Application of Laser metal deposition for fabrication of titanium matrix wear-resistant coating and its wearing performance

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Abstract: TiC reinforced titanium matrix functionally graded materials (FGM) has been produced by processes of laser metal deposition through changing the powder feed rate of Ti and Cr3C2 powder. The OM, SEM, EDS methods were used to analyze the components and microstructure of the coatings. Microhardness and wearing resistance at room temperature of the FGM coating were examined by microhardness tester and wear tester respectively. The results show that FGM coating reinforced by in-situ TiC apparently improved hardness of Ti alloy; the microhardness can reach HV1100, and present gradient distribution along deposition direction. Dry sliding wear properties of these FGM coatings have been compared with substrate materials wearing. The observed wearing mechanisms are summarized and related to detailed microstructural observations. The results show the wear resistance of the coating can be improved by 46.6 times.

Introduction

Titanium alloys have higher specific strength, stiffness, fatigue resistance and good high-temperature strength. They also have excellent corrosion resistance to seawater and aqueous chloride solution over a wide range of temperatures and concentrations. These superior properties made titanium alloys widely used for structural applications in the chemical industry, medical engineering, and the leisure sector[1-2]. However, all titanium alloys exhibit poor tribological characteristics, which include abrasion resistance, metal-to-metal wear resistance, and solid particle erosion and cavitations. These poor tribological properties have limited the applications of titanium alloys in many sliding components, tools and parts that are related to wear resistance [2].

The main reasons for such limitations are the low surface hardness and high friction coefficient of titanium alloys. It is a good choice to clad wear-resisting layers on the surface to solve these problems. Laser Metal Deposition (LMD) is an advanced laser materials processing technique, which is wildly used in manufacturing, part reparation, surface modification. The main characteristic that distinguishes LMD from other surface treatment is excellent metallurgical bonding, no pollution, high productivity, easy to realize automation, what’s more, the tendency to form pores and cracks is also reduced [3]. So LMD process can take the requirements (meet requirement) as the first choice.

As one of research area of rapid prototyping (RP) technology, LMD processes have drawn much attention lately because of their ability of forming small quantities of functional prototypes and structural parts at very low cost to the buyers. Several commercialized LMD processes existed already, including laser-engineered net shaping (LENS), directed-light fabrication (DLF), and laser additive manufacturing (LAM). All LMD processes are similar in a three-dimensional part in a computer-aided design file sliced into layers, and it in turn defines laser scan trajectories. A high-power laser is used to heat and melt metal powder, which solidifies to form a fully dense layer. The addition of multiple layers will produce a three-dimensional, fully dense part having net or near-net shape [4-6].
This paper reports the investigations in-situ synthesis TiC reinforced layer on Ti6Al4V alloy by LMD, using Cr<sub>3</sub>C<sub>2</sub> and Ti powders mixtures and the subsequent friction characteristics and wear-resistant properties.

**Experimental Procedures**

**Materials.** The experimental substrate is Ti6Al4V with nominal chemical composition is shown in Table 1. The Ti6Al4V specimens were cut into pieces of 100mm × 55mm × 10mm, and then grounded with 320 SiC paper, and degreased using acetone and ethanol before deposition [7]. Mixtures of Cr<sub>3</sub>C<sub>2</sub> powder and pure Ti powder were thoroughly mixed by ball milling in an argon atmosphere. The powder has a mesh size of -100/+325 (the particle size between 45 and 150 μm). The powder was exsiccated in drying vacuum cabinet for 10 hours with the temperature of 150°C and the substrate was preheated to 500°C by home-made preheater [8].

**Table 1 The composition of Ti6Al4V alloy (wt%)**

| Elements | Al  | V   | Fe  | O   | Si  | Ti  | Others |
|----------|-----|-----|-----|-----|-----|-----|--------|
| Percent  | 5.5–6.8 | 3.5–4.5 | <0.30 | <0.20 | <0.15 | Bal  | 0.40   |

**Set-up and Process.** Experimental set-up consists of high-power CO2 laser source and control system including laser beam delivery system, vacuum chamber and vacuum acquiring system, powder feeding system and powder delivery nozzle, positioning devices and CAM software. The real photograph and diagram of the LMD system are presented in Fig. 1. The processing parameters of LMD are listed in table 2.

