Microstructure of B₄C/TiC/TiB₂ reinforced surface titanium matrix composite produced by laser cladding

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Abstract. Ti+30%B₄C/Ni (nickel-coated boron carbide) was used as cladding material and the titanium metal was prepared on the TC4 titanium alloy substrate by using the unmelted particle reinforced and in-situ autogeneous enhancement technology using a-hundred-watt grade fiber laser heat source to produce the B₄C/TiC/TiB₂ composite reinforced coating. We analyzed the phase composition, distribution and microstructure characteristics of the coating. The results show that the multicomponent composite strengthening coating prepared by adding B₄C/Ni powder is mainly composed of metal-based α-Ti, unmelted particle-phase B₄C, in-situ as-grown TiC, TiB₂, TiB, and intermetallic Ti₂Ni. Each ceramic particle is reinforced and intertwined, depending on growth. With the addition of 30%B₄C/Ni, the average microhardness of the coating was 917.7 HV0.3, the coefficient of friction was stable at 0.19-0.22, and the minimum amount of atmospheric wear was 7.2 mg. The coating had good antifriction and wear resistance.

1. Introduction

Depending on test conditions, there are several materials with high hardness property, boron carbide is a super hard material after diamond and cubic boron nitride (c-bn) in nature [1,2]. When the temperature is above 1300°C, its hardness is higher than that of diamond and cubic boron nitride. Its near constant temperature hardness index (greater than 30 GPa) is unmatched by any other found material. B₄C as an important engineering material [3-6], has been widely used in self-lubricating materials [7-9] and wear-resistant materials, Due to its high hardness and excellent wear resistance [10-12]. In order to improve the wear resistance of titanium alloy, it has been a hotspot to study the titanium matrix composites by using surface hardening technology to obtain the coatings with excellent comprehensive properties [13-15]. By means of laser cladding and adding B₄C cladding powders, TiC/TiB₂ in-situ particle reinforced titanium matrix composites have been successfully synthesized on TC4 substrate. However, in previous studies, B₄C is only used in situ reaction to prepare TiC, TiB₂ ceramic particle-reinforced phase, for the formation of TiC and TiB₂ particles to provide carbon and boron elements. The B₄C ceramic particle phase is not seen in the cladding, and the B₄C ceramics near the constant temperature hardness index have not played a dominant role [16-19].

The purpose of this study was to prepare a composite titanium alloy coating using laser cladding technology [20-22]. The deposited layer is a B₄C/TiC/TiB₂ composite coating comprising a B₄C particle
reinforcement phase and TiC/TiB$_2$ in-situ autogenous particle reinforcement phases. By comprehensively exploiting the special properties of different ceramic particle reinforcement phases, coatings that meet specific performance requirements are prepared.

2. Experimental
The laser cladding test base material of Ti-based particle reinforced coatings is TC4 (Ti-6Al-4V), which is a typical α + β Ti alloy material as shown in Table 1.

| Components% | Al  | V   | Fe  | C   | O   | Ti  | Allowance |
|-------------|-----|-----|-----|-----|-----|-----|-----------|
| Sample quality fraction | 6.20 | 4.30 | 0.19 | 0.02 | 0.18 | 0.17 |

The deposited material is titanium and B$_4$C/Ni mixed powder, and the mass ratio of B$_4$C/Ni to Ti powder is 3:7. B$_4$C/Ni is prepared by a coating process. The mass ratio of B$_4$C and Ni is 3:7, and the particle size of B$_4$C/Ni powder is 5-150 μm, which is irregular granular. The titanium powder has a purity of 99.9%, particle diameter of 2-100 μm, and had an irregular form of particles.

Using a RFL-C1000 1 kW fiber laser, the multi-channel lap laser coating was deposited. After optimization, the laser cladding processing parameters were: Laser power $P=600$ w, scanning speed $v=6$ mm·s$^{-1}$, laser beam spot diameter $d=2$ mm, lap connection rate was 40%, the protection gas was purity 99.9% argon, flow was 20l·min$^{-1}$.

