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ARTICLE

Dry Sliding Wear Behavior of Hot-Dip Aluminized Ti-6Al-4V Alloy Against GCr15 Steel

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Abstract: An aluminized coating of $TiAl_3$ was prepared on Ti-6Al-4V alloy by hot-dip aluminizing (HDA) and subsequent high-temperature diffusion at 650 °C. Dry sliding wear behavior for the aluminized Ti-6Al-4V alloy against GCr15 steel was investigated by a pin-on-disc wear tester. The morphology, phase and composition of worn surface of the HDA coatings were characterized by SEM, XRD, EDS and XPS. The wear mechanism was also explored. The result demonstrates that with an increase of sliding velocity, the wear loss of the aluminized Ti-6Al-4V alloy decreases to a lower value at 0.75 m/s, then increases to the highest value at 2.68 m/s, and finally decreases to the lowest at 4 m/s. At different sliding velocities, the wear loss increases with the increase of load. Tribo-layers notably affect the wear behavior and mechanism. At 4 m/s, oxide-containing tribo-layers (TiO and TiO_2) possess an obvious wear-reduced function; conversely, at 2.68 m/s, no-oxide layers show no protection from wear. Compared with uncoated Ti-6Al-4V alloy, the aluminized coating improves the wear resistance of the titanium alloy under various conditions, especially 4 m/s. The improved wear performance is attributed to Ti-Al coating and tribo-oxide layer.

Key words: aluminized Ti-6Al-4V alloy; sliding wear; wear behavior; tribo-layer; wear mechanism

Titanium alloys are widely used in aerospace, seawater desalination, automobile and other fields because of their high specific strength, low density, and excellent corrosion resistance[1-4]. However, Ti-6Al-4V alloy is considered to possess very poor wear resistance like other titanium alloys, which greatly restricts its application under wear conditions[5,6]. $TiAl_3$ is the only one of Ti-Al intermetallic compounds that form protective oxides in air, and its hardness is so higher that it can improve wear resistance and oxidation resistance of titanium alloys. It is well known that many methods can be used to prepare the coatings, such as pack boronizing, laser cladding and hot dip aluminizing. Compared with other routes, hot dip aluminizing is considered to be a competitive method owing to its low cost, simple operation and thick coating so it has aroused great attention by numerous researchers in recent years[7-11]. At the present time, more research on the hot dip aluminizing of steel is conducted. But the study on the wear behavior of aluminized titanium alloys as a function velocity is sparsely reported.

In the present research, the aluminized coating of $TiAl_3$ was prepared on Ti-6V-4V alloy through hot-dip aluminizing, and subsequently diffusion-annealed at 650 °C. Dry sliding wear tests were conducted for an aluminized Ti-6Al-4V alloy against GCr15 steel at 0.5~4 m/s. The wear behavior and wear resistance of aluminized Ti-6Al-4V alloy were studied, compared with uncoated Ti-6Al-4V alloy under various conditions. The wear mechanisms of aluminized Ti-6V-4V alloy were also explored.

1 Experiment

A commercially available Ti-6Al-4V alloy (wt%, Ti-6.3Al-4.0V) as the substrate was machined into a pie-shaped specimen with a dimension of Φ30 mm×23 mm. The surface of the substrate was polished (R_a=0.38 μm) and ultrasonically cleaned in acetone, and then dried in air. The pretreated Ti-6Al-4V alloy was immerged into a molten high pure

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aluminum (Al≥99.99 wt%) at 760 °C for 15 min, then taken out at a modest speed and cooled in air. Subsequently, a diffusion annealing treatment for the encased Ti-6Al-4V alloy was carried out in a GSL-1300X high temperature tube furnace at 650 °C for 0.5 h to achieve an aluminized coating. $TiAl_3$ was identified by XRD as the main phase of the aluminized coating, as shown in Fig.1a. The cross-section morphology of the aluminized coating is illustrated in Fig.1b.

