Improved interfacial adhesion between TiAlN/DLC multi-layered coatings by controlling the morphology via bias

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A B S T R A C T

By combining the advantages of the thermo-mechanical properties of TiAlN and self-lubricating properties of diamond-like carbon (DLC), a multi-layered TiAlN/DLC coating is fabricated by filtered cathodic vacuum arc and magnetron sputtering. According to the different morphology and mismatch between the physical and chemical properties of TiAlN and DLC, multiple methods are used to study the growth mechanism of crystalline TiAlN and amorphous DLC in the combined system. The morphology evolution depending on the bias is studied and the brittle interface is assessed by scratch experiments. The results show that an interlamination failure occurs at the top of first DLC layer due to the cluster morphology obtained by small bias, however, the failure moves to the interface above the substrate when the clusters are refined by increasing bias. By adopting the stepwise decreased bias, the 4.5 μm thick TiAlN/DLC multi-layer coating is fabricated and does not exhibit interfacial failure at any interface between TiAlN and DLC in the scratch experiments up to a load of 100 N. Excellent adhesion (Lc = 63 N) is also achieved from coatings deposited on high-speed steel with optimized Cr/CrCx/CrC interlayers prepared by high-power impulse magnetron sputtering.

1. Introduction

Owing to the excellent mechanical properties and thermal stability, TiAlN coatings are commonly applied as protective layers to cutting and forming tools as well as other applications [1–3]. However, the friction coefficient of TiAlN, especially under dry conditions, is quite large reaching 0.9–1.0 at room temperature and 1.5 at 400 °C [4]. Diamond-like carbon (DLC) coatings, especially hydrogenated DLC coatings (a-C:H), are known for their excellent tribological properties such as small friction coefficients (0.05–0.2) and wear rates (< 10−15 m3/N·m) [5,6]. However, the hardness of a-C:H films are typically < 20 GPa which is smaller than that of TiAlN or TiAlSiN.

Multi-layered coatings with alternating and different compositions can combine the advantages of the constituent layers and are preferred to enhance integrated performance over single-layered coatings [7–9]. Both hard and self-lubricating multi-layered coatings are expected to prepared by choosing the proper combinations, for example, multi-layered TiAlN/VN, TiAlN/WC, TiAlN/MoN, and so on [10–12]. However, although the wear resistance can be improved and friction can be reduced, the self-lubrication effects of these coatings are still worse than that of a-C:H. However, when a-C:H coatings are used to construct a multi-layered structure with TiAlN, problems occur. For instance, it is difficult to prepare amorphous DLC on crystalline TiAlN and vice versa due to the mismatch between the physical and chemical properties of the two materials and film adhesion is also an issue in the system combining TiAlN and DLC [13,14].

In this study, TiAlN/DLC multi-layered coatings are prepared by filtered cathodic vacuum arc (FCVA) and magnetron sputtering and the growth mechanism of the crystalline TiAlN and amorphous DLC layers on each other are studied. The brittle interface is assessed by scratch experiments and the adhesion mechanism is investigated by controlling the morphology and stress. By adopting the suitable bias and composition, the 4.5 μm thick TiAlN/DLC multi-layered coating is fabricated without failure happening at any interface between TiAlN and DLC and an adhesion strength of 63 N is achieved with optimized Cr/CrCx/CrC interlayers fabricated by high-power impulse magnetron sputtering (HiPIMS).
2. Experimental details

