Original Article

Fabrication of CNTs–TiC–Ti₂(Ni,Al)–Ni₃Ti reinforced Ti-based composite coating by laser alloying processing

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In-situ formation of TiC, Ni₃Ti and Ti₂(Ni,Al) with CNTs reinforced Ti-based composite coatings were fabricated by laser alloying processing. The effect of laser specific energy on the microstructure, micro-hardness and wear property of the composite coatings were studied. The results showed that the composite coatings exhibited free from cracks and pores. Cypress leaf-like and flower-like TiC dendrites, as well as block-like Ti₂(Ni,Al) and rod-like Ni₃Ti intermetallic compounds were in-situ formed and distributed uniformly in the coating. With the increasing of laser specific energy, TiC dendrites coarsened and amount of TiC reduced. The micro-hardness and wear resistance of the coatings first increased and then decreased with the increasing of laser specific energy. When laser specific energy was controlled with 4.167–5 kJ/cm², coatings with high micro-hardness and wear resistance were obtained. Wear resistance of the coatings were 2.3–6.9 times of that of substrate. Wear behavior of the dominant wear mechanism of the composite alloying coatings was adhesive wear, however, the Ti6Al4V substrate exhibited serious abrasive wear, adhesive wear and plastic deformation.

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1. Introduction

Owing to high specific modulus, excellent corrosion resistance, superior strength-to-weight ratio and good biocompatibility, titanium (Ti) and titanium alloy have been widely applied in marine, chemical and aerospace industries, as well as medical science. However, they are easily subject to heavy wear under the severe wear condition due to low hardness and poor sliding wear resistance. To improve their wear properties, surface modification techniques were used to fabricate metal-ceramic composite coatings on the surface [1–6]. For example, TiB–TiC/Ti [1], TiC/Ni [2], TiN/Co [3] and TiB–TiB/Ti [4] composite coatings have been fabricated on the surface of titanium alloys. The results revealed that micro-hardness and wear resistance of titanium alloys were improved after employing composite coating.

In recent years, TiC has been received interest worldwide as reinforcement in metal matrix composites (MMCs) due to its lower density, high hardness and high thermal stability [7–10].
There are mainly two methods to fabricate TiC particles reinforced Ti-based composite coatings. One is that TiC particles were directly added to the coating, the other is that the reinforcing phases were formed through chemical in-situ reaction. For the former, interface between ceramics and matrix is prone to contamination during fabrication processing. The latter can overcome this shortcoming. In situ formation of TiC requires metallurgical reaction between titanium and carbon. It is reported that graphite, sucrose, BaC and CNTs were of carbon origin [11–14]. Among those carbon sources, CNTs are made of one or more graphene sheets rolled-up to form tubes [15], they possess a high aspect ratio and large specific area. Moreover, it is well known that the walls of the CNTs are hexagonal carbon with strong SP² covalent carbon bonds, and the end caps contain pentagonal rings [16]. Those characteristics are facilitating the reaction between carbide formation elements and CNTs. In addition, CNTs have self-lubrication effect, high mechanical properties and chemical stability properties [17]. In recent years, CNTs have attracted much researchers’ attention in the field of metallic composite and ceramic composite coatings. Rodríguez et al. [18] prepared WC/Co–CNTs composite coatings by HVOF spaying processing. Yazdani et al. [19] produced Ni–B–CNT coatings on the surface of 1045 steel by electroless deposition technique. Pei et al. [20] fabricated a functionally graded CNTs/hydroxyapatite composite coating on pure titanium substrate by laser cladding. Li et al. [21] employed pure titanium and CNTs powders to fabricate TiC reinforced Ti-based composite coatings by laser cladding. Those researches showed that micro-hardness and wear properties of the coatings were improved by addition of CNTs. However, regarding carbides and intermetallic compounds reinforced Ti-based composite coatings by laser alloying processing, and to the authors’ knowledge, there are only few studies.

The aim of the present study is to fabricate in situ formation carbides, intermetallic compounds and CNTs reinforced Ti-based composite coatings by means of laser alloying processing. The effects of laser parameters on the crystallographic structure, micro-hardness and wear behavior of the composite coatings were investigated.

