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Microstructure and wear resistance of laser clad TiB−TiC/TiNi−Ti_2Ni intermetallic coating on titanium alloy

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Abstract: A wear resistant TiB−TiC reinforced TiNi−Ti_2Ni intermetallic matrix composite coating (TiB−TiC/TiNi−Ti2Ni) was prepared on Ti−6.5Al−2Zr−1Mo−1V titanium alloy by the laser cladding process using Ti+Ni+B_4C powder blends as the precursor materials. Microstructure and worn surface morphologies of the coating were characterized by optical microscopy (OM), scan electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDS) and atomic force microscopy (AFM). Wear resistance of the coating was evaluated under dry sliding wear test condition at room temperature. The results indicate that the laser clad coating has a unique microstructure composed of flower-like TiB−TiC eutectic ceramics uniformly distributed in the TiNi−Ti_2Ni dual-phase intermetallic matrix. The coating exhibits an excellent wear resistance because of combined action of hard TiB−TiC eutectic ceramic reinforcements and ductile TiNi−Ti_2Ni dual-phase intermetallic matrix.

Key words: intermetallic; composite; coating; laser cladding; wear

1 Introduction

Titanium alloys are widely used as structural components in aerospace, chemical, petrochemical and marine industries owing to their low density, high specific strength, exceptional corrosion resistance and high temperature mechanical properties [1−3]. However, the range of applicability is limited by their poor tribological functionality. One of the most efficient approaches to enhance the tribological properties and hence to expand the industrial application for titanium alloys as tribological machinery components is to fabricate a hard and wear resistant coating on the titanium components.

Since the last two decades, TiNi-based intermetallic alloy has attracted increasing interest from tribologists due to its many superior properties, such as pseudo-elasticity, toughness, ductility and biocompatibility. In addition, TiNi alloy exhibits an outstanding wear resistance because of its special deformation behavior caused by a thermoelastic martensitic transformation [4−6]. However, wear resistance of TiNi needs to be improved due to its low load-bearing capability and low hardness. One of the most efficient approaches to enhance the tribological properties of TiNi alloy is to produce a composite by addition of hard phases.

Having a good combination of ductility owing to its face-center-cubic crystal structure and good wear resistance due to its high hardness of approximately HV700 [7], the hard intermetallic compound Ti_2Ni is a suitable reinforcing phase for the ductile TiNi alloys for wear resistance. Several researches [6−8] indicated that TiNi−Ti_2Ni dual-phase intermetallic alloys indeed exhibit a higher yield strength and wear resistance. Nevertheless, the tribological applicability of those multi-phase alloy composites is still limited by their relatively low hardness. Obviously, the wear resistance would be further enhanced if the TiNi−Ti_2Ni matrix composite could be reinforced in-situ by hard ceramic particles.

Due to high hardness, low density, high melting temperature, high modulus as well as good wear and corrosion resistance, TiB and TiC are widely used as the reinforcements for iron, aluminum and titanium matrix composites [9−13]. However, along with the use of monolithic TiC and TiB, several limitations such as low

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toughness have been found [14]. Consequently, the attention of researches has now turned to the multiple-phase ceramic particles as the reinforcing phases. Recently, a number of studies [14−17] on the mechanical and tribological behaviors of TiB−TiC reinforced composites have been reported. It has been shown that the fracture toughness and wear resistance of the TiB−TiC composites are significantly higher than those of the monolithic TiC and TiB materials. Hence, a TiNi−Ti_2Ni intermetallic matrix composite coating reinforced by TiB−TiC composite particles is expected to have outstanding combination of tribological properties and toughness. To our knowledge, such a composite coating prepared by laser cladding has not been reported in literatures.

In this work, a TiC−TiB/TiNi−Ti_2Ni intermetallic matrix composite coating is fabricated on substrate of a Ti−6.5Al−2Zr−1Mo−1V titanium alloy (here after refers to TA15 titanium alloy) by laser cladding using Ni–Ti–B_4C powder blends as the raw materials. Microstructure, microhardness and wear resistance of the composite coating are investigated.

