Vacuum 157 (2018) 442–446

Contents lists available at ScienceDirect

Vacuum

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

Short communication

Multi-phase carbonaceous coating with super wear resistance

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ARTICLE INFO

Keywords:
Multi-phase carbonaceous coating
Microstructure
Sputtering
Friction
Wear

ABSTRACT

This paper achieved the pure multi-phase carbonaceous coating matrix by magnetron sputtering technique with pulse bias voltage. Raman spectroscopy and transmission electron microscopy analysis demonstrated that three kinds of phases including amorphous, fullerene-like and nano-crystalline carbons were interleaved inside the coating matrix with similar fine size around 6 nm. Most of the ordered fullerene-like and nano-crystalline carbon phases were spherical, while, the disordered amorphous carbon phases distributed among ordered carbon phases with irregular shapes. The synergy of these phases generated rather low friction coefficient 0.05 and extremely low wear rate $8.23 \times 10^{-17} m^3 N^{-1} m^{-1}$ under dry-sliding condition in ambient air. The multi-phase carbonaceous coating has great potential to be used as the wear-resistance working surface for mechanical moving components when the liquid lubricant is lacking or forbidden.

The shortcomings of the traditional integral materials and the eagerness for high performance working surfaces of the modern mechanical components have been driving the development of the protective coatings with high mechanical properties, especially the tribological protective coatings. Since the carbonaceous coatings could exhibit the good self-lubricating effect as well as the high wear resistance, various carbonaceous structures were investigated, including the amorphous carbon coating, the hydrogenated amorphous carbon coating, fullerene-like amorphous carbon coating, tetrahedral amorphous carbon coating, nanocrystalline diamond coating, nanocrystalline graphite coating, glassy carbon coating, polymeric hydrogenated amorphous carbon coating, high hardness graphite-like carbon coating, etc. [1,2]. The common structural characteristic of these carbonaceous coating materials was the mixture of the sp^2-and sp^3-hybridized carbon. While, the diversity of these microstructure could further promote the formation of rigid carbonaceous matrixes composed with different disorders and the generation of lubricating nano-layers between contact interfaces, leading to the low wear and the low friction [3]. The different clustering feature of the carbonaceous bonding structure as well as the different doping elements such as H, N, Si, Al, Ti, Cr, Mo and W would generate different physical and chemical properties, which deeply affected the wear performance under certain friction conditions [4].

It was found that the pure amorphous carbon coating without –H could show low sensitivity to the environment, the fullerene-like microstructure would result in the high toughness and the nano-crystalline carbon would strengthen the amorphous matrix [5–7]. Therefore, in this work, the pure multi-phase carbonaceous coating with amorphous carbon, fullerene-like carbon and nano-crystalline carbon was developed by magnetron sputtering technique with pulse bias voltage on Si wafers and 316L steel substrates. Prior to deposition, the substrates were cleaned ultrasonically in ethanol and acetone baths in succession and dried with a blower. When the base pressure of the vacuum chamber pumped to 1.0×10^{-3} Pa by a turbo, Ar gas with a constant flow 100 sccm was introduced to the chamber and the vacuum pressure was adjusted to 1.0 Pa by a throttle. After that, the substrates were sputter-cleaned for 15 min at pulse bias voltage −1000 V (duty cycle 75%). Then Cr interlayers were firstly deposited on the substrate surfaces for 10 min to improve the adhesion between substrates and as-deposited carbonaceous coating. The middle frequency (40 KHz) current of the twin born Cr targets was 2.0 A, and pulse bias voltage supplied on substrates was −500 V (duty cycle 50%). On top of the Cr layers, carbonaceous layers were deposited for 100 min with DC current 0.8 A, and the pulse bias voltage for the deposition of carbonaceous

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https://doi.org/10.1016/j.vacuum.2018.09.023
Received 28 June 2018; Received in revised form 21 August 2018; Accepted 11 September 2018

layer was −300 V (duty cycle 50%). Different to our previous study in which the distance between sample and target was constant during deposition (rotation axis of sample was perpendicular to the surface of graphite target) [8], the distance between sample and target in this work was fluctuant (rotation axis of sample was parallel to the surface of graphite target). After the deposition, Raman spectroscopy and transmission electron microscopy (TEM) were carried out to reveal the structure of the deposited films. Furthermore, the ball-on-disc tribometer in reciprocating regime was used to test the tribological performance. The scanning electron microscopy (SEM) was also employed to analyze the microstructure of the as-fabricated carbonaceous coating before and after tribological test.

