

Article Effect of TiB₂ Content on Properties of Nickel-Coated Graphite Self-Lubricating Coating Prepared by Laser Cladding

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Abstract: To improve the anti-wear and friction-reducing properties of self-lubricating coatings, Ni60/Nickel-coated graphite/TiB₂ composite coatings with different contents were prepared by laser cladding. The coating properties were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM), energy spectrometer (EDS), electrochemical workstation, micro-Vickers hardness tester, and friction and wear tester. The results showed that with the increase in TiB₂ content, the graphite morphology changed from spherical at 0 wt.% TiB₂ content to a little black graphite alone at 14 wt.% TiB₂ to irregular agglomerates at 22 wt.% TiB₂. Furthermore, the hardness of the coatings increased with increasing TiB₂ content, and the 63% Ni60 + 15% nickel-coated graphite + 22% TiB₂ coating had the highest hardness. TiC and Cr₇C₃ were generated in the coatings with the addition of nickel-coated graphite. In addition, the 71% Ni60 + 15% Ni-coated graphite + 14% TiB₂ coating had the lowest friction coefficient, wear loss, and wear volume, thus exhibiting excellent friction reduction and anti-wear properties. The 71% Ni60 + 15% nickel-coated graphite + 14% TiB₂ coating had excellent corrosion resistance.

Keywords: laser cladding; TiB₂; nickel-coated graphite; wear resistance

1. Introduction

Q235 steel has excellent overall properties such as high strength, good toughness and combination properties, low carbon content, and high economy [1-3]. It can be used in the transmission components of new power units. Under operating conditions, its transmission components have small mating clearance and the load is greatly increased, which will cause severe wear on the surface of the steel plate. The use of conventional lubricants to reduce wear on the surface of the parts is difficult to adapt to the harsh operating environment. The only way to solve the problem of lubrication under high loads is to use solid-lubricated wear-resistant coatings [4,5]. Several methods for preparing solid lubricated wear coatings are electrospark deposition, compression molding, and thermal spray techniques, electroplating, magnetron sputtering, and laser cladding [6–9]. Each of these techniques has its limitations in terms of material selection, deposition thickness, adhesion, and molding deformation. However, these drawbacks can be overcome by laser cladding technology, which can provide new processing methods for the repair of critical components and the preparation of protective layers [4]. In addition, because of the low adhesive strength between the substrate and coating, the coating fabricated by thermal spraying is easily peeled off in a high-frequency working environment. The electroplating is harmful to the environment, and the deposition rate of magnetron sputtering is relatively slow [5]. Laser cladding is characterized by high power density, fast cladding speed, and the ability to achieve precisely localized cladding. It also has the advantage that the coating can be matched to the material according to the functional requirements of the



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part surface and that the coating and the substrate are metallurgically bonded [10]. Several studies have been conducted on the preparation of laser cladding over solid lubricated wear-resistant coatings.

Some studies on solid lubricating and wear-resistant coatings of metal sulfides (MoS₂, WS_2) have been carried out. Qu et al. [11] studied the effect of MoS_2 content on the microstructure evolution and wear behavior of the laser cladding coating. When the content of MoS_2 was more than 6 wt.%, the anti-friction lubricating phase MoS_2 could be synthesized in situ in the coating, which significantly improved the wear resistance of the substrate. Wang et al. [12] produced a nickel-based alloy submicron WS₂ selflubricating composite coating, which found that the wear resistance of the laser cladding Ni60-WS₂ coating was remarkably higher than that of the Ni60 coating. Yan et al. [13] studied a laser cladding WS₂/NbC/Co-based self-lubricating coating, which found that the multilayer structural coating had lower friction coefficient and wear volume at room temperature. Gao et al. [14] studied the Ti–Ni/TiN/TiW + TiS/WS₂ self-lubricating wear resistant composite coating prepared by laser cladding. It was found that the 50%Ni-30%TiN-20%WS₂ coating had good anti-wearing and friction reducing effects. Although WS_2 and MoS_2 have excellent self-lubricating properties, in the laser cladding process, high temperatures will cause WS₂ and MoS₂ to oxidize and decompose to form SO₂ gas. The escape of SO_2 gas not only increases the porosity of the coating, but also leads to the adhesion of the coating decline, which causes the coating to break under the action of tensile load [15].

Some studies on solid lubricating and wear-resistant coatings of inorganic (graphite) have been carried out. Liu et al. [16] studied the friction and wear properties of the laser cladding Ti-containing Ni60/graphite self-lubricating composite coatings. It was found that the friction coefficient of the Ti-containing composite coatings was higher than that of the Ti-free composite coatings. Liu et al. [17] prepared Ni-based coatings decorated by graphite particles, which found that the coating had excellent wear resistance. The above studies found that the graphite self-lubricating materials had superior lubricating and anti-friction properties. At the same time, graphite is an excellent solid lubricating material due to its high melting point and strong thermal stability.

