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Sandwich-zigzag structure enhanced erosion resistance of TiN coatings

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1. Introduction

In the early days of developing anti-erosion coatings fabricated by various physical vapor deposition (PVD) techniques, the hardness of protective coating was considered to dominate the erosion resistant performance. Till now, many binary nitrides and carbides, such as TiN, CrN, ZrN, WC, etc, have been focused as candidates for harsh environments [1–[4\].](#page-3-0) In particular, TiN coatings showed the great priority to suppress the erosion damage of metallic components, due to their superior mechanical properties. However, TiN coatings with high hardness are still prone to suffering from the serious erosion damages under the severe impact of solid particles, because of the strong brittleness and poor fracture toughness [5–[8\].](#page-3-0) How to design and fabricate TiN coatings with required comprehensive mechanical performance is of significant importance for aeronautical high-technology development.

In this work, we synthesized the multilayered sandwich TiN coatings by tilting magnetron sputtering source, in which the middle layer exhibited a dedicated grain boundary orientation, named with zigzag structure. Compared to the normal TiN coatings, the enhanced erosion resistance was noticed for multilayered sandwich-zigzag TiN coatings by a factor of 9. This favored the easy way to dissipate crack energy and deflect cracks on the tilted interface within the zigzag layer, and promoted for absorbing and balancing the external impact stress from erosion.

2. Experimental

TiN-zigzag coatings with the designed sandwich structure were prepared by a direct current magnetron sputtering (DCMS) technique, where the direction of the substrate was tilted angle at 45° and 135° with respect to the target normal at the deposition of zigzag layer. Single-crystalline Si (100) wafers and Ti–6Al–4 V titanium alloy were used as substrates. A rectangular Ti target with the size of 400 mm \times 100 mm \times 7 mm was applied as sputtering source. The base pressure of chamber was vacuumed less than 2.7×10^{-3} Pa. During deposition, high purity Ar and N_2 with the flow rate of 1:1 were introduced into the chamber with a working pressure of 0.4 Pa. The DC sputter current was controlled at 3 A, and a DC negative bias voltage of 300 V was applied on the substrates. The chamber was heated to 450 ◦C. Under the same deposition conditions, the normal TiN coatings were deposited for comparison. The coating thickness was controlled at about $2 \mu m$. Fig. 1 shows the schematic diagram of as-deposited TiN coatings with two kinds of structures.

The morphology and crystallographic structure of the coatings were investigated by scanning electron microscope (SEM, S4800) and grazing incidence X-ray diffraction (GIXRD, Bruker D8 Advance diffractometer). Transmission electron microscope (TEM, Talos F200x) was employed to address the microstructures of coatings. The nano-indentation (MTS NANO200) with continuous stiffness measurement method was used to measure the hardness (H) and elastic modulus (E) of coating. Adhesion

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Fig. 1. (a) Schematic diagram of the experimental arrangement, (b) the normal TiN coatings, (c) TiN-zigzag coatings.

Fig. 2. Cross-sectional morphologies: (a) the normal TiN coatings, (b) the TiN-zigzag coatings; (c) Chemical composition and (d) GIXRD patterns of the TiN coatings.

strength of the coatings with substrates was determined by scratch tests (CSM, Switzerland). The erosion tests were performed at room temperature by a home-made test rig according to the ASTM G76-13 standard [\[9\]](#page-3-0).

3. Results and discussion

Fig. 2a-b presents the cross-sectional micrographs of the normal TiN coatings and TiN-zigzag coatings. The total thicknesses of the TiN and TiN-zigzag coatings were controlled at about 2.0 μm and 1.9 μm, respectively. For the substrate tilting angle of 0° , most of the energetic particles of sputtering flux impacted the substrate surface at a normal direction. This led to the formation of a typical columnar nanocrystalline coatings, which were composed of straight elongated grains extending through the coating thickness (Fig. 2a) [\[10\]](#page-3-0). In contrast, when the incident particles were dominated on the substrate surface at an oblique direction (45◦ and 135◦), the inclined columnar crystal with zigzag-like structure was subsequently evolved in the deposited coatings (Fig. 2b). Despite the different structures, the atomic ratio of N and Ti of two kinds of coatings were both identified to be close to 1:1, according to the EDS result (Fig. 2c). Moreover, both the coatings exhibited the cubic TiN phase (PDF#87–0632) with (200) preferred orientation due to its lowest surface energy compared with other orientations which required a long diffusion distance (Fig. 2d) [\[11\],](#page-3-0) According to the modified structure zone model by A. Anders [\[12\]](#page-3-0), the high deposition temperature at 450 ◦C causes an enhanced diffusion ability of absorbed atoms, which gives rise to the formation of (200) texture. The TiN-zigzag coatings presented much higher FWHM (0.904) than that of the normal one (0.696), suggesting the smaller grain size formed in TiNzigzag coating.

