Microstructure and mechanical properties of laser-cladded WC–Co composite coatings on Ti–6Al–4V

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Abstract
WC-Co powder reinforced coatings were prepared on the Ti-6Al-4V substrate for improving the hardness and wear resistance by laser cladding technique. The effects of different laser power and Co content on the microstructure and properties of the cladding layer were studied. The results showed that when the laser power was too low, there were unmelted WC-Co powders on the surface of the cladding layer. In contrast, when the laser power was too high, the coating materials were prone to over-burning and evaporation, cracks and pores were aggravated. The WC-25Co coatings without cracks and pores could be formed when power is set at 1300 W, and its average micro-hardness was higher than other specimens. The addition of Co was helpful to the bonding of clad and Ti-6Al-4V substrate. New hard phases of TiC and CoTi2 were mainly distributed in the cladding coatings. The micro-hardness of the cladding coatings increased by 2–4 times than that of the Ti-6Al-4V substrate, and the maximum hardness reached 1349 HV. Under the same dry sliding wear condition, the wear resistance of the WC-25Co coatings was significantly improved and increased by 15.7–34.1 times compared with the substrate.

1. Introduction

Ti-6Al-4V alloy has been widely used in aerospace, marine, automobile, and other fields due to its characteristics of high specific strength, excellent corrosion resistance and low density [1–3]. However, the low hardness (280–360 HV), poor wear resistance and high friction coefficient (0.5–0.7) severely limit its applications under several wear and friction conditions [4–6]. Hence, improving the wear resistance of titanium alloys is of great significance for expanding the range of applications.

The surface treatment is an effective way to improve wear resistance and service life of titanium alloys. Traditional surface modification methods for titanium alloys include ion implantation [7, 8], chemical vapor deposition (CVD) [9], physical vapor deposition (PVD) [10], and etc. However, these methods afford coatings of micron thickness and weak adhesion to the substrate, due to which they are unable to meet the application requirements under high contact stress conditions. Recently, laser cladding technology has been extensively used in the preparation of precision defect-free composite coating, which can significantly improve the surface hardness, strength, wear resistance and corrosion resistance of materials [11, 12]. The laser cladding process usually involves the melting of a thin surface layer of the substrate and subsequent combination with the additive materials to form coatings of typically 0.5–3 mm thickness with good metallurgical bonding [13]. In addition, the laser cladding technique is characterized by several advantages such as limited heat-affected zone, small distortion of the substrate, and low internal dilution rate [14].

Generally, the process parameters and material characteristics considerably influence the microstructure and properties of the laser coatings [15]. In laser cladding technology, the melting width increases with the increase of laser power, while the melting depth decreases with the increase of scanning speed. Emamian et al [16] found that a higher amount of fed powder coming from lower scan speed increased the fraction of in situ
formed microstructure in the clad, and resulted in higher values for hardness. Song et al [17] fabricated denser Ti-6Al-4V parts without post-processes during selective laser melting. The experimental results indicated that with the increased in the scan rate, the microstructures exhibited more and more pores and the layer structures were more and more obvious. Weng et al [18] studied the effect of process parameters on the microstructure evolution and wear properties of the laser-clad Co42 + B4C mixed powders on Ti-6Al-4V alloy. The results indicated that the hard particles (TiB and TiC) were refined with the decrease in laser specific energy.

The reinforced particles (such as TiC, TiN, SiC and WC) [19–22] are usually directly added to improve the hardness and wear resistance of titanium alloy substrates. Li et al [23] fabricated a (TiB + TiC)/Ti composite coating on Ti-6Al-4V alloy by laser cladding. The results indicated that the wear resistance of the coating is significantly superior to that of the Ti-6Al-4V substrate. Savalani et al [3] investigated the in situ formation of titanium carbide using titanium and carbon-nanotube powders by laser cladding. They found that the coating comprised α-Ti and TiC reinforced phases, and the micro-hardness (1125 HV0.5) of Ti-20wt% carbon nanotubes was the highest. Feng et al [24] obtained Ti3Al and TiB particles in situ in an α-Ti matrix by laser cladding. The wear resistance and high-temperature oxidation resistance of the coating significantly increased compared with that of the matrix.

