Effect of Graphene Oxide on the Performance of Co-Based Coatings on Ti6Al4V Alloys by Laser Cladding

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Abstract: In order to improve the hardness and wear resistance of Ti6Al4V alloys, Co-based coatings with different contents of graphene oxide (GO) were prepared on Ti6Al4V alloys by laser cladding. The effects of the graphene oxide content on the microstructure, hardness, and wear resistance were analyzed. It was found that carbides and undissolved graphene oxide films existed in the coating. Carbides contribute to grain refinement and improve the hardness of the coating. Graphene oxide films can improve the wear resistance of the coating. However, an excessive addition of graphene oxide affects the laser energy absorption of the coating. The results show that when the graphene oxide content is 0.5 wt.%, the performance of the coating is the best. Compared with the Co-based coating without graphene oxide addition, the hardness increased by 32.3%, the friction coefficient decreased by 27.2%, and the wear rate decreased by 66.5%.

Keywords: Ti6Al4V alloy; laser cladding; graphene oxide; Co-based coating; microstructure; microhardness; wear resistance

1. Introduction

The titanium Ti6Al4V alloy has the advantages of a small density, high specific strength, and excellent corrosion resistance [1,2], and is widely used in aerospace [3,4], chemical industry [5], biomedical [6,7], and other fields. However, there are some restrictions for the applications of the Ti6Al4V alloy due to its low wear resistance and poor hardness properties [8,9]. Laser cladding is a promising method for the surface modification of material. The surface performance can be improved by laser cladding a coating on the Ti6Al4V alloy [10]. Cobalt has a strong precipitation hardening effect, intrinsic high strength properties, and the ability to maintain the hardness over a wide temperature range [11,12]. The thermal expansion coefficient of cobalt is close to that of the Ti6Al4V alloy, so it is an ideal material for coating a titanium alloy surface [13–15].

It has been found that the addition or formation of some carbides can effectively improve the performance of the coating. Hu et al. [16] produced Ni-based composite coatings via mixing different contents of TaC by laser cladding on the Ti6Al4V alloy. It was found, through an analysis of the microstructure and corrosion behavior of the coating, that the addition of TaC has a positive effect on the corrosion resistance of the coating. Chen et al. [17] prepared TiC bioinert coatings on the Ti6Al4V alloy surface by using mixed TiC and ZrO2 powders as the cladding material. The microhardness and wear resistance of the coating were greatly improved compared with the substrate Ti6Al4V alloy. Li et al. [18] prepared a micro- and nano-structured WC reinforced Co-based coating on the Ti6Al4V alloy by laser cladding. The results showed that the wear resistance of the coating was obviously improved compared with the substrate. Due to the accumulation of carbides or oxides, it is easy for the coating to harden and become brittle. Yang et al. [19] prepared...
WC7Co/Ti6Al4V composite coatings on a pure Ti substrate by laser cladding. It was found that the mean hardness of different structures exhibits a significant gradient distribution in the coating. The abrasive mechanisms of the coating are mainly adhesive wear and oxidation wear during the dry sliding process. Li et al. [20] prepared Ti + SiC coatings on the Ti6Al4V alloy by laser cladding. It was found that the hardness and wear resistance of the coating were significantly improved compared with the substrate.

Graphene oxide is an important derivative of graphene. The addition of graphene oxide (GO) can greatly improve the performance of the coating, which has been a research hotspot in recent years. Li et al. [21] employed GO-filled sol-gel films of a plasma electrolytic oxidation layer on the Ti6Al4V alloy. It was found that the addition of GO significantly improved the corrosion resistance and wear resistance of the coating. The improvement of wear resistance of the coating may be due to the solid lubrication property of GO nanoflakes. Sadeghi et al. [22] deposited double-layer coatings of GO-poly on the Ti6Al4V alloy by electrophoretic deposition. The friction coefficient was reduced from 0.5 to less than 0.03 due to the combination of the double-layer coatings. Zuo et al. [23] prepared GO particle-inserted coatings with different GO concentrations on a titanium alloy by micro-arc oxidation treatment. The results showed that the addition of GO significantly improved the tribocorrosion resistance. When the GO concentration was 10 mL/L, the performance of the coating was the best. Liu et al. [24] prepared ceramic coatings with GO addition on the Ti6Al4V alloy by plasma electrolytic oxidation technology. It was found that the wear resistance of the GO-added coating was significantly improved due to the physical barrier of GO. Wang et al. [25] grafted GO on the surface of the Ti6Al4V alloy. The corrosion resistance and tribological mechanism of the coating were discussed. The results show that the relative slip of GO sheets and entrapment of wear particles of the surface topography are the main factors contributing to the improved tribological behavior. Palaniappan et al. [26] used neodymium-decorated GO as the corrosion inhibiting barrier for the Ti6Al4V alloy. As a result, the corrosion resistance of the Ti6Al4V alloy was improved. Bulbul et al. [27] prepared hydroxyapatite (HA) reinforced by reduced nano-GO using the sol-gel method. The results showed that a crack-free coating was formed on the surface of the Ti6Al4V alloy by replacing HA with GO. The adhesion strength was also significantly improved.

