DLC Film Fabricated by a Composite Technique of Unbalanced Magnetron Sputtering and PIII

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DLC multilayer films were deposited on an AISI 304 stainless steel substrate by the composite technique of unbalanced magnetron sputtering and plasma immersion ion implantation (PIII). Structure characterization was performed on the films by Raman spectroscopy (RS) and Glancing X-ray Diffraction (GXRD). Composition analysis of the surface layer on the implanted substrates was carried out using auger electron spectroscopy (AES). The mechanical properties of the films were evaluated by nanoindentation. The results showed that the Raman spectra were divided into a “D” disordered peak and a “G” graphite peak with the integrated intensity ratio between them (I_D/I_G) being 1.30. The implanted carbon penetrated the substrate resulting in complete interfacial mixing. The hardness, elastic modulus, fracture toughness and interfacial fracture toughness of the films were about 19.84 GPa, 190.03 GPa, 3.75 MPa·m1/2 and 5.68 MPa·m1/2 respectively. Compared with that of a DLC coating deposited directly by the PIII technique, the interfacial fracture toughness of the multilayer films increased, which is mainly attributed to the interfacial mixing at the interface.

1. Introduction

Diamond-like carbon (DLC) thin films have great potential as wear-resistant coatings in spacecrafts or vacuum technology due to their high hardness, low friction coefficients and excellent chemical inertness. Various synthesis methods have been studied for fabricating carbon films to date, such as ion beam assisted deposition (IBAD), laser deposition and plasma enhanced chemical vapor deposition (PECVD). However, since the mechanical properties of the films are different from that of the substrate, hard layers of diamond-like materials deposited directly on the metallic substrate result in a high residual stress at the fracture. The fracture would be easily generated at the sharp interfaces between the film and the metallic substrate. Therefore, it is reasonable to elect fabricating a gradient interlayer between carbon films and metallic substrates, which release the residual stress and improve the adhesion of DLC films on metallic substrates. Glozman et al. investigated a CrN interlayer to improve the adhesion. K. Choy demonstrated also that both of the two functionally graded structures, Ti/TiC/DLC and Ti/TiN/TiN/C/DLC prepared by the magnetron sputter ion plating technique, could improve the adhesion and wear resistance of the DLC coatings on metallic substrates. However, the coatings were not good enough for aerospace application, due to the existence of an obvious interface between interlayers.

Plasma immersion ion implantation (PIII), invented by Tendys, has been used to make carbon films. Compared with ion implantation, this technique solves the line-of-sight problem in the conventional ion implantation, and also generates better adhesion to the substrate than other surface coating processes since there is no abrupt interface to suffer debonding. Based on the research of Tendys, the composite process of the unbalanced magnetron sputtering technique and PIII was employed to fabricate DLC gradient films in our present work. GXRD and Raman spectroscopy were used to investigate the structural character of the films. The mechanical properties of the multilayer films were compared with that of the DLC film and C/TiC/DLC multi-layer films.

2. Experimental

2.1 Preparation of films

DLC multi-layer films were prepared in an industrial prototype DLZ-01 PIII installation. The base pressure in the vacuum chamber was 1 × 10−4 Pa. The plasma was generated by the application of a 500-W r.f. power on the antenna located inside the chamber. With a maximum voltage and current of −50 kV and 3.5 A, respectively, the repetition ranged from 100 to 161 Hz during the implantation process, and the maximum pulse duration was 1% of the repetition period. Commercial AISI 304 stainless steel was used as the substrate. After mechanically polished to a mirror-like surface, the substrates were placed into the vacuum chamber. When the chamber was pumped down to the base pressure, ions were introduced into the chamber to bring the pressure up to 4 × 10−4 Pa. Subsequently, the substrates were cleaned using high energy ion bombardment before implantation, operating at a bias of 2000 V for 10 min, to remove the undesirable oxide layers on the substrate surfaces.

Three kinds of layers, i.e. a DLC layer prepared by the PIII technique and two multi-layer films prepared by the composite technique of unbalanced magnetron sputtering and PIII, were fabricated on the substrate. During the preparation of N/TiN/Ti(N,C)/DLC multi-layer and C/TiC/DLC multi-layer films, several processes were conducted consecutively.