Traditionally, tungsten carbide is one of the most effective wear-resistant materials [25]. However, using single ceramics as cladding materials has some shortcomings, since ceramics eventually exhibit brittleness in addition to their high hardness. Defects easily form in these coatings, especially at a certain location between the reinforced phases and the matrix. In this case, some scholars have found that the addition of a cobalt binder is helpful in the bonding of the clad and Ti-6Al-4V substrate [22, 26, 27]. However, there have been few reports that the WC-Co composite powder was directly coated on the surface of the titanium alloy by laser cladding technology to improve wear resistance.

Consequently, in the present study, WC-Co reinforced coatings were prepared on the Ti-6Al-4V substrate with the aim of improving the hardness and wear properties by the laser cladding technique. The effects of Co content and different laser power on the properties of the laser-cladded WC-Co coatings were investigated, and the formation mechanism of the hard phase in the coating was analyzed.

2. Experimental details

Commercially available Ti-6Al-4V alloy (30 mm × 30 mm × 10 mm) was chosen as the substrate. WC-12Co and WC-25Co powders were selected as reinforcing materials. The typical morphology of the two powders is shown in figure 1. Specifically, both powders of 80–120 mesh and 120–230 mesh, respectively, with good spherical morphology and small surface roughness were prepared in the laboratory. The chemical composition of the substrate and clad powders are provided in table 1. Prior to laser cladding, the Ti-6Al-4V surfaces were polished with silicon carbide abrasive papers and degreased in acetone to eliminate surface contaminants.

An LMD8060 laser 3D printing system was used to form composite coatings on Ti-6Al-4V alloy. The instrument was equipped with Laserline LDF 3.000–60 laser (power: 0–3 kW, adjustable) and Precitec laser cladding head (beam spot diameter: 1–6 mm, adjustable). The parameters of laser processing after initial
experimental explorations were as follows: laser scan speed: 500 mm min\(^{-1}\); beam spot diameter: 2 mm; scanning overlap rate: 50%; synchronous powder feed rate: 1.0 rpm; laser power: 900–2000 W. Argon was used as a shielding gas at a flowing rate of 10 L min\(^{-1}\) to protect the cladding from oxidation.

After the laser cladding process, coatings were machined to dimensions 16 mm \(\times\) 16 mm \(\times\) 5 mm via wire-cut electrical discharge machining. The microstructure characterization of the cross-section coatings was performed using a field emission scanning electron microscope (SEM, FEI Quanta 200FEG) equipped with an incident energy dispersive spectrometer (EDS). Phase analysis was performed using an x-ray diffractometer (XRD, PANalytical Empyrean x-ray diffractometer). Vickers hardness test (HVS-1000) was performed on the cross-sectioned layers under an applied load of 200 g for 15 s, starting from the surface of the cladded area toward the Ti-6Al-4V substrate. The average value of 5 points at the same depth was taken as the measured value.

Wear resistance of coatings at room temperature were tested by using a ball-on-disk tribometer (THT-1000) under dry friction condition. The Al\(_2\)O\(_3\) ball with a diameter of 6 mm was used as the friction pair because it is a ceramic material with high hardness. The sliding speed was 20 cm s\(^{-1}\), the sliding distance was 200 m and the test time was 20 min at a load of 5 N. An OLYMPUS LEXT OLS4100 laser scanning confocal microscope was used to observe the wear marks. Through the analysis and simulation of OLYMPUS Stream microscopic image software, the three-dimensional structure of the wear marks was obtained, and the wear rate was calculated. The wear rate is defined as the wear volume per unit load and per unit wear distance, and is calculated using the following formula [28]:

\[ W_r = V / (F \times L) \tag{1} \]

where \(W_r\) is wear rate (mm\(^3\) \(\cdot\) N\(^{-1}\) \(\cdot\) m\(^{-1}\)), \(V\) is the wear volume volume loss (mm\(^3\)), \(F\) is the vertical load (N), and \(L\) is the sliding distance (m).