Dry sliding wear tests were carried out in air using an MPX-2000 type pin-on-disc wear tester. The aluminized and uncoated Ti-6Al-4V alloys were machined into Φ5 mm×23 mm pin specimens. Commercial GCr15 steel (wt%, Fe-1.02C-1.55Cr) was selected as the mating material and machined into Φ40 mm × 10 mm disk specimens. It was austenitized at 850 °C, then oil quenched, and finally tempered at 400 °C for 2 h to achieve a hardness of 50 HRC. The sliding conditions were as follows: 0.5, 0.75, 1.5, 2.68 and 4 m/s for the sliding velocity; 10~50 N with an interval of 20 N for the normal load; room temperature at 23~28 °C for the experimental temperature; 840 m for the sliding distance. The wear losses of pins were achieved through measuring mass loss before and after tests by an electronic balance with an accuracy of 0.01 mg. The mean value of the three tests was provided as the experimental result. Scanning electron microscopy (JSM-7001F SEM), energy dispersive spectroscopy (Inca Energy 350 EDS), and X-ray diffractometer (D/Max-2500/pc XRD) were used to investigate the morphology, composition, phase

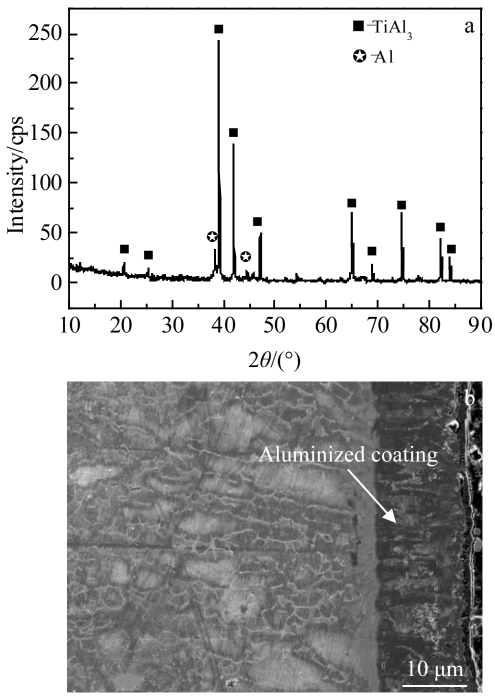

Fig.1 XRD pattern (a) and cross-section morphology (b) of the aluminized coating on Ti-6Al-4V alloy

of the aluminized coating and worn surfaces, respectively. Trace oxides formed on worn surfaces were further identified by X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD XPS). The microhardness of the aluminized coating and worn subsurface was measured by a digital microhardness tester (HVS-1000 type) with a load of 0.49 N and a holding time of 15 s. The hardness of the steel after heat treatment was determined by an HR-150A type Rockwell apparatus.

2 Results and Discussion

2.1 Wear behavior of aluminized and uncoated Ti-6Al-4V alloy

The wear loss of the aluminized Ti-6Al-4V alloy as a function of sliding velocity and load is shown in Fig.2a. The wear loss of the aluminized Ti-6Al-4V alloy increases with the load under various velocities, and a sharper increase occurs at 2.68 m/s. With an increase of sliding velocity, the wear loss firstly decreases until a turning point of 0.75 m/s, then increases slowly at 0.75~1.5 m/s and increases rapidly at 1.5~2.68 m/s. It reaches the top value at 2.68 m/s, then decreases and finally reaches the lowest value at 4 m/s.

The comparison between the wear loss of the aluminized and uncoated Ti-6Al-4V alloy is shown in Fig.2b~2d. It is obvious that the aluminized and uncoated Ti-6Al-4V alloy almost present the same variation regularity in wear loss with the increase of sliding velocity under various loads. This is similar to Li's research results on the wear behavior of Ti-6Al-4V alloy[12]. Clearly, the aluminized Ti-6Al-4V presents absolutely lower wear loss than uncoated Ti-6Al-4V alloy at different sliding velocities, no matter what the applied load is. This means that the aluminized coating sub- stantially improves the wear resistance of the Ti-6Al-4V alloy. At higher velocity and load, in particular, the aluminized coating presents more remarkable decrease of wear loss. It can be suggested that the aluminized coating can protect Ti-6Al-4V alloy from wear.