Some studies have been conducted on self-lubricating wear-resistant composite coatings with the addition or in situ generation of lubricant phases and hard reinforced phases. Li et al. [18] investigated laser cladding Ti₃SiC₂ lubricating cobalt-based alloy coating. The dissolution of the lubricating phase Ti₃SiC₂ generated the reinforcing phase TiC, which led to a significant increase in the hardness and wear resistance of the coating. Yan et al. [19] prepared Ti₃SiC₂/Ti₅Si₃/TiC/Ni-based self-lubricating composite coating by laser. It was found that not only was the friction coefficient of the composite coating reduced, but it also had a relatively smooth wear surface. Dai et al. [20] used B4C and graphite to prepare a selflubricating TiB₂-TiCxNY ceramic coating on a Ti–6Al–4V alloy by laser, and found that the wear resistance of the coating was markedly improved. Xia et al. [21] investigated a laser cladding TiB_2 /graphite coating on the surface of 9Cr18 stainless steel, and found that the presence of carbides greatly increased the hardness of the coating, and the wear resistance of the coating was higher than that of the substrate stainless steel. Chi et al. [22] prepared in situ TiB₂–TiC reinforced Fe–Al composite coatings by laser alloying. It was found that when Ti was added at 30 wt.%, the volume loss was reduced by 92.8% compared to the substrate, indicating a significant increase in wear resistance. Tran et al. [23] studied the Cu/TiB_2 wear resistance composite coating on H13 steel prepared by in situ laser cladding, which found that the in situ synthesis of Cu/TiB_2 composite coating could improve the friction and wear properties of H13 steel. Li et al. [24] fabricated Al₂O₃-TiB₂-TiC ceramic coatings on carbon steel by laser cladding, and found that the white granular TiB₂ and TiC distributed on the Fe substrate significantly increased the microhardness and wear resistance. Lin et al. [25] prepared TiB_2 -TiB reinforced titanium matrix composite coating by laser cladding. It was found that the wear volume loss of the center of the coating was approximately 30% less than that of the Ti–6Al–4V substrate. The addition or in situ

formation of the lubricating phase and hard reinforcing phase in the above coating not only reduces the friction coefficient before the friction pair, but also increases the hardness of the coating. In addition, the toughening phase that plays the role of bonding and supporting can also be added to improve the comprehensive properties of the coating.

Ni60 self-fusing alloy powder, with high hardness and good wear and corrosion resistance, is widely used to improve the wear resistance of substrate surfaces [26]. When using laser cladding to prepare wear-resistant lubricating coatings, a solid lubricating phase is often introduced into nickel-based powders [27,28]. The solid lubricating phase reduces the wear rate and friction coefficient of the friction pair components, thereby improving their wear resistance. Whereas, graphite is an ideal and excellent solid lubricant with a high melting point, good heat resistance, and excellent lubricity [17]. TiB₂ is considered to be a good reinforcement material choice due to its hardness, second only to diamond and cubic boron nitride. In addition, TiB₂ has high hardness, high elastic modulus, low friction coefficient, and excellent chemical stability [25]. The addition of TiB₂ hard reinforced phase in the composite coating can improve the hardness, fracture toughness, and wear resistance of the coating [29].

At present, although some studies related to self-lubricating coatings have been investigated, due to the relatively low hardness of the lubricant phase, the introduction of the lubricant phase can reduce the friction coefficient of the coating, but will lead to the reduction in the hardness of the coating, so the biggest bottleneck at present is the integrated control of the anti-wear and friction reduction performance of the coating. To break through the technical bottleneck of existing research, this paper used TiB₂ as the reinforcement phase, Ni60 as the toughening phase, and nickel-clad graphite as the lubrication phase to prepare the self-lubricating composite coating by laser. Exploring the influence of the change in TiB₂ content on the performance of the coating, which provides support for the process optimization of the self-lubricating coating in engineering.

