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Surface modification of Ti alloys with WC-TiB₂-reinforced laser composite coatings

Abstract: Laser cladding of the TiAl/Fe+Co-coated WC+TiB₂ pre-placed mixed powders on a Ti-6Al-4V alloy substrate can be used to form TiB₂/α-W₂C-reinforced composite coating, which improved the wear resistance of the substrate. To further improve the TiB₂/α-W₂C-reinforced composite coating, yttria partially stabilized zirconia (YPSZ) was added into the pre-placed powders. A metallurgical bonding was formed between the YPSZ-infused composite coating and the substrate. Many amorphous alloys were produced in this composite coating due to the action of YPSZ, and such coating showed fine microstructure. Thus, it is feasible to further improve the wear resistance of the laser clad TiB₂/α-W₂C-reinforced composite coating through the addition of YPSZ.

Keywords: interfaces; metal-matrix composites (MMCs); surfaces; tribological properties.

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1 Introduction

Laser cladding is a laser processing technique used to achieve required surface modification. Laser clad composite coating is an effective method to improve the surface performance of titanium alloys [1–3]. Previous studies have focused on the use of alloy powders for the

in situ fabrication of TiC particle-reinforced composites [4, 5]. Meanwhile, fewer studies have been carried out on WC-TiB₂-YPSZ system, especially via laser cladding technique. The W-C ceramics combine many favorable properties, such as high hardness, plasticity, and good wettability by the molten metals. Dearnley et al. [6] reported that the WC-Co-coated materials are being increasingly used in aeronautical applications owing to their tribological properties. Ti-B ceramics also have many good properties, such as high hardness, good wear resistance, and thermal stability.

In the current study, we confirm that the laser cladding of the TiAl/Fe+Co-coated WC/TiB₂ pre-placed mixed powders on a Ti-6Al-4V substrate can form the composite coating, which in turn, improved the wear resistance of substrate. Another investigation [7] indicated that laser clad yttria partially stabilized zirconia (YPSZ)-modified composite coating is an effective way to improve the surface performance of the metals. Through the experiment, we confirm that the addition of YPSZ into the TiAl/Fe+Co-coated WC/TiB₂ pre-placed powders on Ti-6Al-4V fabricated by laser cladding can form a composite coating, which possesses fine microstructure and high wear resistance. In this study, the influence of YPSZ on the microstructures and wear resistance of the TiAl/Fe+Co-coated WC/TiB₂ laser clad composite coating is introduced in detail.

2 Materials and methods

The materials used in this experiment are detailed in this section. First, we used Ti-6Al-4V alloy samples (10 mm×10 mm×30 mm), and the thickness of the pre-placed layer ranged from 0.7 to 0.9 mm. These were polished with SiC grit paper prior to the coating operation. Alloy powders of Fe (≥99.5% purity, 50–200 μm), TiAl (≥99.5% purity, 50–200 μm), Co-coated WC (≥99.5% purity, 50–150 μm, wt.%25 Co), TiB₂ (≥98.5% purity, 150–250 μm), and YPSZ (8 wt.%Y₂O₃, 50–100 μm) were used for the laser cladding. Water glass (Na₂O·nSiO₂) was used as binder. A 5 kW continuous wave of CO₂ laser with a beam diameter of 4.5 mm was employed to melt the surface of the samples. Three-track lap coating was formed on the substrate, and the lap

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rate was approximately 25%. During the laser cladding process, the surface oxidation was prevented by inert gas (Ar) with a flow rate of 30 l/min. The parameters of laser cladding process included a laser power of 850–1150 W and scanning speed of 2.5–8.0 mm/s. The compositions of the pre-placed powders used in this experiment were 17.5wt.% Fe+25wt.%TiAl+35 wt.%Co-coatedWC+20 wt.% TiB₂+2.5 wt.%YPSZ.