The Raman spectroscopy is a nonintrusive, nondestructive, room ambient method to probe the microstructural information of carbonaceous coatings, which places non-constraints on substrate size, shape or material. Normally, diamond has a single Raman active mode at 1332 cm^{-1}, which is a zone center mode of T_{2g} symmetry [9]. Single crystalline graphite has a single Raman active mode at 1580 cm^{-1} of E_{2g} symmetry labelled 'G' for 'graphite' [10]. Disordered graphite has a second mode at around 1350 cm^{-1} of A_{1g} symmetry labelled 'D' for 'disorder' [10]. Both of G and D peaks dominate the Raman spectra of amorphous and nano-crystalline carbons, even though these carbons do not have widespread graphitic ordering. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains, which does not require the presence of sixfold rings. The D peak is due to the breathing modes of A_{1g} symmetry involving phonons near the K zone boundary, which is forbidden in perfect graphite and only becomes active in the presence of disorder. Different microstructural information of the carbonaceous coatings can be deduced from the dispersion, peak fitting and intensity comparison of the Raman spectrum [11]. The Raman spectrum of the as-fabricated carbonaceous coating is shown in Fig. 1, which has typical feature with D and G bands. The extremely high intensity of D peak informed a significant content of ring graphitic and sp^2 bond, which was consistent with the concept of graphite-like amorphous carbon. After peak fitting in Gaussian deconvolution procedure, as shown in Fig. 1(a), the intensity ratio of D and G peak (ID/IG) was obtained. The area ratio and height ratio of ID/IG were 4.46 and 1.84, respectively. In comparison with other carbonaceous coatings, the as-fabricated coating in this work possessed extremely high values of ID/IG. According to the interpretation of Raman spectra, these values of ID/IG informed that more than 90% sp^2 bonds were existed inside the carbon matrix [10,11]. As for the graphite-like carbon, the concept believes that the sp^2 sites can connect with each other to form configurations with poor in-planer order and high bond-angle disorder inside a carbonaceous matrix [12,13]. The distortion in the sp^2 bond angle will give rise to the formation of non-six-membered rings which allow curvature and the formation of a cross-linked three-dimensional network. The strong sp^2 σ-bonded three-dimensional carbon structure provides the network rigidity and therefore high hardness. Consequently, the hard graphite-like structure even composed of 100% sp^2 bonds can be obtained if the carbonaceous matrix is perfectly disorder [13]. However, it was realized that the fitting curves (D and G bands) were difficult to fix the basic spectrum very well, which informed that the microstructure of as-deposited film was rather special in comparison with common amorphous carbon. Actually, the Raman spectrum can also decomposed into four Gaussian peaks with wave number 1260, 1383, 1470, and 1560 cm^{-1} when the carbon coating was composed of significant ring or ball structures as shown in Fig. 2(b) [14–16]. The peaks located at around 1260 and 1470 cm^{-1} could be attributed to curved graphite structure from five-member and seven-member carbon rings, respectively. The D mode can be considered as breathing vibrations of aromatic rings include five, six, and seven-membered rings [17]. Therefore, four vibrational bands including three with A-type symmetry (from five, six, and seven-membered rings) and one with stretching (E-type) symmetry (from six-membered rings) associated with G mode are used to decompose the Raman spectra of fullerene-like carbons. If the four peaks at 1260, 1383, 1470, and 1560 cm^{-1} were assigned to the vibrational model of $7A_1$, $6A_{1g}$, $5A_1$, and $6E_{2g}$, the ID/IG would be determined by $(I_{7A1} + I_{5A1g} + I_{5A1})/I_{6E2g}$. According to the 4-peak fitting in Gaussian deconvolution procedure, the area ratio and height ratio of ID/IG of the as-fabricated multi-phase carbonaceous coating in this work were 4.51 and 2.17, respectively. Both the increase of ID/IG values in area and height, combined with the highly coincident between the 4-peak fitting curve and basic spectrum, indicated the more fine curved graphite-like rings were formed inside the as-fabricated coating than that inside typical amorphous carbon matrix.