2. Experimental Materials and Method

Q235 steel, with dimensions of 51 mm \times 31 mm \times 11 mm, was used as the substrate. The coating materials were Ni60 (Kennametal Stellite, Shanghai, China), nickel-coated graphite (Nangong Xindun alloy, Nangong, China), and TiB₂ (Huarui Metal, Beijing, China) powder in different proportions. The particle size of the powder was 150-300 mesh. The proportions (wt.%) of nickel and graphite in the nickel-coated graphite were 60% and 40%, respectively. Two sets of comparisons were made for the coatings, which were divided into variable TiB₂ content (0 wt.%, 6 wt.%, 14 wt.%, 22 wt.%) and variable nickel-coated graphite content (0 wt.%, 15 wt.%). The chemical composition is shown in Table 1. The material composition of the coating is shown in Table 2. Before the experiments, the oxide layer on the surface of the substrate was removed with sandpaper, and then cleaned with alcohol. An Nd: LDF 4000-40 solid-state laser (Laserline, Koblenz, Germany) with a rated power of 4.4 kW was used to manufacture the coatings (laser power 1.5 KW, scanning speed 8 mm/s, spot size 4 mm, Ar flow 6.5 L/min, the synchronous powder feeding method was adopted, and the rate was 1.5 r/min). The experimental parameters are the results of the pre-experimental preferences, and the selected laser parameters do not allow for complete melt of TiB₂. The experiment used a single-layer laser cladding, and the laser scanning direction was the length of the substrate.

Table 1. Chemical composition of the coated materials (wt.%).

Element	Ni	Cr	Si	В	С	Fe
Ni60	Bal.	15.5	4.0	3.5	0.8	15.0

Sample No.	Powder Composition (wt.%)
W1	85% Ni60 + 15% nickel-coated graphite + 0% TiB ₂
W2	79% Ni60 + 15% nickel-coated graphite + 6% TiB ₂
W3	71% Ni60 + 15% nickel-coated graphite + 14% TiB ₂
W4	63% Ni $60 + 15%$ nickel-coated graphite + $22%$ TiB ₂
W5	86% Ni60 + 0% nickel-coated graphite + 14% TiB ₂

Table 2. Material composition of the coatings (wt.%).

The metallographic specimens were cut by a wire-cut machine (ZhongXin, Taizhou, China) in the vertical to the scanning direction. It was ground by #60 to #2000 metallographic sandpapers and polished by a polish-grinding machine (ZMP-1000) (Xinruisi, Tianjin, China). Then, the cross-section of the sample was corroded with 50% nitric acid solution for 25–49 s, and then washed with alcohol, and dried by cold air. The microstructure and composition of the samples were characterized by a scanning electron microscope (phenom g5 pure, Hitachi S-3400) (phenom, Eindhoven, The Netherlands) (Hitachi, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS).

The hardness on the cross-section of the coating was evaluated using a hardness tester (HVS-1000Z) (LiDun, Shanghai, China) with a load of 500 g for 10 s along the vertical direction. The hardness was measured every 100 μ m from the coating surface to the substrate.

In the electrochemical corrosion experiment, the sample was a dimension of $10 \text{ mm} \times 10 \text{ mm} \times 11 \text{ mm}$, and the characterization area was polished. The electrochemical corrosion experiment was measured by a CHI660D electrochemical analyzer (Huake, Beijing, China). The electrochemical corrosion test was carried out after immersion in 3.5% NaCl electrolyte solution for 30 min. A three electrode system was used in the electrochemical test, in which the reference electrode was calomel, the working electrode was the coating, and the auxiliary electrode was pt.

The phase composition of the coating was identified by an X-ray diffractometer (D/max-2500) (Rigaku, Tokyo, Japan). It was collected in the diffraction range of $20^{\circ} \sim 90^{\circ}$ with a diffraction speed of 4 (°)/min.

In the friction and wear experiment, the sample was a dimension of 15 mm \times 10 mm \times 9 mm. The room temperature friction and wear experiments were performed in MPX-3G friction wear tester (HengXu, Jinan, China) with the following conditions: test load 30 N, test time 60 min, and rotating speed 300 r/min. The grinding ball was a Si₃N₄ ceramic ball with a diameter of 6.35 mm.

3. Results Analysis and Discussion

3.1. The Influence of TiB₂ and Nickel-Coated Graphite Content Change on the Macro Morphology of the Coatings

Figure 1 shows the macro morphology of the cross section of the coating. It also shows that obvious cracks and hole defects could be observed in all five coatings. This was due to the mixing of moisture and air in the melt pool and reaction with the graphite, causing pores to appear in the coating. In addition, the fast scanning speed allowed the melt pool to flow insufficiently, resulting in the creation of pores [19]. Cracking may be caused by thermal mismatch between the reinforced, toughened, and lubricated phases, which may have increased the thermal stress in the TiB₂ phase and the surrounding coating, leading to the formation of cracks [30]. Moreover, there was a clear boundary between the coating and the substrate. A metallurgical bond was formed between the coating and the substrate. The thickness of the coating is shown in Figure 1. The thicknesses of the coatings with TiB₂ additions of 0 wt.%, 6 wt.%, 14 wt.%, and 22 wt.% were approximately 0.956, 1.29, 1.19, and 0.921 mm, respectively. The thickness of the coating without nickel-coated graphite was approximately 1.42 mm. This was due to a combination of factors such as the high thermal conductivity of graphite in the nickel-coated graphite, leading to fast heat dissipation from the melt pool, resulting in the deepest coating depth without graphite.