2 Experimental

A commercial $\alpha+\beta$ TA15 titanium alloy plate (50 mm×20 mm×10 mm) was used as substrate for laser cladding to fabricate the TiB−TiC/Ti−Ni composite coating using a 4 kW YLS−4000 fiber laser in argon shielding atmosphere. Commercial powder blends of pure titanium (with the average particles size of 120−200 μm), pure Ni (40−70 μm) and B_4C (60−120 μm) in nominal chemical composition (mass fraction, %) of 50.47Ti−46.69Ni−2.84B_4C were selected as the precursor materials. Before laser cladding, the TA15 titanium alloy substrate was polished with silicon carbide abrasive papers and degreased in acetone. The powder blends, with approximately 1.2 mm in thickness, preplaced on the surface of the titanium substrate, were melted under the scanning of the laser beam. The laser cladding parameters were: laser beam power 3.5 kW, laser beam diameter 4.5 mm and laser beam scanning speed 500 mm/min.

Metallographic samples were prepared using mechanical polishing procedures and were etched in HF+HNO_3+H_2O water solution with volume rate of 1:4:5 for approximately 3 s. Microstructure was characterized on a Leica optical microscope (OM), Apllo−300 and JSM−6700F scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) was conducted using the Rigaku D/max 2200 pc automatic X-ray diffractometer with Cu target K_α radiation to identify the phase constitution. In addition, microhardness profile along the depth direction of the laser clad coating was measured using a MH−6 semi-automatic Vickers microhardness tester with a testing load of 9.8 N and a dwelling time of 10 s. Volume fraction of the TiB−TiC ceramic phase was measured by quantitative metallographic analysis method using a commercial contrast-based image analyzing software.

Room-temperature dry sliding wear tests were carried out on an MM−200 block-on-wheel dry sliding wear tester under a test load of 196 N. TA15 titanium alloy was selected as the reference material. The coupling wheel was the hardened 0.45%C steel with an average hardness of HV645. The test parameters were as follows: sliding speed 180 r/min, sliding time 60 min. Each test was repeated three times. Wear mass loss was measured using Sartorius BS110 electronic balance with an accuracy of 0.1 mg and was utilized to evaluate the relative wear resistant properties of the laser clad coating in comparison with the reference material TA15 alloy. Worn surface and subsurface morphologies of the coating and wear debris were characterized using CS−3400 and Apllo−300 scanning electron microscopes. The realistic three-dimensional image of the worn surface was analyzed by atomic force microscope (AFM, Multimode Nanoscope IIIa, Veeco Instruments, USA).

3 Results

3.1 Microstructure and microhardness profile

The laser clad TiB−TiC/TiNi−Ti_2Ni intermetallic matrix composite coating has a uniform microstructure and is metallurgically bonded to the TA15 titanium alloy substrate, as indicated in Fig. 1. Only a few pores and incompletely dissolved B_4C particulates are observable in the coating. As indicated in Fig. 2, the phase constituents mainly consist of TiNi (M), Ti_2Ni, TiB and TiC.

SEM micrographs of a gently etched composite coating, as shown in Fig. 3, clearly reveal the morphology of each phase. The flower-like TiB−TiC eutectic ceramics are dispersed in the dual-phase intermetallic matrix which is mainly composed of the TiNi dendrite (49.43Ti−48.80Ni−1.18Al−0.59V according to the EDS analysis in mole fraction, %) and interdendritic Ti_2Ni (62.75Ti−31.39Ni−5.26Al−0.60V). The dark regions in Fig. 3(c) by the electron back scattering TiB−TiC eutectic ceramics are due to low atomic mass of light elements B and C. A more detailed SEM image of the dual-phase TiB−TiC ceramic microstructure is shown in Figs. 3(b) and (d). It is clear that the eutectic consists of coarse needle TiB with hexagon cross section (analyzed in Refs. [18,19]) and near-equiaxed TiC particulates. Quantitative image analysis shows that the volume fraction of TiB−TiC eutectic is approximately 8%.

