Microstructure and wear resistance of bimodal cemented carbide coating prepared by direct laser powder deposition

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Abstract
Compact spherical WC-12Co composite powder was deposited on 304 stainless steel substrate by multi-layer laser powder deposition (LPD) to fabricate cemented carbide coating. The phase constitution and microstructure of the coating as well as the feedstock powder were characterized. Microhardness and dry sliding wear tests were also performed to assess the mechanical properties of the coating. The results showed that the coating exhibited distinct microstructures and phase constitutions at different depths due to the various thermal cycles and the resulting heat damages of feedstock powders. The upper region of the coating (i.e. the wear resistant layer) exhibited bimodal microstructure in which the incompletely dissolved WC-Co composite particles preserved the original submicron sintered structure and secondary carbides were precipitated around them. Owing to the fine-grained strengthening of submicron WC grains in the undissolved areas, the microhardness of wear resistant layer was enhanced to 8 times that of the substrate. The wear rate of the cemented carbide coating was about three orders of magnitude lower than that of the substrate when dry sliding against Al2O3 ball under 10 N normal load. The bimodal structure of the wear resistant layer and the synergistic enhancement of differently sized carbides are the key factors for the excellent wear resistance of the coating.

1. Introduction
The applicability of austenitic stainless steel alloys is hindered by their limited strength and poor wear resistance in harsh working conditions [1, 2]. Therefore, it is necessary to strengthen the surface of such materials. An effective approach to strengthening stainless steel components is to deposit ceramic-metal composite (CMC) coatings with high hardness and high wear resistance on their surfaces. Such association of materials with distinct natures can not only maintains the plasticity and toughness of the stainless steel matrix, but also exerts the high hardness and wear resistance of CMC coatings [3]. WC-Co cemented carbides are widely employed in tribological files of cutting, dieing, mining, and drilling on account of their high hardness, outstanding wear resistance, high heat stability and reasonable toughness [4, 5]. Many surface modification techniques have been used to prepare WC-Co cemented carbide coatings, such as thermal spraying, arc welding, and laser cladding. Among them, laser cladding can fabricate much better coatings with extremely fine microstructure, minimal dilution from the substrate, small heat-affected zone (HAZ), and metallurgical bonding with the substrate [6, 7]. However, laser cladded CMC coatings exhibit high crack sensitivity, which restricts their further application in many industrial fields [8, 9].

Laser powder deposition (LPD) is an additive manufacturing (AM) technology based on laser fusion and powder injection [10, 11]. It has also been considered as a surface coating technology when deposited powders generate a functional layer onto the substrate [12–14]. The LPD process not only can adapt to complex
workpieces, but also has wide parameters window and high deposition efficiency \([15, 16]\). During LPD, the laser beam is directed onto the substrate surface to create a moving molten pool, simultaneously, additive powders are injected into the melt pool through coaxial nozzle by carrier gas stream. There is no sharp thermal gradient and dramatic composition change across the interface of the CMC coatings and substrates because the added powders are deposited directly into the molten pool of the substrate in LPD \([17]\). Consequently, crack initiation induced by residual thermal stress and structural stress is eliminated.

Recently, a series of multimodal WC-Co cemented carbide coatings have been fabricated by various spraying techniques to improve the mechanical properties and wear resistance of the coatings \([18–20]\). Skandan \textit{et al}\([21]\) reported that the multimodal WC-Co coating had significantly improved abrasive wear resistance without an associated increase in hardness. Yang \textit{et al}\([22, 23]\) proposed a concept of WC-(nanoWC-Co) multimodal cemented carbide and obtained such structured coating by cold spraying WC-Co powder with bimodal-sized WC particles. They found that the wear performance was significantly improved by the simultaneous hardening and toughening effects of WC-(nanoWC-Co). Wang \textit{et al}\([24]\) deposited a novel bimodal-grained WC-Co coating by high velocity oxy-fuel (HVOF) spraying, using the raw materials consisting of the nanoscale WC-Co composite powder as major component and a certain of ultra-coarse WC particles as addition. Due to the high energy density of the laser beam, the CMC coatings prepared by laser surface technologies are incapable to inherit the original structure and mechanical properties from the raw materials \([25]\). So far, no attempt has been made to deposit multimodal CMC coatings by laser surface technology.

In this work, cemented carbide coating with bimodal structure was deposited on 304 austenitic stainless steel substrate by optimized LPD process. The compact spherical WC-12Co composite powder with submicron-grained WC was used as feedstock. The phase constitution, microstructure, microhardness, and wear performance of the deposited coating were characterized. In addition, the formation mechanism of microstructure distinction in the different regions of the coating and the relationship between microstructures and mechanical properties were discussed in detail.