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Table 1 The processing parameters for DLC multi-layer film.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Implantation parameters</th>
<th>Sputtering parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bias Voltage Kv</td>
<td>Pulse width µs</td>
</tr>
<tr>
<td>N implantation</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>Ti, N implantation</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>TiN deposition</td>
<td>0.8</td>
<td>38</td>
</tr>
<tr>
<td>C implantation</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>DLC deposition</td>
<td>15</td>
<td>26</td>
</tr>
</tbody>
</table>

processing parameters for N/TiN/Ti(N,C)/DLC multi-layer film are shown in Table 1.

The composite times of DLC monolayer and C/TiC/DLC multi-layer films were 280 min with the same processing parameters for C-implantation as described in Table 1.

2.2 Characterization

Chemical structure of the surface layer of the substrate was determined using Glancing X-ray diffraction analysis (GXRD), with Cu Kα diffraction, voltage 40 kV, current 40 mA. Raman spectroscopy (EQUINO-X55 FT-Raman scattering spectroscopy) was also used to determine the molecular structure and composition of the amorphous carbon film. The elemental depth profiles of different films were obtained using Auger Electron Spectroscopy (AES). The Ar ion peelingetching rate was about 12 nm/min.

In order to investigate the mechanical properties of the multi-layer films, indentation experiments were carried out at room temperature using a Nano-indenter (CSEM Instruments) with a load resolution of 1 µm and a displacement resolution less than 1 nm. Ten indents were made on each sample and averaged. A simple cycle of loading and unloading was used in all the experiments, and the loading rate was equal to $2 \times P_{\text{max}}$ min where $P_{\text{max}}$ was the maximum load.

3. Results and Discussion

3.1 Structural characterization

GXRD analysis in Fig. 1 shows the presence of TiN, Ti(N,C) and carbon structures in the N/TiN/Ti(N,C)/DLC film on the stainless steel substrates. In order to distinguish graphite from diamond in the outer carbon layer, Raman scattering spectroscopy is adopted with the result shown in Fig. 2. The spectral profile can be fitted by two Gaussian profiles, with one centered at 1518 cm⁻¹ corresponding to the G-line assigned to the graphite structure, and the other at 1335 cm⁻¹ corresponding to the D-line assigned to the disordered structure. The positions of the G-line and D-line, as well as the integrated intensity ratios ($I_D/I_G$), had been correlated with sp³/sp² bonding ratios. Based on the research of Miyoshi et al., the deposited multi-layer DLC films consisted of amorphous hydrogenated carbon with graphitic domains. Such DLC structures were also observed in the C/TiC/DLC films.

Figure 3 shows the elemental depth profiles of N/TiN/Ti(N,C)/DLC multi-layer film. It can be found in Fig. 3 that nitrogen and titanium atoms had penetrated into the substrate and a well-mixed area at the interface had been formed, which
suggests that the inner layer should match well with the metallic substrate. Moreover, Fig. 3 shows that the carbon concentration curve intersects with the N and Ti concentration curve (about at 30 at% and 28 at% respectively), during sputtering, indicating that carbon ions had penetrated into the deposited TiN layer and resulted in complete interfacial mixing, which improves the adhesion between the outer carbon layer and the TiN layer. The multilayer was about 0.3 µm in thickness.

3.2 Mechanical properties

The mechanical properties of the films were evaluated by nano-indentation. The composite hardness, effective elastic module and fracture toughness of the gradient film/substrate system were calculated by means of a typical indentation load-displacement curve, as shown in Fig. 4.

For coatings of about 0.3 µm thickness, the load-displacement curves of indentation with a load of 1, 5 and 10 mN are smooth [Figs. 4(a)–(c)]. A distinct change is observed in the slope of the load-displacement curve at a load of 18.2 mN [Fig. 4(d)], which is related to the onset of radial cracking in the coating. The critical load at which the radial cracking started is independent of the coating thickness. The elastic modulus and fracture toughness of coatings can be obtained from the load-penetration depth curves.

