Wear properties of alloyed layers produced by laser surface alloying of pure titanium with B_4C and Ti mixed powders

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Titanium and its alloys are extensively used in aeronautical, marine and chemical industries due to their intrinsic properties such as high specific strength, good oxidation and corrosion resistance. Nevertheless, the applications of titanium alloys under severe wear conditions are highly restricted due to their low hardness and poor tribological properties.

Surface treatment can enhance the properties of Ti alloys. But conventional chemical heat treatments like nitriding, carburizing and boronizing, have some disadvantages such as long processing time, thin treated layer and easy deformation of the workpiece being treated. Thermal spray coatings also have some demerits such as low coating density and limited bond strength between the coating and the substrate. Laser beams, owing to their excellent coherence and directionality, are widely used in surface modification of many kinds of metals. So the disadvantages of pure titanium and its alloys can be overcome by laser surface modification treatment on the special surfaces of the workpieces where they suffer in operation. Laser treatments have several advantages over commonly used heat treatment methods, including precise control over the width and depth of processing, ability to selectively process specific areas of a component, and ability to process complex parts.

Different laser surface modification techniques have been used to treat titanium alloys for improving their wear resistance. Among them, laser nitriding is the commonly used method. Jiang *et al.* [1] have carried out laser nitriding of Ti–6Al–4V and found that the wear resistance of the treated samples is enhanced noticeably under both two-body abrasive and dry sliding wear conditions. The results of laser nitriding after plasma spraying of Ni and Cr on the surface of pure titanium show that both sliding and fretting wear resistance are improved greatly [2]. The experiment of laser surface alloying pure titanium with N_2 and CO-mixed reactive gases shows that the laser alloyed layers exhibit a lower friction coefficient and a higher wear resistance than as-received sample [3]. Cui *et al.* [4] fabricated gradient Ti/TiN composite coating on the surface of commercial pure titanium using laser-alloying technique and the test results show that the hardness and wear resistance of the samples are markedly enhanced. Ref. [5] reported that the composite coatings produced by laser alloying of pure titanium with aluminium powder in a nitrogen atmosphere present a surface Al–$TiAl_3$ composition which gradually evolves to Ti_3Al close to the titanium base and dendritic titanium nitrides (TiN and Ti_2N) and titanium aluminium nitrides (Ti_2AlN) are formed throughout the laser track. Pang *et al.* [6] investigated the effect of laser treatment parameters on the microstructure, microhardness and wear resistance of alloyed layers. They found that, with a constant thickness of preplaced alloy powders, the dilution level of the alloyed layers is proportional to the incident laser energy density, and is inversely proportional to the microhardness of the alloyed layers.

Nevertheless, although titanium nitrides can significantly enhance the wear resistance of titanium alloys, the dendritic morphology is not desirable because it is apt to induce cracks in the alloyed layers [7]. As known to all of us, titanium borides and carbides have very high hardness, excellent wear and corrosion resistance and stability at elevated temperature (1000 °C) [8–10]. These characteristics make them very attractive for surface modification of metal materials such as steel and titanium alloys. The composite coatings containing TiB and TiC compounds fabricated onto Ti–10V–2Fe–3Al alloy substrate by using high-energy electron beam irradiation exhibit excellent high-temperature microhardness [10]. The results of deposition of TiB_2 onto hardened hot work steel by PACVD show that the coatings with a microhardness of 33 GPa, appear to be a promising material for the wear protection in various tribological systems [11].

So, the aim of the present work is to produce alloyed layers containing titanium borides and carbides on the surface of pure titanium by means of laser surface alloying technique and investigate the wear resistance of the alloyed layers and the effect of laser processing parameters on the microstructure of the alloyed layers.