Microhardness profile along the depth direction of the laser clad coating is shown in Fig. 4. Because of the

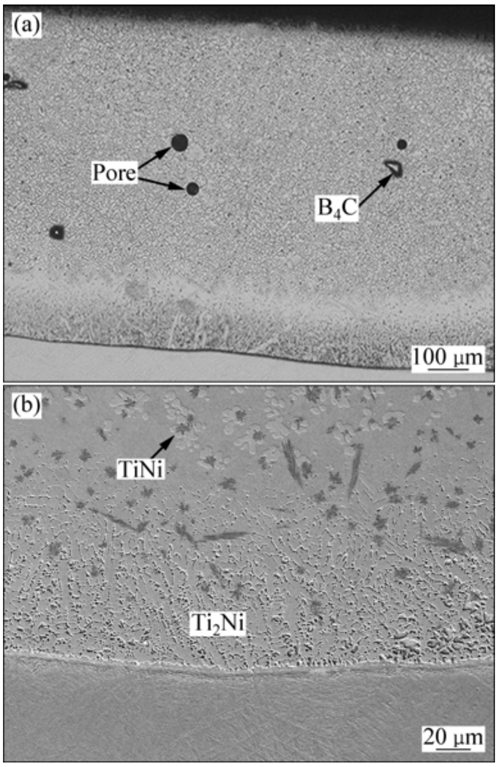

Fig. 1 OM micrograph showing overview longitudinal cross-section (a) and SEM micrograph showing microstructure in coating/substrate transition zone (b) of laser clad coating on substrate of TA15 titanium alloy

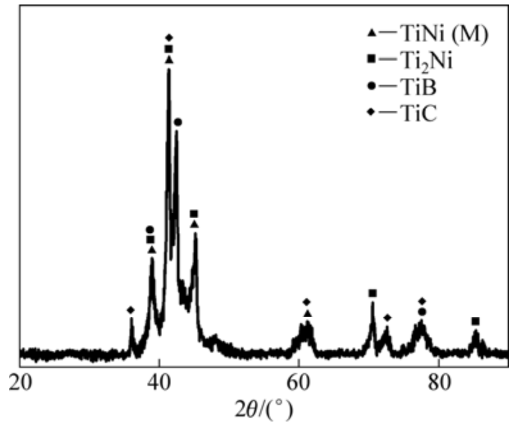

Fig. 2 X-ray diffraction pattern of laser clad coating

fine microstructure of hard TiB−TiC reinforcing phase uniformly distributed in TiNi−Ti_2Ni dual-phase intermetallic matrix, the coating has an average value of HV580 higher than that of TA15 substrate (HV345), and a uniform hardness distribution. It is worth noting that there is a hardness peak of approximately HV700 near the substrate in the coating. That is because the main phase constitution near the substrate is the hard intermetallic Ti_2Ni, as shown in Fig. 1(b).

3.2 Wear resistance

In comparison with the TA15 titanium alloy, the laser clad coating exhibits outstanding wear resistance under room-temperature dry sliding wear test condition coupling with the hardened 0.45%C steel wheel, as

