Tribocorrosion Behavior of Laser Cladded Ti-Al-(C, N) Composite Coatings in Artificial Seawater

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Abstract: MAX phase containing Ti-Al-(C, N) composite coatings is promising in marine engineering due to the improved tribocorrosion performance of titanium alloys. Therefore, novel Ti-Al-(C, N) composite coatings were prepared in this study using laser cladding on TC4 substrate. Electrochemical performances of as-obtained composite coatings were then analyzed under static and dynamic conditions in an artificial seawater environment, and their tribocorrosion behaviors and corrosion–wear synergism mechanism were examined by a tribocorrosion test system. The results showed that the existence of self-lubricating phases Ti$_2$AlC and Ti$_2$AlN in composite coatings and the corrosion products with a certain lubrication effect generated during the friction process kept the average friction coefficient at a low level. With the increase of load, the mechanical failure of the passive film in the friction process was enhanced, the adsorption of corrosive medium on the surface of the passive film led to its active dissolution, and the wear volume increased from $1.45 \times 10^{-2}$ to $3.24 \times 10^{-2}$ mm$^3$. The corrosion of composite coatings in artificial seawater was not extensive, and volume loss caused by tribocorrosion was mainly determined by wear behavior. In summary, the coatings exhibited good bearing capacity in the marine environment, thereby showing broad prospects for marine equipment applications.

Keywords: tribocorrosion; laser cladding; synergism mechanism; composite coatings

1. Introduction

The moving parts in the marine environment often suffer tremendous losses due to corrosion and wear. Corrosion–wear synergism does not simply combine both corrosion and wear, but results in certain synergistic effects different from both properties [1,2]. Titanium alloys are also called “marine metal” because of their low densities, high specific strengths, and strong corrosion resistances in seawater and ocean atmosphere. Hence, titanium alloys are widely used in submarine, deep submarine, and other marine equipment [3,4]. However, titanium alloys suffer from poor wear resistance. Additionally, surface passive film formed on the alloys can easily be destroyed by friction, thereby exposing the fresh surface to the corrosive environment and bearing the synergistic damage of corrosion and wear. These features have limited further applications of titanium alloys in marine equipment [5].

Laser cladding technology is a surface treatment tool used to effectively improve the corrosion and oxidation resistances of titanium alloy surfaces. This method has recently attracted increasing attention due to its various advantages, such as fast-melting and solidification speed, small heat-affected area, and small residual stress [6]. In this view, Weng et al. [7] used laser cladding technology to prepare coatings on TC4 with CoTi, CoTi$_2$, NiTi, TiC, TiB$_2$, TiB, Cr$_7$C$_3$, and Ti$_5$Si$_3$ as reinforcement phases. Their data suggested an increase in hardness and wear resistance by 4- and 10-fold, respectively. Liang et al. [8] prepared a TiB$_x$ + TiC-enhanced Ti$_2$Ni + TiNi-based gradient composite coating on TC4. The surface hardness of the coating reached 1555.1 HV, while the friction loss was reduced by 57%. However, the surface modification of titanium alloys by traditional ceramic or refractory alloys still suffers from some problems, such as coating brittleness and interface...
binding defects. These features make it difficult for the coating to cope with the complex environment under mechanical-chemical conditions [9,10].