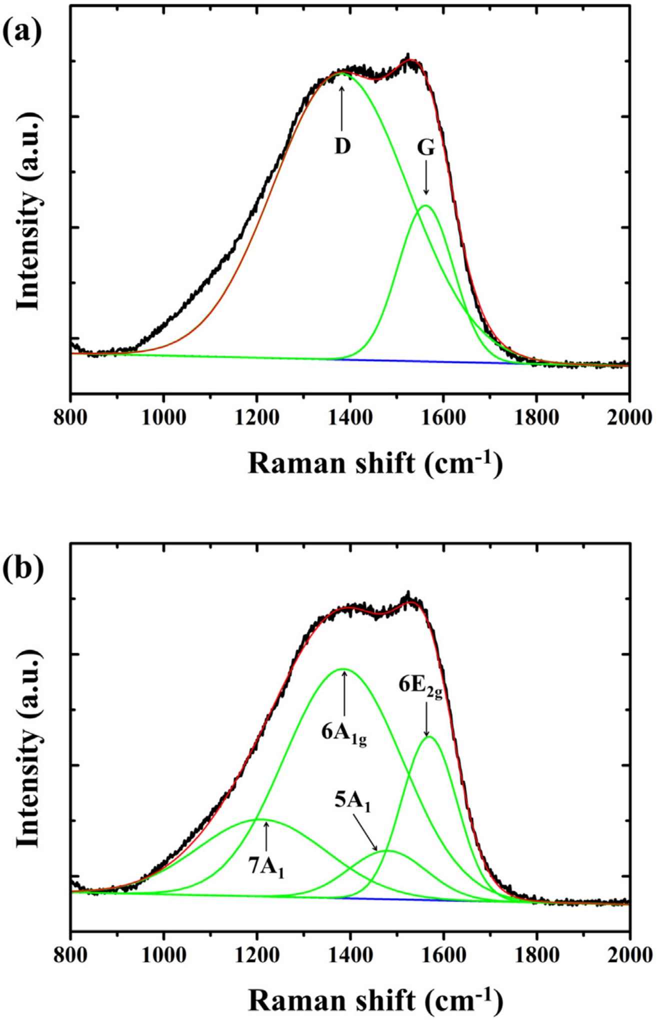

Fig. 1. Raman spectrum: (a) 2-peak fitting; (b) 4-peak fitting.

Besides of the Raman spectrum, more structural details were given in TEM micrographs and selected area electron diffraction (SAED) pattern as shown in Fig. 2. As shown in Fig. 2(a), the low resolution TEM image clear displayed a composited carbonaceous matrix embedded with plenty of fine clusters in nano-scale. Most of nano-clusters had the diameter of 6 nm, approximately. According to the SAED pattern shown in Fig. 2(b), the diffraction halo corresponding to amorphous microstructure was blurred, however, the diffraction rings related to crystalline microstructure were dim as well. Two relatively clear diffraction rings matched closely with cubic nano-diamond. One d-spacing was 2.09 Å, and the other was 1.25 Å, approximately. These patterns could be attributed to cubic diamond {111} and {220}, respectively [18,19]. Though the cubic diamond in nano-scale might be included inside the carbonaceous matrix, the size or quantity must be small due to the faint patterns. In order to clarify the ordered carbon, high resolution image was obtained as shown in Fig. 2(c). Different to