The sample was cut by an EDM wire-cutting machine. Metallographic specimen specification was 12×10×9 mm$^3$ (cladding thickness of 1 mm), the preparation process includes interception, mosaic, sample grinding and throwing, according to the proportion of HNO$_3$:HF:H$_2$O=43:7:50 to configure corrosive, 10 s~30 s etching, immediately after the etching with water, and then rinse with alcohol and air-dry standby.

The X-ray diffraction analysis (XRD) sample size is 10×10×9 mm$^3$, and the surface of the sample deposition layer is coarsely ground and finely ground using 200-1200 mesh metallographic sandpaper to make the surface of the cladding smooth and flat. It is then polished using a diamond polishing agent of 0.25 um.

Friction and wear specimen dimensions were 25×8×9 mm$^3$, and their deposited layer surfaces were subjected to coarse grinding, fine grinding, and polishing.

A sliding wear test was performed on the surface. The samples with dimensions of 25×8×9 mm$^3$ are used for this purpose.

A Zeiss Sigma 300 field emission scanning electron microscope (SEM) was used to observe the macroscopic morphology and microstructure of the deposited layer at low magnification and high magnification. The phase composition of the deposited layer was analyzed by an D8 X-ray diffraction analyzer (XRD). The diffraction analysis parameters were set to: acceleration voltage of 40 kV, current of 40 mA, diffraction range from 20 to 100°, and diffraction speed of 8°·min$^{-1}$.

The micro-hardness test of the cladding cross-section was carried out with the HV1000 digital micro-hardness tester, and the loading load was 300 g and the time was 12 s. Starting from the position of 0.05 mm from the specimen surface, the direction from the outside to the inside was measured per each 0.1 mm, until the base material position. Horizontal direction interval was 100 μm, the total of three points being tested. At the same level, the average value of three sets of data was measured as the micro-hardness of the cladding on the thickness.

The friction and wear test of M-2000 type friction and wear tester was carried out in atmosphere and vacuum, the grinding wheel material was GCr15 steel after quenching treatment, the diameter of grinding wheel was 40 mm, the rotation speed was 200 rad·min$^{-1}$, the load was 100 N, the grinding time was 30 min, and the vacuum degree was 1.0×10$^{-3}$ Pa.

3. Results and discussion
The specific phase of the cladding layer was analyzed by XRD to obtain a diffraction peak of the
contained phase. Each diffraction peak in the map was calibrated using the Jade data analysis software. Figure 1 shows the results of the analysis calibration. The XRD results show that the phase composition of the coating was as follows: B$_4$C, TiC, TiB$_2$, TiB, and Ti$_2$Ni. XRD test results show that during the surface strengthening of laser cladding, the titanium element in the powder and the titanium element in the molten substrate reacted in situ with elements such as carbon and boron to form ceramic phases such as TiC, TiB$_2$, and TiB. Titanium and nickel also reacted under laser irradiation to form Ti-Ni intermetallic compound Ti$_2$Ni. Meanwhile, the phase reaction of the added B$_4$C particles was incomplete, and unmelted B$_4$C particles were present in the coating.

![XRD result of 30% B4C/Ni titanium matrix cladding layer](image)

**Figure 1.** XRD result of 30% B4C/Ni titanium matrix cladding layer.

![SEM showing 30% B4C/Ni cladding layer](image)

**Figure 2.** SEM showing 30% B4C/Ni cladding layer. (a) zoning of the cladding layer, (b) upper part, (c) middle part, and (d) bottom part.

Figure 2 shows the microstructure of the cladding SEM. As shown in figure 2(a), the coating is divided into three layers according to the distance from the free surface of the coating: Zone I, Upper part of the cladding layer; Zone II, middle part of the cladding layer; Zone III, bottom part of the cladding part. Zone IV is TC4 substrate.

Figure 2(b) shows the most of the particles in the upper part of the cladding layer in Zone I are dendritic or rod-like and light grey block-shaped phases also appeared. A closer examination of the particles shows that there is a belt reaction zone surrounding each particle.

Figure 2(c) shows the particles in the middle part in Zone II are of large black granular, stick or short branches, light grey block-shaped. There are a large number of small white particles near the large black particles. And a network of phases is distributed between light grey particles.

Figure 2(d) shows the particles in the bottom part are light grey block-shaped. There are a large number of small granular phases near the large black particles.

