Tribological behavior of TiAlN-coated TA19 alloy at elevated temperatures

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Abstract. TiAlN coating was deposited through the magnetron sputtering technology on the TA19 titanium alloy. The microstructure, composition, and binding force of the TiAlN coating were systematically evaluated. The friction and wear performance of coated specimens at elevated temperature were studied in detail. For elastic modulus E, the values of hardness H, H/E, and H/E² of the TiAlN coating were much higher than those of the matrix, which directly reduced the friction coefficient, wear volume, and wear rate of the TiAlN coating in high-temperature friction and wear. The friction mechanism of matrix and coating was mainly abrasive wear at room temperature. However, the coating and matrix suffered from tribo-oxidation at 300 and 500°C. In the process of friction and wear, the coating had no obvious characteristics of spalling and mechanical failure, showing good abrasive resistance at high temperature. This makes the TiAlN coating an effective high-temperature protective coating for titanium alloys.

1. Introduction

Due to high specific strength, outstanding corrosion resistance, and relatively low density [1-3], titanium alloys have been used in various kinds of aero-engine components. However, a notoriously poor wear resistance of titanium alloys largely restricts their structural applicability [4, 5]. For further stable application in aero-engine components, the wear resistance of titanium alloy should be improved by a series of specific surface treatments. Among the suitable surface treatments, cemented carbide materials can be effectively used to improve the wear resistance [6], especially the TiAlN coating prepared by the physical vapor deposition (PVD) technology, has been widely used to improve the properties of various structural materials because of their high hardness, good high-temperature oxidation resistance and wear resistance [7-9]. For example, Ti-6Al-4V alloy coated with TiAlN/TiAlSiN composite coating by the magnetron sputtering method significantly improved the cutting performance and the wear resistance of this titanium alloy [10]. Geng et al. [11] proved that patterned TiAlN coatings fabricated by a finish milling engraving machine allowed one to reduce the adhesion and wear of sliding parts of engines at high temperatures. Qi et al. [12] reported that Ti0.34Al0.66N coatings on the ceramic carbide prepared by the arc ion plating displayed significant improvements in wear resistance at elevated temperatures.

As a typical high-strength material, TA19 titanium alloy (Ti-6Al-2Sn-4Zr-2Mo-0.1Si) has been used in the compressor power-brake of aircraft engine [13-15]. However, the wear resistance of TiAlN coating deposited on TA19 alloy at high-temperature has been seldom reported. In this study, TiAlN coating was deposited on the surface of TA19 alloy by the magnetron sputtering technology. In addition,
the mechanical properties and elevated-temperature tribological behavior of the TiAlN coating were systematically studied.

2. Materials and Methods
The TA19 (Ti-6Al-2Sn-4Zr-2Mo) titanium alloy specimens with dimensions of 15 mm×15 mm×5 mm were used as the matrix in this experiment. Prior to coating deposition, specimens were abraded using the set of SiC emery paper. After that, the matrix was polished to a surface roughness of 3.3 nm. After the polishing process, samples were ultrasonically cleaned in alcohol and then dried by N2 gun. Pure Ti0.5Al0.5 (at. %) alloy was used as sputtering target and N2 was used as the reaction gas. The experimental parameters of magnetron sputtering are summarized in table 1. The in-air wear experiments were carried out and the change trend of the friction was recorded using a ball-disk friction and wear tester (HT-500, CAS, China). The friction and wear test parameters are shown in table 2.

| Parameter                              | Set value |
|----------------------------------------|-----------|
| Duration of the deposition (h)         | 3         |
| Sputtering power (V)                   | 250       |
| Operation pressure (Pa)                | 35        |
| Flow ratio of Ar and N2                | 3:4       |
| Work pressure (Pa)                     | 0.5       |
| Distance between target and substrate (mm) | 20       |

Table 2. The parameters of friction and wear.

| Temperature (℃) | Friction pair | Load (g) | Sliding speed (m/min) | Duration (min) |
|-----------------|---------------|----------|-----------------------|---------------|
| 20 ± 5          | Si3N4         | 230      | 10                    | 15            |
| 300 ± 5         |               |          |                       |               |
| 500 ± 5         |               |          |                       |               |

The phase formation was identified by the X-ray diffraction (XRD) through Cu-Kα radiation (λ=1.5418 Å, 30°≤2θ≤80°). The microstructure was examined by a scanning electron microscopy (SEM, Hitachi S4800). The average Young modulus and micro-hardness were measured by nano-indenteter (DUH-85 W201/W201S, Japan). The average roughness (Ra) of samples was examined by an atomic force microscope (AFM, FSM FM-Nanoview 6600, China). By measuring the width and depth of grinding marks, the wear volume and wear rate were calculated to evaluate the wear resistance of coatings and substrates. The surface profilometer system (UP series, RTEC Inc., USA) was used to determine the width and depth of the wear track.

