Thermal stability and oxidation properties of magnetron sputtered diamond-like carbon and its nanocomposite coatings

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Abstract

Diamond-like carbon or amorphous carbon (a-C) and its nanocomposite nc-TiC/a-C(Al) coatings have been exposed to temperatures up to 600 °C for one hour. Hardness and oxidation resistance have been studied using nanoindentation, Raman Spectroscopy, X-ray Diffraction and X-ray Photoelectron Spectroscopy. Pure a-C becomes thermally unstable at temperatures higher than 300 °C when coating hardness drastically drops with temperature because of graphitization that causes increase of sp² and decrease of sp³ bonding structure. nc-TiC/a-C(Al) is stable up to 600 °C. Its hardness is not sensitive to temperature because the hardness mainly comes from the TiC nanocrystallites rather than sp³ bonding. As such, the coating hardness experiences only a slight drop after annealing at 600 °C. The oxidation resistance of nc-TiC/a-C(Al) nanocomposite is much better than that of the pure a-C. Even after annealing in air at 600 °C for 1 h, nc-TiC/a-C(Al) coating still maintains its original thickness (while the pure a-C loses 60% of it).

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1. Introduction

Though diamond-like carbon (DLC) has been studied extensively and applied in industry during the past decade, there is still much room for improvement. For tribological applications, aside from hardness and toughness, coatings should have excellent adhesion to substrate, good thermal stability and be “thick” enough to sustain long working hours. As engineering coatings, DLC needs to be designed to satisfy the following requirements: high hardness and toughness, low residual stress, low coefficient of friction, good thermal stability and oxidation resistance. How to increase the adhesion and toughness of hard or superhard amorphous carbon (a-C) coatings deposited on engineering substrates (steels, cemented carbide, etc.) is the subject of recent intensive study. Substrate bias grading [1] creates a graded sp³/sp² bonding structure along the thickness direction with softer but tougher interface and harder surface. That works well if pure DLC is desired. But to further increase the toughness or hardness, one of the solutions is the application of the nanocomposite structure. Veprek and Reiprich and Veprek et al. [2,3] designed their superhard nanocomposite in such a way that the nanocrystallites (3–4 nm in diameter) of a strong phase were embedded in an amorphous matrix of another strong phase with the grain separation of about 1 nm. But this design was thought of lacking toughness [4] because the plasticity is suppressed. Toughness of a hard coating can be improved by facilitating grain boundary sliding via increasing grain separation coupled with random orientation [5], i.e., high angle grain boundaries to minimize incoherent strain and facilitate nanocrystallite to slide in the amorphous matrix to release the strain under high applied loads. Nanocomposite coatings based on DLC are made mostly through doping of one metal at a time, such as Ti, W, Cu, Ni, Cr, or Al [6–10]. In our previous studies, two metals (Ti and Al) are simultaneously sputtered into DLC [11]. Ti is to form the strengthening phase nanocrystalline titanium carbide (nc-TiC), while Al is to toughen the DLC amorphous matrix. The resultant coating overcomes the drawbacks of traditional DLC and meanwhile maintains the desirable properties, very low residual stress and adequate hardness. The newest developments on this subject (bias grading and metal doping) together

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with findings in adhesion and tribological studies are summarized in our recent paper [12].

In high speed machining or medium temperature molding, etc, thermal stability and oxidation resistance of DLC is a concern. Studies showed that hydrogen-free DLC is better in thermal stability than hydrogenated counterpart, and works at temperatures up to 350–400 °C [13]. Beyond that temperature, DLC is oxidized and the loss of coating thickness takes place quickly. This paper concentrates on thermal stability and oxidation properties of DLC-based nanocomposite nc-TiC/a-C(Al) coating. Pure hydrogen-free DLC is also deposited and thermally treated for comparison.