The wear volume loss was measured at 10-min intervals. Wear properties of the laser clad composite coating was tested by a MM-200 block-on-wheel dry sliding wear tester (Jinan Hengxu Testing Machine Technology Co., Ltd., Jinan, P.R. China). The rotational speed of the wear tester was 465 r/min, and the linear velocity of the friction surface was 0.88 m/s. An SMX-1000/1000L X-ray diffractometer (XRD) (SHIMADZU Co., Ltd., Kyoto, Japan) was used to determinate the phase constituent of such composite coating, and its microstructural morphology was analyzed using S-520 scanning electron microscope (SEM) (Hitachi Limited, Tokyo, Japan). Their distributions were measured using an energy dispersive spectrometer (EDS) (Hitachi Limited, Tokyo, Japan) and an electron probe micro-analyzer (EPMA) (Hitachi Limited, Tokyo, Japan). An HV-1000 microsclerometer (Shanghai Zhongyan Instrument Manufacturing Plant, Shanghai, P.R. China) was used to test the micro-hardness of such coating.

3 Results and discussion

3.1 SEM analysis

With the addition of YPSZ, the laser clad composite coating shows a fine microstructure (Figure 1A). As shown

in (Figure 1B), a great number of fine piece-like or Ti-B stick-like precipitates are produced. It can be deduced that the growth of the Ti-B crystals may be retarded by those piece-like precipitates to a certain extent. In addition, tetragonal ZrO₂ was present in such coating (Figure 1C). A previous investigation [8] reported that as the stabilizer of ZrO₂, Y³⁺ in Y₂O₃ can suppress c→t→m transformation; furthermore, the Y³⁺ content had a different suppression effect on ZrO₂ transformation, which enabled metastable phase tetragonal ZrO₂ (t-ZrO₂) to exist. Meanwhile, t-ZrO₂ phase structure possesses stress-induced transformation character, which can produce a transformation toughness effect [9].

3.2 XRD analysis

The composite coating mainly consists of γ -Co, Ti₃Al, Al₁₃Fe₄, M₁₂C (Co₆W₆C), α -W₂C, TiB₂, ZrO₂ and Al₁₆Co₇Zr₆, along with many amorphous alloys; these phases are produced through the *in situ* metallurgical reactions, as shown in Figure 2. Due to the addition of YPSZ, the diffraction peak of ZrO₂ can be observed in the XRD pattern, indicating that Fe reacts with Al in laser molten pool, which then leads to the formation of Al₁₃Fe₄. Moreover, a number of YPSZ show a very marked trend of floating on the surface of the molten pool due to its low density; thus, the diffraction peak of ZrO₂ can be detected.

3.3 EDS/EPMA analysis

When the fine piece-like precipitates in the coating were scanned by electron probe micro-analyzer (EPMA), the diffraction peaks of Al, Co and Zr reached high value

Figure 1: SEM images of the TiAl/Fe+Co-coated WC/TiB₂+YPSZ laser clad coating. (A) The clad zone, (B) TiB₂, and (C) t-ZrO₂.

Figure 2: XRD pattern of the laser clad coating.

(Figures 3A and B). Combined with the XRD results, it can be deduced that there is a $\text{Al}_{16}\text{Co}_7\text{Zr}_6$ phase in the fine piece-like precipitates, reinforcing the fact that laser cladding is an effective method to prepare the amorphous alloy coatings on titanium alloys, and is a significant approach in improving the surface properties of materials. An earlier work [10] reported that the production of the amorphous alloys can help improve the wear resistance of metals.

Figure 3: EPMA line scan results of the clad zone in the $\text{TiB}_2/\alpha\text{-W}_2\text{C}$ -reinforced composite coating. (A) The clad zone and (B) Al, Co, Zr.

Figure 4: SEM images of the the $\text{TiB}_2/\alpha\text{-W}_2\text{C}$ -enforced composite coating. (A) The block-shape precipitate, (B) nanocrystals, and (C) the needle-like location; (D) Location 1 and (E) location 2.

Table 1: EDS results of the different locations in the composite coating of the sample.

