Wear Performance of Ti/Al Composite Coating Based on Magnetron Sputtering

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Abstract: In order to study the wear performance of Ti/Al coating under different loads, split-target magnetron sputtering device was used to prepare a Ti/Al composite coating on the surface of 304 stainless steel, the friction and wear test of the coating with 3.5%NaCl treatment was carried out. Scanning electron microscope (SEM), scratching instrument, EDS, three-dimensional surface topography instrument and other equipment were used to investigate the physical and chemical properties of the coating. During magnetron sputtering coating, Ti and Al atoms are stacked to form a Ti-Al binary phase, and TiAl3 intermetallic compounds are enriched in the coating. The wear experiment shows that the wear rate of the Ti/Al coating is significantly lower than that of the substrate, moreover, the wear rate increases uniformly with the load. The friction coefficient of the Ti/Al coating is lower than the friction coefficient of substrate in the table wear stage under different loads. The friction coefficient of the coating decreases as the load increases. At low loads, the coating main form of wear is the surface abrasive wear with furrows. With increasing the load, the coating wear form is mainly represented that the reduction of abrasive wear and the generation of micro-cracks on the surface, which in turn produces scaly flaking.

1. Introduction
Ti and titanium alloys have the advantages of high specific strength, good corrosion resistance, high heat resistance, good mechanical properties at low temperature, and non-magnetic properties. However, due to the weak resistance to high-temperature oxidation, Ti and titanium alloys are prone to high-temperature embrittlement in high-temperature environments, which reduces their toughness and hardness, which severely limits the development of titanium industry technology [1]. In the friction and wear gaps of aviation ship fasteners, local high temperature is easily generated due to self-friction and air friction. The study found that Al element is the best element of oxygen-philic element, it can generate aluminum oxide film at high temperature, and the Ti-Al phase is a typical ordered binary phase, with high melting point, low density, good oxidation resistance and other advantages, which will protect the substrate well [2]. Fan [3] used Mechanical alloying to produce a dense Ti/Al coating with excellent anti-wear properties. A large number of studies have reported the oxidation resistance of...
titanium-based alloys, including aluminide coatings and ceramics. Ti/Al coating is a modified aluminide coating that can form protective Al2O3, so it has been widely used as an anti-oxidation coating, and due to its excellent anti-wear performance, it has excellent performance in corrosion and wear. Zhang [4] changed the rolling temperature of multilayer Ti/Al to conduct tensile experiments, and found that the main fractures of multilayer Ti/Al alloy were shear toughness fracture, delamination fracture and crack fracture. Liu [5] prepared the intermetallic compound TiAl3 reinforced Al-based composite coating on the surface of ZL117 aluminum piston parts by laser cladding. The prepared coating has high strength and poor plasticity, and crack expansion occurred in the friction and wear experiment. Shahzad, A [6] used a vibrating ball mill to synthesize the Ti/Al intermetallic compound, and then used laser heat treatment, which changed the problem of its coating surface roughness. X.T.Lib [7] used hot infiltration and heat treatment processes to prepare a dense network structure of Ti/Al silicon coating on TiB/Ti6Al4V composite material, and found its excellent shielding and high temperature oxidation resistance. More scholars are engaged in the comprehensive modification of the surface of Ti/Al coatings. Common addition items for Ti/Al coating include N [8], V [9], Mg/Si [10], Cu [11] etc. Duan [2] deposited an Al coating on the Ti surface and performed laser cladding, so that the coating performed excellent oxidation resistance under the action of Ti/Al metal compounds.

This paper mainly uses magnetron sputtering technology to prepare Ti/Al composite coating on the surface of 304 stainless steel. And through friction and wear test, artificial seawater immersion friction and wear test, scratch test, etc. to explore the evaluation of Ti/Al composite coating friction and wear performance.

2. Experimental and coating preparation
The deposited Ti/Al composite coating adopts a Ti target (99.99%) and an Al target (99.99%). Before the experiment, the substrate was washed with deionized water and absolute ethanol for 20 minutes, and deionized fan was used for drying. The TGP-500 magnetron sputtering equipment was used for the coating experiment. The Ti target and Al target were sputtered with radio frequency power. The specific parameters are shown in Table 1 below. During sputtering, the temperature of the cavity is increased due to ion ionization. The temperature of the chamber after the completion of sputtering is 210°C. The pressure in the cavity is taken out for 8 hours, and the temperature decreased to 50°C when the coating was taken out.

| Project parameter | time (min) | Power(Ti) (W) | Power(Al) (W) | Pre-pumping gas pressure (Pa) | working gas pressure (Pa) | Temperature (°C) | Hold time (H) | Argon flow (sccm) |
|-------------------|-----------|--------------|--------------|-------------------------------|--------------------------|-----------------|-------------|-----------------|
|                  | 60        | 196          | 200          | 2*10-3                        | 0.5                      | 150             | 8            | 30              |

The friction and wear test was carried out at room temperature using the MFT-4000 friction and wear test machine. The friction pair is a 6mm diameter SiC ball, the wear speed is 200mm/min, the wear time is 100min, and sliding distance is 5mm. The S4800 scanning electron microscope (SEM) was used to observe the microscopic surface characteristics of the coating before and after the wear. The EDS instrument was used to analyze the chemical characteristics of the coating surface. Bruker's Contour Elite K three-dimensional surface profilometer was used to measure the shape and depth of friction and wear of the sample, and statistically analyze the friction depth. The X'Pert PRO MPD type XRD was used to qualitatively analyze the composition of the coating, and the Jade software was used to quantitatively test and calculate the coating elements.