A multi-functional plasma surface modification and coating deposition system designed by our lab with a vacuum chamber (diameter of 100 cm and height of 80 cm) was used for the deposition at 200 °C and a base pressure of $8 \times 10^{-4}$ Pa. High-speed steel (HSS) and single-crystal silicon (100) samples were used as substrates. The target-substrate distance was fixed at 14 cm in the experiment. The HSS substrates ($\Phi 25 \times 4$ mm) were polished with abrasive SiC paper from 320 to 1500 grits and then up to 1 $\mu$m with diamond paste with a velvet cloth manually. All the substrates were ultrasonically cleaned for 30 min in alcohol, acetone, and deionized water sequentially and dried at 120 °C. Before deposition, the substrates were further cleaned for 20 min with an Ar plasma (40 sccm, 0.8 Pa) using an anode layer ion source (Cehis 100, Plasma Technology Ltd. Hong Kong) at a power of 300 W and bias of $-500$ V in the deposition chamber. To enhance film adhesion, an optimized Cr/CrCx/CrC interlayer was produced under Ar (99.999% pure) and C2H2 (99.8% pure) using a 530 × 100 mm Cr target (99.99% pure) by HiPIMS with pulses voltage of 750 V, frequency of 50 Hz, pulse width of 300 $\mu$s (SIPP 2000, Melec GmbH, Germany). The DLC film was fabricated using a 530 × 100 mm C target (99.99% pure) under the same conditions with a DC power of 2400 W (480 V, 5 A) (SIPP 2000 Melec GmbH, Germany). To obtain a gradient transition of C at the interface between the DLC and TiAlN layers, the on/off flow of C2H2 and N2 (C2H2 flow changed from 40 sccm to 0 sccm while N2 flow from 0 sccm to 15 sccm and vice versa before DLC deposition) was controlled carefully and slowly when the TiAlN layer was deposited by 90° curved magnetic FCVA (FCVA133, Plasma Technology Ltd. Hong Kong) using a Ti70Al30 target ($\Phi 71 \times 50$ mm, 99.99% pure) in the presence of a carrier gas (Ar) and reactive gas (N2). The arc voltage and current were 35 V and 60 A, respectively, and a 10 A current was applied to the coil to produce the extraction magnetron.

The morphology was observed by field-emission scanning electron microscopy (FE-SEM, ZEISS SUPRA® 55) equipped with an energy-dispersive X-ray spectrometer (EDS), atomic force microscopy (AFM, Bruker multimode 8) and transmission electron microscopy (TEM, JEM-3200FS) equipped with an energy-dispersive X-ray spectrometer (Thermo UltraDry, America). A scratch test instrument (WS-2005, Zhongke Kaihua Technology, China) equipped with acoustic emission was employed in the scratch test to evaluate the adhesion strength between the films and substrate. Normal loads were applied progressively from 0 N to 100 N for 3 mm/min at a sliding rate of 50 N/min. The scratch tracks and depths were examined by 3D laser confocal microscopy (KEYENCE, VK-×200) and the results were verified by EDS.

3. Result and discussion

In order to enhance the adhesion strength between the coating and substrate, a gradient Cr/CrCx/CrC interlayer is introduced to reduce the mismatch in thermal expansivity and element compositions. To obtain a gradient transition of C at the interface between the DLC and TiAlN layer, the C2H2 and N2 flow rates are controlled carefully and gradually during deposition of the TiAlN layer. The C2H2 flow rates are changed from 40 sccm to 0 sccm while that of N2 are rising from 0 sccm to 15 sccm gradually at the same time and vice versa before DLC deposition.
deposition. However, the adhesion was poor. Fig. 1 shows the cross-sectional morphology of the failed interface in the TiAlN/DLC multilayered coating and the magnified images of the coatings that did not peel off. Failure always occurs at the interface between the first DLC layer and the next TiAlC(N) layer (Interface 1 in Fig. 1(b)) although the transition processes at each TiAlC(N)/DLC and DLC/TiAlC(N) interface are the same (as shown in Fig. 1(a)). Fig. 1(b) gives the enlarged view of the coatings that did not peel off. Further study of the morphology of each layer reveals that growth of the first DLC layer is more distinct than that of the other DLC layers and adhesion between the first DLC layer and the next TiAlN layer is weaker, as shown in Fig. 1(b). The first DLC layer shows an apparent clustery and rough structure which is different from the fine and smooth morphology observed from the TiAlC(N) layer. The cluster size decreases in the subsequent DLC layers.
similar to TiAlC(N) and this may explain the better adhesion at the other interfaces. Considering the large columnar grain structure of the Cr/CrCx/CrC interlayer under the first DLC layer, the large DLC cluster formed during “coping profile” growth along the large columnar CrC grains in the interlayer may determine the morphology of the first DLC layer. However, the TiAlC(N) layer always shows a fine grain structure and the morphological difference may contribute to the adhesion.

