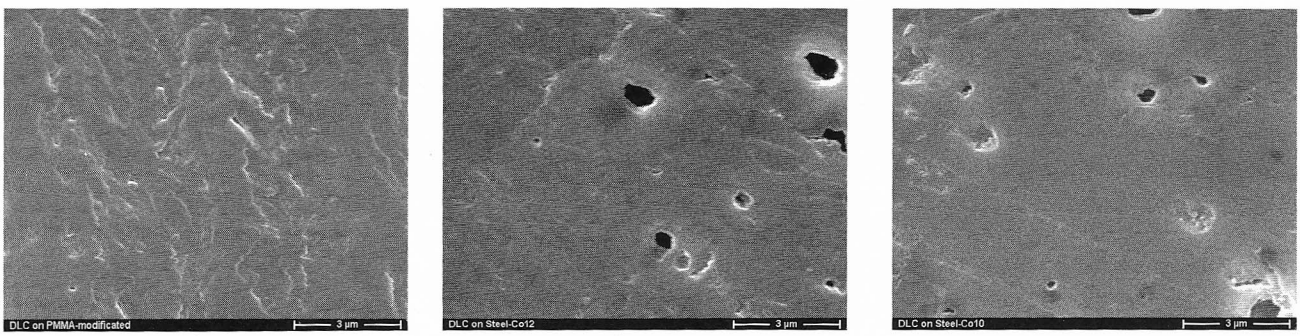
4. RESULTS AND DISCUSSION

4.1 Pre-treatments

For the tool steel substrates passivated with the corrosion process, the nucleation of DLC on the chromia after the passivation is not possible and graphite is produced, maybe because the Cr_2O_3 is not a tip of surface protrusion for a preferential nucleation of DLC as occurring with carbide phases, such W, Si, Mo and so on. This implication of the model is supported by a large number of observations on diamond nucleation on other surface protrusions[4]. The adherence on the tool steels was improved by the production of $CoO/CoSO_4$ passivating layers. In the case of the PMMA substrates, the samples with a surface modification show stronger adherence that the one with a Ti buffer layer

Table 1 Chemical composition of the tool steels used as substrates

Material	C %	Si %	Mn %	P≤ %	S≤ %	Co %	Cr %	Mo %	V %	W %
13.202	1.30-1.45	≤0.45	≤0.40	0.030	0.030	4.50-5.00	3.80-4.50	0.70-1.00	3.50-4.00	11.5-12.5
13.207	1.20-1.35	≤0.45	≤0.40	0.030	0.030	9.50-10.5	3.80-4.50	3.20-3.90	3.00-3.50	9.00-10.0



(a) (b)

Fig. 1 SEM of DLC deposited by PLD on PMMA and tool steels; 3,3 J/cm², 6000 pulses, p = 10^{-5} mbar. (a) PMMA with the surfaces grinding modification, (b) DLC on the tool steel 1.3207 passivated, (c) DLC on the tool steel 1.3202 passivated.

4.2 Optical and Scanning Electron Microscopy

Fig. 1 shows the SEM results of the systems with the improved adherence and hardness obtained for this investigation. The growth of DLC on PMMA with the mechanical surface modification (fig. 1a) is observed. The inhomogeneous surface morphology and microcracks in the films are also observed. For the virgin PMMA samples the deposition of DLC as observed by optical microscopy show delamination of the coating. According to [8] a partial delamination of Al_2O_3 films with more than 500 nm in thickness takes place at the Al_2O_3-PMMA interface. The delamination is caused by large compressive stresses in the films and low adherence of the film. A titanium buffer layer a few nanometer in thickness between the PMMA substrate and the DLC film does not change the adherence significantly. Similar results are obtained using a buffer ZrO_2 layer for the deposition of Al_2O_3 on PMMA and also PC substrates [8].

The adherence of the films deposited on polished tool steels without a passivation process was not possible and the thin films are easy removable from the surface. For the deposition on passivated tool steels the formation of a CoO/ $CoSO_4$ film is the more interesting method because this layer improves the adherence between the DLC/steels interface [7]. Figs. 1b and 1c show the DLC films deposited on tool steels after the passivation process and these coating show an excellent adherence, but the pinholes on the coatings are produced from the previous pinholes in the original steels surface. This problem was detected from the analysis by optical microscopy before the corrosión-passivation process.

4.3 Raman Spectroscopy

The Raman spectra of the films deposited on tool steels are shown in fig 2.

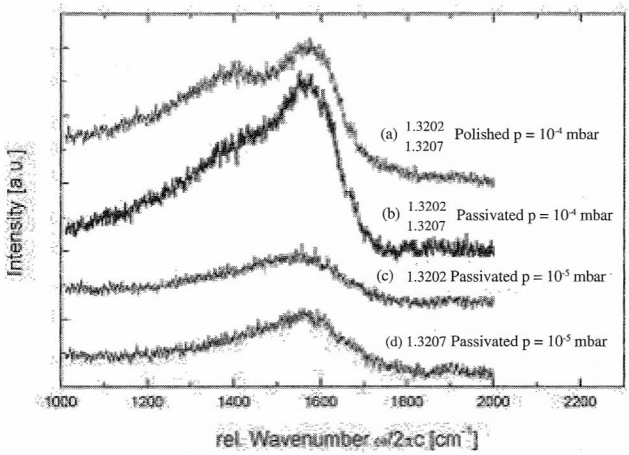


Fig. 2 Raman Spectra from DLC deposited by PLD on tool steels, 3,3 J/cm², 6000 pulses. (a) Both steels show a identical spectra, p = 10^{-4} mbar; (b) Both passivated steels show the same spectra, p = 10^{-4} mbar; (c) 1.3202 passivated tool steel, p = 10^{-5} mbar; (d) 1.3207 passivated tool steel, p = 10^{-5} mbar.