2. Materials and methods

2.1. Experimental material and preparation method

Multi-walled CNTs with a diameter from 10 to 20 nm and a length of 30 μm (as shown in Fig. 1(a)) and pure nickel powder with size of 10–20 μm were used as precursor materials. Mass ratio of the CNTs and Ni powder is 15:85. Firstly, a certain amount of CNTs was dispersed in aqueous solution with cetyltrimethylammonium bromide as dispersant. It was dispersed by ultrasonic wave for 1 h. And then, pure nickel powders were mixed into the aqueous solution of polyvinyl alcohol at high speed magnetic stirring to form suspension. At the same time, CNTs suspension was dripped into the nickel aqueous solution. Finally, the obtained blend liquids were dried in oven for 3 h. Subsequently, CNTs/Ni composite agglomerated powders were grounded by a QM-1SP2 planetary ball mill to fabricate the CNTs/Ni powder mixture. To improve the mill efficiency of the powders, Nylon ball-milling pot (500 mL) with Agate balls (diameter 0.5–2.0 cm) was used and the ball-to-powder weight ratio was selected as 5:1. The morphology of Ni coated CNTs was shown in Fig. 1(b).

A Ti6Al4V alloy with size of 50 mm × 40 mm × 6 mm was used as substrate for laser deposition, whose nominal chemical composition in wt.% is 5.5–6.5 Al, 3.5–4.5 V, Fe less 0.25, C less 0.08, and the balance Ti. Surface of the samples to be depositing were polished with SiC paper, etched in 4% HF solution for 2 min, ultrasonic cleaned in acetone, ethyl alcohol and deionized water for 10 min, respectively, and finally dried in air. CNTs/Ni mixed powders were pre-placed with thickness of 0.2 mm on the cleaned surface of substrate. Pre-coated samples were baked in the oven to dry moisture and other volatile components from the pre-placed coating at 100 °C for 1 h.

A Rofin FL-010 fiber laser processing system was employed to fabricate the alloying coatings. Laser deposition parameters used to fabricate the CNTs/Ni composite coatings are shown in Table 1. Argon with a flow rate of 101/ min was used as the protection gas to purge into the chamber to prevent the specimens from oxidation during processing.

2.2. Microstructure characterization

After laser deposition, each representative sample was cut into 10 mm × 10 mm × 6 mm, washed with distilled water and air dried for the following experiment. The samples were then etched with HF-5 vol.% and HNO₃-15 vol.% water solution for approximately 20 s at room temperature to reveal the microstructure. Microstructure of the coatings was investigated by a JSM-7800F scanning electron microscope (SEM). The local element composition and distribution were analyzed by a JXA-8530F electron probe micro-analyzer (EPMA). Phase identification was carried out by D/max 2500PC X-ray diffractometry (XRD) with Cu-Kα radiation operated at a voltage of 50 kV, a current of 100 mA, step of 0.02° and a scanning rate of 10°/min.

2.3. Micro-hardness and wear properties test

Micro-hardness of samples was measured by a DHV-1000 Vickers hardness tester with a load of 1.96 N and a dwell time of 15 s. Wear resistance of the composite coatings without lubricant was conducted by using a HSR-2M type ball-on-disk reciprocating abrasive wear testing machine at a load of 10 N, reciprocating velocity 15 mm/s and ambient temperature for 20 min. A schematic representation of the test performed in this work was shown in Fig. 2. The counterpart material was a Si₃N₄ ball with a diameter of 4 mm and hardness of 79 HRC. Surface of the wear samples were prepared by grinding with SiC paper, final surface roughness of the samples was about 0.08 μm, and then, the samples were degreased with acetone. To evaluate wear volume loss, wear groove profile and worn tracks section area were measured by a LSM-800 non-contact laser confocal microscopy. And then, wear volumes were calculated by calculating the wear groove section area of the worn tracks multiplied by length of the worn tracks. Each wear volume loss value was the average of three samples under the same test conditions. Wear scars were observed by SEM after the wear test.
3. Results and discussion

3.1. Thermodynamic analysis and predictions

Thermodynamic analysis helps us to predict what potential reactions in the Ti–Al–V–Ni–C systems are possible and which is the most favorable. Several researchers [22–28] have studied thermodynamics of Ti–Ni–C, Ti–Al–C, Ni–Ti–Al–C and V–Ni–C system. It has been revealed that the system is very active and complex owing to the temperature and activities of the elements. For the Ti–Al–V–Ni–C system, possible reactions between Ti–C, V–C, Ti–Al, Ni–Ti, Al–C and Ni–C should be considered. The possible products and the changes of Gibbs free energy, which are calculated using thermodynamic data from Ref. [22–29] are shown in Fig. 3. As can be seen, the formation Gibbs free energy of other carbides and intermetallic compounds are always less than 0 except Ni3C in the system, while the temperature is less than 2000 K. It indicates that formation of those carbides and intermetallic compounds are possible. However, the absolute values of Gibbs free energy in the reactions of TiC is lowest among carbides in the system, implying that formation of TiC is most favorable in view of thermodynamics. As well as, Ni3Ti has lowest Gibbs free energy among the intermetallic compounds in the system, meaning that Ni3Ti has a strong intermetallic compound formation tendency.

