Diamond & Related Materials 42 (2014) 58–63

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Effect of carbonitriding temperature process on the adhesion properties of diamond like-carbon coatings deposited by PECVD on austenitic stainless steel☆

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ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 3 December 2013
Accepted 18 December 2013
Available online 27 December 2013

Keywords:
Steel
Carbonitriding
Carbon-based coating
CVD coating
Scratch testing

ABSTRACT

The deposition of adherent coatings such as diamond-like carbon (DLC) on substrates of iron-based materials is difficult to obtain for two reasons: high residual compressive stress occurs in the inner film formation, and the mismatch of thermal expansion coefficient between steel and DLC film generates delamination effects. In order to determine the carbonitriding temperature prior to film deposition, the steel substrate and the DLC films were analyzed for their microstructure and mechanical properties of adhesion as a function of temperature. The technique used to deposit the coating was DC-pulsed plasma enhanced chemical vapor deposition. The delamination distances and the critical load of the film were obtained by scratch testing. The surface analysis by X-ray diffraction indicated the formation of nitride phases on the steel. Raman spectroscopy showed the fraction of sp^3 carbon bonds in DLC films. Hardness profiling was used to verify the extent of the interface modified by carbonitriding along the cross section. For this, the steel sample with the appropriate surface modification to have high adhesion of the DLC film was used.

1. Introduction

Diamond-like carbon is an interesting type of coating because of its high hardness and chemical inertness. It contains fractions of sp^3 and sp^2 carbon bonds, and has no crystal lattice [1]. However, their industrial application is limited due to the poor adhesion between the film and iron based substrates. In recent years, improvements have been sought in the deposition process in order to increase the adherence, especially on metals. Thus, through a variety of assisted deposition methods, such as ion beam [2], filtered pulsed laser [3], plasma immersion ion implantation [4], plasma enhanced chemical vapor deposition [5] and unbalanced magnetron sputtering [6], a variety of DLC films have been produced. Some practical applications of DLC films are related to the reduction of friction coefficient and antibacterial action [7]. In terms of coatings, DLC on steels such as AISI 304 could be applied as coatings on surgical equipment, since they require a low friction coefficient and biocompatibility [8–10]. However, for technological applications of the coated steel, it is advantageous that the substrate is as hard as possible to avoid fracture of the coating by brittle deformation and to improve the load support [11]. Consequently, the physical and mechanical properties of DLC are essential for the mechanical industry, particularly on metal surfaces, since they could increase resistance to corrosive, adhesive, abrasive and diffusive wear [12]. It is difficult to nucleate DLC on steel due to the high internal compressive stress and a high coefficient of thermal expansion mismatch between the steel and the DLC [5,13]. Also, the effects of delamination and cracking of coated materials have often been observed due to internal compressive stress of the film [14]. After an investigative study on the ideal temperature of treatment of the steel surface by carbonitriding and carburizing, a study of the influence of temperature on the adhesion of the DLC is presented in this paper. Some authors have used a thin intermediate layer [6,15], but in this study, a number of carbonitriding and carburizing steel pretreatments were applied to promote a gradual hardening of the surface and thus the deposition of DLC on the substrate. Here, one advantage of the process is that the pre-treatment and film deposition were performed in the same chamber without breaking vacuum. Based on the ISO 20502: 2005 (E) standard, we evaluate the adhesion performance of the film. Scratch tests were made in order to verify the delamination of the film and the critical load [16]. The surface modification results of the steel after pre-treatment were analyzed by X-ray diffraction [12,17]. The DLC film quantitative evaluation was based on Raman scattering spectroscopy, which was used to determine the sp^3 carbon bonds in the coating [18]. Finally, the hardness profile of the steel was obtained from the cross section in order to evaluate the gradual mechanical changes.

☆ Presented at the International Conference on Diamond and Carbon Materials (DCM 2013), September 2–5, 2013, Riva del Garda, Italy.

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http://dx.doi.org/10.1016/j.diamond.2013.12.004