Figure 1. Macro morphology of the cross section of the coatings. (**a**) W1 coating, (**b**) W2 coating, (**c**) W3 coating, (**d**) W4 coating, (**e**) W5 coating.

3.2. The Influence of TiB₂ and Nickel-Coated Graphite Content Change on the Phase of Coatings

Figure 2 shows the XRD analysis of the phase of the self-lubricating coating by laser cladding. Figure 2a shows the phase of the coating with TiB_2 contents of 0 wt.%, 6 wt.%, 14 wt.%, and 22 wt.%. Figure 2b shows the phase of the coating with a nickel-coated graphite content of 0 wt.% and 15 wt.%.



Figure 2. XRD analysis diagram of composite coatings (**a**) varying in TiB_2 content and (**b**) varying nickel-coated graphite content.

Figure 2a shows that the phases of the coating without TiB₂ were mainly Cr1.12Ni2.88, γ -Ni, Ni3Fe, Cr7C3, and graphite. In addition, Ni₃B, TiC, TiB, and TiB₂ were also detected after adding TiB₂. The formation of γ -Ni and TiB phases is consistent with the TiB₂-containing composite coating synthesized by Yan et al. [31]. The diffraction peak of the hard phase TiC enhanced with the increase in TiB₂ content. Because the laser power cannot completely melt TiB₂, the molten Ti element had a stronger affinity with carbon atoms in the molten pool than boron atoms, leading to TiC being formed before TiB [19], and then the TiC diffraction peaks were enhanced. As the TiB₂ content increased, more TiB₂ decomposed in the molten pool, creating conditions for the solidification of the molten pool to form more TiC.

Figure 2b shows that the coating without nickel-coated graphite is mainly comprised of Cr1.12Ni2.88, γ -Ni, Ni3Fe, Ni3B, TiB, and TiB₂. Moreover, after adding nickel-coated graphite, new phases Cr₇C₃, TiC, and graphite were also detected. This was due to the reaction of the C element with Ti and Cr elements in the molten pool, and then Cr₇C₃ and TiC were formed. Zhang [32] also achieved similar results.

3.3. The Influence of TiB_2 and Nickel-Coated Graphite Content Changes on the Microstructure

Figure 3 shows the back-scattering electron (BSE) images of the five coatings. Figure 3(a1,b1,c1) shows the microstructures of the coating without TiB₂, which was mainly composed of a fine dendrite (A) black aggregated structure (B). Figure 3(a2-a4,b2-b4,c2-c4) shows the microstructures of the coating with 6 wt.%, 14 wt.%, and 22 wt.% TiB₂ content, respectively. It can be observed that the coating was mainly composed of fine peritectic crystals with black aggregate structures (F, H), and cruciform and sheet structures (E, G, K).



Figure 3. The effect of TiB₂ and nickel-coated graphite content changes on the microstructure of the coating. **(a1)** W1 upper part, **(b1)** W1 middle part, **(c1)** W1 lower part; **(a2)** W2 upper part, **(b2)** W2 middle part, **(c2)** W2 lower part; **(a3)** W3 upper part, **(b3)** W3 middle part, **(c3)** W3 lower part; **(a4)** W4 upper part, **(b4)** W4 middle part, **(c4)** W4 lower part; **(a5)** W5 upper part, **(b5)** W5 middle part, **(c5)** W5 lower part.

Figure 3(a5,b5,c5) shows the microstructures of the coating without adding nickelcoated graphite, and the coating was distributed with a long coarse strip of structure (M) and gray structure (N). Figure 3(a3,b3,c3) shows the microstructures of the nickel-coated graphite coating with 15 wt.% content. Compared with a5, b5, and c5, it can be seen that there was a cruciform structure (G) and black aggregate structure (H) in the image of a3, b3, and c3.