2. Experimental

2.1. Materials and LPD processing

The substrate used in this work was an AISI 304 stainless steel plate with dimensions of 100 mm × 50 mm × 10 mm. Commercially available compact spherical WC-12Co composite powder (Jiangxi Qisheng New Materials Co., Ltd., China) with an average particle size of 93.6 μm was used as raw material. Before LPD, the surface of the substrate was sandblasted and then cleaned ultrasonically by ethanol. The purpose of the sandblasting is to roughen the substrate surface so as to improve the laser-power absorptivity.

The cemented carbide coating was fabricated on 304 stainless steel substrate with a direct laser powder deposition system. A schematic diagram of the LPD process is displayed in figure 1. A 3 kW fiber-coupled diode laser (Laserline, LDF 3000-60) with a wavelength of 1070 nm and circular beam shape was used as energy source,
and the high purity argon was used as the carrier and shielding gas. The laser spot diameter on the surface of the substrate was adjusted to 2.0 mm. The multiple tracks with an overlapping rate of 40\% were deposited for each layer and three layers were cladded on the substrate to produce the desired coating. The other parameters of laser deposition were set as follows: laser power of 1.4 kW, beam scanning speed of 0.3 m \text{min}^{-1}, powder feeding rate of 10.2 g \text{min}^{-1}, which had been optimized by our previous study \cite{26}.

2.2. Coating characterization and tests

After LPD, the transverse cross section of the cemented carbide coating was cut perpendicularly to the scanning direction. The top region of the coating was worn off about 100 \(\mu\text{m}\) along the thickness to form the wear resistant surface. The cross-sectional and surface samples were then ground and polished. The microstructures of samples were observed by a scanning electron microscopy (SEM, FEI Quanta 200F) with the backscattering (BSE) mode. The phase constitutions of both composite powder and as-deposited coating were identified by x-ray diffraction analysis (XRD, PANalytical X’Pert Pro) with Cu-K\(\alpha\) radiation (\(\lambda = 0.15406 \text{nm}\)). Energy dispersive spectrometer (EDS, Oxford X-Max 80) analysis was used to measure the chemical composition in different locations of the cemented carbide coating.

Microhardness tests were performed along the thickness of the cross section at intervals of 100 \(\mu\text{m}\) using a digital Vickers hardness tester (Shanghai, HXS–1000AK). An indentation load of 0.3 kg and dwelling time of 15 s were used in this study. To assess the wear performance of the cemented carbide coating and the substrate, dry sliding wear tests were executed on the samples surface using a ball-on-disk tribometer (Anton Paar, THT–1000) at ambient temperature. Figure 2 shows a schematic illustration of the dry sliding wear test. The sample was fixed on a rotating stage of the ball-on-disk configuration, while the counterpart ball was contacted with the sample to cause wear under an applied load. A 6 mm diameter sintered \(\text{Al}_2\text{O}_3\) ceramic ball with the hardness of 1840 HV was selected as the counterpart. The rotational sliding tests were carried out at a normal load of 10 N and a wear track radius of 2 mm. The sliding velocity was set to a constant of 9 m \text{min}^{-1}, and the total sliding distance was 200 m with a duration of 22.22 min The coefficient of friction (COF) was continuously recorded by the computer connected to the tribometer. The profile of the wear track was simulated by using a laser confocal microscope (Olympus, LEXT OLS 4100) and then quantified as a measure of the cross-sectional area. The wear rate \(\omega\) was calculated by the equation (1):

\[
\omega = \frac{V_{\text{loss}}}{F \times L} \quad (1)
\]

\[
V_{\text{loss}} = A_{\text{loss}} \times l \quad (2)
\]

where \(V_{\text{loss}}\) is the volume loss of the worn surface as calculated b is the contact load (N), L is the sliding distance (m), \(A_{\text{loss}}\) is the cross-sectional area, and \(l\) is the perimeter equation (2), Fr of the worn track. After the friction and wear tests, the worn surfaces were also characterized by SEM.

Figure 2. Schematic illustration of the dry sliding wear test: (a) ball-on-disk tribometer and (b) wear track.
**Figure 3.** Morphology and cross-sectional microstructure of the WC-12Co composite powder: (a) overall view, (b) surface morphology, (c) cross-sectional view and (d) enlarged BSE microstructure of the rectangular region in (c).