Position	Elements (Atomic%)						
	C	O	Ti	Zr	Al	W	Fe
1	13.75	–	24.5	–	26.63	27.98	7.14
2	–	6.78	42.63	2.72	24.36	–	23.51

As shown in Figure 4A, the block-shape precipitate is produced. The EDS pattern indicates that C, Al, Ti, Fe, and W are in location 1 (Figures 4A and D). Combining the results of Table 1 and the XRD diagram, it can be deduced that the block-shape precipitates mainly consist of α -W₂C and Al₁₃Fe₄/Ti₃Al. The SEM image demonstrates that the nanocrystals are produced (Figure 4B). In general, the metallic liquid solidifies immediately into the crystalline phases due to the unstability of metallic liquid at temperatures below the ideal melting temperature. The stability of supercooled liquid plays an important role in the fabrication of the bulk metallic glass. Okai et al. [11] reported that the amorphous alloys have attracted increasing interest as a precursor to producing nanocrystalline alloys containing a remaining amorphous phase by partial crystallization, or alloys consisting of a nano crystalline single phase by full crystallization. These nanocrystalline alloys exhibit unique characteristics, such as good mechanical properties. The EDS pattern of location 2 indicates that there are O, Zr, Fe, Ti, and Al in the needle-like location (Figures 4C and E). According to this result, it can be assumed that m-ZrO₂ has been produced in the coating matrix. In accordance with the report of Chen et al. [12], the transformation from t-ZrO₂ to

m-ZrO₂ (t-m) has proven to be nucleation controlled and martensitic in nature.

3.4 Micro-hardness

The micro-hardness distribution of the composite coating is shown in Figure 5. As can be seen, the micro-hardness of such coating is in a range of 1700–1830 HV_{0.2}, which is approximately five times higher than that of the substrate (360 HV_{0.2}). Combined with the XRD analysis, it is known that the phase constituent of such coating is beneficial in increasing micro-hardness; moreover, the production of amorphous alloys and their fine microstructure are also beneficial in increasing micro-hardness. Owing to the rapid cooling rate of the molten pool, a small amount of elements, such as Al and Si, have had no time to be precipitated from the liquid and solution in γ -Co to form a supersolution. This strengthened the solution and improved micro-hardness.

3.5 Wear resistance

The wear test result indicates that the wear volume loss of the TiB₂/α-W₂C reinforced composite coating is about 1/4 of Ti-6Al-4V when the load is at 49 N (Figure 6). The high wear resistance of such coating is primarily attributed to the characteristics of coating with a phase constituent showing excellent wear resistance. It should be mentioned that the production of the amorphous alloy and t-ZrO₂/m-ZrO₂ play dominant roles in resisting wear attacks during the dry sliding wear process, preventing

Figure 5: Micro-hardness distribution of the TiB₂/α-W₂C-reinforced composite coating. **Figure 6:** Wear volume loss of the TiB₂/α-W₂C-reinforced composite coating and Ti-6Al-4V.

the alloy from serious deformation, such as micro-cutting or micro-plowing. Thus, the coating exhibits good wear resistance compared with Ti-6Al-4V.

4 Conclusions

Laser cladding of the TiAl/Fe+Co-coated WC/TiB₂+YPSZ pre-placed mixed powders on a Ti-6Al-4V alloy substrate can form the TiB₂/α-W₂C-reinforced composite coating. There are mainly γ-Co, Ti₃Al, Al₁₃Fe₄, M₁₂C (Co₆W₆C), α-W₂C, TiB₂, ZrO₂ and Al₁₆CoZr₆ in this composite coating, and its phase constituent improves wear resistance of the substrate. The addition of YPSZ can further improve the microstructure and wear resistance of this coating. The amorphous alloys and t-ZrO₂/m-ZrO₂ are produced the coating due to the action of YPSZ, which is beneficial in improving wear resistance. The micro-hardness distribution is in a range of 1700–1830 HV_{0.2}, and the wear volume loss of coating is about 1/4 of Ti-6Al-4V. Thus, it is feasible to improve the wear resistance of the titanium alloys via the laser cladding of the TiAl/Fe+Co-coated WC/TiB₂+YPSZ mixed powders.

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