With increasing processing gas pressure during the PLD the intensity of the G-band decreases and the D-band appears, in agreement with the previous observations [9]. For all the samples deposited at 10^{-5} mbar and different pre-treatment the spectra are identical with a peak at 1594.5 cm^{-1}, corresponding to a sp^3-fraction of 60% [10] The D-band is

not observed. By increasing the processing gas pressure to 10^{-4} mbar the films show the two usual features seen in sp^2-bonded carbon, the G peak around 1560 cm^{-1} and the D-band with a mode around 1360 cm^{1}, attributed to a disorder-activated mode of sp^2-bonds [10]. This is reasonable, since during PLD the kinetic energy of the film–forming particles is drastically reduced with increasing processing gas pressure [8], so that less kinetic energy and momentum is available for the formation of sp^3-bonds in thermal spikes or by subplantation effects.

4.4 XPS Analysis

The XPS spectra of the films deposited on tool steels and PMMA are compared with previously reported values for DLC (fig. 3). P_0 is the C1s line and the loss peaks P_1, P_2 and P_3 have been referenced to P_0. For the graphite sample, a P_1 at about 7 eV is characteristic for π-type plasmon losses, while a P_3 at 28 eV arises due to bulk plasmon losses. Diamond does not have π-type electrons and hence does not exhibit the peak P_1 at 7 eV. Data from pure diamond report an intense loss peak (P_3) about 34 ± 4 eV and the maximum of this bulk plasmon loss (P_3) is centred at 33 eV for the DLC coatings. There is another loss peak (P_2) around 12 eV which was unidentified for a ion beam deposited diamond-like carbon film and is not present on the DLC deposited by PLD or in pure diamond [11].

4.5 Hardness Measurements

The hardness of the films deposited on PMMA and tool steels is measured by nanoindentation. As the load is continuously increased, the maximum indenter depth is 10% of the film thickness. The state-of-the-art of high quality DLC thin films is characterised by the high values of the Young modulus and hardness of E ≥ 800 GPa and $H_V \geq 40$ GPa, respectively [9]. For DLC thin films deposited in this investigation, the elastic modulus and hardness show a middle values of E = 300 GPa and H_V = 20 GPa for the 1.3207 tool steel, and E = 310 GPa and 30 GPa for the 1.3202 tool steel, respectively, because the presence of pinholes in the substrate decrease these values. For the case of PMMA substrate an influence of the PMMA is indicated (EPMMA = 5.2 GPa, H_V = 300 MPa). The amount of sp^3-bonds is determined from the Raman spectra by the position of the G-band. The content of sp^3-bonds in the films is about 60%. This amount of sp^3-bonds may be has also influences in the value of hardness of this coatings, because the increase of the hardness in the DLC thin film is directly proportional to the amount of sp^3-bonds present in the thin film [9]

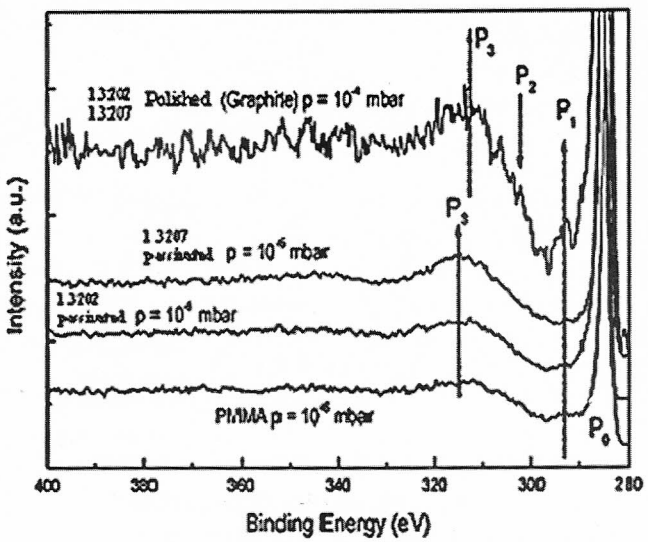


Fig. 3 XPS spectra from DLC deposited by PLD on tool steels and PMMA with surface grinding modification; 3,3 J/cm^2; 6000 pulses. Both polished steels show identical graphite spectra, p = 10^{-4} mbar. For PMMA, 1.3207 passivated steel and 1.3202 passivated steel the DLC spectra are shown, p = 10^{-5} mbar.

5. SUMMARY

The adherence of the DLC thin films on tool steels is improved significantly by the passivation pre-treatment with H_2SO_4/H_2O_2 solution. Pinholes appear on the substrate surface because the DLC thin film made a exact copy of the surfaces on which it is deposited and the substrate shown a pinholes in its structure, with this morphology influencing the measured values of hardness and elastic modulus. On polished steel the nucleation of DLC was not possible. There was no adhesion of the thin films. With increasing processing gas pressure the amount of sp^3-bonds in the thin films on tool steel decreases (G-band decreasing and the D-band appear in Raman spectra). The deposition of adherent DLC on PMMA was not possible. The titanium buffer layer located at the DLC/PMMA interface had no influence on increasing the adherence of DLC thin films on PMMA, improved coatings were produced on PMMA with a mechanical pre-treatment, but more work is needed to check other pre-treatments. The values of hardness and elastic modulus for the DLC thin films produced by PLD on PMMA with a mechanical surface modification indicate an influence of the PMMA (E = 3 GPa) on the nanoidentation measurements. Further investigations have to concentrate on the substrate pre-treatment and the development of better buffer layers to allow the increase the film thickness to 2-10μm and also high adherence, which are desirable for tribological applications.

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