2.2 XRD analysis and morphology of worn surfaces

XRD patterns of worn surfaces for the aluminized Ti-6Al-4V alloy sliding under 10 and 50 N at 0.75, 2.68, and 4 m/s are shown in Fig.3. At 0.75 m/s, it can be noticed that the $TiAl_3$ coating disappears, but Ti and TiO appear on the worn surfaces; the oxide amount seems to increase slightly with the increase of load (Fig.3a). This means that at 0.75 m/s, the $TiAl_3$ coating is not strong and totally delaminated after sliding 840 m. Clearly, at 4 m/s, more TiO and TiO_2 appear and the oxide amount increases with the increase of load. In this case, a small amount of $TiAl_3$ was identified on the worn surface under 50 N (Fig.3c). This demonstrates that at 4 m/s, the $TiAl_3$ coating becomes strong and partly delaminated after sliding 840 m. Oppositely, at 2.68 m/s, trace of TiO appears under 10 N, but no oxide remains under 50 N on the worn surfaces (Fig.3b). Similarly, the $TiAl_3$ coating is not strong and totally delaminated after sliding. It is clear that tribo-

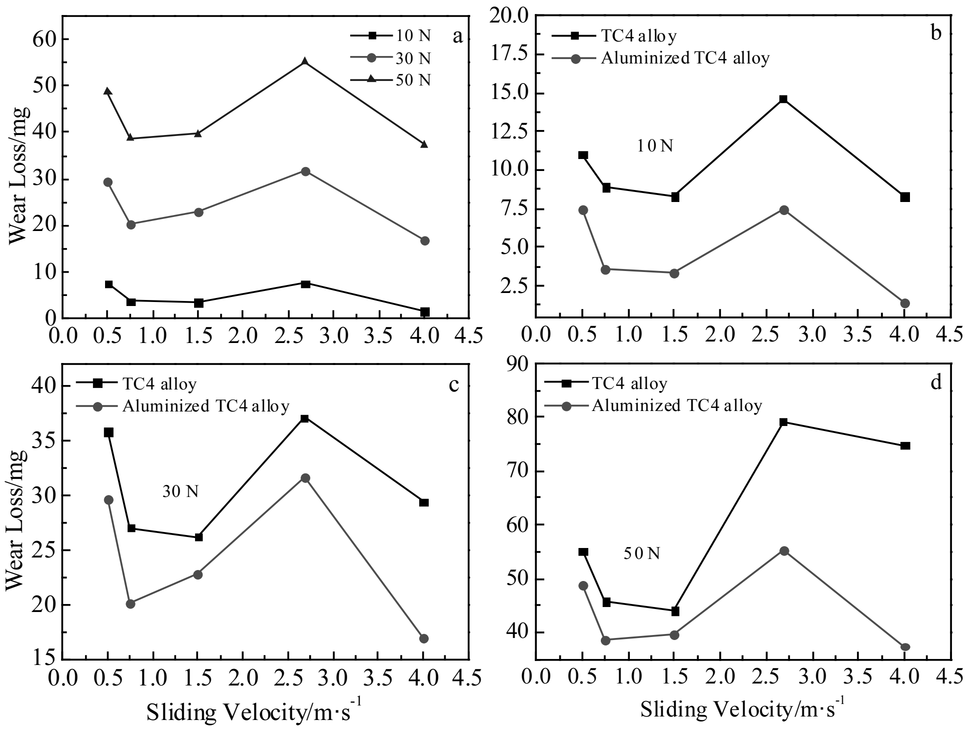

Fig.2 Wear losses of aluminized Ti-6Al-4V alloy (a) and wear loss comparison (b~d) between the aluminized and uncoated Ti-6Al-4V alloys