Pure titanium samples of 10 mm × 10 mm × 40 mm in size were polished with SiC grit paper prior to the coating operation. Fine mixed powders of size 10 μm, consisting of 50 wt.% B_4C and 50 wt.% Ti, blended

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TABLE I The experimental parameters

Sample	Power (W)	Scanning velocity (mm s^{-1})
1	1200	0.85
2	1200	3.85
3	1200	6.80

with dilute sodium silicate solution were coated on the surface of samples to a thickness of about 0.5 mm and then dried. A 1.5 kW continuous wave CO_2 laser, with a beam diameter of 4 mm, was employed to melt the surface of samples and the tracks were 40% overlapped. During the process of laser surface melting, the prelaced B_4C was decomposed and dissolved into the melted pool, leading to alloying the surface of pure titanium with boron and carbon. To protect the melted pool from oxidation during processing, argon gas shield at a pressure of 3.0 kg/cm^2 was fed through a nozzle which was coaxial with the laser beam. In addition, there was a side argon gas flow through a nozzle at an angle of 30° to melted pool. The experimental parameters are shown in Table I.

The hardness and microstructure of the samples were evaluated using Shimadzu Vickers hardness tester, JXA-8800R electron probe microanalysis (EPMA) and JXA-840 scanning electron microscope (SEM), respectively. Compounds formed in the laser-alloyed layers were investigated using D/max-rC XRD with Cu K_α radiation operated at a voltage of 40 kV, a current of 40 mA, and a scanning rate of 5°/min. For EPMA and SEM observation, the polished samples were chemically etched in a solution of HF, HNO_3 and H_2O in volume ratio of 1:1:48 to reveal the microstructure of the alloyed layers.

Sliding wear tests were performed using MM200 wear test machine with a load of 5 kg. A sintered carbide abrasive wheel (rotation speed: 400 rpm) with a diameter of 40 mm was selected as the wear couple. The samples of laser treatment and as-received are annealed at 750 °C for 1 hr prior to the wear test. The weight loss was evaluated every 10 min using an electronic balance with an accuracy of 0.1 mg.

Result of XRD (Fig. 1) indicates that the main phase compositions of the alloyed layers are TiB_2, TiB and TiC compounds. It means that, during the irradiation process, the B_4C decomposed and combined with Ti to form titanium borides and carbides *in situ* in the melt pool. Zhang *et al.* [12] reported that TiC, TiB and TiB_2

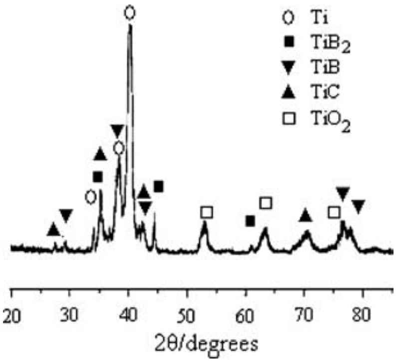

Figure 1 XRD spectrum of sample 2.

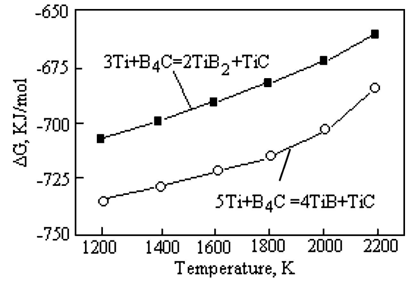

Figure 2 Change of Gibbs free energy ΔG as a function of temperature for reactions (1) and (2).

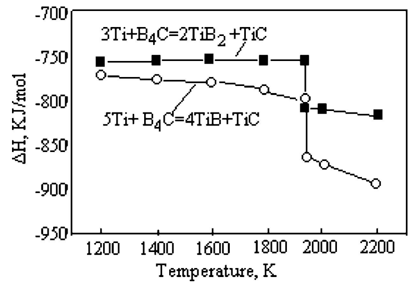

Figure 3 Change of formation enthalpy ΔH as a function of temperature for reactions (1) and (2).