The sample bias has been reported to change the morphology of DLC coatings, that is, from large grains or clusters to small ones with increasing ion energy [15]. Hence, four samples were fabricated at different biases in our experiments to control the morphology of the first DLC layer and the results are shown in Fig. 2. The TiAlN/DLC bi-layer is repeated 2.5 times for each samples to achieve an overall coating thickness of 3 μm including the Cr/CrCx/CrC interlayer with a thickness of about 1 μm. The thickness of each DLC layer is 400 nm and the TiAlN layer possesses a sandwich structure with a 140 nm thick TiAlN film infiltrated by two 130 nm graded transition layers (from TiAlC to TiAlN or TiAlN to TiAlC) on each side because of the varying deposition atmosphere to improve adhesion with the DLC layer. As expected, the large clusters in first DLC layer shown in Fig. 2(a) change to a fine and smooth morphology when the bias is changed from −50 V to −200 V. At the same time, the TiAlN layers retain the fine and smooth structure regardless of bias [16,17] and the interface between the first DLC layer and the next TiAlN layer is smooth and continuous without defects at high bias indicating an good adhesion as shown in Figs. 2(a) to 2(d).

In order to confirm the detailed chemical transition at the interface between the first DLC layer and TiAlN, the TEM and EDS are performed and the results are shown in Fig. 3. For comparison, two samples prepared with the bias of −50 V and −200 V are selected. The TEM results show that the interface between the first DLC layer and TiAlC(N) is bumpy and depends on the DLC morphology when the bias is −50 V, however, it becomes smooth and flat when the bias increases to −200 V due to the refined DLC particles. The chemical transitions (without been given in the article due to the little difference) are similar with the transition zone of about 20 nm from DLC to TiAlC(N) whatever the bias is because of the same deposition parameters of the follow layer.

To monitor the morphology evolution of the first DLC layer, samples with only the first DLC layer are prepared at different biases and the AFM images are depicted in Fig. 4. The sample prepared at −50 V has a roughness of Ra = 5.35 nm (Rq = 7.09 nm) due to the presence of clusters with a diameter of about 300 nm. With increasing bias, both the cluster size and surface roughness decrease. This phenomenon is more obvious compared to the samples deposited at −150 V (Ra = 3.74 nm, Rq = 4.93 nm) and −200 V (Ra = 3.25 nm, Rq = 4.19 nm) which are relatively flat. As the sample bias is increased, the C ion energy goes up and C mobility is enhanced [18,19] giving rise to reduced surface roughness and cluster size [20].

The scratch morphology of the TiAlN/DLC multi-layered coatings formed at different biases is presented in Fig. 5. The scratch is obtained by applying a progressively increasing normal load from 0 to 100 N at a sliding speed of 3 mm/min and loading speed of 50 N/min. Five scratches are performed for each sample and no significant difference is obtained. The one presented in this work has the critical load value closest to the average value. The four samples show critical loads of

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**Fig. 5.** Scratch morphology of the TiAlN/DLC multi-layered coatings prepared at different biases: (a) −50 V, (b) −100 V, (c) −150 V, and (d) −200 V.

**Fig. 6.** Magnified morphology of the representative scratch positions of the TiAlN/DLC multi-layer coatings prepared at different biases: (a) −50 V, (b) −100 V, (c) −150 V, and (d) −200 V.
27 N, 36 N, 55 N, and 33 N, respectively, based on when breakage first occurs, indicating improved adhesion initially with increasing bias and decreased adhesion when the bias is larger than −150 V. There are differences in the morphology of the failed regions as shown in Figs. 5(a)–5(d). As shown in Figs. 5(a) and 5(b), delamination occurs at the edge of the scratch. Although delamination continues to the end, no obvious exposed substrate can be observed from the failed locations, indicating poor adhesion at some interlamination interfaces which is even worse than that between the coating and substrate. When the bias is larger than −150 V, the coating shows peeling and the silvery surface seen at the failed locations is likely that of the HHS substrate or Cr/ CrC interlayer, indicating the interlamination adhesion is enhanced. When the bias is −200 V, significant cracking and flaking occur at a critical load of 33 N.