3.2. Phase analysis and microstructure characteristics

The X-ray diffraction results of precursor powders, laser alloying coating of Sample S2 and substrate is shown in Fig. 4. The results show that ceramic particles TiC and intermetallic compounds NiTi2, AlTi2 and Ni3Ti are in situ formed by laser alloying process, which help to improve the hardness and wear resistance of the coating. However, no any CNTs peaks are observed in the coating. One possibility is that there are no CNTs in the coating. Another possibility is that there exists a few of CNTs in the coating, but the diffraction peaks of CNTs are too weak to show in XRD pattern. In addition, there are also no Ni peaks in the coating, implying that Ni has completely reacted with Ti or dissolved into matrix of the coating.

Fig. 5(a), (c) and (d) is typical microstructure feature of the upper part, middle and bottom of the coating in cross section taken by Sample S2, respectively. Fig. 5(b) is a local enlargement of Fig. 5(a). As can be observed, lots of random orientation cypress leaf-like dendritic phases, flower-like phases, irregular block-like phases and tripe-like phases are found in the coating, and those structures distribute dispersedly in the coating. As well as, it can also be seen that the dendritic structures are relatively more in the upper zone of the coating and less on the bottom of the coating from the cross section observation. It is well known that the solidifi-
In general, the temperature gradient has increased and the growth rate has decreased from the upper part of the laser molten pool towards the bottom. It means that there are larger G/R and smaller GR at the bottom of the laser molten pool, but contrary at the upper part of the coating. Therefore, a large number of coarser dendrites are found in the upper part of the laser molten pool, while only a few of finer dendrites are found in the bottom of the laser molten pool. However, the main structure is mostly clearly directional cellular dendrites in the regions near the interface and the interface (as shown in Fig. 5(d)). The cellular dendrites grow directionally and epitaxially from the substrate in the coating, which indicates that the bonding of the coating to the substrate is of high quality metallurgical bonding. In addition, it can be found from Fig. 5(b) and (e) that a few of un-melted CNTs with size about 40–80 nm remain in the matrix of the coating, which will be favorable to reduce the friction coefficient of the coating.

In order to make clear the composition of cypress leaf-like dendrites, the sample was analyzed by EPMA. Secondary electron images and elemental face analysis at the upper zone of the alloying coating are shown in Fig. 6. It reveals that cypress leaf-like dendritic phases are rich in Ti, G elements and as a few of V elements. Combined with the XRD results, it can be confirmed that cypress leaf-like dendritic phases are TiC, and few of vanadium is dissolved into TiC dendrites.

Fig. 7 shows the EPMA elemental line and point analysis results. Fig. 7(b) is the locally enlarged image in the Fig. 7(a). As can be seen from Fig. 7(c), irregular block-like phases are rich in Ti, Ni and Al elements, but without C element. It reveals from spectrum point 3 and point 4 (as shown in Fig. 7(d), (e), respectively) that the atomic percent contents of point 3 is about 65.2 at.% of Ti, 23.2 at.% of Ni, 9.2 at.% of Al and 2.0% of V, and point 4 contains about 66.2 at.% of Ti, 23.3 at.% of Ni, 8.3 at.% of Al and 2.2% of V. It can be found that atomic ratios of Ti:(Ni + Al) are 2.01:1 and 2.09:1 for point 3 and point 4, respectively. Thus, it can be concluded that irregular block-like phases are Ti<sub>3</sub>[Ni,Al] type intermetallic compounds. Moreover, as can be seen from the result of spectrum point 5 (as shown in Fig. 7(f)), rod-like structure is mainly composed of 66.8 at.% of Ni, 22.7 at.% of Ti and 7.4 at.% of Al. The atomic ratio of Ni:Ti is about 2.94:1, which implies that rod-like structures are Ni<sub>3</sub>Ti. However, flower-like phase is mainly enrich in Ti and C elements (as shown in Fig. 7(g)), furthermore, the atomic ratio of Ti to C is about 1.01:1, meaning that flower-like phases are also TiC carbides. In addition, it can be seen form Fig. 7(h) that the matrix is mainly enrich in Ti element, but a few of Al, V and Ni can also be found in the matrix. It implies that matrix of the coating is still a α-Ti phase of Ti6Al4V alloy, and Al, Ni, V dissolves into the matrix.