The distribution of the particle phases in the three regions is substantially the same, but the number of distributions is significantly different. In the middle and lower parts, due to the short residence time of the melt liquid, the distribution of black particles is more, and the dendritic or rod-like white particles are less; in the upper middle part, due to the long liquid residence time, the black particle phase is
significantly reduced, and strips or rod-shaped white particles increase. The EDS analysis results of points A, B, C, D, E, and F in Figure 2, are listed in Table 2.

**Table 2. EDS analysis results of points A, B, C, D, E, and F in figure 2.**

| Location | Ti Wt% | B Wt% | C Wt% | Ni Wt% | Al Wt% | V Wt% | Ti At% | B At% | C At% | Ni At% | Al At% | V At% |
|----------|--------|-------|-------|--------|--------|-------|--------|-------|-------|--------|--------|-------|
| Point A  | -      | 80.01 | 19.81 | -      | -      | -     | 81.74  | 18.22 | -      | -      | -      | -     |
| Point B  | 84.32  | -     | 15.68 | -      | -      | -     | 57.41  | 42.59 | -      | -      | -      | -     |
| Point C  | 70.51  | 18.62 | 2.95  | 7.29   | 1.36   | 1.27  | 43.07  | 44.15 | 6.94   | 3.63   | 1.48   | 0.73  |
| Point D  | 66.50  | 27.28 | 4.85  | -      | -      | 1.37  | 31.97  | 58.11 | 9.30   | -      | -      | 0.62  |
| Point E  | 84.32  | -     | 15.68 | -      | -      | -     | 57.41  | 42.59 | -      | -      | -      | -     |
| Point F  | 78.86  | -     | 4.57  | 10.44  | 3.60   | 2.32  | 68.86  | -     | 15.91  | 7.44   | 5.58   | 1.91  |

**Figure 3.** EDS analysis results of line and surface scanning: (a) scanning zone, (b) surface scanning results on C, (c) surface scanning results on Ti, (d) line scanning results on B, (e) line scanning results on C, and (f) line sweep of Ti.

In Figure 3(a), areas A and B contain large black particles and adjacent areas, while area C is an overlapping area of areas A and B. In the experiment, three areas (A, B and C) are determined as typical areas of line and area scanning. The line D indicates the direction and path of the line scanning.

Figure 3(b) shows the carbon element surface scanning spectrum. The concentration of carbon elements in the region changes greatly. A significant carbon-rich region is formed between the near-black large particle region and the adjacent two particles.

Figure 3(c) is a surface scan of the titanium element, which can be seen in a typical area of black large particle phase titanium.

Figure 3(d) shows the line scanning of boron element. The concentration of boron in the whole region is opposite to that of titanium (Figure 3(f)). The concentration of boron in the titanium-rich region is evenly distributed, and it has the highest peak in all regions. The peak value is about 400, and the lowest horizontal region of the titanium element peak level completely overlaps with the highest level of the
boron element peak level.

Figure 3(c) shows a line scan of carbon, which shows a high level of gradient, but with an average peak of only 50 compared to titanium and boron, at a lower level; the gradient of the line scan shows two peaks near the black particle, up to 130, about three times the regional average.

Figure 3(f) is a line sweep of titanium element with a peak value of up to 1.2k. The overall concentration of titanium is balanced, which is consistent with the position of titanium as a cladding metal base. At the same time, the spectrum of titanium in a typical region shows a very gradient. Large rises and falls, the peaks and valleys are close to zero peak, and maintain a long distance (about 20 \( \mu m \)). After crossing the area, the peak returns to the pre-crossing level, indicating that the area is seriously depleted in titanium.

Due to the large deviation of carbon and boron in the energy spectrum analysis, the results of line scan and surface scan were analyzed based on the XRD diffraction analysis.

The phase of each phase is analyzed as follows: Figure 2(c) black particle phase A, no titanium element is found. Only carbon and boron are found, and the atomic ratio of carbon to boron is 1:4, which is judged to be unmelted B\(_2\)C particles, which is dispersed in the coating; in the vicinity of the black particle phase, there are obvious carbon-rich regions and in the boron-rich region, there is a high peak of titanium, and it is judged that the white small particle B is TiC. The rod-shaped and dendritic phase C is TiB. Due to the adjacent unmelted B\(_2\)C particle phase, a large amount of TiB\(_2\) is generated in situ, and TiB is not completely formed. The short-rod phase D is TiB\(_2\); the point analysis results show that the gray granular phase F is the coating matrix structure \( \alpha \)-Ti. The network structure E between the \( \alpha \)-Ti particles is the Ti\(_5\)Ni intermetallic compound.