To determine the locations of failure on each sample, profiles are acquired by 3D confocal microscopy as shown in Fig. 6. The depth information along lines 1, 2, 3, and 4 in Fig. 6 and elemental composition at points 1, 2, 3 and 4 determined by EDS are presented in Fig. 7. The height of the step between the coating surface and flakes for lines 1 and 2 is about 1.6 μm, indicating that the fragile position is the interface between the first DLC layer and next TiAlN layer consistent with SEM (Fig. 2). However, the height of the step for lines 3 and 4 is about 3 μm corresponding to the thickness of the whole coating, indicating that failure occurs at the interface between the Cr interlayer and HSS substrate. The same conclusion can be drawn based on the composition at the scratch in Fig. 7. The main element at points 1 and 2 is carbon whereas points 3 and 4 show mainly iron. According to film growth theory, a smooth surface is suitable for ion migration and diffusion for adhesion improvement [21,22]. Owing to the rough surface of the first DLC layer, the coating peels off at this interface. As shown in Figs. 2, 3 and 4, the cluster size of the first DLC layer decreases with increasing bias resulting in improved adhesion at the interlamination interfaces. However, although the film morphology can be adjusted with the bias, the bias also affects the properties of TiAlN and DLC, especially the internal stress which can influence adhesion of multi-layered coatings [23,24]. Therefore, when the bias exceeds 150 V, adhesion becomes poor again as manifested by structural failure of all the layers.

As aforementioned, the morphology mismatch between the DLC clusters and TiAlN layer occurs at the interface above the first DLC layer and induces interlamination failure. In comparison, no failure is observed at the other interfaces. Failure at the interface above the substrate may be attributed to the stress accumulated until the end of deposition. Hence, gradually decreasing biases are applied during deposition. A −150 V bias is used for the first DLC and TiAlN layer (first modulation period) and is decreased by 10 V each during subsequent modulation periods. Finally, a 4.5 μm thick TiAlN/DLC multi-layered coatings is fabricated and the cross-sectional SEM images are shown in Fig. 8. As expected, the morphology of the first DLC layer is refined and smoothed and matches the TiAlN layer well. The transition is smooth and continuous at all the interfaces thus giving rise to excellent interfacial adhesion. The scratch morphology in Fig. 9(a) confirms excellent adhesion with a value of 63 N. The 3D profile of line 5 and composition of point 5 in Fig. 9(a) are shown in Figs. 9(b) and 9(c). The step height between the coating surface and failed position is about 4.5 μm.
corresponding to the coating thickness and the composition exposed is confirmed to be HSS. These results suggest that failure occurs at the substrate-interlayer-interface and not through delamination in between the functional DLC/TiAlN multilayers.

4. Conclusion

In an attempt to obtain hard and self-lubricating coatings, TiAlN/DLC multilayers are fabricated by FCVA and magnetron sputtering. The growth and adhesion mechanisms of the amorphous DLC layer and crystalline TiAlN layer are studied. When the bias is small, “coping profile” growth plays an important role in the DLC layers but when the bias is increased, the high atomic mobility and nucleation rate as a result of the larger ion energy refine and smooth the DLC clusters. The morphology of TiAlN layer is found to be independent of the bias and it always shows a fine and smooth structure. Adhesion failure occurs at the interfacial interface for small biases and commences at the interface above the substrate for large biases. A 4.5 μm thick TiAlN/DLC multi-layered coating with excellent adhesion (Lc = 63 N) is obtained by means of stepwise decreasing bias in order to accommodate the growth morphology and internal stress.

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