The EDS results of the above-mentioned spots are shown in Table 3. Combining XRD and EDS analysis in Table 3, the fine dendrite (A) was mainly composed of Cr element, and C element was also detected near it. According to the literature [33], Cr and C elements are enriched on the dendrites mainly in the form of carbides. It can be seen that the dendritic strip structure was the hard phase Cr_7C_3 . B, F, and H show that the black aggregated structure was mainly composed of carbon elements, which was graphite. From the mass fraction of (J) in Table 3, the ratio of the number of Ni and Fe atoms was 3.6:1, and the highest chemical formula was Ni3.6Fe, which was presumed to be Ni₃Fe. The continuous matrix (C, D, I, J) and the long strip of structure (M) mainly included nickel, iron, and other elements such as titanium, carbon, and chromium, hence, it is speculated to be a Ni₃Fe eutectic structure and γ-Ni solid solution [31,34]. E, G, and K structures are cross-shaped and flake-shaped, inferred to be the hard phase TiC [35]. From the mass fraction of (K) in Table 3, the ratio of the number of Ti and C atoms was nearly 1.48:1, and the highest chemical formula was Ti1.48C, which was presumed to be TiC. The gray structure (N) was rich in the Ti element, which was the element precipitated by TiB₂ in the molten pool. Furthermore, it was also detected that the white small dot structures (L, O) were rich in B elements, and nickel and iron elements were also detected. The B element was the element precipitated by TiB₂ in the molten pool, and the B element was distributed around the Ti element. This is because laser cladding is a process of rapid high-temperature melt, and part of TiB₂ decomposes in the molten pool. The rapid melting and solidification process causes the B element to not diffuse to the surroundings in time, so it is distributed around the Ti element.

7			Element	ts (wt.%)		
Zones	Ni	Fe	Cr	Ti	С	В
А	26.03	32.36	36.88	_	4.72	_
В	18.80	8.70	11.40	-	60.30	-
С	73.13	20.68	2.50	-	1.70	-
D	77.91	15.16	2.91	-	1.71	-
Е	2.70	0.80	29.30	46.10	13.40	-
F	21.31	3.52	9.85	4.32	57.69	-
G	10.93	7.12	7.12	51.65	13.34	-
Н	18.42	19.52	6.11	2.00	47.75	-
Ι	42.60	42.60	4.50	1.00	4.60	-
J	73.85	19.64	1.30	-	1.50	-
Κ	6.4	7.00	13.60	59.60	10.10	-
L	32.00	15.05	6.32	-	2.91	40.12
Μ	16.28	54.87	27.14	-	1.71	-
Ν	6.21	5.81	17.42	67.47	-	0.90
О	15.73	23.85	9.02	5.01	5.21	35.97

Table 3. Chemical compositions of the phases with different morphologies in the coatings.

Figure 3(a1,b1,c1) demonstrates that when the content of TiB₂ was 0 wt.%, the shape of graphite was mostly spherical. Figure 3(a2,b2,c2) shows that when the content of TiB₂ was 6 wt.%, the shape of graphite was a large aggregate. Figure 3(a3,b3,c3) indicates that when the content of TiB₂ was 14 wt.%, there was very little black graphite alone in the coating. It can be seen from Figure 3(a4,b4,c4) that when the content of TiB₂ was 22 wt.%, the black graphite in the coating was also less, and the shape was irregular. The addition of high-melting-point phase TiB₂ caused the fluidity of the molten pool to decrease, the ability to exchange heat with the outside world became worse, and the cooling rate of the molten pool became slower, providing more time for the diffusion of graphite. Besides, low-density phase graphite showed a large difference in density from other phases, which will also cause agglomeration. Meanwhile, because laser cladding is a rapid heating process, the graphite gradually decomposes, and then the C element gradually diffuses in the molten pool. The melting of carbon is an exothermic process, and then a large temperature gradient and concentration gradient will be formed in the melting area of

carbon. Graphite diffuses from a high concentration to low concentration area under the action of temperature gradient and concentration gradient [17], next, the large diffusion and aggregation shapes in Figure 3(b2,c2) in are formed. Furthermore, as the content of TiB₂ increases, the content of titanium in the molten pool increases. The diffused carbon element and the titanium element in the molten pool form the carbide TiC. As a result, the graphite in Figure 3(a3,b3,c3,a4,b4,c4) was reduced. Due to the strong affinity between titanium and carbon, the diffusion speed of graphite in the molten pool increased, and the shape of the graphite changed from spherical to irregular diffusion.

Through the addition of nickel-coated graphite, it was observed that the structure of the coating with the nickel-coated graphite was denser than the structure of the coating without addition. This is because the nickel-coated graphite melts in the molten pool, which leads to the full combination of titanium, chromium, and carbon in the molten pool, thereby increasing the precipitation of carbides. In addition, there is a relatively low-temperature zone between the graphite and the surrounding intermetallic alloy during the melting process, which increases the heterogeneous nucleation rate of the intermetallic alloy and leads to the refinement of the coating structure [36].

3.4. The Influence of TiB₂ and Nickel-Coated Graphite Content Changes on the Corrosion *Performance of the Coatings*

Figure 4 shows the electrochemical corrosion polarization curves of different contents of TiB₂ and nickel-coated graphite. The corrosion parameters listed in Table 4 present a clearer comparison between the different samples. Coating W1 without TiB₂, and coatings W2, W3, W4 with 6 wt.%, 14 wt.%, and 22 wt.% TiB₂ had self-corrosion potentials of -0.45, -0.427, -0.416, -0.431 V, respectively. The minimum self-corrosion current density of coating W3 was $3.925 * 10^{-5}$ (A·cm⁻²). The self-corrosion potential of the coating with TiB₂ was positively shifted and the self-corrosion current density was basically reduced.