2. Experimental

2.1. Deposition

The deposition was carried out at the E303A magnetron sputtering system (Penta Vacuum-Singapore). Details of the deposition system have been described elsewhere [14]. Graphite (99.999% purity), Ti (99.995% purity), and Al (99.995% purity) targets were located about 100 mm above the Si (100) substrate. From mono or multi target co-sputtering, two kinds of coatings were deposited: a-C and TiC/a-C(Al). For all samples, a bias voltage of −150 V was applied and the power density of graphite target was kept constant at 10.5 W/cm². Power density of metal targets was varied for desirable composition. The base pressure of the deposition chamber was pumped to $1.33 \times 10^{-5}$ Pa and the process pressure was kept constant at 0.4 Pa with 50 sccm Ar flow. The substrates were ultrasonically cleaned for 20 min in acetone followed by 10 min ultrasonic cleaning in ethanol prior to be introduced into the vacuum chamber. After loading, the substrates were heated to and maintained at 150 °C for 20 min before plasma cleaning for 30 min at RF induced bias voltage of 300 V to remove possible oxides and contaminants on the surface. During deposition, the substrate temperature was maintained at 150 °C.

2.2. Oxidation and characterization

The oxidation resistance tests were carried out by subjecting the coatings to heat in a furnace in open air (relative humidity 75%) at fixed temperature between 100 and 600 °C and held at the temperature for 60 min. In order to study the thermal effect alone (to compare hardness without influence of surface oxidation), the coatings were also treated in argon atmosphere. After unloading from the furnace, the samples were cooled down in ambient air to room temperature followed by Raman,
nanoindentation hardness testing and X-ray Photoelectron Spectroscopy (XPS) analysis using a Kratos–Axis spectrometer with monochromatic Al Kα (1486.6 eV) X-ray radiation (15 kV and 10 mA) and hemispherical electron energy analyzer. The base vacuum of the chamber was 2.66 × 10−7 Pa. The survey spectra in the range of 0–1100 eV were recorded in 1 eV step for each sample followed by high-resolution spectra over different elemental peaks in 0.1 eV step, from which the composition was calculated. Curve fitting was performed after a Shirley background subtraction by non-linear least square fitting using mixed Gauss–Lorentz function.

3. Results and discussion

3.1. Pure DLC

Fig. 1 shows the Raman spectra of a pure DLC coating after thermal exposure for 60 min at different temperatures. As seen from the figure, the spectrum does not change much as the temperature increased up to 300 °C. The increase in G peak frequency (ranging from 3 to 15 cm⁻¹, c.f., Fig. 2) indicates some change in the structure of the DLC coating, corresponding to a slight decrease in sp³/sp² fraction of the coating. As the temperature goes beyond 300 °C, the structural changes in coating become apparent. At 400 °C, the appearance of the Raman band near 1350 cm⁻¹ coincides with a further shift of the G band to higher frequencies and a considerable increase in the I_D/I_G ratio from 1.2 (at 300 °C) to 1.9 (at 400 °C)(c.f., Fig. 2). This indicates a high rate of graphitization occurred in the coating, which led to a decrease in hardness from 28.6 (at 300 °C) to 16.6 GPa (at 400 °C) as seen from Fig. 3.

As annealing temperature increases to 500 °C, the hardness of the coating decreases to a very low value of 8.1 GPa, corresponding to a high I_D/I_G ratio of 3.6. Since the thickness of the coating after 60 min annealing at 600 °C reduces to about 350 nm, the hardness measurement is not carried out for this sample. Fig. 4 plots the DLC coating thickness measured using a profilometer from a step. Clearly, the coating thickness does not change after the 1 h annealing up to 300 °C. A slight reduction in thickness is seen at 400 °C (about 15%). At temperatures higher than 400 °C, the loss of thickness drastically aggravates (about 35% at 500 °C and 62% at 600 °C). The loss of coating thickness

Fig. 5. Raman spectra of nc-TiC/a-C(Al) nanocomposite annealed at different temperatures for 60 min in an Ar environment.