**Figure 4.** XRD pattern of the WC-12Co composite powder.
3. Results

3.1. Characterization of the feedstock powder
Figures 3(a) and (b) display the appearance of the WC-12Co composite powder in which the spherical morphology and slightly rough surface can be clearly distinguished. The cross-sectional morphology of the composite powder (see figure 3(c)) indicates that the particles are almost fully densified. Result from the XRD analysis (see figure 4) confirms that the WC-12Co composite powder is composed of WC and Co phases only. Figure 3(d) shows the inner microstructure of a single feedstock particle. The WC grains with triangle or quadrangle shapes are densely and uniformly embedded in Co binder matrix, exhibiting typical microstructure characteristics of the sintered cemented carbide. As measured by the linear intercept method, the WC particles have a grain size ranging from 80 nm to 370 nm with a mean value of about 230 nm.

3.2. Phase constitution and microstructure of the coating
The cross-sectional macrostructure of the cemented carbide coating prepared by LPD is shown in figure 5(a). It can be seen that the laser deposited coating with a thickness of \( \sim 1.6 \) mm which has a metallurgy bonding with the substrate is obtained. The coating is fully dense and absence of defects in the form of porosity and crack. Visible thermal damage of the substrate in the heat-affected zone (i.e., the dark gray region under the interface) occurs alternately because the energy intensity of the laser beam follow a Gaussian distribution. It is noted that...
the coating can be divided into two regions according to the different microstructures, namely the upper region and the lower region, as marked in figure 5(b).

Figure 6 presents the phase constitutions of the substrate and each region marked in figure 5(b). Specifically, the test planes of the lower region and upper region are approx. 800 μm and 200 μm away from the surface of the coating, which represent the typical phase constitution in each region. It confirms that the only phase in the substrate is γ-Fe. The lower region of the coating mainly composed of γ-Fe, WC and M3W3C (M=Fe, Co) type carbide. According to the diffraction peak intensity, the dominant phase of the lower region is WC, while the contents of M3W3C and γ-Fe phases are relatively low. The existence of M3W3C carbide phase can be attributed to the reaction of dissolved WC-Co composite particles with liquid Fe-based substrate in the molten pool during LPD [27]. As compared with the phase constitution of the lower region, γ-Fe and M3W3C phases are absent in

| Location | W   | Co  | C   | Fe  | Cr  | Ni  | Possible phase       |
|----------|-----|-----|-----|-----|-----|-----|----------------------|
| 1        | 10.18 | 8.46 | 0.42 | 71.05 | 7.50 | 2.39 | γ-Fe solid solution |
| 2        | 65.73 | 4.51 | 1.00 | 25.77 | 2.39 | 0.60 | Fe3W2C                |
| 3        | 90.95 | 2.65 | 3.74 | 1.85 | 0.81 | —   | WC                   |

Figure 7. (a) Microstructure of the bonding zone; (b) linear distribution of elements along the red dashed.

Table 1. EDS analysis results of typical phases marked in figure 7.

Figure 8. (a) Cross-sectional microstructure of the lower region of the coating, (b) local enlargement of (a).
the upper region of the coating, and substitutive phases of Co and Co₄W₂C are present. The dominant phase in the upper region is also WC, but the diffraction peaks of WC are higher and sharper in comparison with that of the lower region.

Figure 7 shows the microstructure and elements distribution around the bonding zone. EDS analysis of the typical phases marked in figure 7 (a) is listed in table 1. It can be seen from figure 7 (a) that the substrate metal presents a planar growth with the thickness of 4 ~ 6 μm at the coating-substrate interface. With increasing distance from the interface, the relatively coarse columnar dendrites and herringbone eutectics are observed. The EDS analysis indicates that the gray columnar dendrite (marked 1 in figure 7 (a)) is γ-Fe, which is a typical supersaturated solid solution with high content of W and Co. Moreover, the herringbone eutectics (marked 2 in figure 7 (a)) can be identified as M₃W₃C type carbide corresponding to Fe₃W₃C composition.

The linear distribution of the Fe, W, Co and Ni elements across the bonding zone is depicted in figure 7 (b). It can be observed that the W, Co elements increase gradually from the substrate to the bonding zone. Meanwhile, a large amount of Fe element from the substrate diffuses into the coating layer and dilutes it. Analyses of microstructural and elements distribution demonstrate that the metallurgical bonding, which can enhance the adhesion of the coating to the substrate and protect it from peeling, has been generated between the coating and the substrate. It can also be seen that some WC particles (marked 3 in figure 7 (a)) tend to sink towards the bottom of the coating, which is attributed to the density and melting point of the WC particles are much higher than the Fe-based alloy substrate [28, 29].