In the current literature, few people have used laser cladding to prepare coatings with GO addition. Due to the high temperature of the laser cladding process, most of the GO in the coating will be dissolved even under the protection of inert gas. However, the performance of the coating can be effectively improved by undissolved GO and formed carbides if the amount of GO added is appropriate. Therefore, in this study, a Co-based coating with GO addition was prepared by laser cladding on a titanium alloy, and the effect of the addition of GO on the coating performance was analyzed.

2. Materials and Methods

In this study, the Ti6Al4V alloy was taken as the substrate, and its chemical composition is shown in Table 1. The cobalt powder (CoCrMo) used was self-fluxing alloy powder, and its chemical composition is shown in Table 2. The GO used in this paper included single-layer films, which were provided by Suzhou Tanfeng Graphene Technology Co., Ltd (Suzhou, China). The purity of GO powder was 99.0 wt.%. The CoCrMo and GO powders were divided into six groups and mixed. The content of GO was 0 wt.%, 0.2 wt.%, 0.5 wt.%, 0.8 wt.%, 1.1 wt.%, and 1.4 wt.% respectively. In order to ensure the uniformity of powder dispersion, the mixed powder was ball-milled. The ball-milling speed was 250 r/min and the ball-milling time was 3 h. In order to ensure the consistency of the experiment, the cobalt powder without GO addition was treated in the same way. The process parameters of laser cladding are shown in Table 3.

| Table 1. Chemical composition of the Ti6Al4V alloy. |
|--------------------------------------------------|
| **Element** | **Ti** | **Al** | **V** | **Fe** | **Others** |
| Content (wt.%) | 88.99 | 6.0 | 4.33 | 0.3 | 0.38 |
Table 2. Chemical composition of cobalt powder.

| Element | Co | Cr | Mo | Fe | Others |
|---------|----|----|----|----|--------|
| Content (wt.%) | 76.68 | 12.93 | 10.86 | 0.12 | 0.41 |

Table 3. Process parameters.

| Parameters | Value |
|------------|-------|
| Laser power (W) | 1200 |
| Scanning speed (mm/s) | 6 |
| Supply speed (r/min) | 1.2 |
| Spot size (mm) | 4 |

The substrate Ti6Al4V alloy was cleaned and kept at 403.15 K for 30 min. Then, the experiment of laser cladding was carried out immediately, in order to reduce the cracks and pores of the coating in the process of cladding. Argon was used as protective gas during the experiment. At the end of the experiment, the sample was cooled at constant temperature and sampled by wire electrical discharge machining (WEDM). Then, the etchant reagent (HF:HNO₃:H₂O = 2:3:15) was prepared, and the cross-section of the sample after grinding and polishing was etched for about 15 s. The microstructure of the sample was observed with a LEICA-DM-2700M optical microscope (Leica, Heerbrugg, Switzerland) and Sigma300 scanning electron microscope (Carl Zeiss, Oberkochen, German). The Vickers-hardness of the sample was measured with an HVS-1000ZCM-XY digital microhardness tester (Suoyan Testing Instrument, Shanghai, China). Taking the upper surface of the substrate as the starting point, the measuring points were taken every 0.15 mm along the depth direction. The hardness of each sample was measured at 12 points. The wear resistance of the sample was tested by an MFT-5000 friction wear testing machine (Rtec Company, Wilmington, DE, USA). The diameter of the ball was 5 mm, the normal load was 25 N, the loading time was 30 min, the frequency was 1 Hz, and the stroke was 10 mm. The wear marks were observed by an MFP-D white light interferometer (Rtec Company, Wilmington, DE, USA). The wear resistance of the coating was studied by analyzing the friction coefficient, wear morphology, and wear rate.