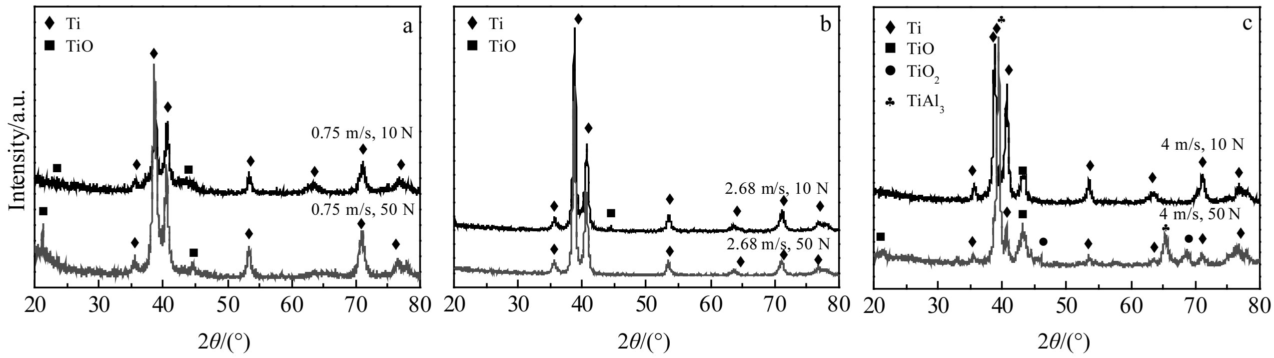

Fig.3 XRD patterns of worn surfaces of aluminized Ti-6Al-4V alloy sliding under various conditions: (a) 0.75 m/s, (b) 2.68 m/s, and (c) 4 m/s

oxidation occurs during sliding. XRD patterns of worn surfaces present the formation and delamination of tribo-oxides under various sliding conditions. It is well known that the existence of tribo-oxides affects the wear behavior and even wear mechanism. More importantly, the amount of tribo-oxides as a function of load tends to unchange and the tribo-oxides show a delamination.

Morphologies of worn surfaces for the aluminized Ti-6Al-4V alloy are shown in Fig.4. As shown in Fig.4a and 4b, a composite pattern containing adhesive and tribo-oxide vestiges at 0.75 m/s is presented. However, at 2.68 m/s, tribo-oxide vestiges totally disappear. The worn surfaces reveal many furrows and deeper delamination places. This appears to be resulted from the plowed marks and the delamination of matrix (Fig.4c and 4d). While at 4 m/s, the worn surfaces of the aluminized coating present totally different morphologies compared at 2.68 m/s. It was observed that compacted tribo-layers and shallower delaminated regions appear on worn surfaces (Fig.4e and 4f).

2.3 Cross-section analysis of worn surface and sub-surface

Fig.5 shows the cross-section morphologies of worn sub-surfaces of the aluminized Ti-6Al-4V alloy. Regardless of velocities, more or less tribo-layers invariably exist on the worn surfaces. At 0.75 m/s, the tribo-layer seems to be uncompacted with a thick plastically deformed layer. But as the load increases to 50 N, it becomes more compacted with a thinner plastically deformed layer (Fig.5a and 5b). At 2.68 m/s,