2. Experimental

In this experiment, AISI 304 steel with dimensions of 5 × 10 × 6 mm was used as a substrate. According to the manufacturer, the tensile strength of rolled steel after heat treatment and annealing was 420 MPa. The composition of the as received AISI 304 is shown in Table 1. All samples were polished using standard metallographic techniques up to one micron diamond paste and then degreased in an ultrasonic bath before introduction into the deposition chamber DLC films were deposited after a series of surface modification processes involving four steps such as carburizing and carbonitriding. All in situ pretreatments and depositions were performed in a pulsed DC PECVD. The substrate was assembled on a cathode diameter of water cooled of 50 mm, which is pressed by an asymmetric bipolar pulsed DC source, consisting of pulses with amplitude of 30 V fixed and followed by a negative pulse with peak amplitude ranging from −250 to −900 V in 20 kHz. The substrates were first cleaned in an argon discharge for ten minutes. Surface treatments prior to the deposition of DLC were as follows: First, the steel substrate was subjected to a carbonitriding plasma treatment, in a mixture of methane, hydrogen and nitrogen (5:15:80) ratio of flow rates for 2 h at 250 Pa. Second, the total pressure was kept constant and the flow rates were changed to methane: hydrogen:nitrogen (15:5:80) for 1 h. Third, the gas mixture was changed to methane and hydrogen (ratio 60:40) to perform the carburizing treatment. This step was carried out at 250 Pa for 0.5 h. And fourth, the overall pressure and temperature were reduced to 40 Pa and 150 °C respectively, while the ratio of methane/hydrogen was maintained constant. This step lasted for 1 h to thermally equilibrate the system. At the end of these four stages, the deposition of DLC was performed, operating with pure methane at 150 °C and 40 Pa for 1.5 h. AISI 304 specimens were named according to the carbonitriding temperature prior to deposition of the coating. The pre-treatment temperatures were 450 °C, 480 °C, 510 °C, 540 °C and 570 °C, respectively. The pre-treatments were monitored using a thermocouple located below the sample holder. The temperature indicated in each sample refers to temperature below the sample. Consequently, the temperature of thermo diffusion is greater and will be discussed forward. The adhesion of DLC coating was qualitatively determined by scratch testing using diamond with Rockwell C geometry. The scratch testing used here is based on the ISO 20502:2005 (E). That standard describes a method which consists of generating scratches by drawing the indenter across a coating-substrate system. In our study, we chose a normal progressive force. The rate of normal force and table traverse speed was 0.067 N/s and 0.5 mm/min, respectively. The vertical position tip and the friction coefficient were gathered simultaneously in a UMT CETR Tribometer. The images of scratches and indentations were taken by scanning electron microscopy (SEM) Hitachi S-3400®. The X-ray diffraction (XRD) Philips PW1840® was used to analyze the nitride phases of the modified steel substrate. The carbon coating bond contents in the film were verified in a Raman spectroscopy Renishaw® 2000 using wavelength of 514 nm in backscattering geometry. The spectra were analyzed using deconvolution of the bands into two components (*G* and *D*) followed by calculating the I_D/I_G ratio of their intensities, determining the *G* peak position (ω_G) on the frequency scale, and measuring its full width at half maximum (Γ_G). The hardness profile perpendicular to the steel surface (from the sample with high DLC film adherence) was obtained by micro-UMIS tribometer.

Table 1
Chemical composition of the steel substrate (AISI 304).

Element	C	Mn	P	S	Si	Cr	Ni
wt.%	0.03	<2.00	<0.04	<0.03	<1.00	18.0–20.0	8.0–12.0

3. Results and discussion

We name the normal force at which failure occurs as the critical normal force Lc. In a scratch, a number of consecutive coating-failure events were observed at increasing critical normal force values. Failure by cracking through the coating thickness (through-thickness cracking) usually occurs at lower normal forces than full detachment of the coating [16]. The surface of the specimen has a uniform statistical roughness. The surface roughness (Ra), measured according to the ISO 20502:2005 procedures do not exceed 0.5 μm. Table 2 shows the Ra values, which were 67 and 326 nm, respectively, for samples at 450 °C and 570 °C. The surface roughness was affected by temperature of carbonitriding, probably due to interdiffusion of elements such as nitrogen and carbon in the grain boundaries [19]. Microscopic examination of the scratch track remains the only reliable manner of associating a failure event with a critical normal force [20]. Thus, the delamination distance was measured by SEM to evaluate the quality of adhesion between the samples. In Fig. 1, four images can be observed from one of the three tests done on the scratched DLC film. In Fig. 1-a, a portion of the AISI 304 surface is shown (the area of the film was not presented here, but it is completely covered with the DLC film). The film follows the topography of the surface. In Fig. 1-b, the three arrows show the stages of deformation of the film: the first cracking (Lc 1), the first adhesive failure (Lc 2) and the full delamination (Lc 3). It is notable in the magnification of the image that, in Fig. 1-c, the DLC film did not release after the plastic deformation of the substrate. Fig. 1-d shows the delamination of the film. The same scratch test was repeated for all samples between 450 and 570 °C. However, the example in Fig. 1 only shows the DLC film sample which was pretreated at 450 °C. Fig. 2 is related to the scratch test of the sample which was pretreated at 570 °C. It seems that the morphology of DLC film follows the substrate morphology (with greater average roughness), and this was detrimental to the film coalescence. In Fig. 2-a, the film is homogeneous over the sample, but cracks between the grains can be seen. That occurred because, after the system equilibrates at room temperature, the internal structure of the atomic arrangement of the DLC does not support the difference between the thermal expansion coefficient of both the substrate and the film, indicating the influence of the interfacial free energy to obtain DLC films with thicknesses above 0.25 μm on steel substrate [21]. Moreover, the difference of thermal expansion significantly affects the adhesion between the DLC (~1×10^{-6} /K) and the steel (~11.8×10^{-6}–14.7×10^{-6} /K). Furthermore, excessive internal compressive residual stress in DLC films (on the order of tens of GPa) [22] that usually accompanies the growth of DLC, is a limiting factor of the formation of DLC films on metallic surfaces [23]. In Fig. 2-b, the critical loads Lc1, Lc2 and Lc3 were pointed out. It is notable in Fig. 2-c that the first point of delamination occurred in the first contact between the indenter and the film. Next, in Fig. 2-d, the complete plastic deformation of the steel without the DLC inside the track was observed. Fig. 3 shows the information of friction coefficient, acoustic emission and load during a scratch test. Three measurements were performed, but just one from the sample held at 450 °C is shown as an example. The friction coefficient between the diamond tip and DLC film varied ranging from 0.10 to 0.15. This means that the frictional

Table 2
Comparison of the D and G band characteristics between DLC deposited at different temperatures of pre-treatments of the steel substrate (AISI 304). Comparison of the Roughness (Ra and Rq) changes in the steel.

Temperature (°C)	I_D/I_G	ω_G (cm^{-1})	Γ_G (cm^{-1})	Ra (nm)	Rq (nm)
450	0.365	1542.6	170.1	67	103
480	0.370	1542.7	170.5	130	184
510	0.378	1543.2	168.3	234	314
540	0.378	1544.3	166.8	305	399
570	0.380	1544.7	167.8	326	425