3. Results and Discussion

3.1. Microstructure

Figure 1a–f shows the optical microscope (OM) images of the coatings with different GO contents. The GO content of the coating shown in Figure 1a was 0 wt.%. In the absence of GO, the coating consisted of a large number of dendrites. Dendrites grew from multiple centers to all around the sample. However, when the content of GO was 0.2 wt.%, some carbides appeared in the coating. The corresponding EDS result demonstrated that they were TiC. The added GO absorbed energy and dissolved into C and O atoms during laser cladding. Then, TiC were formed by reactions with the substrate. At this content, the grains were undeveloped dendrites. The introduction of TiC causing grain segregation on the grain boundary, which reduced the driving force of the Gibbs free energy, hindered the grain growth and disrupted the branching. In addition, because the dissolution of GO consumed a lot of energy, the laser energy absorption rate of the coating was affected. Obviously, the laser energy absorption rate has a great effect on the microstructure [28]. Figure 2 presents an OM image of the bottom of the coating by laser cladding. It can be seen from the figure that the grain distribution at the bottom of the coating is layered. This is because the absorption of laser energy at the bottom of the coating is much weaker than that in the upper part. When the content of GO increased to 0.5 wt.%, the grains in the coating were undeveloped fine dendrites, as shown in Figure 1c. The dendrites were further refined. However, when the addition of GO increased to 0.8 wt.%, the grain size increased, as shown in Figure 1d. An excessive addition of GO weakens its ability to refine grains. With the continuous increase of the GO content, the grain size further increased, as shown in Figure 1e. When the content of GO was 1.4 wt.%, large cracks appeared in the coating, as shown in
Figure 1f. Due to the accumulation of carbides or oxides, the coating easily hardened and became brittle [18]. Therefore, the cracking of the coating was caused by the excessive addition of GO.

Figure 1. Optical microscope (OM) images of Co-based coatings with different graphene oxide (GO) contents: (a) 0 wt.%; (b) 0.2 wt.%; (c) 0.5 wt.%; (d) 0.8 wt.%; (e) 1.1 wt.%; and (f) 1.4 wt.%.

Figure 2. Grain distribution at the bottom of the coating: (a) bottom; (b) middle; (c) upper.
Figure 3a,c,d presents the energy dispersive X-ray spectroscopy (EDS, BRUKER AXS GMBH, Karlsruhe, Germany) results of the coating with a 0.8 wt.% GO content. Figure 3b shows a scanning electron microscopy (SEM) image of the coating with a 1.4 wt.% GO content. It can be seen from Figure 3a that there are many thin films embedded in the grains. The results of EDS show that the substance contains a large number of carbon and oxygen elements, and the atomic quantity ratio of carbon to oxygen is about 4.6, as displayed in Figure 4a. It can be inferred that the substance is GO. When the content of GO is 0.8 wt.%, there is much undissolved GO in the coating. In comparison, when the content is 1.4 wt.%, GO agglomerated, as shown in Figure 3b. A small amount of GO is helpful for improving the tribocorrosion resistance of the coating [21–25]. However, whilst the dissolution of some GO will consume a lot of energy, the existence of excessive undissolved GO will also affect the absorption of laser energy. A loss of energy greatly limits the growth of grains. Figure 3c shows the area without a film-shaped substance. The EDS results in this area indicate that carbon accounts for a relatively low percentage, as shown in Figure 4b. Figure 3d shows the distribution of carbon. Compared with Figure 3c,d, it is not difficult to find that carbon is mainly distributed along the grain boundary.

Figure 3. EDS and SEM images of the case of a 0.8 wt.% GO content: (a) Undissolved GO films; (b) agglomeration of GO; (c) area without GO films; and (d) mapping of carbon atoms.
Figure 4. EDS results (a) of the films and (b) of the area without GO films.

Figure 5 presents the carbon contents of different zones of the coating with a 1.4 wt.% GO content. The EDS results are shown in Tables 4 and 5. Due to the excessive content of GO, not only large cracks, but also some micro cracks, appeared in the coating, as shown in Figure 5. The EDS results show that the carbon content in the lower part of the coating is higher than that in the upper part of the coating. It can be seen that the distribution of carbon is uneven. Such a distribution also has an effect on the delamination of grains at the bottom of the coating. This should be related to the flow characteristics of the molten pool.

Figure 5. Different positions of the coating. (a) lower part; (b) upper part.

**Table 4.** EDS results of the lower part of the coating.

| Spectrum | C  | Al | Ti  | V  | Cr  | Co  | Mo  |
|----------|----|----|-----|----|-----|-----|-----|
| 1        | 7.01 | 1.91 | 57.27 | 3.66 | 10.10 | 18.01 | 2.04 |
| 2        | 2.62 | 2.24 | 60.50 | 4.22 | 10.76 | 16.34 | 3.32 |
Table 5. EDS results of the upper part of the coating.

| Spectrum | C     | Al    | Ti    | V     | Cr    | Co    | Mo    |
|----------|-------|-------|-------|-------|-------|-------|-------|
| 1        | 5.38  | 1.21  | 31.42 | 2.52  | 28.71 | 24.73 | 6.03  |
| 2        | 2.10  | 0.79  | 36.64 | 3.01  | 15.93 | 40.56 | 0.96  |