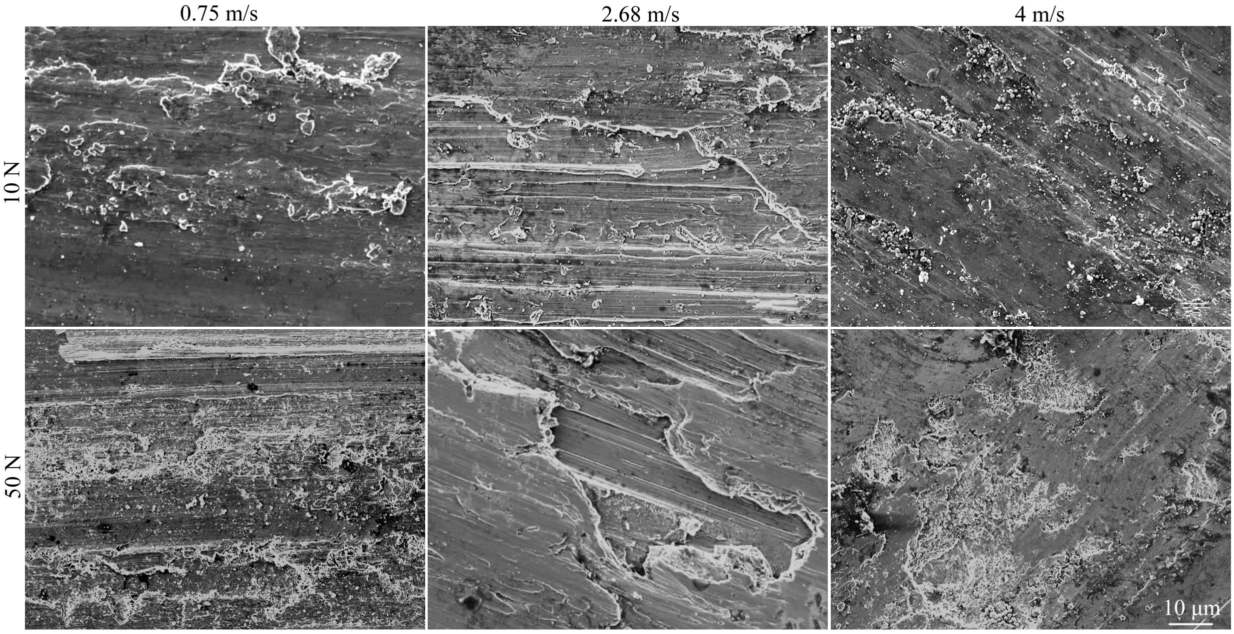

Fig.4 Morphologies of worn surfaces of the aluminized Ti-6Al-4V under 10 and 50 N at different sliding velocities

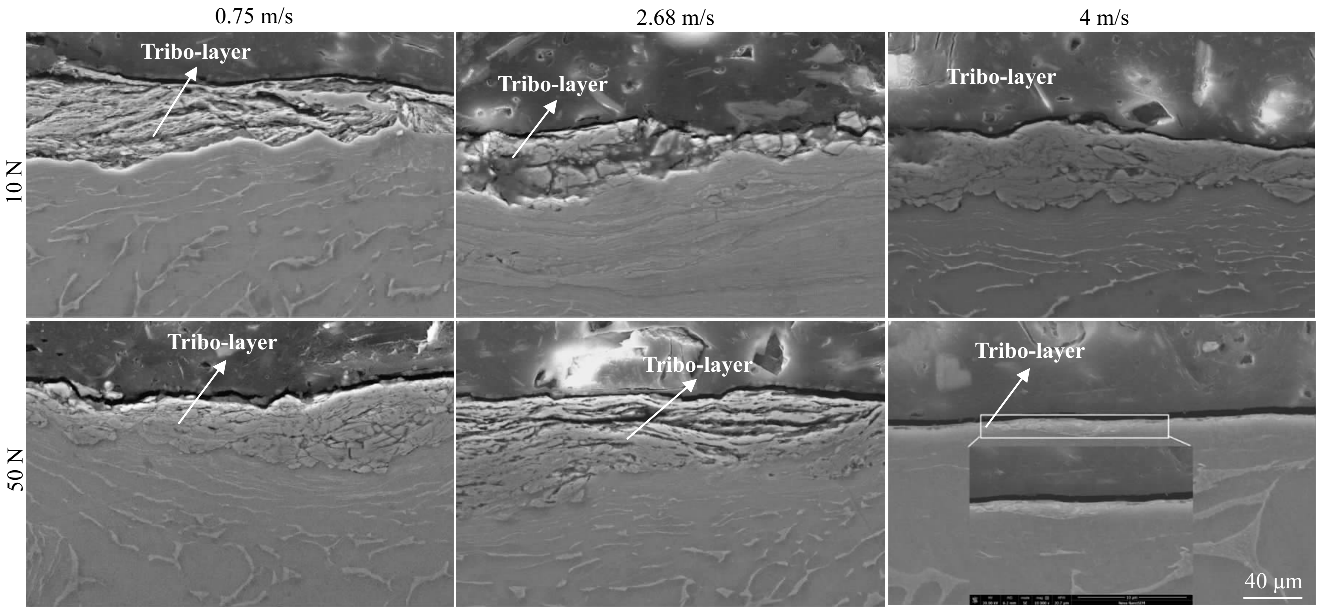

Fig.5 Cross-section morphologies of worn surfaces of the aluminized Ti-6Al-4V under 10 and 50 N at different sliding velocities

there is a discontinuous tribo-layer and a thicker plastically deformed layer (Fig.5c and 5d). On the contrary, at 4 m/s, compact and continuous tribo-layers appear to possess a higher load-bearing capability. In this case, the plastic deformation region becomes smaller, and even disappears under 50 N (Fig.5e and 5f).