Fig. 6. Hardness of nc-TiC/a-C(Al) nanocomposite as a function of annealing temperature.

Fig. 7. XRD patterns of nc-TiC/a-C(Al) coating before and after 60 min annealing in an Ar environment at 600 °C.

Fig. 8. XPS spectra (Al 2p) of nc-TiC/a-C(Al) nanocomposite coating at different annealing temperatures in air for 60 min.
is attributed to the oxidation of carbon following the reaction: \( \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \uparrow \). The carbon dioxide formed moves out of the coating causing the loss of thickness.

### 3.2. Nanocomposite nc-TiC/a-C(Al)

Fig. 5 shows the Raman spectra of the DLC-based nanocomposite coating nc-TiC/a-C(Al) of composition C\(_{56}\)Ti\(_{31}\)Al\(_{13}\) and hardness 19.5 GPa after 60 min annealing in Ar at different temperatures. The \( I_D/I_G \) ratio of a-C in the matrix increases with increasing temperature. This behavior is the same with that of pure DLC where a more graphite-like structure is formed at high temperatures. The change of the a-C structure takes place as temperature exceeded 300 °C. At high temperatures (>500 °C) carbon in the matrix is almost graphite-like with a large cluster size. Further increase in temperature does not cause much increase in \( I_D/I_G \) ratio (\( I_D/I_G \) ratio increased from 4.5 to 4.6 as the temperature increased from 500 to 600 °C). As temperature is high enough, structural change occurs, i.e., DLC is graphitized thus more sp\(^2\) forms [13]. Although the amount of graphite-like structure increased with temperature the coating hardness does not change much but remains as high as the original value of about 19 GPa up to 400 °C (c.f., Fig. 6). In a pure DLC coating of 32.5 GPa in hardness, its hardness drops to 16 GPa (only half of the original value, c.f., Fig. 3) after annealing for 60 min at 400 °C. After 500 °C, only a quarter of the hardness remains. This drop in hardness comes from the structure change—fraction sp\(^2\) increases while sp\(^3\) drops; in pure DLC, majority of the

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**Fig. 9.** XPS spectra (Ti 2p) of nc-TiC/a-C(Al) nanocomposite coating at different annealing temperatures in air for 60 min.

**Fig. 10.** The coating thickness of nc-TiC/a-(Al) nanocomposite coating before and after annealing in air at 600 °C obtained from profilometer.

**Fig. 11.** XPS depth profile of nc-TiC/a-C(Al) nanocomposite coating (a) without annealing and after annealing in open air for 60 min at (b) 300 °C and (c) 600 °C.
hardness contribution comes from the sp$^3$ fraction, as sp$^3$ drops, the hardness drops. However when nc-TiC/a-C(Al) is heated up the same way, although the amount of graphite-like structure increases, the coating hardness holds up to 400 °C. Even after the coating is annealed at 600 °C for an hour, its hardness only drops a little. In absolute value, the hardness of nc-TiC/a-C(Al) coating keeps constant at 19 GPa after 1 h annealing at 400 °C, then little drop to 17 GPa after 1 h at 600 °C. This is so because in the DLC-based nanocomposite, hardness mainly comes from the hard nanocrystalline TiC, which is stable even at 600 °C. Also, from Fig. 7, the XRD patterns of nc-TiC/a-C(Al) before and after annealing are not noticeably different. Therefore, the hardness of the nanocomposite coating is less sensitive to temperature than that of pure DLC.