can be synthesized by the chemical reactions between titanium and B_4C:

$$5Ti + B_4C = 4TiB + TiC \quad (1)$$

$$3Ti + B_4C = 2TiB_2 + TiC \quad (2)$$

The Gibbs free energy ΔG and reaction formation enthalpy ΔH of reactions (1) and (2) have been calculated using the thermodynamic data from Ref. [13] and the results are shown in Figs 2 and 3, respectively. From Fig. 2 we can see that the ΔG of above two reactions are all negative, which indicates that the above reactions all can take place. The ΔG of reaction (1) is less than that of reaction (2), which indicates that the reaction (1) is liable to take place, namely TiB forming in preference to TiB_2 throughout the temperature range. Moreover, the reaction formation enthalpy ΔH of two reactions are also negative (see Fig. 3), indicating that the reaction is exothermic, making it favored to occur.

Fig. 4 shows us the different micrographs of the samples. It can be seen that coarse needle-like compounds (see Fig. 4a) are formed when the scanning speed is lower (0.85 mm/s). With the scanning increasing (3.85 mm/s), point-like compounds appear and the size of needle-like compounds decreases (see Fig. 4b). When scanning speed is up to 6.80 mm/s, the morphology of the compounds turns into fine needle-like but the point-like is disappear (Fig. 4c). Clearly, laser-processing parameters have a significant effect on the compound morphology, which can be explained as following: with a lower laser scanning speed (0.85 mm/s), the melted pool (0.9 mm in depth measured) absorbed more heat energy. Thus, coarse needle-like compounds are formed because of relatively slow solidification cooling rate of the melt after the laser beam movement. As the scanning speed increase (6.80 mm/s), less heat energy is absorbed by the melt pool (0.65 mm in