3.2. Microhardness

Figure 6 shows the hardness of the coatings with different GO contents. Figure 6a presents the hardness distribution along the coating depth. When the GO content is 1.1 wt.% and 1.4 wt.%, the hardness of the coating fluctuates, which is related to the quality of the coating. The change of hardness along the depth direction can be divided into three stages. With the increase of depth, the hardness of the coating remains unchanged at first (part I in the figure), and then decreases sharply (part II in the figure), before finally stabilizing (part III in the figure). The area with a higher hardness is the coating, and the area with a lower hardness is the substrate. The area where the hardness decreases sharply should be the transition zone between the coating and the substrate, which is called the heat-affected zone. Figure 6b shows the average hardness of the substrate and the coatings under different conditions. The hardness of the substrate is 390.6 HV. With the increase of the GO content, the average hardness of the coating first increases and then decreases. The hardness of the coating without GO is 762 HV, which is 95.1% higher than that of the substrate. When the GO content is 0.5 wt.%, the hardness of the coating is 1008.3 HV. It is 2.58 times that of the substrate and 32.3% higher than that of the coating without GO addition.

Figure 6. The hardness of the coatings with different GO contents: (a) Hardness distribution and (b) average hardness.

3.3. Wear Resistance

The changes of the friction coefficient with time of the substrate and the coatings with different GO contents are shown in Figure 7a. It is easy to observe that the friction coefficient of all coatings is lower than that of the Ti6Al4V alloy. As shown in Figure 7b, the friction coefficient of the coating with a 0.5 wt.% GO content is the minimum value. It is 40.1% lower than that of the substrate and 27.2% lower than that of the coating without GO addition.
Figure 7. The friction coefficient of the coatings with different GO contents: (a) The changes of the friction coefficient with time and (b) the friction coefficient.

Figure 8 shows the 3D morphologies of the wear surfaces of the substrate and the coatings with different GO contents. The coating without GO addition has a lot of pits and severe wear, as shown in Figure 8a. The wear of the coatings with 0.2 wt.% and 0.8 wt.% GO addition is low, but the wear scar boundary can be clearly seen, as shown in Figure 8b,d. When the GO content is 0.5 wt.%, the wear of the coating reaches the minimum, as shown in Figure 8c. The wear of the substrate Ti6Al4V alloy is the most serious, as shown in Figure 8e. The width and depth of the wear scars are presented in Table 6. It can be seen from the table that the width and depth of the wear scars of the coatings with different GO contents are smaller than those of the substrate, and the width and depth of the wear scars of the coatings with GO addition are smaller than those of the coating without GO addition. When the GO content is 0.5 wt.%, the width and depth of the wear scars are the minimum values.

| Different Conditions | Width/mm | Depth/μm |
|----------------------|----------|-----------|
| 0 wt.% GO            | 0.90     | 18        |
| 0.2 wt.% GO          | 0.85     | 10        |
| 0.5 wt.% GO          | 0.70     | 10        |
| 0.8 wt.% GO          | 0.90     | 12        |
| Substrate            | 1.05     | 38        |
Figure 9 shows the wear rates of the substrate and the coatings with different GO contents. It can be seen from the figure that the wear rate of the substrate is very high. The wear resistance of the coating without GO addition was significantly improved, and the wear rate was reduced by 56.8%. Compared with the coating without GO addition, the wear resistance of the coating with GO addition has been further improved. When the GO content is 0.5 wt.%, the wear resistance of the coating is the best. The wear rate of the coating decreased by 85.5% compared with the substrate and was 66.5% lower than that of the coating without GO addition.

4. Conclusions

With the addition of GO, the formed carbides and undissolved film-shaped GO exist simultaneously in the coating. The existence of the carbides refined the grain and improved the hardness and wear resistance of the coating. The existence of the undissolved GO enhanced the lubrication performance of the coating.

When the content of GO is excessive, the ability of grain refinement decreases. The dissolution of GO consumed a lot of laser energy. Moreover, the existence of excessive undissolved film-shaped GO weakened the laser energy absorption of the coating. The hardness and wear resistance of the coating decreased instead.

When the GO content is 0.5 wt.%, the performance of the coating is the best. The hardness of the coating is 2.58 times that of the substrate, and 32.3% higher than that of the Co-based coating without GO addition. The friction coefficient is reduced by 40.1% compared with the substrate and is 27.2% lower than that of the Co-based coating without GO addition. The wear rate is 85.5% lower than that of the substrate and 66.5% lower than that of the Co-based coating without GO addition.

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