Fig. 3 – Variation of Gibbs free energy of carbides and intermetallic compounds with temperature: (a) carbides; (b) intermetallic compounds.

Fig. 4 – XRD patterns of precursor powders, alloying coating and substrate.
3.3. Effect of laser parameters on the microstructure of the coatings

Fig. 8 reveals the effect of laser parameters on the morphology of TiC and Ti2(Ni,Al) intermetallic compounds reinforcements in the coatings. As can be seen, except for sample S5, the number of dendrite phases increase, but grain size of the dendrites become coarser with the increasing of laser specific energy. On the one hand, laser heat input increases with increasing of laser specific energy, more substrate is melted, which provides more Ti for the laser molten pool and promotes the reaction between Ti and CNTs, as well as Ti and Ni, in hence, more reinforcements are formed. On the other hand, the high temperature dwelled time of the molten pool increases with the increasing of laser specific energy, which leads to reduce the solidification rate of the laser molten pool. Thus, grain size of reinforcements increases. Furthermore, the amount of CNTs and Ni added in the precursor materials is constant, thus, the number of reinforcements produced by reaction in laser molten pool does not increase with the increasing of laser specific energy. On the contrary, the dilution rate increases with the increasing of laser specific energy, which leads to reduce the concentration of reactants and increase the volume of laser molten pool. As a result, the volume fraction of reinforcements in unit volume decreases, when laser specific energy exceeds a certain value.

3.4. Effect of laser parameters on the hardness and wear behaviours of the coatings

Fig. 9(a) shows the typical micro-hardness distribution along the depth of the alloying coating for sample S2 and S3. Fig. 9(b) presents the variation of average micro-hardness on the top surface of the coatings with laser specific energy. As can be seen from Fig. 9(a), the micro-hardness at middle parts of the coating is higher than that of upper parts and bottom parts of the coating. This distribution is related to the flow of laser molten pool fluid and the density of reinforcements. In general, metal fluid of in the laser molten pool is affected by surface tension force, gravity and buoyancy force [31]. The comprehensive effect of the surface tension force, gravity and buoyance results in intense convection in laser molten pool, which is favorable to the uniform distribution of the reinforcements. On the other hand, density of TiC (4.93 g/cm²) is quite similar to that of Ti6Al4V alloy (4.51 g/cm³), which is helpful for the uniform distribution of TiC in coatings. In addition, density of NiTi2 (6.4–6.7 g/cm³) and Ni3Ti (7.5–7.9 g/cm³) are somewhat larger than that of Ti6Al4V alloy, which leads to Ti2(Ni,Al) and Ni3Ti intermetallic compounds having a tendency to sink down to the bottom of molten pool. However, as we known, laser surface alloy technology has a high cooling rate. It is reported that the solidification rate of the molten pool can up to 10³–10⁶ °C/s during solidification and the coating is
solidified in 50 μm–2 ms [32,33]. As a result, reinforcements have not sunk down to the bottom of the coating, and the coating has solidified. Therefore, the reinforcements can still be evenly distributed in the coating. On the other hand, owing to the influence of dilution and low density of CNTs, effective concentration of CNTs at the bottom is less than that of upper and middle parts of the coating, which leads to form less TiC reinforcement at the bottom of the coating. In hence, the micro-hardness at the bottom of the molten pool is relatively lower. In addition, it can be seen from Fig. 9(b) that micro-hardness first increases and then decreases with the increasing of laser specific energy. When the specific energy of laser exceeds 5 kJ/cm², the reason for the decrease of micro-hardness is a large dilution rate and less reinforcements in the coating at high laser specific energy. Therefore, laser specific energy should be controlled within 4.167–5 kJ/cm² for the present study.

The 2D geometry of the wear scar and wear volume loss of the samples are shown in Fig. 10. It can be seen that the maximum wear width and depth of the wear scar, as well as wear volume loss of the coatings are less than that of the substrate. It means that wear resistance of the coatings is higher than that of the substrate at the same test conditions. It can also be found that, the maximum wear depth and wear volume loss of the coatings first decrease and then increase with the increase in the laser specific energy. The main reason is that, when laser specific energy is less than 5 kJ/cm², the volume fraction of reinforcements increasing with the increasing of laser specific energy. So that, wear resistance of the coatings increases with the increasing of laser specific energy. However, when laser specific energy is beyond a certain value, the volume fraction of reinforcements reduces due to increasing of dilution, result in reducing the wear resistance of the coatings. In addition, it can be also found from the Fig. 10(b) that wear volume losses of the alloying coatings are less than that of Ti6Al4V alloy substrate, meaning that coatings process a higher wear resistance than that of substrate. Furthermore, it can also be drawn from Fig. 10(b) that wear resistance of the composite coatings is 2.3–6.9 times of that of Ti6Al4V alloy substrate.