Figure 8 (a) shows the cross-sectional microstructure of the lower region of the coating. It can be seen that the sintered WC-Co composite powders are almost dissolved completely, and the coarse carbides are precipitated in the lower region. These precipitated carbides fall into two main categories, viz. polygonal block carbides and penniform dendritic carbides, which magnified microstructure is presented in figure 8 (b). According to the EDS results (see table 2), XRD analysis (see figure 6) and morphological features, the polygonal block carbides can be identified as WC particles with abnormal growth, and the penniform dendritic precipitates are FeCo₂W₃C carbides with M₃W₃C type.

Figure 9 (a) shows the cross-sectional microstructure of the upper region of the coating, and bimodal distribution in microstructure is clearly observed. It can be seen that the upper region of the coating contains many round ultrafine-grained aggregates, whose magnified internal microstructure is shown in figure 9 (b). The EDS analysis (see table 3) reveals that the atomic ratio of the square area (marked 1 in figure 9 (a)) is W:Co: C = 87.2:8.4:3.9. In combination with XRD analysis (see figure 6), it is confirmed that these submicron-grained aggregates are incompletely dissolved WC-Co composite particles with primary round shape. Comparing figure 9 (b) with figure 3 (d), we can found that the undissolved areas inherit the submicron sintered structure form the raw composite powders, and the WC grain size still remains no more than 420 nm.

It can also be seen from figure 9 (a) that the outer layer of the sintered WC-Co composite particles is partially dissolved, and micron-sized carbides with different morphologies are precipitated around the undissolved areas.

Table 2. EDS analysis results of typical phases marked in figure 8.

| Location | W    | Co   | C     | Fe    | Cr     | Possible phase         |
|----------|------|------|-------|-------|--------|------------------------|
| 1        | 92.42| 1.70 | 3.83  | 1.41  | 0.64   | WC                     |
| 2        | 70.94| 17.23| 0.76  | 10.28 | 0.79   | FeCo₂W₃C               |
Figure 9(c) shows the detailed microstructure of the precipitated carbides between undissolved areas. As seen, these precipitated carbide particles exhibit regular trapezoidal and symmetrical petaloid shapes, which are completely different from the adding powders. The EDS results combined with XRD analysis demonstrate that the micron-sized carbides with trapezoidal and petaloid shapes are WC and Co4W2C, respectively. It should be noticed that the precipitated WC particles in the upper region are relatively small ($2 \sim 7 \mu m$) because of the rapid solidification. However, the larger WC particles with grain size of 15–30 $\mu m$ appear in the lower region, as seen in figure 8(b). This distinction in morphology and size of precipitated carbides observed at different regions can be attributed to the various thermal cycles at different depths of the coating.

**Table 3.** EDS analysis results of typical phases marked in figure 9.

| Location | W   | Co  | C    | Fe  | Cr    | Possible  | Possible phase          |
|----------|-----|-----|------|-----|-------|-----------|-------------------------|
| 1        | 87.21 | 8.38 | 3.89 | —   | 0.52  | WC-Co composite | WC-Co composite         |
| 2        | 92.91 | 2.03 | 4.15 | 0.27 | 0.64  | WC         | WC                      |
| 3        | 53.70 | 38.37 | 1.05 | 5.11 | 1.77  | Co4W2C    | Co4W2C                  |

Figure 10. Microhardness profile along the cross-section of the cemented carbide coating.

Figure 11. Coefficient of friction (COF) curves of the substrate and the cemented carbide coating.
3.3. Microhardness and sliding wear performance

Figure 10 depicts the microhardness profile along the cross section of the cemented carbide coating. Four different hardness zones can be observed in this profile, viz. substrate, interface zone, lower region and upper region of the coating. It is clear that the hardness distribution of the coating is closely related to the microstructures of different regions. The Vickers microhardness of the lower region of the coating is steady with the average value of 1225 HV0.3, which is greater about 6.4 folds than the 304 stainless steel substrate (191 HV0.3). The formation of massive reinforced carbides in the form of WC and M₆W₃C in micron is the key factor for this hardness. In addition, the profile shows that the microhardness of the upper region is significantly enhanced compared with that of the lower region, reaching the average hardness value of 1536 HV0.3, which is about 8 times higher than that of the substrate. Besides, the microhardness gradually increased in the heat affected zone (at distance of -200 ~ 0 μm). This hardness increase may be ascribed to the local metallurgical changes that occur by rapid heating and cooling above the austenizing temperature.