Figure 4. Polarization curves of TiB₂/Ni-coated graphite with different contents.

No.	Self-Etching Voltage Ecorr/V	Self-Etching Current Density $10^{-6} \text{ A} \cdot \text{cm}^{-2}$
W1	-0.450	$1.251 imes 10^{-4}$
W2	-0.427	$2.405 imes10^{-4}$
W3	-0.416	$3.925 imes 10^{-5}$
W4	-0.431	$7.263 imes 10^{-5}$
W5	-0.439	$7.324 imes 10^{-5}$

 Table 4. Self-corrosion voltage and self-corrosion current density.

The self-corrosion potentials of coating W5 without nickel-coated graphite and coating W3 with 15 wt.% nickel-coated graphite was -0.439 and -0.416 V, respectively. The self-corrosion current densities of coatings W5 and W3 were 7.324×10^{-5} and 3.925×10^{-5} (A·cm⁻²), respectively. The self-corrosion potential of the coating with nickel-coated graphite was positively shifted, and the self-corrosion current density was reduced.

According to the relevant corrosion theory, the minimum corrosion current represents the corrosion resistance of the sample in the solution. Generally speaking, the smaller the corrosion current, the stronger the corrosion resistance of the material surface. Furthermore, the self-corrosion potential characterizes the sensitivity of the metal to corrosive media. The higher the corrosion potential, the stronger the corrosion resistance of the material surface [37]. Compared with other samples, W3 had superior corrosion resistance. The main reasons for the excellent corrosion resistance of W3 coatings are as follows. (1) The passivated oxide film that formed on the coating surface could effectively prevent the penetration of corrosive ions and improve the corrosion resistance of the coating. Metal atoms such as titanium and chromium in the coating can form a dense passivation film on the surface of the coating, which effectively separates it from the chloride ions in the NaCl solution [38]. Figure 3(a3,b3,c3) implies that the W3 coating was rich in dendritic and cladlike nickel-based structures. The Ni-rich element in the nickel-base was thermodynamically unstable and easily passivated, thereby forming a corrosion-resistant film with good protection during the corrosion process [39]. (2) Figure 3(a3-c3) show that the coating microstructure was uniform and dense. The addition of a moderate amount of TiB₂ helps to make the reinforcing phase and the toughening phase in the structure combined with lubrication more dense, thus reducing the oxidation rate. Similar findings were also found by Zhang et al. [40]. (3) According to XRD analysis data, it can be seen that compared with coating W5 without nickel-coated graphite, coating W3 with the nickel-coated graphite generated carbides Cr_7C_3 and TiC, which improves the corrosion resistance of coating W3 [41,42]. Furthermore, Diao found that ultrafine structured TiC and TiB₂ could improve the corrosion performance of composite coatings [43].

3.5. The Influence of TiB_2 and Nickel-Coated Graphite Content Changes on the Hardness Performance of the Coatings

Figure 5 shows the hardness test results from the surface of the coating to the substrate. It can be seen from the Figure 5 that the hardness of the coating gradually decreases from the coating to the substrate. With the increase in TiB_2 , the hardness increased successively. The average hardness of coating W1 without TiB_2 was 1272 $HV_{0.5}$, and the average hardness of the coating with 6 wt.% (W2), 14 wt.% (W3), and 22 wt.% (W4) TiB₂ was 1488, 1776, and $2109 \text{ HV}_{0.5}$, respectively. In particular, coating W4 had the highest hardness, and its highest hardness was $2275 \text{ HV}_{0.5}$. The main reason for this change is that TiB₂ was added to the composite coating as a hard phase to increase the hardness of the coating. The W4 coating had a maximum TiB_2 addition of 22 wt.%, so the hardness of the W4 coating was the highest. In addition, the added hard phase TiB₂ and the synthesized TiC enhanced phase were heterogeneously nucleated to achieve grain refinement. the finer the grains, the larger the grain boundaries. With grain refinement, the grain boundaries increased the blocking effect on dislocations, which in turn led to an increase in hardness [44]. Moreover, as Cr, Si, C, and B in the molten pool were captured and dissolved into the γ -Ni matrix, it caused lattice distortion and solid solution strength [45]. The enhanced phase TiB generated in the coating could also further increase the hardness [46].