Ternary metal ceramics phase $M_nAX_{n-1}$ has excellent properties, combining those of metal and ceramic materials due to the special bonding and layered structure, including good electrical conductivity, high damage tolerance, elevated hardness, superior modulus, and excellent wear and corrosion resistances. The unique layered structure and density distribution of electronic states may lead to various energy absorption mechanisms, making $M_nAX_{n-1}$ phase useful in the production of protective coating materials for various applications [11,12]. For instance, Richardson et al. [13] used elemental powders Ti, Al, and C to prepare coatings containing Ti$_2$AlC, TiC$_{0.64}$, Ti$_3$Al, and TiAl phases on pure titanium substrate. The hardness of the resulting coatings reached up to 811 HV. Cao et al. [14] produced coatings containing Al$_2$O$_3$, TiO$_2$, Ti$_2$AlC, and Al$_2$TiO$_3$ on low-carbon steel surfaces. They recorded a decline in the friction coefficient by 50% of the matrix, as well as a reduction in matrix stress by 41.3% due to self-lubrication and phase transformation of MAX phase Ti$_2$AlC. Yan et al. [15] manufactured coating reinforced by Ti$_3$SiC$_2$, Ti$_5$Si$_3$, TiC, TiNi$_x$, and γ-Ni solid solution. Their data revealed hardness values of the coatings reaching 2.36-fold that of the substrate. The existence of self-lubricating phase led to a reduction in the surface friction coefficient to 0.33, and the wear rate reached $13.5 \times 10^{-5}$ m$^3$/(N·m). The wear mechanism was based on small amounts of adhesive wear and plastic deformation. Wang et al. [16] deposited a Ti$_2$AlC coating on a martensitic stainless-steel surface. The continuous 75 h corrosion test in the NaCl vapor environment revealed a corrosion layer well-bonded to the coating, with defects that can be repaired by Al$_2$O$_3$ amorphous phase to increase the coating corrosion resistance. Overall, coatings containing MAX phase prepared by laser cladding on surfaces of titanium alloys may effectively improve the wear and corrosion resistances of titanium alloys.

Current works have mostly investigated the single failure mechanism of corrosion or wear of MAX phase coatings. The presented study mainly focuses on the tribocorrosion behavior and corrosion–wear synergism of MAX phase containing composite coatings in artificial seawater. This study provides support for the development of corrosion- and wear-resistant MAX phase containing composite coatings in marine engineering equipment. Accordingly, Ti-Al-(C, N) composite coatings reinforced with Ti$_2$AlC and Ti$_2$AlN MAX phases are fabricated in this work by laser cladding on TC4 substrate. The tribological properties of the as-obtained Ti-Al-(C, N) composite coatings are studied under different loads in artificial seawater to analyze the influences of applied loads on corrosion and wear behaviors of composite coatings, as well as to clarify the mechanism of corrosion–wear synergism.

2. Materials and Methods

2.1. Materials’ Preparation

TC4 alloy (size 40 mm × 20 mm × 10 mm) was used as the substrate. After polishing, TC4 alloy was cleaned with acetone and anhydrous ethanol followed by drying. Ti4822 powder (99%, 15–53 µm), TiC powder (99%, 2–4 µm), and AlN powder (99.5%, 1–3 µm) were all employed as cladding materials. The three powders were mixed in a planetary ball mill (MIQI, Guangzhou, China) at the ratio of 1:0.5:0.5, with a ball to material ratio of 5:1, rotation speed of 200 r/min, and ball grinding time of 120 min. The powders were then evenly mixed and placed under 100 °C vacuum drying for 10 h. The resulting powder material (thickness about 2 mm) was pre-laid on TC4 surface using a self-made tool. An YSL-6000 fiber laser (YUCHENG, Dezhou, China) was used for laser cladding under argon at the flow rate of 10 L/min. The spot size was set to 10 mm × 2 mm, laser power was 3000 W, and scanning speed was 120 mm/min. The natural seawater was simulated according to standard ASTM D1141-98 (Table 1), and pH was adjusted to 8.2 using 0.1 M NaOH solution.
Table 1. Chemical constituents of experimental seawater (g·L\(^{-1}\)).

| Compound | NaCl | MgCl\(_2\) | NaSO\(_4\) | CaCl\(_2\) | SrCl\(_2\) | KCl | NaHCO\(_3\) | KBr | H\(_3\)BO\(_3\) | NaF |
|----------|------|------------|------------|------------|------------|-----|-------------|-----|-------------|-----|
| Concentration/(g·L\(^{-1}\)) | 24.53 | 5.20 | 4.09 | 1.16 | 0.025 | 0.695 | 0.201 | 0.101 | 0.027 | 0.003 |

2.2. Materials’ Characterization

The microstructures and wear morphologies of the materials were observed and analyzed by scanning electron microscopy (ZEISS Gemini 300, Jena, Germany) and energy dispersive spectrometry (OXFORD Xplore, Oxford, UK). The crystal phases of the materials were identified by X-ray diffraction (Bruker-D8 Advance, Bremen, Germany). The X-ray wavelength of the Cu target was 1.54056 Å, the tube voltage was 40 kV, the tube current was 40 mA, the scanning speed was 0.02 °/s, and the scanning range was 10°–80°. The Vickers hardness tester (DHV-1000Z, TIANXING, Changsha, China) was used to measure the hardness distribution of the coating. The load was 9.8 N, the holding time was 10 s, and the coating was tested along the top of the coating to the substrate direction with a 0.15 mm interval.

