Structure and properties of graphene reinforced Ti-based composite coatings on TC4 alloy by argon arc cladding

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Abstract. The TiC coating was prepared on TC4 alloy using argon arc cladding method of graphene and titanium powder to improve wear resistance. The microstructure and phase of coating was observed by XRD, OM and SEM. The properties of coating were tested by microhardness-tester and dry slipping friction tester. The results show that the coating consists of TiC and Ti, and the composite coatings have good bonding with substrate. The in-situ synthesis of TiC particles are uniformly distributed in the composite coatings, and the morphology of TiC particles are composed of particle-shaped, rod-like and flower-like morphologies. The average microhardness of composite coating can reach 835 HV, about 2.8 times of the substrate. The composite coating has excellent tribological properties.

1. Introduction

The TC4 is a kind of titanium alloy which have the characteristics of light quality, high strength, corrosion resistance and easy to processing, and it can be applied to aviation, aerospace, petroleum, transportation and so on [1-3]. However, the application of TC4 alloy is limited due to low hardness, and low wear resistance [4,5]. Therefore, surface modification of TC4 alloy is necessary. The mainly surface modification methods of the TC4 alloy include ion implantation [6,7], spraying technology[8,9], sol-gel method[10,11] and surface cladding technology [12,13], especially the surface cladding technology has become one of the most widely studied at present. Ceramic composites exhibits high microhardness, excellent wear resistance can be employed as cladding materials. Zhang et al[14] have studied the microstructure of TiC/Ti composite coating by laser cladding technology. The results showed that the highest haredness of coating is HV1400, about 4.5 times of the substrate. Li, et al[15] have studied SiC reinforced Ti-based composite coatings produced by in laser cladding technique using titanium and silicon carbide powder. The result that the maximum hardness of cladding layer can reached 1607.9HV. Yang et al[16] evaluated the microstructure and properties of TiCp/Ti composite coating by tungsten inert gas cladding.

Graphene is a two-dimensional carbon nano-material composed of carbon atoms and sp² hybrid orbital with hexagonal honeycomb lattice. Graphene has excellent optical, strength and modulus, electrical and mechanical properties [17-19]. A small amount of graphene can significantly improve the tensile strength and wear resistance of the pure Ti composites [20]. Compare to other cladding technology, the argon arc cladding features easy operation, energy concentration, low cost and non-oxidation and so on other advantages [16,21,22]. However, there was little research about graphene reinforced Ti-based composite coatings by argon arc cladding. So the present study employed the
argon arc cladding to deposit graphene and titanium powder on the surface of TC4 to synthesize coating. The phase, microstructures and components of the composite coating was analyzed.

2. Experimental metal

2.1. Materials and cladding processing

The TC4 alloy was used as the substrate material with a dimension of 50 mm × 10mm × 10 mm. The surface of TC4 alloy need be polished with 320 grit silicon carbide sandpaper and washed with acetone and alcohol. The Ti powder (99.5% purity, ~20μm diameter) and graphene powder (99.0% purity; Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, Chengdu, China) initial materials were used for synthesizing materials. The total mass of powder is 20 g, and the mass fraction of the graphene in the powder is 3%. Figure 1 shows that the SEM images of graphene powder and the pre-processed titanium powder. Next, the pre-processed Ti powder (97% by mass) and graphene (3% by mass) were mixed in the ball milling (F-P400H) for 4 h under argon (99.99% Ar) atmosphere. The EDS of mixed powders show that the powder did not occur reaction by ball milling(figure 2). Then coatings were carried out by MW3000 welding machine. The optimum cladding parameters are the cladding current (90A), cladding voltage (14.5V), cladding speed (140mm/min), respectively. argon flow rate: 10L/min. Furthermore, argon gas (99.99%) was used as shielding gas in the cladding processing and the argon gas flow rate 10 L/min.

![Figure 1](image1.png)  
**Figure 1.** SEM images of the pre-processed titanium powder (a) and graphene powder (b).

![Figure 2](image2.png)  
**Figure 2.** The SEM and EDS patterns of graphene and titanium powders after the ball milling.

2.2. Microanalysis and performance testing

The phase structure of the cladding coatings were analyze by DX-2700B X-ray diffraction with Cu Kα irradiation (λ = 0.1540nm). The scanning speed was 4°/min and the step size was 0.02°. The microstructure and components of the cladding coatings were observed by MX-2600 SEM and EDS.

The microhardness tester (type: MHV-2000) used to measure the microhardness of cladding coatings. The loading force is 2.942 N and the time is 15 s. The wear properties of cladding coatings were measured by wear machine (type: MMS-2A). The friction pair was GCr15 steel with a rock well...
hardness of 58HRC. The wear conditions were a normal load of 200 N, a sliding speed of 200 r/min, and the time of abrasion of 30 min.