The average hardness of coating W5 without nickel-coated graphite was 1189 HV_{0.5}, which was lower than that of coating W3 with 15 wt.% nickel-coated graphite, and its hardness was 1776 HV_{0.5}. The high hardness of the coating with the addition of nickel-coated graphite (W3) is mainly attributed to the dispersion distribution of the hard phase Cr7C3 formed in situ in the coating structure [47]. The hard phases TiC and Cr₇C₃ formed a dispersive strengthening effect. Therefore, the coating with nickel-coated graphite had a higher hardness than the coating without nickel-coated graphite.



Figure 5. The hardness of the coating under the change in TiB_2 and nickel-coated graphite content: (**a**) hardness profile; (**b**) average hardness.

3.6. The Influence of TiB_2 and Nickel-Coated Graphite Content Changes on the Friction and Wear Properties

Figure 6 demonstrates the average friction coefficient/mass loss and wear volume of the coating. According to the Archard wear equation [48,49], the wear volume V can be described as

$$V = K \frac{WS}{H}$$

where *W* is the normal load; *S* is the sliding distance; *H* is the hardness of coating; and *K* is a wear coefficient. The value of *K* is 5.0×10^{-3} [48].



Figure 6. Average friction coefficient, mass lose, and wear volume of the coating: (**a**) average friction coefficient and mass loss; (**b**) wear volume.

It can be seen from Figure 6a that the average friction coefficient of the coating decreased and then increased with the increase in TiB₂ content. When the TiB₂ content was 0 wt.% (W1), 6 wt.% (W2), 14 wt.% (W3), and 22 wt.% (W4), the average friction coefficients of the coatings were 0.51, 0.33, 0.23, and 0.46, respectively. Similarly, the mass loss first decreased and then increased with the increase in TiB₂, and the mass loss was 3.975, 0.6, 0.17, and 2.875 mg, respectively. In addition, the wear volume calculated from Archard's model is also shown in Figure 6b. With the increase in TiB₂ content, the wear volume gradually decreased. When the TiB₂ content was 0 wt.% (W1), 6 wt.% (W2), 14 wt.% (W3), and 22 wt.% (W4), the wear volume of the coatings were 0.00267, 0.00239, 0.0019, and 0.002 mm³, respectively. Figure 6a shows that the average friction coefficient of the coating without adding nickel-coated graphite (W5) and adding 15 wt.% nickel-coated graphite (W3) was 0.42 and 0.23, respectively, the mass loss was 4.46, and 0.17 mg, respectively. Figure 6b shows that the wear volume was 0.00258 and 0.0019 mm³, respectively. Nickel-coated graphite was added as a lubricating phase to the composite coating to play a lubricating effect, so the friction coefficient and wear volume of the composite coating to play

of 15 wt.% nickel-coated graphite was lower than that of the composite coating of 0 wt.% nickel-coated graphite. Compared to other coatings, the W3 coatings had excellent self-lubricating and tribological properties. This is because at low load (30 N), the W3 coating with low volume ceramic reinforcing phase added exhibited better wear resistance due to the uniform distribution of the reinforcement and small pore size. It can be seen from Figure 3 that the W3 coating had a more uniform combination of the reinforcing phase and the surrounding structure with smaller pore size, so the wear resistance was better than the W4 coating with the highest hardness [50]. In addition, the hardness results showed that the hardness of the composite coatings increased with increasing TiB₂ content, with the W4 coating having the highest hardness. However, the increase in hardness will be accompanied by a very low toughness, resulting in a more brittle W4 coating than the other coatings. The reinforcing particles on the surface of the coating are easily pulled out and flaked off during the wear process, which in turn aggravates the wear of the W4 coating. Similar results were observed in the study by Meng [51].