3. Result and Discussion
3.1 Coating structure
Figure. 1 shows the morphology and the cross-sectional morphology of the coating that was analyzed...
by SEM. The surface of the coating fabricated by RF magnetron sputtering technology is flat, the overall coating surface is uniform, and no obvious protrusions appear. The surface density of the magnetron sputtering coating is more excellent than the previous Ti/Al coatings using ball milling process, laser cladding and other preparation processes [5, 6]. The thickness of the coating is about 3.17 μm.

Figure 2 is the EDS image of the coating. There are obvious Ti and Al peaks in the figure. The Ti and Al contents are 56.9% and 36.24% respectively. According to the area of the Ti and Al atoms in figure 2, the Al peak and Ti peak ratio in the coating is close to 3:1. The molar ratio is close to 1:3, so it can be speculated that TiAl3 may be present in the coating [12]. Many studies have shown that the presence of TiAl3 compound can greatly improve the wear resistance and increase the hardness of the coating [13]. Relevant scholars have also used Ti:Al molar ratio of 1:3 to prepare coatings rich in Ti-Al compounds, and found that the activation energy of Ti-Al compounds is: Ti3Al> TiAl2 > TiAl > TiAl3 [13]. Therefore, this paper suggests that a large amount of TiAl3 compound in the coating.

Figure 3 shows the XRD analysis of the coating. It can be seen from the figure that there are abundant AlTi3, AlTi, Al2O3, Al1+xTi1-x, Al3Ti. Magnetron sputtering, as an ion coating technology, ionizes the metal in the chamber to react to form a variety of compounds. Compared with the traditional heat infiltration method and laser cladding method, its operating temperature is higher and the coating performance is stable. It can greatly reduce the bubbles in the coating produced by the laser cladding coating and mechanical alloy manufacturing method, and due to the later thermal insulation effect, the residual stress inside the coating can be reduced. The existence of Al2O3 in the coating is mainly due to the passivation of the Al element of the coating at room temperature. According to the activation energy sequence of metal compounds mentioned above [13], this article speculates that the coating is rich in TiAl3 phase, and the micro-hardness of TiAl3 can reach 11.17 GPa [12]. Using Jade software to calculate the grain size of 27.5nm, fine grains is another important reason for excellent coating performance [14].
3.2 Analysis of Friction and Wear Performance of Coating

Figure 4(a) shows the friction coefficients of the 304 stainless steel. As shown in the figure, the friction coefficient of the 304 stainless steel substrate increases with the time during the first 20 minutes under the load of 2N, and the friction coefficient between the 304 stainless steel and the friction ball pair gradually increase after 20 minutes. The friction coefficient has a small effect, which may attribute to the relatively dense oxide film was produced by the 304 stainless steel in the air medium. The overall wear under load of 2N is the wear of the oxide film on the surface of 304 stainless steel [15]. At the later stage of friction loss, the behavior of friction coefficient during stable wear is positively correlated with load.

As shown in Fig. 4(b), in the initial wear phase of the Ti/Al coating, the friction coefficient increases as the load increases, and the amplitude of the friction coefficient also increases as the load increases. At the beginning of the wear, friction coefficient of the loading force of 10N is high; in the first four minutes and under the load of 20N, the average friction coefficient is the highest. As the wear time increases, the friction coefficient tends to be stable at 16 minutes, and at about 25 minutes, the friction coefficient began to jump obviously, and with the increase of the load, the behavior of the friction coefficient tends to be a nonlinear relationship. The overall friction coefficient curve under different loads has different degrees of increasing, moreover, the friction coefficient lines of 10N and 20N increase faster, and the friction coefficient with a loading force of 5N is the most volatile. In the later stage of stable wear, the overall friction coefficient and load tend to be negatively correlated. At 2N, due to the enrichment of aluminum in the coating, an oxide film is formed on the surface of the coating. Its wear form is mainly the removal of the surface oxide film, the formation of abrasive particles, and the formation of furrows on the surface. At 5N, the friction pair begins to enter the coating. Due to the mechanical extrusion stress, micro cracks are generated on the surface. The wear is mainly manifested by the reduction of the furrow phenomenon on the coating surface, the generation of micro cracks and the movement of the coating cracked plates. With the peeling of the coated microchip, it sticks to the friction pair and begins to form a shear slip film. In the later stage of stable wear, the friction coefficient of the coating is low at 10N and 20N, and the friction coefficient of the coating is stable, which is about 0.25. The wear form of the coating is further reduced with the increase of the load, meanwhile, the shear of the coating appears. The shear slip phenomenon is more prominent with the increase of the load, so a negative correlation of friction coefficient changes occurs in the late stage of coating wear. This kind of research on the negative correlation of friction coefficient also appears in MoS2 and other materials. The initial friction coefficient of the coating is higher than that of the 304 stainless steel substrate, and the coating overall friction coefficient is lower than the 304 substrate. The main reason for lower friction coefficient under larger load may attribute to
the cracks in the coating. Due to the effect of plastic cutting and bonding, the coating produces a lot of flaky abrasive debris, the abrasive debris is not discharged in time, and intermittent slippage occurs at the wear interface transfer, and forms a transfer film mechanism.