3. Results and discussion

3.1. Microstructure and phase of the composite coatings

Figure 3 shows the XRD diagram of the composite coating. It reveals that the composite coatings comprised of Ti and TiC phases. There is no graphene in the cladding coating, because of carbon titanium in the coatings, in which the graphene and titanium have happened in-situ reaction. The result of the XRD analysis confirms that the TiC reinforced titanium matrix composite coatings have been produced by argon arc cladding technique.

![Figure 3. X-ray diffraction patterns of the cladding coating.](image)

The cross-section morphologies of the composite coating by argon arc cladding is given in figure 4. It reveals that the surface of the composite coating is relatively smooth, free from pores and cracks, and has metallurgical bonding with matrix. There is an obvious bright intermediate belt between cladding coating and the substrate, forming good metallurgical bonding[23].

Figure 5 shows the upper surface SEM images of the composite coating’s cross-section. For the top surface of the coating, as shown in figure 5(a), the amount of particles is smaller and the size of the in-situ formed particles is bigger. For the coating in which depth from surface is equal to 300 μm, as we can see in figure 5(b), it can be observed clearly that the microstructure in the clad zone exists in the form of fine dendrites. The particles are formed by direct metallurgical reaction and distributes evenly in the coating. Argon arc cladding is an integrated physical and metallurgical process of the quick heating and quick cooling far away from the equilibrium state, which determines the particles synthesized in-situ were fine. SEM micrographs of composite coating, as shown in figure 6, clearly reveal the morphology of each phase. It can be found that, the composite coating are composed of particle-shaped and rod-like morphologies, and around the rod-like structures, where there are lots of particle-shaped phases (figure 4(a)). As shown in figure 4(b), the microstructure is composed mainly of flower-like structures. From the component content and element in table 1, the particle-shaped, rod-like and flower-like morphologies were found to be Ti and C by EDX analysis, and so they are presumably the TiC phase identified by XRD. The spectrum 2 were found to be rich in Ti, Al, and V, and so we can infer that they are α-Ti phase. The TiC particles are dominated by fine particles with an average grain size of less than 1 μm and the rod-like structures with average particle size of 4 μm×500 nm. The results show that graphene and titanium powder generate a large number of TiC particles by in-situ reaction in the composite coating. These TiC particles play the role of particle reinforced.
Figure 5. SEM images of the composite coating (a) Top surface; (b) Surface at about 300 μm.

Figure 6. The high magnification morphology of different reinforcement shape.

Table 1. Component content and element of different zone in figure 6.

| Position   | Element and content (Wt. %) |
|------------|------------------------------|
| Spectrum1(a) | C 17.7, Al - , Ti 82.3, V 14.2 |
| Spectrum2(a) | C 1.32, Al 5.70, Ti 89.73, V 3.25 |
| Spectrum3(a) | C 20.36, Al - , Ti 79.64, V - |
| Spectrum1(b) | C 15.61, Al - , Ti 84.39, V - |
| Spectrum2(b) | C 1.47, Al 5.58, Ti 89.86, V 3.09 |

3.2. Microhardness

Figure 7 shows the microhardness of the composite coating. As seen from figure 7, the composite coating presents higher microhardness. From distribution of the microhardness curves, there are three main regions: the coating zone, heat-affected zone and substrate. The microhardness of the composite coating is decreased gradually from the coating through the interface to substrate, and the microhardness of top surface of composite coating is relatively lower than that of central region of the coating. The average microhardness of composite coating is 835HV, which is about 2.8 times of the initial hardness. This is mainly attributed to the fine hard particles on the near surface region of the cladding coating. The TiC particles have higher hardness(3400HV)[24, 25]. Therefore, the hardness of the cladding coating can be improved.

3.3. The wear weight loss
Figure 8 shows the wear weight loss of the composite coating surface and TC4 alloy. The argon arc cladding coatings has better wear resistance under dry sliding wear condition in comparison to the TC4 alloy substrate. Wear mass loss of the composite coating is 1/90 of that of the TC4 alloy. The main strengthening mechanism of the composite coating is fine-grain strengthening and dispersion strengthening. These in-situ synthesized TiC reinforcements inhibit the dislocation motion and result in the strengthening effect. The high hardness TiC particles which is formed at the substrate will improve the hardness and wearable ability of the coating, which decrease the mass-loss wear of composite coating.

![Figure 7. Microhardness profiles across the depth of composite coating.](image)

![Figure 8. Comparison of wear loss weight for TC4 alloy substrate and the composite coating.](image)

4. Conclusions

(1) The titanium matrix composite coating reinforced by TiC particles being prepared by argon arc cladding with reactions of graphene and titanium powder.

(2) The main phase of the composite coating was TiC phase and α-Ti phase. The morphology of TiC particles are composed of particle-shaped, rod-like and flower-like morphologies.

(3) The microhardness of the composite coating from the surface to the substrate is gradually decreased and the microhardness was up to 835 HV. The argon arc cladding coating exhibits excellent wear resistance under dry sliding wear test conditions due to in situ formation of high hardness of TiC ceramic reinforcements.

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