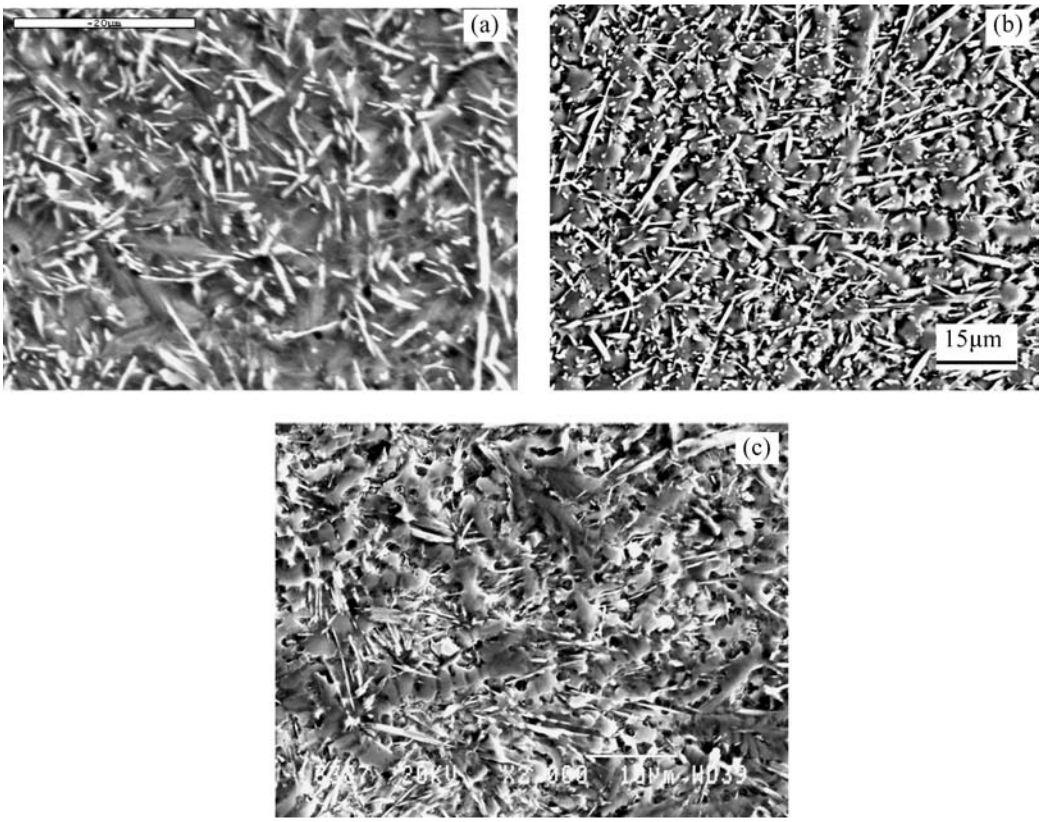

Figure 4 Micrographs of samples irradiated with deferent scanning speed, (a) 0.85 mm/s (b) 3.85 mm/s (c) 6.80 mm/s.

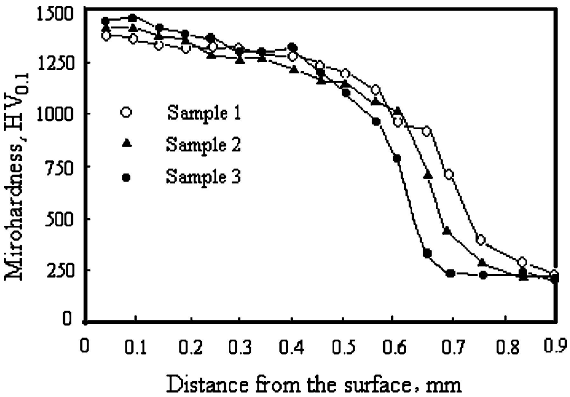

Figure 5 Microhardness profile of the samples.

depth measured). Under the condition of relatively fast cooling rate fine needle-like compounds are formed in the melt pool.

The microhardness profiles along the depth direction of the laser alloyed layers of samples are showed in Fig. 5. It can be found that the total depth of the alloyed layer is in a range of 0.65–0.90 mm and with the depth increasing the microhardness decreases gradually to about 230 HV for the matrix. In addition, with the scanning speed decreasing, the depth of the alloyed layers increase, which means that the laser scanning speed has also an effect on the depth of the alloyed layers.

Results of the sliding wear test, as shown in Figs 6 and 7, indicate that the alloyed layers have excellent sliding wear resistance compared with as-received sample and the friction coefficient of alloyed layers are lower than that of the matrix. Fig. 8 is EMPA

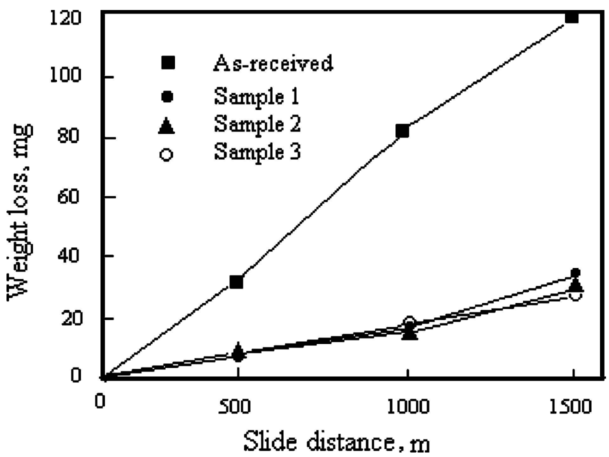

Figure 6 Wear weight loss as a function of sliding distance.