3. Results and discussion

3.1. Microstructure of the WC-12Co/WC-25Co coatings

Figure 2 shows the microstructure of the WC-12Co coatings laser-cladded on the Ti-6Al-4V substrate at different laser power. With the increase of laser power (1100 W, 1300 W and 1500 W), the cladding layer thickness increases, forming a coating with a thickness of 1.9–2.4 mm. In the WC-12Co composite coatings, the cross-section images clearly show that coated layers have defects with cracks and pores. SEM analysis was performed around the region of a micro-crack (P = 1100 W), as shown in figure 2(a). We can observe that the crack originated from the surface of the cladding layer, propagated along the depth and ended at the center of the coating. Cracks appear in the cladding layer because the thermal expansion coefficient and thermal conductivity between the substrate and cladding layer are quite different, which easily causes high internal stress. The linear analysis of the crack region in figure 2(b) shows that the elemental content of O increases sharply in the crack area, resulting in the formation of an O-rich alpha-titanium phase with high brittleness and high crack sensitivity on the surface. As shown in figures 2(c) and (e), pores are observed between the coating and the substrate. A large number of pores are formed because the reaction gas in the molten pool cannot escape in time during the laser cladding process. Furthermore, it may be due to the uneven temperature distribution in the cladding layer. As shown in figure 2(d), due to high density and melting point of the WC-12Co composite powder, it easily deposits at the bottom of the molten pool during laser cladding, which results in the aggregation of ceramic particles and the uneven structure of the coating. In contrast, on employing higher processing power (1500 W), no WC-12Co-deposited powder was observed.

The SEM images of the cross-section of the WC-25Co composite coatings at different laser power are shown in figure 3. An excellent metallurgical bond forms between the substrate and the coating by partial mutual diffusion of the elements. Furthermore, it is evident that the morphology of the laser-cladded coatings largely depends on the laser power. A close comparison of the images revealed that the energy from employing lower laser power (900 W or 1100 W) is too small to melt enough cladding material and substrate surfaces. Therefore, a

| Material       | Element (wt%) |
|----------------|---------------|
| Ti-6Al-4V      | Bal. 0.15     |
| WC-12Co       | 5.70 12.20 Bal. |
| WC-25Co       | 5.20 25.03 Bal. |

Table 1. Chemical composition of the substrate and clad powders.
small amount of unmelted WC-25Co spherical particles adheres to the cladding layer surface. In contrast, on employing higher laser power (2000 W), the surface of the cladding layer is evidently smoother. At condition of higher laser power, the substrate and powder absorb relatively more energy to heat up and melt. The coating thickness is reasonably small on employing low laser power, but with the increase in laser power, the coating thickness increases significantly. The thickness of the WC-25Co coating obtained in this study is 1.2–1.7 mm. The higher the laser power, the greater the probability of generating pores. With the increase in laser power (P) to 2000 W, the depth of the cladding layer increases, the molten metal fluctuates sharply, and the surface solidifies...
quickly. In this case, the cladding materials are prone to over-burning and evaporation, and cracks and pores are aggravated, as shown in figure 3(e). In this study, the optimized coatings without pores and cracks can be formed only when P is set at 1300 W.

Compared with the results shown in figures 2 and 3, we found that the WC-25Co cladding layer obtained using the optimized processing parameters has small pore size, and more uniform phase structure. This may be due to the increase in the Co content, which can enhance the bonding strength between the coating and Ti-6Al-4V substrate. A CoTi2 solid solution produced by the reaction of Co and Ti can also promote the metallurgical bonding between the cladding layer and the substrate [22]. Based on the morphological analysis of WC-12Co and WC-25Co cladding layers, the WC-25Co coatings with good morphology were analyzed in detail.

Figure 3. SEM images of cross-section of WC-25Co coatings at different laser powers: (a) 900 W; (b) 1100 W; (c) 1300 W; (d) 1500 W; (e) 2000 W.
3.2. Phase composition of the WC-25Co coatings

Figure 4 shows the XRD analysis of the WC-25Co laser-cladded coatings at different powers (900 W, 1100 W, 1300 W, 1500 W and 2000 W). The coatings mainly comprised of W, WC, TiC, α-Ti, and CoTi2. No oxides of Ti and Co were detected according to the XRD results, profiting from the effective protection of the shielding gas (Ar). With the rapid heating enabled by the laser, WC powders easily decomposed and reacted due to the high temperature of the molten pool. The following chemical reactions occur [22]:

\[ \text{WC} \rightarrow \text{C} + \text{W} \]  
(2)
\[ 2\text{WC} \rightarrow \text{W}_2\text{C} + \text{C} \]  
(3)
\[ \text{W}_2\text{C} \rightarrow \text{C} + 2\text{W} \]  
(4)

As \( \text{W}_2\text{C} \) is an unstable phase in the W-C system, it further reacted to form W and C, according to equation (4). A small amount of Ti in the substrate enters the molten pool through convection and diffusion in the laser cladding process, which reacts with C to in situ form high hardness TiC owing to the higher affinity of C to Ti. At the same time, the reaction of equation (5) consumes a lot of C, which further promotes the decomposition of WC. [29–31]

\[ \text{C} + \text{Ti} \rightarrow \text{TiC} \]  
(5)
\[ \text{Co} + 2\text{Ti} \rightarrow \text{CoTi}_2 \]  
(6)
\[ \text{Co} + \text{Ti} \rightarrow \text{CoTi} \]  
(7)