The wear properties of the cemented carbide coating and the substrate were examined by dry sliding wear against Al₂O₃ ceramic ball at normal of 10 N. Figure 11 illustrates the evolution of the COF as a function of...
sliding time for specimens. The average COF of the cemented carbide coating is 0.463, which is lower than that of the substrate (average value of 0.629). The lower COF is ascribed to the lower surface roughness and higher hardness of the coating. It is noted that the COF of the substrate experiences a fluctuation within a wide range as the sliding time increased. On the contrary, the wear process of the coating is relatively stable, while the COF fluctuates within a narrow range. In details, after a sliding time over 520 s, the COF value of the coating increases gradually with the increase of the sliding time.

Figures 12(a) and (b) present the surface mappings of the wear tracks generated on the substrate and the cemented carbide coating after dry sliding wear tests. Cross-sectional profiles of the corresponding worn tracks are revealed in figures 12(c) and (d), respectively. With the trajectory data and cross-sectional area of the wear tracks, the wear rates (ω) were calculated through equation (1). Figure 13 shows a comparison of the average COFs and wear rates of the substrate and the cemented carbide coating. As seen in figure 12, the wear track geometries of the cemented carbide coating are much smaller compared to the substrate. Numerically, the wear rate of the cemented carbide coating with \(6.05 \times 10^{-7} \text{mm}^3\text{N}^{-1}\text{m}^{-1}\) is about three orders of magnitude lower than that of the substrate \((5.522 \times 10^{-4} \text{mm}^3\text{N}^{-1}\text{m}^{-1})\), which confirms that the coating exhibits excellent wear resistance. This result appears to be supported by the microstructures, hardness and the phases identification.

4. Discussion

4.1. Microstructure formation mechanism

The characteristic microstructures of cemented carbide coating depend on the various thermal cycles at different depths and the resulting heat damages of WC-Co composite particles. Since the melting point of WC is 2870 °C, while the normal temperature in a laser induced molten pool is about 1800 ~ 2300 °C [8], the WC particles are not directly melted but dissolved into the molten pool. The damage extent of the WC-Co composite powders is dependent on the temperature and duration of the molten pool. However, the dissolution of the primary WC particles more depends on their size and content in the molten pool [30]. The relative solubility of WC particles with different size in Fe(Co)-based alloy solvent can be calculated by Ostwald-Freundlich equation [31]:

\[
\frac{S_1}{S_2} = \exp \left( \frac{2\sigma M}{RT\rho} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \right)
\]

(3)

where \(R\) is the gas constant, \(T\) is the absolute temperature, \(\rho\) is the density of WC particle, \(M\) is the molecular weight of WC particle, \(\sigma\) is the interfacial tension between WC particle and Fe-based alloy solvent, and \(S_1\) and \(S_2\) are the solubilities of WC particle with radius \(r_1\) and \(r_2\) \((r_1 > r_2)\), respectively. Equation (3) indicates that the solubility of WC in Fe(Co)-based alloy solvent increases with the decrease in WC particle size. And besides, owing to the low free-formation enthalpy of WC \((38.5 \text{kJ mol}^{-1})\) [8], the WC particles with submicron grain size can be easily dissolved in the Fe(Co)-based molten pool.

Thus, the formation mechanism of the characteristic microstructures of cemented carbide coating can be explained as follows. During LPD process, the laser beam is conducted onto the substrate surface to create a moving molten pool, and the composite powders are simultaneously injected into the metal pool by carrier gas. The Co binder in the outer layer of the composite powders is firstly melted because of the relatively low melting point of 1495 °C. At the same time, the unbonded submicron WC particles dissolved immediately and release a large number of free W and C atoms, resulting in the formation of Fe(Co)-W-C alloy solvent in the molten pool. With the rapid decrease of temperature and the solidification of molten pool, the incompletely dissolved WC-Co composite particles are locked in position in the deposited layer and preserve the original sintered structure. Meanwhile, the secondary carbides with different morphologies and melting points precipitated successively around the undissolved areas. The formation mechanism of secondary carbides is a typical dissolution-precipitation process, and the reaction can be expressed as follows:

\[
\text{WC} + \text{Co} + \text{L} \rightarrow \text{Fe(Co)} + \text{W} + \text{C} \rightarrow M_xW_yC (M = \text{Fe}, \text{Co}; \ x + y = 6)
\]

After the first layer is deposited, the coating and substrate remain in a high temperature. When the second layer deposition is carried out, the previous layer is treated as the substrate which will be reheated to form a molten pool. Since the large heat accumulation in the first deposited layer, accompanied by overall reduced thermal gradient and the slower solidification rate, provides enough energy and time for the complete dissolution of residual WC-Co composite particles. Subsequently, the high solute concentration in the molten pool and long solidification time also provide favorable kinetic and thermodynamic conditions for the growth of secondary carbides. As a result, a large number of coarse polygonal WC and penniform M_xW_yC carbide particles are formed in the lower region of the coating. The above deposition process repeats again, eventually forming a coating structure as shown in figure 5. The wear resistant layer presents bimodal microstructure, and the lower region of the coating is mainly composed of coarse precipitated carbides.
4.2. Hardness and wear resistance enhancement