2.4 Discussion

Rigney[13] pointed out that the sliding wear of metal alloys can be described by the evolution of the following phenomena: surface and subsurface plastic deformation, formation of debris and material transfer, reaction with the environment and mechanical mixing, and the formation of a mechanically mixed layer (MML) on worn surfaces. It was observed from the cross-section morphology of worn surfaces that tribo-layers always exist, as shown in Fig.5. The tribo-layers consist of wear debris from the sliding pin and counterface metal resulted from transfer as well as their reaction products with oxygen. It is clear that they are mechanically mixed layers (MML) from identifiable particles or composition of tribo-layers. Pauschitz et al[14] divided the tribo-layers into transfer layer, mechanically mixed layer (MML) and composite layer. They pointed out that mechanically mixed layer (MML) has an effect on reducing wear. However, whether the tribo-layer has an influence on wear behavior and wear mechanism depends on the characteristics of tribo-layers, which are determined by their formation processes under different sliding conditions[12].

According to wear rate and XRD analysis of worn surface, aluminized Ti-6Al-4V alloy presents a lower wear loss than uncoated Ti-6Al-4V alloy and has almost no $TiAl_3$ on worn surfaces. This means that aluminized Ti-6Al-4V alloy should possess a slightly better wear resistance than untreated ones at lower velocities because of the function of $TiAl_3$ intermetallic compounds. However, at high velocity, the $TiAl_3$ coating possessed a better wear resistance and still remained after wear, as shown in Fig.3c. Because of the brittleness of the $TiAl_3$ intermetallic compounds at room temperature, it was gradually consumed by brittle delamination during sliding, although the brittleness of the $TiAl_3$ intermetallic compounds would be slightly ameliorated with an increase of velocities. Thus, tribo-layers indeed play a key role in improving wear resistance of aluminized Ti-6Al-4V alloy, regardless of the existence and inexistence of the intermetallic coating.

The characteristics of the tribo-layer are summarized in Table 1. Continuously increased velocity made tribo-layers contain more oxides and possess higher hardness, thus reducing wear loss obviously. Moreover, with the increase of sliding velocity, a higher temperature on the worn surface made the tribo-layer to be readily compacted; thereby its protective function would be benefited. However, on the other side, a higher temperature on the worn surface would cause the thermal softening of the worn matrix, presenting obvious plastic deformation of subsurface. Clearly, the softened matrix cannot support the tribo-layers. Thus they would be readily delaminated. This absolutely damaged the protective function of tribo-layers. In this case, under the action of pressure and frictional force, a lot of cracks appeared in tribo-layers, even if they were totally delaminated because tribo-oxide layers lost the solid support of substrate. At 0.75 m/s, the thickness of tribo-layer was about 10~20 μm, and the tribo-layer seemed to be uncompacted with cracks and a plastic deformed layer of about 5~10 μm in thickness under 50 N. At 2.68 m/s, the thickness of tribo-layer became thinner. Under 50 N, particularly, it was only 5~8 μm due to much delamination. The tribo-layers seemed to be uncompacted with a lot of cracks and a thicker plastically deformed layer (about 10~25 μm). On the contrary, at 4 m/s, the tribo-layer became thinner but was very compacted with a slight plastically deformed layer. Under 50 N, in particular, the plastically deformed layer could not be noticed. Meanwhile, the O content and oxide amount of the worn surfaces could be detected to be 28.71 wt%~29.88 wt% and trace TiO at 0.75 m/s, 13.01 wt% and a little TiO under 10 N, zero and no oxide under 50 N at 2.68 m/s, 37.27 wt%~ 45.33 wt% and TiO and TiO_2 at 4 m/s, respectively.

Oxygen content and oxide amount directly determine the characteristics and properties of tribo-layers. At 0.75 m/s, the existence of oxides endowed tribo-layers with ceramic-partly characteristics. Clearly, at 4 m/s, tribo-layers presented more obvious ceramic characteristics because of more oxides. Oppositely, at 2.68 m/s, tribo-layers merely presented metal characteristics because of no oxides. It is clear that the characteristics and properties of tribo-layers can be evaluated by microhardness. After sliding at various velocities, the tribo-layers presented a much higher microhardness than the substrate, especially at 4 m/s; the hardness value reached 7040 ~7720 MPa. However, at 2.68 m/s, the hardness of tribo-layer was substantially reduced because of the delamination of oxides, especially under 50 N. The protective function of tribo-layers can be roughly estimated through their hardness as a function of load. At 0.75 m/s, the hardness of tribo-layers increased from 3970 MPa to 5100 MPa with the increase of load. At 4 m/s, the hardness of tribo-layers increased from 7040 MPa to 7720 MPa with the increase of load. This means that tribo-layers become strong with the increase of load. Thus, such tribo-layers are protective. Conversely, at 2.68 m/s, the hardness of tribo-layers decreased from 4910 MPa to 3900 MPa with the increase of load. Clearly, the latter approaches the hardness of substrate (3080~3440 MPa). This demon-