**Fig. 6** – Secondary electron images (EPMA) and elemental face distribution of the coating: (a) image (b)V element (c) Ti element (d) Al element (e) C element (f) Ni element.
Fig. 7 – Secondary electron images (EPMA) and elemental results of some typical phases in the coating: (a) image; (b) locally enlarged image in Fig. 7(a); (c) elemental line distribution; (d) spectrum point 1; (e) spectrum point 2; (f) spectrum point 3; (g) spectrum point 4; (h) spectrum point 5.

Morphology of wear scars at different laser specific energy are shown in Fig. 11. As can be seen from Fig. 11(a), surface of the substrate exhibits the serious effect the micro-plowing and plastic deformation, as well as local wear debris from the surface of the substrate. When the substrate contacts with the friction pairs during dry wear process, some micro-humps on the surface of friction pairs are squeezed into the relatively soft surface of the substrate at normal applied load. Metals in the contact zone are pushed at the thrust load produced by reciprocating motion of specimen, resulting in forming numerous wide and deep grooves and plastic flow due to poor bearing and shear capacity of the substrate. At the same time, because of the local contact between substrate and friction pair, the temperature of contact point rises and “welding” is formed, and then welding point are tearing at the effect of at the shear force produced by reciprocating motion of specimen, as a result, local adhesive wear is formed. It can be concluded that wear mechanism of Ti6Al4V alloy substrate is serious abrasive wear and plastic deformation, as well as slight adhesive wear. It can be discerned from Fig. 11(b)–(f) that surface grooves become shallow and plastic deformation reduces, as well as there is no obviously indication of brittle failure or loose debris of reinforcements in the surface of coatings. It implies that the coatings have good abrasive wear resistance properties and brittle fracture resistance. However, compared with substrate, there exists number of local metal tearing zone in the matrix of coatings, implying that the dominant wear mechanism of the coatings is adhesive wear. Among all the coatings, the sample S2 and S3 possess the shallowest groove and the smallest area of tear. It means that the coatings of S2 and S3 have good resistance to adhesion wear, abrasive wear and plastic deformation. However, when the laser specific
energy increases to 6.67 kJ/cm² (sample S5), a lot of narrow and shallow grooves re-emerges on the surface of wear scar and numerous debris produced (as shown in Fig. 11(f)). It implies that wear mechanism of the coating changes from adhesive wear to adhesive wear and abrasive wear after laser specific energy beyond a certain value. Therefore, laser specific energy should be controlled within 4.15 kJ/cm²–5.83 kJ/cm² at present study.
Fig. 10 – Wear scar profile and wear volume loss: (a) 2D geometry of the wear scar, (b) wear volume loss.

Fig. 11 – Wear scar morphology of the substrate and coatings: (a) substrate; (b) sample S1; (c) sample S2; (d) sample S3; (e) sample S4; (f) sample S5; (g) enlarged zone A in Fig. 11(a); (h) enlarged zone B in Fig. 11(d).
4. Conclusions

(1) TiC–TiO2(Ni,Al)–Ni2Ti reinforced composite coatings were fabricated on the Ti6Al4V alloy substrate by laser alloying processing with pure Ni + CNTs mixed powders. Coatings were free from cracks and pores. Cypress leaf-like and flow-like TiC dendrites, as well as block-like TiO2(Ni,Al) and rod-like Ni2Ti intermetallic compounds were in-situ formed during laser alloying process, and some of residual CNTs were found in the coating. TiC, TiO2(Ni,Al) and Ni2Ti reinforcements were uniformly distributed in the coating.

(2) With the increasing of laser specific energy, depth of laser pool and dilution of the coating increased. Volume fraction of reinforcements first increased and then decreased with the increasing of laser specific energy, but grain size of reinforcements became coarse with the increasing of laser specific energy.

(3) Compared with the Ti6Al4V alloy substrate, micro-hardness and wear properties of the composite coatings were improved obviously. When laser specific energy was controlled within 4.167–5.5 kJ/cm², the coating had a high micro-hardness and good wear resistance. Wear resistance of the coating was about 2.3–6.9 times of that of substrate. Wear behavior of the dominant wear mechanism of the composite coatings was adhesive wear, whereas the Ti6Al4V alloy substrate exhibited serious abrasive wear and plastic deformation, accompanied by local slight adhesive wear.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