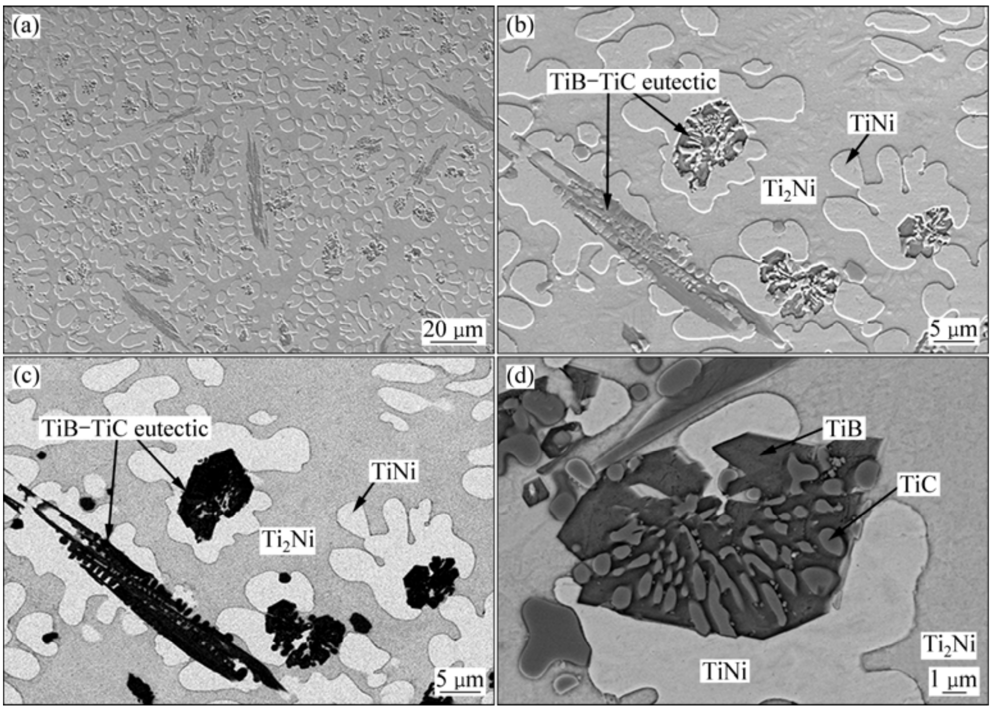

Fig. 3 SEM images showing typical microstructures of laser clad coating (a, b), electron back-scattering micrograph (c) and detailed SEM image of TiB−TiC eutectic (d)

indicated in Fig. 5. Wear mass loss of the coating is 1/200 of that of the TA15 alloy.

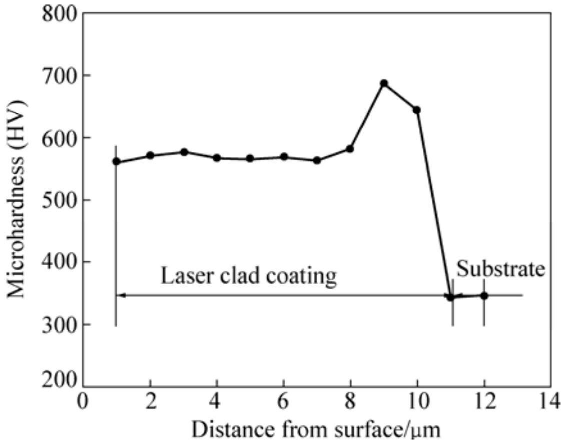

Fig. 4 Microhardness profile along depth direction of laser clad coating

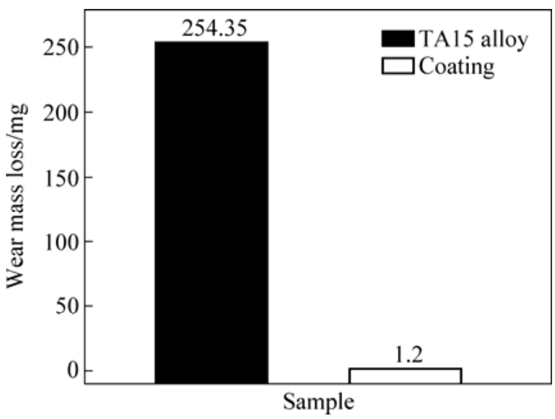

Fig. 5 Wear mass loss of laser clad coating and TA15 alloy at test load of 196 N

The worn morphologies of the laser clad coating and the TA15 alloy after dry sliding wear test for 60 min at a test load of 196 N are shown in Fig. 6. Noticeable plastic deformation and deep plowing grooves shown in Fig. 6(b) are observed on the worn surface of the TA15 titanium alloy, which proves that TA15 titanium alloy suffers severe abrasive and adhesive wear from the mating wheel. On the contrary, worn surface of the laser clad coating is mostly covered by a transferred layer without obvious features of micro-cutting or plowing grooves. Wear debris of the coating mainly consists of tiny powders and a few small flake-like chips, as shown in Fig. 7(a). EDS analysis results indicate that both the smeared layer covering the worn surface and the wear debris particles highly enrich in Fe and O with a negligible amount of Ti and Ni (41.91Fe−56.64O−0.78Ti−0.66Ni), and are identified as the iron oxide particles which primarily originated from the contacting surface of the mating hardened 0.45%C steel counterpart. Figure 7(b) shows the microstructure of the worn subsurface of the laser clad coating. Slightly plastic deformation of the TiNi primary dendrites and a few small cracks from the interdendritic Ti_2Ni are revealed in the worn subsurface. However, the cracks expansion of