Table 1 Characteristics of tribo-layers for aluminized Ti-6Al-4V alloy

Wear characteristics	0.75 m/s		2.68 m/s		4 m/s	
	10 N	50 N	10 N	50 N	10 N	50 N
Thickness of tribo-layer/μm	15~20	10~20	10~15	5~8	10~20	8~10
Morphology of tribo-layer	Continuous, uncompacted	Continuous, compact	Continuous, uncompacted	Discontinuous, uncompacted	Continuous, compact	Continuous, compact
Thickness of a plastically deformed layer/μm	1~5	5~10	10~15	10~25	1~5	0
Oxygen content of worn surface (EDS)/wt%	28.71	29.88	13.01	0	37.27	45.33
Phases of worn surface (XRD)	Ti, TiO	Ti, TiO	Ti, TiO	Ti	Ti, TiO	Ti, TiO, TiO_2
Micro-hardness (HV) of tribo-layer/MPa	3970	5100	4910	3900	7040	7720
Micro-hardness (HV) of substrate/MPa	3200~3800	3200~3600	3120~3360	3080~3440	3200~3730	3030~3500

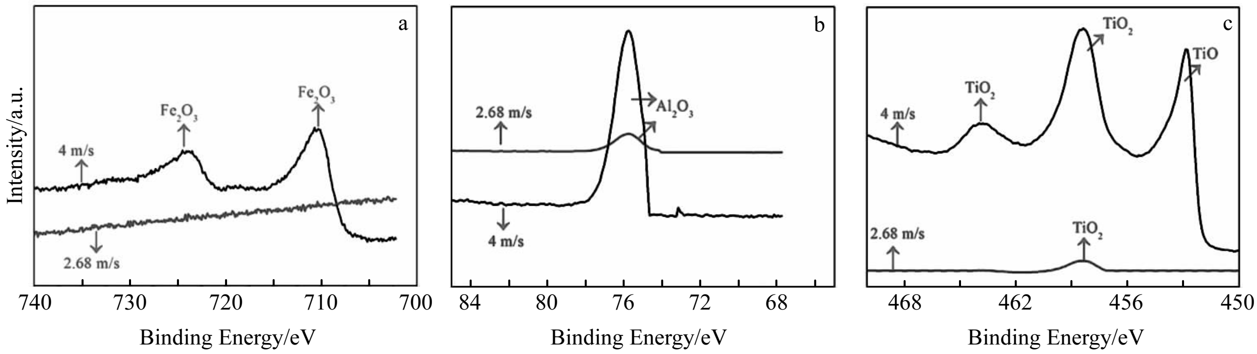

Fig.6 XPS spectra of Fe 2p (a) , Al 2p (b) and Ti 2p (c) on the worn surface of the aluminized coating at a normal load of 50 N and sliding speeds of 2.68 and 4 m/s

strates that tribo-layers become weak with the increase of load. And the tribo-layers present similar characteristics and properties to the substrate alloy. So, such tribo-layers can be considered to be non-protective.

In order to further distinguish trace oxides on worn surfaces, XPS was employed. XPS spectra of Fe 2p, Al 2p and Ti 2p on the worn surfaces under 50 N at sliding speeds of 2.68 and 4 m/s are shown in Fig.6. At 2.68 m/s, there are no XPS peak of Fe 2p and only weak XPS peaks of Al 2p and Ti 2p which are assigned to Al_2O_3 and TiO_2 on the worn surface. Such trace oxides might slightly increase the hardness of tribo-layers, but did not change their metal-predominated characteristics. Thus, they did not provide a protection from wear at 2.68 m/s. On the contrary, at 4 m/s, the XPS peaks of Ti 2p are assigned to TiO and TiO_2 in Fig.6c, which is similar to the XRD results in Fig.3c. The XPS peaks of Fe 2p and Al 2p are assigned to Fe_2O_3 and Al_2O_3 in Fig.6a and 6b, respectively, while no Fe_2O_3 and Al_2O_3 appeared on worn surface according to XRD results because of little amounts. This indicates that Fe and Al elements do exist on the worn surface in the form of Fe_2O_3 and Al_2O_3, respectively. Clearly, the tribo-layers contained not only TiO and TiO_2, but also Fe_2O_3 and Al_2O_3. These trace oxides enhanced the ceramic characteristics and load-bearing capability of tribo-layers further. Thus, they are helpful to reduce wear loss.