For sintered cement carbide composites, the quantitative relationship between the hardness and WC mean grain size generally follows a Hall-Petch type equation, which is given below [32–34]:

\[ H_{WC-Co} = H_0 + Kd_{WC}^{-1/2} \]  

(5)

where \( H_{WC-Co} \) is the Vickers hardness of sintered WC-Co composite, \( H_0 \) is the constant related to Co binder phase content, \( K \) is the grain size coefficient and \( d_{WC} \) is the mean grain size of the WC particles. Therefore, the finer the WC is, the higher the hardness exhibit. Due to the fine-grained strengthening of submicron WC grains in the incompletely dissolved WC-Co composite particles, the upper region of the coating exhibits higher hardness. However, it is worth noting that the microhardness value of the upper region has a significant fluctuation, which mainly attributed to the bimodal distribution of the microstructure.

To further explore the wear mechanisms of the cemented carbide coating, the characteristic SEM images of wear surfaces of the test specimens are shown in figure 14. It is obvious that the substrate is subjected to serious wear damage, as shown in figure 14(a). The worn surface of substrate both exhibit adhesion (protruding plastic deformations) and abrasion (plowing grooves and wear debris) wear characteristics. The coexistence and alternating transition of different wear behaviors are also reflected in the fluctuation of COF value with sliding time (see figure 11). Consistent with the wear rate results, the wear track of the cemented carbide coating presents a clean and smooth surface, as shown in figure 14(b). A dense tribofilm is continuously smeared on the coating surface, without any plowing grooves and wear debris. According to the wear surface morphology analysis, the wear mechanism of the coating is mainly guided by relatively mild adhesion wear. During the sliding wear process, the softer Co binder phase has been extruded from the local position and adhere to the surface of counterpart and hard carbide particles, forming a coherent and dense tribofilm on the wear surface because of the severe contact stress. This tribofilm generated on the worn surface enhances the adhesion between the coating and the counterpart. As a result, the COF value of the cemented carbide coating increases along with the generation of tribofilm, as shown in figure 11. Furthermore, no carbide pull-out can be witnessed on the worn surface. Combining with the microstructure analysis of the upper coating layer (see figure 9), a strong...

Figure 14. SEM images of the worn surfaces of (a) the substrate and (b) the cemented carbide coating; (c) and (d) enlargement of the rectangular regions marked C and D in (b).
interfacial bond is formed between the precipitated carbides and Co binder as well as within the incompletely dissolved WC-Co composite particles.

In the wear test, the counterpart ball slid against the coating surface continuously, whereas the wear performance is primarily affected by relative hardness and microstructural features of the corresponding parts [35]. To further understand the enhancement mechanism on wear resistance of the cemented carbide coating, a comprehensive relationship between microstructure and wear process is discussed as follows. As demonstrated in the above microstructural analyses, the wear resistant layer of the coating exhibits bimodal structure, in which the incompletely dissolved WC-Co composite particles preserve the original submicron sintered structure and coarse secondary carbides are precipitated around them. This structure is believed to has a beneficial effect on improving the wear resistance of the coating. As for dry sliding wear of cemented carbide coating, the wear mechanism under a normal load of 10 N condition is mainly the selective adhesive removal of soft Co binder followed by the exposure of the reinforced carbide particles from the bimodal-structured layer. The carbide particles can construct a load-support skeleton because of the strong interface bonding between the Co binder and precipitated carbides as well as within the incompletely dissolved WC-Co composite particles. As a result, the counterpart is mainly supported by the hard carbides skeleton, which can greatly decrease the contact stress effect and obstruct the further removal of the Co binder. The reduced height loss of the Co binder will in turn effectively maintain the skeleton structure and thereby preventing carbide particles from being pulled out. Furthermore, the differently sized carbide particles play synergetic roles on enhancing wear property of the wear resistant layer [18]. The precipitated coarse carbides protect the Co binder from rapid abrasion by withstanding the contact load (see figure 14(c)). Meanwhile, the submicron-grained WC-Co composite particles provide high hardness and plastic accommodation to enhance the wear-resistant property of the coating (see figure 14(d)) [24]. As a consequence, the loss of coating materials is delayed and a high wear resistance is obtained for the cement carbide coating.