The composite hardness of the film/substrate system can be calculated based on the load-displacement curve. Figure 5 shows the composite hardness of DLC monolayer and C/TiC/DLC multi-layer films (deposited by the PIII technique). It can be found that with the increasing penetration depth into multi-layer films, the hardness of the films decreases and approaches the substrate hardness (0.324 GPa). In order to obtain the true hardness of film without the influence of the substrate, it is generally assumed that the indentation depth should not exceed 10% of the film thickness. Based on this rule, the depth of 20 nm is selected for the measurements of the true hardness and elastic modulus of the film. Therefore, the hardness of the N/TiN/Ti(N,C)/DLC gradient film is about 19.84 GPa, close to the reported values of multi-layer films deposited by other techniques.

The elastic moduli of the films as a function of contact depth were calculated using the unloading curves as indicated in Fig. 4, and the results are shown in Fig. 6. The elastic modulus of N/TiN/Ti(N,C)/DLC and C/TiC/DLC films are about 190.03 and 178.64 GPa, respectively, close to that of the DLC monolayer (202.66 GPa). It is worth noting that some authors reported that the hardness and modulus of DLC
film was in the range of 24–59 GPa and 200–400 GPa, respectively.22,25,26)

A step in the loading curve can be observed in the load-penetration depth curve of these coatings, which indicates cracking of the functional film. So the load at the step should correspond to the peak indentation load which is 18.83 mN for N/TiN/Ti(N,C)/DLC film. According to the theoretical analysis by Li and Bhushan, 20, 27) the fracture toughness of thin films, $K_{IC}$ can be defined as:

$$K_{IC} = \left[ \frac{E}{1 - v^2} \frac{1}{2\pi C_K} \right] \left[ \frac{U}{t} \right]^{1/2} \quad (1)$$

where $E$ is the elastic modulus, $v$ is the Poisson’s ratio (here, $v = 0.30$), $2\pi C_K$ is the crack length in the film plane, $U$ is the strain energy difference before and after cracking, and $t$ is the thickness of the film. $U$ can be assessed from the steps in the the loading curve in Fig. 5(d), and the strain energy releasing in the ring-like cracking can be calculated from the corresponding steps. The fracture toughness value of the DLC layer, N/TiN/Ti(N,C)/DLC and C/TiC/DLC multi-layer films are 4.12, 3.75 and 3.68 MPa-m$^{1/2}$, respectively.

The fracture toughness of the interface between the substrate and the films has also been obtained from the indentation results based on some existing models. According to the results of Rosenfeld et al. 28) the interfacial fracture toughness is linked to the size of the delaminated area and the corresponding indentation load as follows:

$$K_{int} = \frac{0.792H\sqrt{(1-v^2)h}}{1 + v + 2(1-v)Hc^2/P} \quad (2)$$

where $c$ is the radius of the delamination crack, $v$ is the Poisson’s ratio, $H$ is the hardness of films and $P$ the corresponding load. The calculated interfacial fracture toughness of the DLC layer, N/TiN/Ti(N,C)/DLC and C/TiC/DLC multi-layer films, are 5.18, 5.77 and 5.54 MPa-m$^{1/2}$, respectively. The values of nano-scale mechanical properties described above indicate that the DLC multi-layer films are more wear-resistant than the DLC layer film.

4. Conclusions

With the composite technique of unbalanced magnetron sputtering and PIII, multi-layer films were fabricated on an AISI 304 stainless steel substrate. A well-mixed layer was fabricated at the DLC layer/TiNC/TiN layer and TiN/N/substrate interface. Raman spectra were divided into the “D” disordered peak and “G” graphite peak. The deposited multi-layer DLC films consisted of amorphous hydrogenated carbon with graphitic domains. Such DLC structures were also observed in the C/TiC/DLC films.

The indentation test results show that the graded structure improved the coating adhesion. The multi-layer structure N/TiN/TiNC was more efficient than C/TiC in improving the adhesion of DLC coatings onto stainless steel. The fracture toughness and interfacial fracture toughness of N/TiN/Ti(N,C)/DLC multilayer film are about 3.75 and 5.68 MPa-m$^{1/2}$, respectively. Compared with DLC coating and C/TiC/DLC multi-layer film, the N/TiN/Ti(N,C)/DLC is the coating system that had the best mechanical properties for aerospace application.

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