According to the Ti-Co binary alloy phase diagram [32], there are various intermetallics between Co and Ti. Generally, the chemical reactions were affected by both the thermodynamic and kinetic factors. As shown in the reactions in equation (6) and equation (7), a higher amount of Ti in the molten pool was favorable to the reaction in equation (6), according to the stoichiometric coefficients of Co and Ti. Meanwhile, the reaction in equation (7) is not favored to occur owing to its higher \( \Delta G \) compared with that of equation (6). Therefore, in the case of the limited amount of Co in the molten pool, the reaction in equation (7) was restricted (confirmed by several XRD scans analysis).

The Gibbs free energy (\( \Delta G \)) and enthalpy of formation (\( \Delta H \)) of reactions in equations (5) and (6) are both reported to be negative, indicating that the reaction can be spontaneous and exothermic [33]. Studies have shown that Co-containing coatings play a significant role in enhancing the surface properties of titanium alloys [34]. Dutta Majumdar [35] studied the properties of a coating fabricated via the direct laser cladding of Co on Ti-6Al-4V. The wear resistance of the cladding layer was found to be improved due to the combination of CoTi2, CoTi and α-Ti phases. Therefore, TiC and CoTi2 produced by the reaction play an active role in improving the hardness and wear resistance of the coatings.

3.3. Microstructure analysis of the WC-25Co coating (P = 1300 W)

Figure 5 shows the SEM images of the bottom, middle and top regions of the coating at \( P = 1300 \) W. According to the EDS component analysis in table 2, the bright region (point 5, point 8) is mainly composed of W and a
small amount of C, Ti and Co. Combined with the XRD analysis, we infer that the bright region is W and WC solid solution, the black region (point 6, point 9) is mainly CoTi2, and the gray region (point 4, point 7) is TiC.

The structure of each area is different from the top to the bottom of the cladding due to different temperature gradients and cooling rates. At the bottom of the coating, many dendritic TiC particles are evenly distributed. TiC has a typical NaCl structure belonging to the cubic crystal system. Due to the rapid solidification of the molten pool, the solid-liquid interface changes from a smooth interface to a rough interface. Hence, TiC grains tend to grow into TiC dendrites via continuous growth.

In the middle of the molten pool, the grain morphology changes significantly, under the influence of temperature distribution. The dendrite of TiC tends to transform into block TiC. At the top region, where the temperature is higher and the liquid holding time of the molten pool is longer, more reaction time is available for producing larger size TiC particles. Co-Ti exhibits eutectic character and exists in the form of CoTi2, in agreement with XRD analysis.

Figures 3(b), (c) show the linear analysis of the coatings (1100 W, 1300 W, 1500 W), indicating that closer to the substrate, more Ti and less W content is present in the hard phase. A large amount of Ti exists in the coatings due to convection, which provides conditions for the formation of TiC and CoTi2. The interdiffusion of the elements was beneficial to the bonding between the cladding coatings and the substrate. As the laser power increases, the convection of the molten pool becomes more pronounced. The dilution rate is the change in the degree of the composition of cladding alloy caused by the melting substrate during laser cladding. High dilution rate indicates that the substrate over-dilutes the coating, which easily weakens the coating performance and increases the tendency of cracking and deformation. In this study, the content of Ti is observed to be clearly higher in the coating obtained at $P = 1500$ W, indicating that the dilution rate of the coating increases.

3.4. Micro-hardness of the WC-25Co coatings
Figure 6 shows the Vickers hardness analysis results of the WC-25Co composite coatings. It can be seen that the hardness of the cladding coatings decrease gradually with the increase in distance from the surface, and the micro-hardness of the cladding coatings increased by 2–4 fold than that of the Ti-6Al-4V substrate, which was attributed to dispersion strengthening due to the presence of W, WC, TiC, and CoTi2. The maximum value of
micro-hardness was 1349 HV. At the transition zone from the cladding layer to the substrate, the hardness decreases linearly.