3. Results and discussion
3.1. As-deposited TiAlN coating
The surface morphology, AFM image, cross-sectional morphology, EDS analysis, and XRD results for the as-deposited TiAlN coating are presented in figure 1. The prepared TiAlN coatings without obvious hole cracks are observed, which shows a well-organized, compact and uniform distribution for grains. Low average roughness (17.38nm) reflects the low occurrence of growth defects in TiAlN coating, as seen in figure 1(a). At the early stage of friction process, few abrasive particles are produced on the nano-scale roughness coating. The elemental content of the obtained TiAlN coating is shown in the inset in figure 1(a), which shows that the atomic ratio of the three elements is about 1:1:1. The above results indicate that TiAlN hard phase might be formed during reactive sputtering. The hardness, wear
resistance, and high-temperature oxidation resistance of such coatings can be improved by increasing the Al content [7, 16]. However, due to structural stability constraints, the maximum Al content of TiAl-N coating cannot exceed 65%. Otherwise, the crystal structure of TiN-based coating will change from cubic lattice to hexagonal one [17]. The SEM cross-section illustrates a dense TiAlN coating with a thickness of 5 μm, without impurities, cracks or micropores, as shown in figure 1 (c). The element composition of the coating surface is consistent with the target material. The XRD result of the obtained TiAlN coating can be observed in figure 1(e). The obvious peaks correspond well with the diffraction peaks of (Ti,Al)N, Ti₃Al₃N₂, and Ti₃AlN phase, which is consistent with the EDS results.

![Figure 1. Surface morphology with EDS result (a), AFM image (b) cross-sectional morphology (c) and line-scanning result (d), and XRD pattern (e) for the TiAlN coating.](image)

3.2. Mechanical behavior

The bonding force between the TiAlN coating and the TA19 alloy was measured by scratch test. The scratch scar and corresponding acoustic outputs of the TiAlN coating are shown in figure 2. As can be seen, the scratched surface of the coating is smooth and slightly plastically deformed, without peeling phenomenon, indicating a good toughness and a strong adhesion property. As shown in acoustic outputs, a visible critical load (Lc=53.5N) on the coated sample was initiated, when an acoustic signal was captured at the beginning of a coating failure during the scratch test. At the load of 60 N, strong acoustic emission signals appeared continuously, the coating was worn out by the probe at this moment. Therefore, the above results indicate that binding force of the TA19 alloy and the TiAlN coating is ideal [18], which guarantees good wear resistance.

Through data analysis, the hardness (H), elastic modulus (E), H/E, and H⁴/E² of the samples are shown in figure 3. H/E and H⁴/E² are key factors widely used in determining the elastic fracture limit of surface contact, which are also important judgment criteria in preventing wear caused by plastic deformation [8]. H and E values reach 12.519 and 190.834 GPa, respectively, for TiAlN coating, and 4.028 and 147.28 GPa, respectively, for TA19 alloy. The hardness of TiAlN coating is nearly three times higher than that of TA19 alloy, which might be due to the existence of fine grains and hard phases in the coating. H/E and H⁴/E² values of the TiAlN coating are 0.00656 and 0.053876 GPa, respectively, while those the substrate are 0.00273 and 0.0030129 GPa, respectively.
3.3. Friction coefficients and wear performance
The friction coefficient curves for the two samples of different temperatures are plotted as a function of the sliding time in figure 4. At 20, 300 and 500℃, the friction coefficients of all TiAlN coatings are higher than those of the substrate. In addition, the curves of untreated samples strongly fluctuated, indicating ploughing and shearing on the surface. During the wear process, many abrasive grains were easily produced on the substrate. These abrasives were easy to be embedded in the matrix under the loading force, which would produce more severe wear in the process of wear. Although some abrasive particles could also be produced on the surface of the coating, the abrasive particles were not easily embedded in the coating under load due to the high hardness of the coating. Therefore, the rough particles on the coating surface were worn off and the friction coefficient became stable. According to figure 4(d), with the increased temperature, the friction coefficient of the substrate increased considerably, while that of the TiAlN coatings slightly changed. The average friction coefficients of substrates and coatings were 0.5, 0.72, 0.89 and 0.2, 0.25 and 0.29, respectively.

For measuring the wear resistance, the wear volume and wear rate were derived as follows [19-20]:

\[ V = \frac{2\pi hr}{6b} (3h^2 + 4b^2) \]  

(1)

\[ K = \frac{V}{SP} \]  

(2)

where \( V \) is wear volume, \( b \) is the width of wear mark, \( h \) is the depth of wear area, \( r \) is radius of wear area, \( S \) is sliding distance, \( K \) is the specific wear rate, and \( P \) is the applied load.
Figure 4. Friction coefficient curves of TA19 alloy and TiAlN coating at different temperatures.