5. Conclusion

In this work, the cemented carbide coating was prepared on 304 stainless steel substrate by multilayer laser powder deposition method using compact spherical WC-12Co composite powder as raw material. The microstructural evolution and sliding wear behavior of the coating were experimentally analyzed and the main conclusions can be drawn as follows:

(1) The cemented carbide coating has distinct microstructures and phase constitutions in different depths due to the various thermal cycles and the resulting heat damages of the feedstock powders. The wear resistant layer consists of WC, Co and Co4W2C phases and presents bimodal microstructure. The lower region of the coating is mainly composed of coarse precipitated carbides in WC and M3W3C forms and γ-Fe binder phase.

(2) The microhardness in the lower region of the coating is steady with the average value of 1225 HV0.3. Thanks to the fine-grained strengthening of the submicron WC grains in incompletely dissolved WC-Co composite particles, the microhardness of the wear resistant layer reaches 1536 HV0.3, which is about 8 times higher than that of the substrate.

(3) The cemented carbide coating exhibits stable mild adhesion wear with a average COF of 0.463 when dry sliding against Al2O3 ceramic ball at normal load of 10 N. The wear rate of the coating is about three orders of magnitude lower than that of the substrate. The excellent wear resistance of the coating is attributed to the bimodal structure of the wear resistant layer and the synergistic enhancement of differently sized carbide particles.

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References

[1] Wang H, Song G and Tang G 2016 Effect of electropolishing on surface mechanical properties and microstructure of AISI 304 stainless steel during ultrasonic surface rolling process Mater. Sci. Eng. A 662 456–67

[2] Masanta M, Shariff S M and Roy Choudhury A 2011 A comparative study of the tribological performances of laser clad TiB2–TiC–Al2O3 composite coatings on AISI 1020 and AISI 304 substrates Wear 271 1124–33

[3] Zhou S and Zeng X 2010 Growth characteristics and mechanism of carbides precipitated in WC–Fe composite coatings by laser induction hybrid rapid cladding J. Alloys Compd. 585 685–91

[4] Garcia J, Collado Ciprés V, Blomqvist A and Kaplan D 2019 Cemented carbide microstructures: a review Int. J. Refract. Met. Hard Mater. 80 40–68

[5] Liu X, Song X, Wang H, Liu X, Tang F and Lu H 2018 Complexions in WC–Co cemented carbides Acta Mater. 149 164–78

[6] Zhou S and Dai X 2010 Microstructure evolution of Fe-based WC composite coating prepared by laser induction hybrid rapid cladding Appl. Surf. Sci. 256 7395–9

[7] Farayibi P K, Folkes J, Clare A and Oyelola O 2011 Cladding of pre-blended Ti–6Al–4V and WC powder for wear resistant applications Surf. Coat. Technol. 206 372–7

[8] Shui D, Li Z, Zhang K, Yao C, Li D and Dai Z 2017 In situ synthesized high volume fraction WC reinforced Ni-based coating by laser cladding Mater. Lett. 195 178–81

[9] Guo C, Chen J, Zhou J, Zhao J, Wang L, Yu Y and Zhou H 2012 Effects of WC–Ni content on microstructure and wear resistance of laser cladding Ni-based alloys coating Surf. Coat. Technol. 206 2064–71

[10] Wang C, Zhang S, Zhang C H, Wu C L, Zhang J B and Abdullah A O 2018 Phase evolution and wear resistance of in situ synthesized VBC7 particles reinforced Fe-based coating by laser cladding Opt. Laser Technol. 103 58–65

[11] Sun G F, Yao S, Wang Z D, Shen X T, Yan Y, Zhou R and Ni Z H 2018 Microstructure and mechanical properties of HSLA-100 steel repaired by laser metal deposition Surf. Coat. Technol. 353 198–211

[12] Hu Y and Cong W 2018 A review on laser deposition-additive manufacturing of ceramics and ceramic reinforced metal matrix composites Ceram. Int. 44 20599–612

[13] Luo L, Shan X, Zou Z, Zhao C, Wang X, Zhang A, Zhao X, Guo F and Xiao P 2017 A high performance NiCoCrAlY bond coat manufactured using laser powder deposition Corros. Sci. 126 356–65

[14] Liu Y, Liu W, Ma Y, Liang C, Liu C, Zhang C and Cai Q 2018 Microstructure and wear resistance of compositionally graded TiAl intermetallic coating on Ti6Al4V alloy fabricated by laser powder deposition Surf. Coat. Technol. 353 32–40

[15] Wang S, Zhang S, Zhang C H, Wu C L, Chen J and Shahzad M B 2018 Effect of Cr3C2 content on 316L stainless steel fabricated by laser melting deposition Vacuum 147 92–8