On the basis of identified phases and composition on worn surfaces, the SEM analysis (Fig.4) for the worn-surface morphology was used to readily distinguish wear mechanism. At 0.75 m/s, the worn surface presents a composite pattern containing adhesive and tribo-oxide traces, so wear mechanisms should be adhesive wear and oxidative wear. With an increase of sliding speed, the temperature of worn surface became higher because of more released friction heat. In these cases, more oxides would appear. However, at 2.68 m/s, little or trace oxides were noticed; the worn surface presents large piece of delaminated regions and tearing traces, especially under the load of 50 N. Thus, the wear mechanism should be delamination wear. At 4 m/s, a lot of oxides of TiO and TiO_2 appeared; the worn surface presented a compacted tribo-oxide layer region and some delaminated regions. Undoubtedly, the wear mechanism at 4 m/s is typical oxidative wear.

3 Conclusions

1) The aluminized Ti-6Al-4V alloy presents a significant variation in wear loss as a function of sliding velocity. As the sliding velocity increases from 0.5 m/s to 4 m/s, the wear loss slowly decreases at first, then rapidly increases to a climax at 2.68 m/s, and finally substantially decreases to the lowest point at 4 m/s. At different sliding velocities, the wear loss increases with the increase of load, especially at 2.68 m/s.

2) Compared with uncoated Ti-6Al-4V alloy, the aluminized coating improves the wear resistance of titanium alloys under various conditions, especially at 4 m/s. The improved wear performance can be attributed to the existence of $TiAl_3$ coating and tribo-oxide layer.

3) Tribo-layers form on worn surfaces under various conditions. Different characteristics of tribo-layers notably decide the wear behavior and mechanism. At 4 m/s, oxide-containing tribo-layer (TiO and TiO_2) possesses an obvious wear-reduced function; conversely, at 2.68 m/s, no-oxide one shows no protection from wear.

4) During wear at 0.5~2.68 m/s, $TiAl_3$ coating is totally consumed because of its room-temperature brittleness and the weak protection of tribo-layers. At 4 m/s, $TiAl_3$ coating partially remains because of its improved toughness and the strong protection of tribo-oxide layers. The main wear mechanisms are adhesive wear and oxidative wear at 0.75 m/s, delamination wear at 2.68 m/s, and oxidative wear at 4 m/s.

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Ti-6Al-4V 合金热浸铝涂层对磨 GCr15 钢干滑动的磨损行为

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摘　要：Ti-6Al-4V 合金经热浸铝并在 650 ℃下进行高温扩散退火处理，获得 $TiAl_3$ 涂层。采用销-盘式磨损试验机研究铝化后的 Ti-6Al-4V 合金与 GCr15 钢对磨的干滑动磨损行为。通过 SEM、XRD、EDS 和 XPS 等手段分析热浸镀铝涂层磨面的形貌、物相和成分，并且探讨其磨损机制。研究结果表明：随着滑动速度的增加，当滑动速度为 0.75 m/s 时，铝化后的 Ti-6Al-4V 合金的磨损量先减小到最小值，然后在 2.68 m/s 时增加到最高值，最后在 4 m/s 时降至最低值。在不同的滑动速度下，磨损量随着载荷的增加而增加。研究发现，摩擦层结构对磨损的行为和机制有显著的影响。在 4 m/s 时，含氧的摩擦层(TiO 和 TiO_2)具有明显的减磨性能；相反地，在 2.68 m/s 时，没有氧化物的摩擦层并未对磨损显示出保护作用。与未经热浸镀处理的 Ti-6Al-4V 合金相比，在不同工况下，铝化后的涂层提高了钛合金的耐磨性，尤其速度为 4 m/s。耐磨性得到提高是由 Ti-Al 涂层和摩擦氧化物层所引起的。

关键词：铝化 Ti-6Al-4V 合金；干滑动磨损；磨损行为；摩擦层；磨损机制

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