The volume loss and specific wear rate of both TA19 alloy and TiAlN coated samples are shown in Table 3. The results show that the wear volume and wear rate of the coating were significantly reduced by tens of times compared with that of the uncoated specimens under different conditions. The experimental results show that the wear rate of the coating is lower than that of some other similar coatings, indicating the superiority of the coating [21-22].

Table 3. The wear results of the TiAlN coating and TA19 at 20, 300, and 500°C.

| Temperature (℃) | Specimen | Depth h(μm) | Width b(mm) | Volume loss V(mm³) | Specific wear rate K(10⁻⁵·mm⁴·N⁻¹·m⁻¹) |
|-----------------|----------|-------------|-------------|-------------------|--------------------------------------|
| 20              | TA19     | 17.00       | 0.949       | 0.1351            | 39.959                               |
|                 | coating  | 0.96        | 0.255       | 0.0021            | 0.609                                |
| 300             | TA19     | 20.17       | 1.081       | 0.1826            | 54.008                               |
|                 | coating  | 1.30        | 0.358       | 0.0039            | 1.151                                |
| 500             | TA19     | 36.76       | 0.877       | 0.2703            | 79.995                               |
|                 | coating  | 1.59        | 0.380       | 0.0050            | 1.487                                |

3.3.1. Wear analysis at 20°C. Figure 5 shows the SEM morphologies and profilometries of wear tracks at 20°C. Compared with the uncoated specimen, the wear scar of the surface of the TiAlN were smoother and shallower than those of the uncoated sample. As shown in figure 6, SEM micrographs indicate the characteristics of serious grooves, which was the main phenomena of degradation of TA19 alloy. Particle fragments remained on the worn surface became abrasive particles, which could lead to more severe sliding wear. The wear mechanism of TA19 alloy was abrasion and adhesion wear. The large amount of Ti on the substrate (area 1) proved that the particles mainly come from the spalling of the TA19 substrate during the abrasion process. However, the wear mark of the TiAlN coating was very smooth and without visible debris and signs of mechanical damage. Most of the wear surface of the TAIN coated sample appeared to be relatively uncharacteristic. Moreover, the low content of oxygen indicated that there was almost no oxidation wear on the coating and matrix at 20°C (area 1, area 2).
3.3.2. Wear analysis at 300°C. The SEM analysis results and profilometries of wear tracks at 300°C are exhibited in figure 7. The width and depth of the wear track slightly increased with temperature. As seen in figure 8, similar to 20°C, the wear morphology of the matrix presented parallel furrows and lots of debris at 300 ℃. The wear surface of the coating exhibited a smooth appearance with little material removal. With the temperature increased to 300 ℃, the hardness of TiAlN decreased, and some scratches appeared on the surface. However, the coating still showed high abrasion resistance [23]. Different results on EDS can be attributed to the different oxygen content, which indicates that both the coating and substrate suffered from tribo-oxidation.
3.3.3. Wear analysis at 500°C. SEM results and profilometries of wear tracks at 500°C are exhibited in figure 9. Compared with 20°C and 300°C, the wear scar depth and the wear rate of the substrate were greatly increased at 500°C, while the wear rate of the coating was increased slightly. During high-temperature wear process, TA19 alloy was easily oxidized into a mixture of brittle titanium oxides, as shown in figure 10 (a) in white debris (O content up to 47.52 % at. %). Under the pressure of friction pairs, the oxide films were prone to crack fatigue. As the sliding continued, the oxide film gradually broke down and the oxide slipped to produce material removal. On the other hand, due to the high $H/E^2$ ratio, there is no obvious decrease in ploughing furrow and mechanical properties of TiAlN coating during high-temperature wear, which indicates a better wear resistance.

![Figure 9. SEM micrographs and profilometries of the wear tracks at 500°C.](image)

(a) TA19 alloy; (b) TiAlN coating; (c) profilometry of the wear scar.

4. Conclusion
The TiAlN wear-resistant coating with a thickness of 5 μm was successfully deposited on the TA19 titanium alloy. The analysis of TiAlN coating microstructure and composition proved that it was compact, without obvious defects. The critical load $L_c$ of TiAlN coating and matrix was 53.5 N, which indicated that the adhesion was ideal. XRD analysis showed that the coating was mainly composed of (Ti,Al)N, Ti$_3$Al$_3$N$_2$ and Ti$_2$AlN hard phases. The values of $H$, $H/E$ and $H/E^2$ of the TiAlN coating were much higher than those of the matrix, which directly led to the decrease of friction coefficient, wear volume, and wear rate of the TiAlN coating in high-temperature friction and wear. The friction mechanism of matrix and coating was mainly abrasive wear at room temperature. However, the coating and matrix suffered from tribo-oxidation at 300 and 500°C. In the process of friction and wear, the coating had no obvious characteristics of spalling and mechanical failure, showing good abrasive resistance at high temperature.

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