In summary, there are unmelted \( \text{B}_2\text{C} \) particle phase, in-situ TiC, TiB\(_2\), TiB, and other particle-reinforced phases in the laser cladding layer. \( \text{B}_2\text{C} \) particle phase and other particles are interdependent. The in situ reaction generates TiB\(_2\), TiC, and TiB particle phases, which are also coupled and interlaced. The in-situ reaction forms a phase closely surrounding the \( \text{B}_2\text{C} \) particle phase, forming a dense shell, with a binding effect on \( \text{B}_2\text{C} \) particles, which can greatly reduce the friction and wear process, unmelted peeling and shedding of \( \text{B}_2\text{C} \) particles. It can be seen that there are many kinds of ceramic particles, such as \( \text{B}_2\text{C} \), TiB\(_2\), and TiC in the laser cladding layer prepared by Ti+30%\( \text{B}_2\text{C} \)/Ni powder, and the titanium-based \( \text{B}_2\text{C}/\text{TiC}/\text{TiB}_2 \) multi-component composite strengthening coating is successfully prepared.

Microhardness tests revealed that the average hardness of the sample surface was as high as 917.7 HV\(_{0.3}\).

The fundamental reason for the microhardness performance of the coating is the ceramic reinforcing phase in the coating, whether it is in-situ TiC, TiB\(_2\), TiB, and other particles, or unmelted \( \text{B}_2\text{C} \) particles, the coating microhardness value is significantly improved. The coating of 30% \( \text{B}_2\text{C}/\text{Ni} \) powder was added, and the hardness of the coating was 2.11 to 2.74 times higher than that of the TC4 substrate. The retention and distribution of the unmelted \( \text{B}_2\text{C} \) particle phase have a great influence on the hardness. Due to the temperature field distribution characteristics, a certain degree of "condensation" occurs, that is, in the solidification stage, the temperature of the melt near the substrate rapidly drops to the liquid. Below the phase line, more \( \text{B}_2\text{C} \) particles are less than in-situ reaction with titanium, and are intertwined and solidified with the surrounding objects, resulting in more unmelted \( \text{B}_2\text{C} \) particles in the lower part of the coating than in the middle and upper parts. In this regard, the high hardness value (1000 to 1100 HV\(_{0.3}\)) measured from the lower part can be fully proved.

The friction and wear test showed that the friction coefficient of the deposited layer increased rapidly with the wear time and then gradually stabilized. The friction coefficient of the 30% \( \text{B}_2\text{C}/\text{Ni} \) coating was kept between 0.19 and 0.22. Under the same test parameters, the weight loss of the substrate in the atmosphere is 0.028 g, while the wear of the titanium-based \( \text{B}_2\text{C}/\text{TiC}/\text{TiB}_2 \) multi-component composite coating is 0.0072 g, and the wear in vacuum is only 0.015 g.

4. Conclusions

Ti-B\(_2\)C/Ni powder was used to prepare Ti-based multi-component composite surface coating by using 1000w fiber laser in argon atmosphere. Enhancing component comprises a surface coating by TiC, TiB\(_2\),
TiB and B\textsubscript{4}C phase. The TiC, TiB\textsubscript{2} and TiB phases are formed by in situ reaction. The B\textsubscript{4}C phase is the unmelted retention phase of the deposited powder. In-situ formation of TiB\textsubscript{2}, TiC, TiB, and retained B\textsubscript{4}C phase interdependent and staggered growth. In-situ formed TiB\textsubscript{2}, TiC, and TiB particles closely adhere to the growing B\textsubscript{4}C phase, forming a good metallurgical "binding" effect. TiC/TiB\textsubscript{2}/B\textsubscript{4}C composite reinforced coating helps to perform different integrated reinforcement excellent physical and chemical properties. In particular, B\textsubscript{4}C exhibits excellent hardness, high-temperature performance, which improves the coating hardness and wear resistance.

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