As shown in Figure. 4(c). At the initial stage of friction test, the sample that was treated with 3.5%NaCl shows a positive correlation with the increase of the load. This may due to the initial friction of the cutting increases with the increase of the load. The coating sample which treated by 3.5%NaCl has the lowest friction coefficient under 2N. At 5N, 10N, and 20N, there is no obvious relationship between the friction coefficient and the load change. Specifically, the friction coefficient trend is 10N>5N>20N. This may attribute to the accumulation of corrosion products and oxide films on the coating surface at 2N. After treatment with 3.5%NaCl, there are many Cl⁻, Mg⁺, and NaCl microcrystals on the surface of the coating. Due to grinding, these crystals have some particles; the diameter of these particles can reach the nanometer level, which plays a role of solid lubrication when the wear does not reach the coating body. At 2N, the first run-in between the coating and the friction pair is completed, and the initial wear is essentially the coating surface “Impurities” wear. The friction coefficient changes at 5N, 10N, and 20N are also similar to the transfer film phenomenon due to the generation of shear slip film. Regardless of the deionized water or artificial seawater treatment, the friction coefficient in the late wear stage at 20N load is smaller than that at dry friction.

The 3D surface profiler grinding profile and depth are used for statistics. As shown in Figure. 5, the depth and the microstructure statistics of the worn surface are shown. As the load increases, the average width of all matrix wear scars decreases and the depth of wear increases. When the loading force is 2N, the 304 stainless steel (Sample 1) has obvious wear marks. The wear marks of the Ti/Al coating (sample 2) and the Ti/Al coating after 3.5%NaCl treatment (sample 3) are relatively shallow. As the load increases, the four samples all show different degrees of plastic deformation.

As shown in Figure. 6, when the load is 2N, the creep appeared on the surface of the coating, and the migration of the material was in the form of flake-like migration. It can be seen that the initial wear form of the coating is two-body wear, over time, the wear debris of the layer is mixed into the wear
interface which forms three-body wear, meanwhile, a little crack was appeared in the coating; Under 5N, the coating shows initiation of cracks, and a lot of layered cracking failures occurred. The development and cracking of the coating cracks can be seen under this load, the form of coating failures are fatigue wear and fatigue cracks. The unevenness of the crack and the plastic migration of the coating cause the crack to rupture, resulting in scale peeling failure. And this figure clearly shows the transition process of the coating from crack to scale; Under 10N, the coating has uneven material migration, and it can be seen that there are many "hills" in the wear scars. These hills may cause the friction coefficient to increase. The figure also shows that the main form of the coating is a layered structure, which is often accompanied by the initiation of cracks at the beginning of the failure, but the coating does not show pitting; Under 20N, the peeling of the coating is more serious, which is mainly reflected in the large-scale peeling of the coating, and the substrate is beginning to be exposed. Throwing in the flaking flakes is accompanied by the generation of cracks. At this time, the protective effect of the coating slowly decreases, which shows that the main failure modes of the coating under large loads are brittle cracks and large-scale spalling. The whole coating wear process is accompanied by the furrow phenomenon, which decreases with the increase of load.

Fig. 7, it is a comparison graph of the wear depth curve of 304 stainless steel, Ti/Al coating and Ti/Al coating treated by 3.5% NaCl solution. The maximum wear depth loss of the 304 stainless steel after 100min and under 20N is -2.897μm, and the Ti/Al coating is -2.360μm. The Ti/Al coating that was treated by 3.5% NaCl solution gradually increased with increasing load, and the deepest part of the wear scar was -2.497μm. Both the coating and the substrate showed a positive correlation when the load increased. Moreover, all the coatings showed a more uniform wear depth curve, indicating that the Ti/Al coating showed stronger regularity with the load, the change in wear depth was more uniform, and the wear was more stable. The comparison shows that the wear resistance of the fabricated coating is better than that of 304 stainless steel substrate.

4. Conclusion
1. Due to the excellent characteristics of Ti and the oxygen-philic characteristics of Al element, the dry friction of the coating in the air reduces the oxidative embrittlement of titanium. The presence of
Al element seizes the impurity oxygen in coating, and the hardness phase TiAl$_3$ exists in the coating. Therefore, it shows good anti-wear performance, and the overall depth of wear is relatively low.

2. The coating has tiny cracks at lower loads. As the load gradually increases, the cracks of the coating continue to expand. Finally, the main failure mode of the coating is scale peeling caused by fatigue cracks.

3. With the increase of the load, the cracks of the coating gradually expanded and gradually formed a sheet-like failure mode. Furthermore, the cutting failure of the coating became smaller and smaller, which showed the decrease of the furrow phenomenon.

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