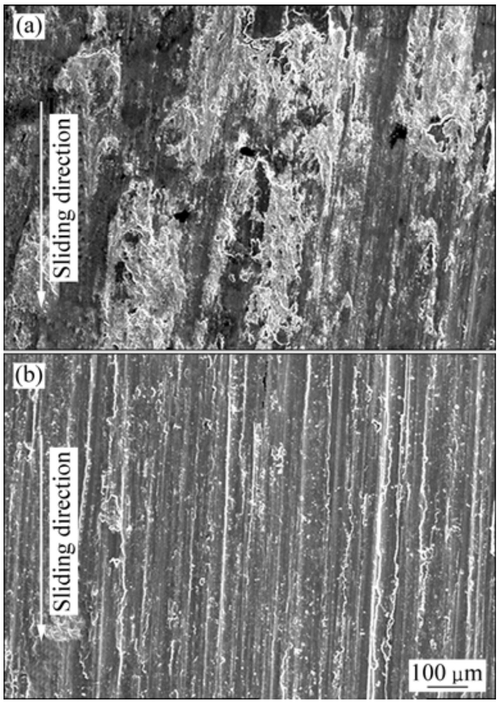

Fig. 6 SEM images showing wore surface morphologies of laser clad coating (a) and TA15 alloy (b) after dry sliding wear test coupling with hardened 0.45%C steel wheel for 60 min at test load of 196 N

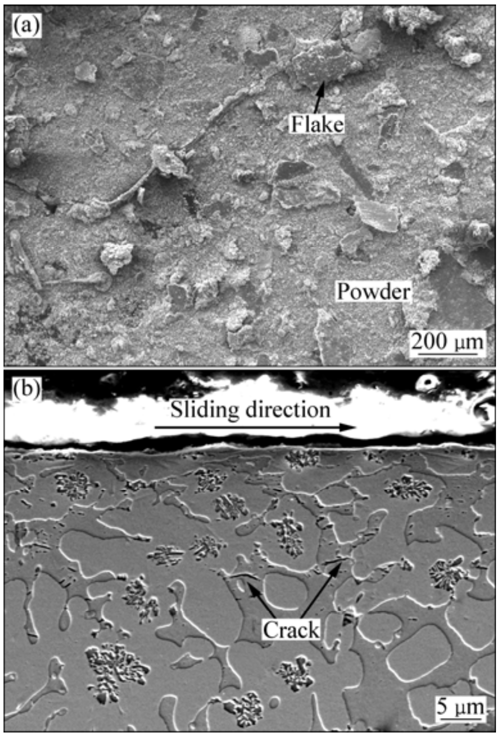

Fig. 7 SEM images showing wear debris morphology (a) and worn subsurface microstructure (b) of laser clad coating

the brittle Ti_2Ni phase is suppressed efficiently due to the presence of ductile TiNi phase.

Atomic force microscope (AFM) was used to characterize the realistic three-dimensional image of worn surface after cleaning by 4% HNO_3−alcohol. Results from several different areas are almost similar to the images as indicated in Fig. 8. As we can see, most areas exhibit exceedingly good smoothness. Surface amplitudes between a peak and a trough are quite small (on average less than 500 nm). This superb worn surface is attributed to the excellent interfacial bonding between the in-situ formed TiB−TiC and the TiNi−Ti_2Ni matrix, and reflects the excellent wear resistance of the laser clad coating indirectly.