Fig. 8 shows Al 2p XPS spectra of the nanocomposite coating after annealing at different temperatures in air. Aluminum oxide (the peak at 74.2 eV) can be seen even for the coating without annealing. It comes from the surface oxide after unloading from the deposition chamber. As the annealing temperature increased to 600 °C, Al–O is the only chemical bond of Al detected. The Ti 2p spectra are shown in Fig. 9. The peaks at 454.9 and 461 eV are attributed to TiC (Ti 2p$^3/2$ and 2p$^1/2$, respectively), at 458.6 and 464.3 eV to TiO$_2$, and at 456.2 and 462 eV to TiC$_4$O$_x$. As the temperature is lower than 300 °C, the oxidation of TiC is very limited and the oxygen exists in TiC$_4$O$_x$. The formation of TiO$_2$ can be seen at an annealing temperature of 400 °C. The oxidation, which leads to the formation of TiO$_2$ can be expressed as the following reaction: TiC + 2O$_2$ → TiO$_2$ + CO$_2$. At 500 °C, a large amount of TiO$_2$ is formed (51 at.% Ti bonded with O) and when the annealing temperature is increased to 600 °C, almost all the surface TiC is oxidized to form TiO$_2$. It can be seen that after 1 h at 600 °C, the thickness of the pure DLC coating drops from 1.1 to 0.45 μm (c.f. Fig. 4) and in the case of nc-TiC/a-C(Al) nanocomposite, the oxidation does not result in thinning of the coating (c.f., Fig. 10). As mentioned earlier, with DLC, the reaction between carbon and oxygen at high temperature (>400 °C) results in the loss of coating thickness. This also occurs on the surface of the nanocomposite coating where the carbon dioxide is formed from the reactions between TiC and oxygen and between C (in the matrix) and oxygen. Aside from carbon dioxide, aluminum oxide (formed at room temperature) and titanium oxide (formed at high temperature) are also products of the oxidation. These oxides remain on the coating and act as a barrier layer (especially aluminum oxide [15]) to prevent the diffusion of oxygen into the coating. Therefore, the loss of coating thickness is limited when annealing the nc-TiC/a-C(Al) nanocomposite in ambient air, even at 600 °C for 60 min (c.f., Fig. 10).

Fig. 11 shows the XPS depth profiles of the coating without annealing (Fig. 11(a)), after 60 min annealing in air at 300 °C (Fig. 11(b)), and after 60 min annealing in air at 600 °C (Fig. 11(c)), from which the thickness of the oxide layer can be determined. The 4 at.% oxygen level is used as the boundary of the surface oxidation layer since this level of oxygen content is throughout the coating, obviously from the deposition process. As seen from the figure, without annealing, the thickness of oxide layer is about 4.2 nm. At 300 °C, the increase in thickness of the oxide layer is not significant (the thickness of oxide layer is about 6.3 nm). It should be noted that the thickness of oxide layer on the nanocomposite (Ti,Cr)CN/DLC (without annealing) was already about 20 nm [10]. At high temperature of 600 °C, the thickness of the oxide layer on nc-TiC/a-C(Al) coating dramatically increases to about 55 nm. Under the same annealing condition, the oxide layer on the TiN coating was reported to be 200 nm and that on TiAlN was 35–180 nm depending on the Al content in the coating [15,16]. These data illustrate the importance of Al in the oxidation resistance of the nanocomposite coating. The addition of Al, even at low amounts considerably enhances the oxidation resistance. Aluminum oxide is a good barrier in preventing oxygen diffusing into and oxidizing the coating.

4. Conclusion

Pure diamond-like carbon is thermally stable up to 300 °C, after which, coating hardness drastically drops with temperature because of the graphitization, which leads to an increase in sp$^3$ and decrease in sp$^3$ bonding structure. In DLC-based nanocomposite, nc-TiC/a-C(Al), the coating hardness is not sensitive to temperature because the hardness mainly comes from the TiC nanocrystallites. As such, the coating hardness experiences only a slight drop after annealing at 600 °C. The oxidation resistance of nc-TiC/a-C(Al) nanocomposite is much better than that of the pure DLC. Even after annealing in air at 600 °C for 1 h, nc-TiC/a-C(Al) coating still maintains its thickness while the pure DLC loses 60% of it.

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