To further explain the reasons affecting the changes in wear, the SEM characterization of the wear morphology of the coating is shown in Figure 7. In Figure 7a,b,d,e all show a large distribution of dark oxide films. According to the EDS data in area B in Table 5, it can be seen that there were large concentrations of O, Ni, and Fe, which indicates the generation of oxide films. The oxide film originates from the frictional heating generated during the reciprocal sliding friction. Wang [52] also found similar oxide films in the wear test. The coating without TiB_2 (W1) in Figure 7a was distributed with shallow grooves and large dark oxide film. Additionally, the oxide film tended to flake off. The oxidation wear characteristics were obvious. Figure 7b shows that the coating with 6 wt.% TiB₂ (W2) addition had more grooves and a small amount of abrasive grain distribution. In addition, the coating adhered to a dark oxide film and the coating showed tear marks at the defects. It belongs to abrasive wear and oxidation wear. The wear pattern of the coating showed signs of tearing, which was caused by plastic deformation of the coating surface. Specifically, when the ceramic ball grinds the coating, the coating is sheared and then ruptured, forming microcracks. Next, the microcracks form tear marks on the wear surface under the action of normal and tangential forces [5]. According to the results of the EDS analysis of white abrasive particle A in Table 5, the main elements were Si and O, and the atomic ratio was 2:1, presumably the abrasive grains are SiO₂. This is due to the reaction of Si_3N_4 on the abrasive balls with water in the air to form SiO_2 during the friction process [53]. In turn, SiO_2 forms abrasive grains during the wear process. Figure 7c shows that the coating added with 14 wt.% TiB₂ (W3) showed extremely high wear resistance, with only a few scratches and oxide films forming on the wear surface, which was almost smooth compared to the other coatings. This was attributed to the effective distribution of the TiB₂ enhanced phase reducing the wear of the composite coating [54]. In addition, the hard phases Cr_7C_3 and TiC generated by the 15 wt.% coating reduced plastic deformation and improved the overall wear resistance of the coating compared to the W5 coating without nickel-coated graphite. Figure 7d shows a large number of parallel rows of elongated scratches and a large amount of abrasive spalling for the coating with 22 wt.% TiB₂ (W4) added. Such a large number of abrasive particles did not occur in coatings W2 and W3 with TiB₂ additions below 22 wt.%. During wear of the coating with 22 wt.% TiB₂ (W4), abrasive grains were shed, leading to three-body abrasive wear. The high hardness of the abrasive grains intensified the wear of the coating surface. These results corresponded to the higher wear weight loss of the W4 coating compared to the W2, W3 coatings. Figure 7e shows the wear pattern of the coating (W5) without nickel-coated graphite. The wear surface of sample W5 showed fewer plow pits and abrasive grains, and a dark oxide film. Therefore, the wear mechanism was mainly oxidative wear and abrasive wear.



Figure 7. The effect of TiB₂ and nickel-clad graphite content changes on the morphology of the wear scar of the coating, (**a**) W1 coating, (**b**) W2 coating, (**c**) W3 coating, (**d**) W4 coating, (**e**) W5 coating.

Table 5. EDS-determined com	positions of the	regions on	the worn	surfaces	marked	in 1	Figure	7
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Positions	Elements (at. %)							
	С	0	Si	Ti	Cr	Fe	Ni	
A	-	67.64	30.76	-	_	0.77	0.83	
В	14.22	42.69	2.75	2.02	4.52	11.13	22.67	

The W3 coating had the best friction wear performance, but not the highest hardness. In contrast, the W4 coating had the highest hardness but poor frictional wear performance. This result indicates that hardness is not the only factor affecting wear resistance. In addition, an appropriate combination of high hardness and high toughness can help to improve the wear resistance [19]. Similar findings were found in the study of Gurusamy [54].

3.7. Improvements

On one hand, the direct incorporation of the hard phase TiB_2 into the coating often leads to a large number of cracks and hole defects due to the large difference in thermal expansion coefficients between the ceramic phase and the rest of the coating material. In future work, we will consider in situ generation of hard phase composite coatings, which is expected to overcome the above-mentioned drawbacks [55]. On the other hand, a considerable amount of graphite in the coating may be oxidized to CO or CO₂ due to the higher and concentrated heat input during laser melting of the coating, resulting in porosity defects in the coating. We can consider a set of suitable laser parameters by adjusting the laser power and speed, thus suppressing the porosity and cracking defects of the coating [16].

4. Conclusions

- 1. With the increase in TiB₂ content, the graphite morphology changed from spherical at 0 wt.% TiB₂ content to a little black graphite alone at 14 wt.% TiB₂ to irregular agglomerates at 22 wt.% TiB₂.
- 2. The W3 coating had the best corrosion resistance. In the W3 coating, the addition of a moderate amount of TiB₂ helps to make the reinforcing phase and the toughening phase in the structure combined with lubrication denser, thus reducing the oxidation rate. Compared with coating W5 without nickel-coated graphite, the carbide Cr₇C₃ and TiC were formed in the W3 coating with nickel-coated graphite, which improved the corrosion resistance of the W3 coating.
- 3. The hardness of the W1, W2, W3, and W4 coatings increased with the increase in TiB_2 content. The W4 coating had the maximum hardness. TiC and Cr_7C_3 were formed in the W3 coating with 15 wt.% nickel-coated graphite, which formed a dispersion strengthening effect, so the hardness was higher than that of the W5 coating without nickel-coated graphite.
- 4. The W3 coatings had excellent self-lubricating and tribological properties. The W3 coating had the best friction wear performance, but not the highest hardness. In contrast, the W4 coating had the highest hardness but poor frictional wear performance. This result indicates that hardness is not the only factor affecting wear resistance. In addition, an appropriate combination of high hardness and high toughness can help to improve the wear resistance.

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