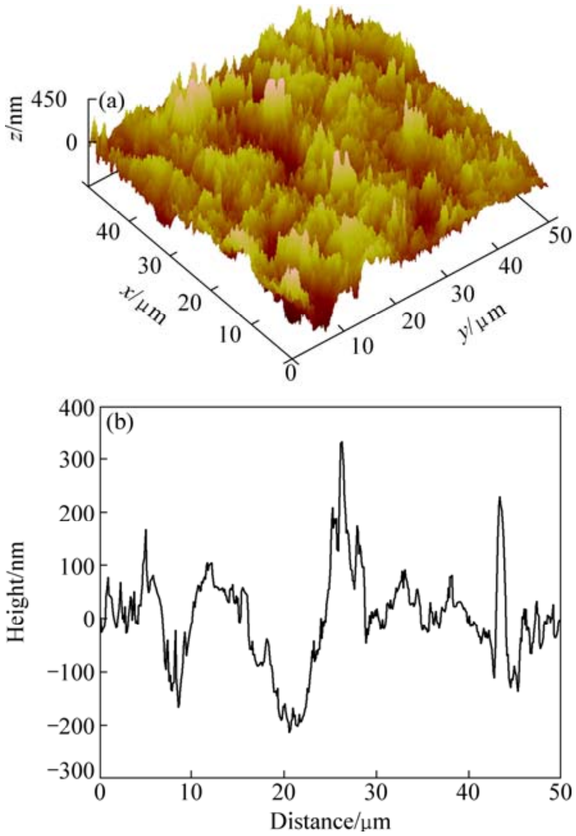

Fig. 8 AFM micrographs of worn surface of laser clad coating after cleaning by 4% HNO_3−alcohol: (a) Photo of realistic image of worn surface; (b) Height profile along wear direction

4 Discussion

4.1 Forming mechanism of laser clad TiB−TiC/TiNi−Ti_2Ni composite coating

On the formation mechanism of in-situ synthesized TiB−TiC reinforced Ti matrix composites [13,14], two mechanisms are prevalent: 1) at a low temperature, the solid-state diffusion mechanism is predominant; 2) at a high temperature, a solution and precipitation mechanism is dominant. The latter mechanism is principal reaction pattern in the synthesis process, evidenced by the obvious existing of TiB−TiC eutectic.

The detailed process could be explained as follows. Firstly, the molten Ti reacts with the solid B_4C to form large aggregation of TiB and TiC [14]. Subsequently, most of ceramics formed by solid reaction would undergo disintegration, dissolution to form Ti−Ni−B−C melting pool due to the high reaction temperature in the laser cladding process. Finally, solidification reaction for composites Ti−Ni−B−C takes place with the gradually decreasing temperature. According to the microstructure shown in Fig. 3, it is suggested that nucleation and growth of TiC occur firstly, then TiB−TiC eutectic precipitates abundantly. The remaining Ti−Ni liquid solidifies as a dual-phase intermetallic matrix, where the dendritic TiNi primary phase precipitates with the flower-like particles as the heterogeneous nucleation sites, producing a unique encapsulated TiNi dendrite with a hard flower-like TiB−TiC core, and the interdendritic residual melt between the TiB−TiC cored TiNi dendrite solidifies as the harder Ti_2Ni.

4.2 Factors of excellent wear resistance

According to the aforementioned results of wear mass loss and worn morphologies shown from Fig. 5 to Fig. 8, it can be concluded that although the average hardness value (HV580) is not very high, the laser clad coating exhibits an excellent wear resistance compared with the reference material TA15 under dry sliding wear test conditions. This outstanding tribological property is the outcome of combined action of hard TiB−TiC eutectic ceramic reinforcements and ductile TiNi−Ti_2Ni dual-phase intermetallic matrix.

On one hand, the TiB−TiC ceramic reinforcements make an important contribution to resisting the abrasive and adhesive wear in the process of the dry sliding owning to the high hardness and strong covalent atomic bonds. When the asperities on the coupling counterpart surface encounter the mixture of TiB−TiC illustrated in Fig. 9(a), the hard TiB−TiC ceramics could smash them to weak the degree of abrasive wear effectively. Meantime, the unique binary-phase ceramic eutectic microstructure improves itself efficiently the toughness of monolithic ceramic, and hence avoids brittle fracture of ceramic particles to some extent.