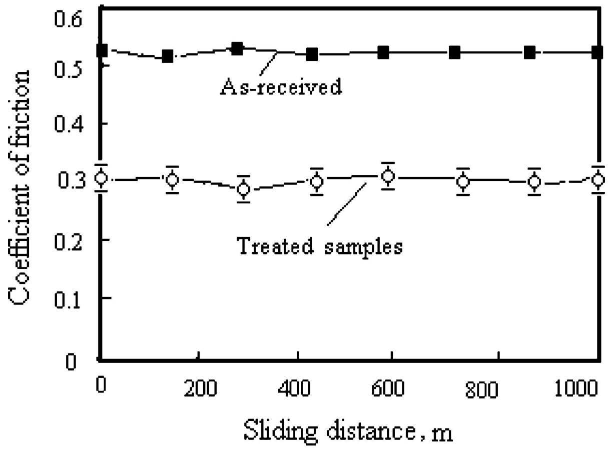

Figure 7 Friction coefficient as a function of distance (The error bars represent the mean deviation of the three laser treated samples).

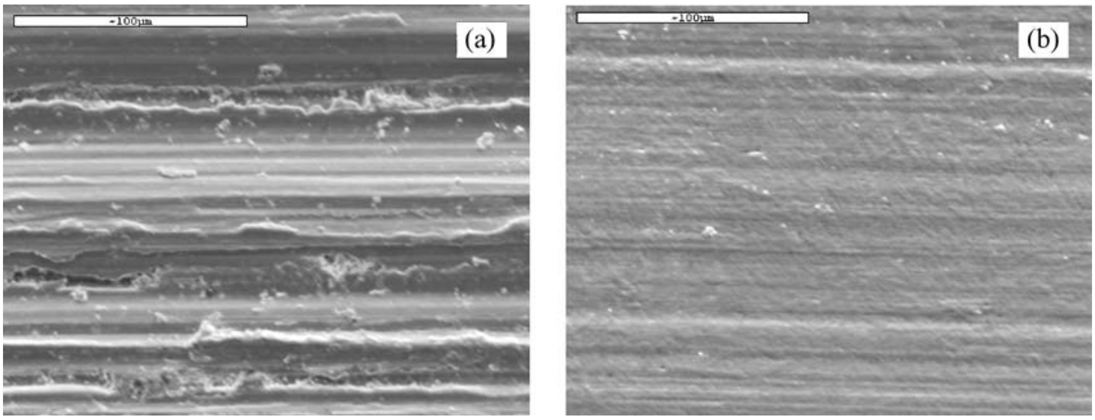

Figure 8 (a) Morphology of worn track of original sample and (b) alloyed layer of sample 2.

micrograph of worn surface of the samples. Clearly, under the sliding wear conditions with the sintered carbide as the counterpart, the sliding worn surface of original pure titanium is easy plastically deformed and grooved. Since the microhardness of pure titanium (about 230 HV) is much lower than that of counterpart (about 1200 HV), the hard asperities on the surface of counterpart can easily penetrate into the sliding surface of pure titanium, resulting in effective micro-cutting. Thus, the wear behavior of the original pure titanium is featured as abrasive and adhesive wear (see Fig. 8a). While the very high hardness of TiB_2, TiB and TiC compounds makes laser surface alloyed layer very difficult to be grooved and plastically deformed, the worn surface is characterized by the presence of much shallower grooves and little adhesive features, as shown in Fig. 8b.

In general, titanium borides and carbides reinforced composite coating exhibits excellent abrasive and adhesive wear resistance under sliding wear test conditions, because the strength and hardness of the surface of samples are significantly enhanced by the *in situ* formed compounds.

Alloyed layers are fabricated by laser surface alloying of pure titanium with B_4C and Ti mixed powders. The phase composition, microstructure, hardness and wear resistance of the alloyed layers can be summarized as follows:

XRD result confirms that the alloyed layer mainly consists of TiB TiB_2, and TiC ceramic phases. The properties of high microhardness, low friction coefficient and excellent wear resistance of the alloyed layer attribute to the formation of hard ceramic compounds. Thus, it can be deduced that the alloyed layers with such an excellent wear resistance can significantly improve the load bearing capability of the substrate. In addition, laser processing parameters have an effect on the morphology of the compounds and on the depth of the alloyed layers.

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