With the change in P, the hardness of the cladding layer also fluctuates to a certain extent. Since the higher the P, the more the energy absorbed by the composite coating; consequently, the phase has more time to be uniform. However, the hardness of the cladding layer is low when P = 2000 W, which is mainly due to the excess dilution rate of the cladding layer. In contrast, the average micro-hardness of the cladding layer on employing P = 1300 W was higher than that of the other specimens. Therefore, P = 1300 W is the best to prepare the WC-25Co coatings, which can be proven from the SEM micrographs and hardness curves.

3.5. Wear properties of the WC-25Co laser cladding coatings

Figure 7 shows the SEM images of the worn surfaces of the Ti-6Al-4V substrate and WC-25Co laser-cladded coatings after wear tests. We can see that the wear marks of the substrate are deeper than those in other cladding coatings. This occurs because of the friction between the hard Al₂O₃ ball and the soft Ti-6Al-4V substrate, which leads to adhesive wear and deep grooves. A large number of abrasive particles fall off with the progress in the wear test. Meanwhile, the abrasive wear on the friction surface is accompanied by a large amount of friction heat, which leads to severe oxidation wear. The wear width of the Ti-6Al-4V substrate is about 3–5 times that of the other cladding coatings. Compared with the Ti-6Al-4V alloy, the surface hardness of the cladding composite layer is higher. After dry sliding friction, a small amount of debris would be produced and slightly abrasive wear would occur. Therefore, there are small abrasion marks, shallow pits and the worn surface is relatively flat. Furthermore, metal adhesion occurs locally on the contact surface of the friction pair. In the process of sliding wear, scratch pits are caused by the destroyed adhesion and metal chips. Furthermore, the surrounding regions of the wear grooves shown in figure 7(c) indicate the occurrence of plastic deformation. The wear of adhesive Co also promotes the transfer of wear debris and increases the surface roughness of the sample.

After the wear test, the produced debris was collected and analyzed. The cladding coating debris (P = 1300 W) is shown in figure 8(a) and the substrate debris in the Ti-6Al-4V alloy is shown in figure 8(c). The images show that the particle size of wear debris in the Ti-6Al-4V substrate is larger than that in the WC-25Co cladding coating. The EDS analysis results show that the content of oxygen is high, which indicates that friction heat induces surface oxidation during the wear process. Furthermore, there is a small amount of Al in the cladding coating, which may come partly from the substrate and partly from the Al₂O₃ friction pair. This indicated that the cladding coating has good dry sliding wear resistance.

Figure 9 shows the wear rates of the Ti-6Al-4V substrate and WC-25Co coatings at different power. As shown in the figure, the wear resistance of each coating is higher than that of the substrate. The wear rate of the substrate (5.8 × 10⁻⁴ mm³ · N⁻¹ · m⁻¹) is about 15.7–34.1 times that of the cladding layers under the same wear conditions, and the wear resistance of the cladding layer is the best at P = 1300 W. Therefore, cladding layers with remarkable improvement in wear resistance can be obtained with suitable laser power and cladding material system.

Figure 6. Cross-section micro-hardness of the WC-25Co coatings.
4. Conclusion

(1) WC-Co reinforced coatings were fabricated on the Ti-6Al-4V substrate at different laser power. The results indicated that there are cracks and pores in the WC-12Co composite coatings, while the WC-25Co composite coatings can be obtained without defects at $P = 1300$ W.

(2) The WC-25Co coatings comprised TiC, WC, W, $\alpha$-Ti and CoTi$_2$ phases. The in situ formed TiC and CoTi$_2$ play an active role in improving the hardness and wear resistance of the coatings.

(3) With varying laser power, the hardness of the WC-25Co laser-cladded coatings increases by 2–4 times than that of the Ti-6Al-4V titanium alloy substrate (360 HV), while the wear resistance of coatings increases by 15.7–34.1 times. Furthermore, adhesion wear and debris wear were demonstrated to be the main wear mechanisms.

Figure 7. Worn morphologies of (a) $P = 900$ W; (b) $P = 1100$ W; (c) $P = 1300$ W; (d) $P = 1500$ W; (e) $P = 2000$ W; (f) Ti-6Al-4V substrate.
The addition of Co is helpful to the bonding of the cladding and the Ti-6Al-4V substrate. Hard phases of W, TiC and CoTi$_2$ are uniformly dispersed in the coatings, in which TiC mainly exists in the form of dendrites and block crystals.

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Figure 8. SEM images and EDS analysis of debris: (a) $P = 1300$ W; (b) EDS analysis of area C; (c) Ti-6Al-4V substrate; (d) EDS analysis of area D.

Figure 9. Wear rate of the WC-25Co coatings.
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