![Fig. 1 The photograph and schematic illustration of the LMD system](image)

**Table 2 The processing parameters for LDM**

| Laser Power | Scanning speed | Spot diameter | Ration of overlap | Thickness of layer | Powder delivery | Focal length |
|-------------|----------------|---------------|-------------------|-------------------|----------------|-------------|
| 1.8~2.1[kW] | 6[mm/s]        | 1.5[mm]       | 30[%]             | 0.3~0.4[mm]       | 6~7[g/min]    | 200mm       |

**Characterization.** All the specimens were sectioned, mounted, polished and etched. The microhardness of the layer was determined, using a HVS-1000 Microhardness Tester with 300g of load, and the loading time being 20s. The microstructure was examined by OLYMPUS-DP71 optical microscope and SSX-550 SEM, while the compositions by EDAX9100 EDS.

A sphere-on-flat geometry was used for the low amplitude oscillating dry sliding tests, in ambient conditions. The fretting apparatus employed for the tests is shown in fig2. the sample disk was in size of 10mm×10mm×2.8mm with a surface polished down to emery paper of 1200 for the test. The coupled pin was a bearing ball of 7mm in diameter with hardness HRC60 made of GCr15 steel with nominal composition: C≤0.95~1.05, Mn≤0.20~0.40, Si≤0.15~0.35, S≤0.02, P≤0.027, Cr≤1.30~1.65 and the rest Fe. The test load was 20N, and the fretting conditions are summarized in Table 3. The speed of the back and forth moving of the disk was 15 mm/s. A Talysurf-4 type profilometer was adapted to measure wearing profiles, from which the volume of wear out of the material was estimated. The morphologies of the wearing surface and also the debris were examined by SEM [9-10].
Table 3 The parameters of wearing test

| Item | Load(N) | Frequency(Hz) | Stroke(mm) | Time(h) |
|------|---------|---------------|------------|---------|
| Value| 20      | 10            | 1          | 0.5     |

Fig.2 Schematic of the wearing tester
1 Normal load, 2 Counterbody, 3 Sample, 4 Supporting stand, 5 sliding vane, 6 crank

Results and discussion

Formation mechanism of TiC. Under laser irradiation between the Cr₃C₂ particles and molten metal might be divided into three stages. In the first stage, the interaction process was a physical one, which involved wetting of the particles by the liquid phase. The second stage was characterized by the inter-diffusion of the two phases. In the third stage a chemical reaction took place and new phases were formed. The type of new phases formed, together with their morphology and distribution in the matrix, was determined by the laser processing parameters used. The reaction between Cr₃C₂ and Ti in the laser process might take place as follows [11]:

\[ 2Ti + Cr₃C₂ \rightarrow 2TiC + 3Cr \]  \hspace{1cm} (1)

The thermodynamic data (in SI units) for the equations above are given in reference [7,9]. The change in the Gibbs free energy for (1) is given by

\[ \Delta G = 2G_{TiC} + 3G_{Cr} - 2G_{Ti} - G_{Cr₃C₂} \]  \hspace{1cm} (2)

The change in the Gibbs free energy for negative (\( \Delta G < 0 \)) at 1600K, indicating that the reaction is spontaneous [12,13]. Microstructure of the coating. Using the optimized parameters listed in the table to produce the in-situ synthesized TiC reinforced LDM layer on Ti6Al4V, and the sample was shown in the Fig.3 with eight wear-resisting layers coated on the substrates.

Fig.3 Wear-resisting sample  Fig.4 Macrostructure of samples  Fig.5 Microstructure of coating

Fig.4 shows the cross section of the clad layer at low magnification. It is clear that with proper laser processing parameters the layers are crack free and porosity free with low dilution and good metallurgical bond to the substrate. Fig.5 shows microstructure of the deposition section of the sample, which was clad with mixture powder containing 20% Cr₃C₂. The microstructure indicates there exists a good compatibility of the reinforcement phase to the matrix material.