[16] Angelastro A, Campellini S L and Casalino G 2017 Statistical analysis and optimization of direct metal laser deposition of 227-F Colmonoy nickel alloy Opt. Laser Techn. 94 138–45

[17] Liu D J, Li L and Fan Y 2008 WC/Fe metal matrix composites produced by laser melt injection Surf. Coat. Technol. 202 1771–7

[18] Ji G C, Wang H T, Chen X, Bai X B, Dong Z X and Yang F G 2013 Characterization of cold-sprayed multimodal WC–12Co coating Surf. Coat. Technol. 235 536–43

[19] Ma N, Guo L, Cheng Z, Wu H, Ye F and Zhang K 2014 Improvement on mechanical properties and wear resistance of HVOF sprayed WC–12Co coatings by optimizing feedstock structure Appl. Surf. Sci. 320 364–71

[20] Guillen-Marín J M, Dosta S and Miguel J R 2006 The enhancement of the properties of WC-Co HVOF coatings through the use of nanostructured and microstructured feedstock powders Surf. Coat. Technol. 201 1180–91

[21] Ganesh Skandan R Y, Kear B H, Qiao Y, Liu L and Fischer T E 2001 Multimodal powders: a new class of feedstock material for thermal spraying of hard coatings Scr. Mater. 44 1699–702

[22] Yang G J, Gao P H, Li C X and Li C F 2012 Simultaneous strengthening and toughening effects in WC–(nanoWC–Co) Scr. Mater. 66 777–80

[23] Yang G J, Gao P H, Li C X and Li C F 2013 Mechanical property and wear performance dependence on processing condition for cold-sprayed WC–(nanoWC–Co) Appl. Surf. Sci. 332 80–8

[24] Wang H, Yang T, Song X, Liu X, Wang X and Wu X 2017 Wear resistance enhancement of bimodal–grained cemented carbide coating Surf. Coat. Technol. 309 759–65

[25] Abioye T E, Farayibi P K, McCartney D G and Clare A T 2016 Effect of carbide dissolution on the corrosion performance of tungsten carbide reinforced Inconel 625 wire laser coating J. Mater. Process. Technol. 231 89–99

[26] Hu M, Tang J C, Chen X G, Ye N, Zhao X Y and Xu M M 2016 Microstructure and properties of WC–Co composite coatings prepared by laser cladding Transactions of Nonferrous Metals Society of China 30 1017–30

[27] Zhong M, Liu W, Zhang Y and Zhuo X 2006 Formation of WC/Ni hard alloy coating by laser cladding of W/C/Ni pure element powder blend Int. J. Refract. Met. Hard Mater. 24 653–60

[28] Ma Q, Li Y Y, Wang L and Liu K 2015 Investigation on cored–eutectic structure in Ni60/WC composite coatings fabricated by wide-band laser cladding J. Alloys Compd. 645 151–7

[29] Ortiz A, Garcia A, Cadenas M, Fernández M R and Cueto J M 2017 WC particles distribution model in the cross-section of laser cladeded NiCrBSi + WC coatings, for different wt% WC Surf. Coat. Technol. 324 298–306

[30] Xia M, Gu D, Ma C, Zhang H, Dai D, Chen H, Li C, Zhou Z, Chen G and Kelbassa I 2019 Fragmentation and refinement behavior and underlying thermodynamic mechanism of WC reinforcement during selective laser melting of Ni-base composites J. Alloys Compd. 777 693–702

[31] Borm P, Klaessig F C, Landry T D, Moudgil B, Pauluhn J R, Thomas K, Trottier R and Wood S 2006 Research strategies for safety evaluation of nanomaterials, part V: role of dissolution in biological Fate and effects of nanoscale particles Tox. Sci. 90 23–32

[32] Zhao S, Song X, Liu X, Wei C, Wang H and Gao Y 2011 Quantitative relationships between microstructure parameters and mechanical properties of ultrafine cemented carbides Jinchu Xuebao/Acta Metallurgica Sinica 47 1188–94 https://www.ams.org.cn/EN/Y2011/V47/1188

[33] Emanı S V, Wang C, Shaw L I and Chen Z 2015 On the hardness of submicrometer–sized WC–Co materials Mater. Sci. Eng. A 628 98–103

[34] Kresse T, Meinhard D, Bermthaler T and Schneider G 2018 Hardness of WC–Co hard metals: Preparation, quantitative microstructure analysis, structure–property relationship and modelling Int. J. Refract. Met. Hard Mater. 73 287–93

[35] Jia Q and Gu D 2014 Selective laser melting additive manufacturing of Inconel 718 superalloy parts: Densification, microstructure and properties J. Alloys Compd. 585 713–21