On the other hand, the existence of TiNi−Ti_2Ni dual-phase intermetallic matrix having excellent properties of ductility and toughness plays a dominate role in preventing TiB−TiC ceramic particles from removal by toughening them and relieving the stress concentration. The excellent interfacial bonding between the in-situ formed TiB−TiC and TiNi−Ti_2Ni intermetallic matrix ensures the smoothness of the worn surface as shown in Fig. 8 and enhances the wear resistance of the laser clad coating.

The excellent adhesion of TiNi intermetallic and frication-induced heating effect make the wear debris particles from hardened 0.45%C steel mating wheel easy adhere to the surface of laser cladding coating, leading to the formation of the transferred layers on the worn surface of the coating, as shown in Fig. 9(a). The presence of the transferred layers prevents the surface of coating from direct contact with the mating wheel and protects the laser clad coating from subsequent sliding wear attacks, as shown in Fig. 9(b).

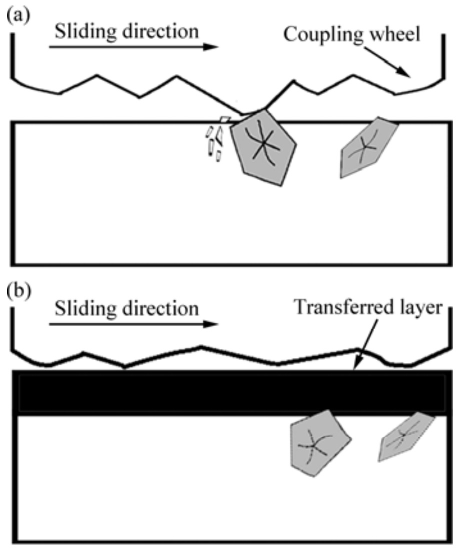

Fig. 9 Schematics of main wear process observed on worn surface of laser clad coating: (a) Initial stage of wear process; (b) Wear process after forming transferred layers

5 Conclusions

1) The laser clad TiB−TiC/TiNi−Ti_2Ni intermetallic matrix composite coating, consisting of the microstructure of the flower-like TiB−TiC eutectic ceramics uniformly distributed in the TiNi−Ti_2Ni dual-phase intermetallic matrix, was fabricated on a substrate of TA15 titanium alloy by laser cladding process.

2) The laser clad coating exhibits outstanding wear resistance under dry sliding wear test conditions due to its combination of high hardness and strong covalent atomic bonds of TiB−TiC ceramic reinforcements and excellent ductility and toughness of TiNi−Ti_2Ni matrix. Wear mass loss of the coating is more than 1/200 of that TA15 alloy.

3) Transferred layer makes an important contribution to the wear resistance of the laser clad coating when coupling with the hardened 0.45%C steel.

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钛合金激光熔覆TiB−TiC增强TiNi−Ti_2Ni金属间化合物复合涂层的组织和耐磨性

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摘　要：以Ti+Ni+B_4C粉末混合物为原料，利用激光熔覆技术在TA15钛合金基材表面制得TiB−TiC共同增强TiNi−Ti_2Ni金属间化合物复合涂层。采用OM、SEM、XRD、EDS及AFM等手段分析激光熔覆涂层的显微组织及磨损表面，测试涂层的室温干滑动磨损性能。结果表明，激光熔覆TiB−TiC增强TiNi−Ti_2Ni金属间化合物复合涂层熔覆具有独特的显微组织，菊花状的TiB−TiC共晶均匀分布在TiNi−Ti_2Ni双相金属间化合物基体中。由于高硬、高耐磨TiB−TiC陶瓷相与高韧性TiNi−Ti_2Ni双相金属间化合物基体的共同配合，激光熔覆涂层表现出优异的耐磨性。

关键词：金属间化合物；复合材料；涂层；激光熔覆；磨损

(Edited by YANG Hua)