Fig.6 The EDS of black grain of fig. 5  Fig.7 Microhardness distribution  Fig.8 Friction coefficient curve
Fig. 6 is EDS of black block in Fig. 5 marked as 1. The EDS maps show that the main component of black particles is Ti and C elements, combined with SEM, EDS and TiC in-situ formation mechanism mentioned above can be concluded that the black particles TiC. Fig. 7 shows the microhardness of deposition direction, where right sides of the dotted line show the hardness of substrate and left sides show the coating's respectively. As can be seen from the figure the hardness present gradient descents form the substrate to cladding layer. The maximum hardness value of layered is HV1000~1100.

Wear and Friction. Fig. 8 shows the friction behavior of the TC4 substrate and coating against GCr15 steel ball under the condition listed in the table 3. It's can be seen from the figure that the friction coefficient of substrate fluctuate over time, showing a gradually increasing trend, while the coefficient of coating changed slowly. Ignoring the unstable data of the first 30 seconds, the wear friction coefficient of the substrate rapidly rose to 0.9 from 0.5 in the first 15 minutes, and then went into stable friction stage and kept maintaining at between 0.9 to 1.0. For gradient distribution of the reinforced phase, the friction coefficient of coating maintained at between 0.9 to 1.0 during the whole friction time.

To investigate the wear performance of the coating, the dry sliding wear resistance at room temperature was performed. The testing conditions were listed at table 3. Thought the test the following results were got: the substrate wear volume is 0.127 mm³, and the coating wear volume is 0.002723 mm³. That is to say the wear resistance of the coating can be improved 46.6 times.

To understand the surface wear mechanism of the coating, the surface morphologies of the Ti6Al4V substrate and coating were examined. Figure 9a and 9b show overall SEM of wearing of substrate and its surface morphologies at higher magnifications.

![Fig.9 Surface morphology of wearing Ti6Al4V](image)

On the surface of Ti6Al4V alloy substrate appears a typical feature of noticeable plastic deformation combined with dense and deep ploughed grooves. Some debris deposited on the edge of the friction surface, there are a large number of chip-like wear debris and a small amount of granular debris on the worn surface, which is the typical feature of abrasive wear and oxidative wear. Since titanium is easily oxidized in air and the wear promoted it, oxidative wear plays a major role in the beginning of the friction process, although the oxide film is destroyed, it can be regenerated soon. As the wear process progressed, the wear was increasing, some wear debris was ejected with the reciprocating motion and some was retained in contact zone which acted as grains, it grinded deep grooves on the substrate surface to enlarge the wear. Therefore the main wear mechanism of substrate is oxidation wear and abrasive wear.

The fretting tack morphologies of coating, as revealed by SEM investigation, are shown in Fig. 10a and Fig. 10b which indicated overview and detail morphology of worn surface respectively. As it can be seen from Fig. 10 that the coating's surface is flat, smooth, and only a slight grinding marks alone sliding direction left on it, and no traces of plastic deformation and spalling. the worn surface of coating showed obvious abrasive wear. Laser in-situ synthesis TiC hard phase dispersed in a good solid solution ductile matrix. Under the normal load, the TiC hard particles were squeezed deeper to the substrate by the ball, which seemed to protect the coating from further wear. At the same time the solid solution Ti(Cr,C) was used as reinforcement to improve the wetting of the carbide phase by the metal matrix, reducing the possibility of TiC spall from Ti matrix. Tic Good combination between TiC and solid solution matrix has effectively improved the wear resistance of the coating.
Wear mechanism analysis shows that the main wear mechanism of substrate is oxidation wear and abrasive wear. And the coating is abrasive wear and few adhesive wear and also the fretting test indicates the coating with Cr₃C₂ has high resistance to wear than substrate.

![Fig.10 Surface morphology of wearing of coating](image)

**a-Overall SEM of wearing of coating**  **b-Partial enlargement SEM of wearing of coating**

**Conclusions**

The tribological behaviour of TiC-based coating has been evaluated under gross slip fretting conditions at room temperature. The following conclusions can be drawn from the present investigation.

A compositionally TiC reinforced Ti₆Al₄V material has been successfully fabricated by laser metal deposition of Cr₃C₂ and Ti powder.

The in-situ TiC particles are distributed uniformly in the Ti₆Al₄V matrix. The fretting test shows that the coating has better wear resistance then substrate. Wear resistance of the coating is about 46 times of TC4 substrate.

The main wear mechanism of substrate is oxidation wear and abrasive wear. The wear mechanism of the coating is abrasive wear and adhesive wear.

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