Fig. 3. (a) Low-magnification TEM images of the normal TiN coatings, (b)(c) Low-magnification TEM and HRTEM micrograph images of the TiN-zigzag coatings.(d) Fast Fourier transform images.

Fig. 4. (a) Hardness, H/E and H^3/E^2 , adhesion strength, and (b) erosion rate of the TiN and TiN-zigzag coatings.

To further elucidate the structural evolution of TiN coatings, Fig. 3 shows the cross-sectional TEM and high resolution TEM (HRTEM) micrographs as well as corresponding selected-area electron diffraction (SAED). Identified from the SAED patterns in Fig. 3a-b, both TiN coatings displayed (111), (200), (220), (311) and (222) planes. However, no (111), (220) and (222) peaks were visible in XRD pattern because of its limited resolution. Furthermore, the change of growth direction within the zigzag layer failed to suppress the continuity of columnar crystal in the kink site (Fig. 3b), where the columnar crystal displayed continuous growth through the coating thickness [\[13\].](#page-3-0)This is more evident in the HRTEM micrograph (Fig. 3c-d), suggesting that no renucleation occurred when the direction of the incident flux was tailored during coating growth.

[Fig. 4a](#page-2-0) presents the hardness, H/E and H 3 /E 2 of the TiN coatings. The hardness of the normal TiN coatings was 22.3 ± 1.8 GPa, while it slightly increased to 25.6 \pm 2.1 GPa for TiN-zigzag coatings. This can be attributed to the smaller grain size of TiN-zigzag coatings compared to the normal one. It is empirically known that the value of H/E and $\mathrm{H}^3/\mathrm{E}^2$ can be assigned to the fracture toughness and the plastic deformation resistance [14,15], respectively. In particular, $\mathrm{H}^3/\mathrm{E}^2$ is considered as a key factor dominating the erosion performance of materials. Compared with the normal TiN coatings, the zigzag structure didn't change the H/E but significantly increased the H^3/E^2 from 0.525 GPa up to 0.065 GPa ([Fig. 4](#page-2-0)a). This indicated that the resistance to plastic deformation of the TiN coatings was improved greatly by introducing the tilted zigzag columnar microstructure within the coatings. Additionally, the similar adhesive strength with a critical load (Lc3) values of 42 N were found for both the normal and TiN-zigzag coatings based on the scratch tests.

[Fig. 4](#page-2-0)b shows the erosion rates of both the TiN coatings. The TiNzigzag coatings presented much lower erosion rate than that of the TiN coatings. The specific erosion rate of normal TiN coatings (0.15 \pm 0.013 mg/g) was 9 times as high as the TiN-zigzag coatings (0.017 \pm 0.004 mg/g . Generally, the monolayer metallic nitride hard coating indicates the poor erosion resistance due to the high internal stress, high brittleness and low fracture toughness, which thus leads to the rapid propagation of cracks [16]. While, the TiN-zigzag coatings exhibiting a sandwich architecture were toughened by the designed middle zigzag structure due to the effects of interfaces, which is adapted to absorb and balance external impact stress. Therefore, the erosion resistance of this sandwich TiN coatings was predominantly improved compared to the traditional TiN coatings.

4. Conclusion

The TiN coatings with sandwich zigzag structure were manipulated by DCMS. The TiN-zigzag coatings displayed a nine-fold reduction of erosion rate at 0.017 \pm 0.004 mg/g than that of normal TiN coatings at 0.15 ± 0.013 mg/g. Such significant improvement of erosion performances for TiN-zigzag coatings was mainly arisen from the dedicated grain boundary orientation in which the zigzag layer along coating thickness enhanced the plastic toughness without deteriorating their high hardness and elastic toughness. This result brings forwards a promising way to achieve excellent erosion resistance for hard coatings used in harsh sandy applications.

Author contributions

Z.Y. Wang and A.Y. Wang conceived and supervised the project; L. Wang designed and carried out the experiments under the supervision of Z.Y. Wang and A.Y. Wang; X. Zuo and L.L. Sun helped to carry out XRD and SEM measurements; R.D. Chen and P.L. Ke measured and analyzed the TEM results; L. Wang wrote the manuscript; All authors discussed the results and commented on the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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