2.3. Tribocorrosion Testing

Tribocorrosion tests require simultaneous testing of electrochemical parameters and wear properties. For friction and wear testing, a ball-disc reciprocating friction and wear tester (Rec MFT-5000, San Jose, CA, USA) was employed, and dual-ball Si\(_3\)N\(_4\) ceramic (diameter 9.525 mm) was selected. The load was set to 10, 20, and 30 N at a reciprocating frequency of 1 Hz, reciprocating length of 5 mm, and test time of 20 min. For electrochemical performance testing, an electrochemical workstation (DH-7000, DONGHUA, Shanghai, China) was used to monitor the electrochemical signals. A saturated calomel electrode was utilized as the reference electrode (RE), platinum sheet as the counter electrode (CE), and test sample as the working electrode (WE). Resin was employed for covering the samples, leaving only a 10 mm × 10 mm test exposure area. Cathodic protection was also performed by applying a cathodic potential of −1 V to avoid corrosion during the sliding process. The wear loss obtained under cathodic protection was entirely generated from pure mechanical wear. Figure 1 presents a schematic diagram of the tribocorrosion test system. The three-dimensional topography instrument (Counter Elite K, Bruker, Billerica, MA, USA) was used to measure the three-dimensional morphology of the wear scar. The profile of the wear scar section and the roughness of the sample surface can be directly obtained by the three-dimensional topography instrument. The scanning mode is VSI/VXI mixed mode, the scanning depth is −40–10 µm, the scanning speed is 1 µm/s, and the threshold is 5%.

![Figure 1. Tribocorrosion experimental device: (a) schematic diagram and (b) experimental layout.](image-url)
steady time range (100 s to the end) can be directly obtained by the friction and wear tester. The potentiodynamic polarization tests of the samples were conducted under dynamic and static conditions at a scanning range from −0.5 to 0.5 V (vs. OCP) and a scanning rate of 1 mV/s. All experiments were carried out at room temperature and repeated three times under the same conditions to obtain the average results.

2.4. Calculation Method

The depth and width of the wear scar can be obtained by the section profile of the wear scar. The wear volume loss, \( V \), of the sample is obtained by integral calculation. The calculation formula is as follows:

\[
V = SD
\]

where \( V \) is the wear volume loss of the sample, \( S \) is the area of the cross-section contour of the wear scar morphology, and \( D \) is the reciprocating length of the friction movement.

According to [17,18], the components of corrosion–wear synergy can be calculated by Equation (3):

\[
W = W_{f0} + W_{c0} + \Delta W
\]

where \( W \) represents the total volume loss of corrosion and wear, \( W_{f0} \) represents pure wear volume loss without corrosion, \( W_{c0} \) refers to pure corrosion volume loss without friction, and \( \Delta W \) denotes the synergistic effect of corrosion and wear. Here, \( \Delta W \) can be defined by Equation (4):

\[
\Delta W = W_{fc} + W_{cf}
\]

where \( W_{fc} \) represents the action of corrosion on wear, and \( W_{cf} \) is the action of wear on corrosion.

After friction and wear testing, both \( W \) and \( W_{f0} \) can be calculated from the cross-section curve of wear marks, while \( W_{c0} \) and \( W_{cf} \) can be obtained by Faraday’s law using static and dynamic current density, \( i_{corr} \).

\[
W_{corr} = \frac{i_{corr}Mt}{nFp}
\]

where \( W_{corr} \) represents the volume loss caused by corrosion, \( t \) is the test time, \( M \) refers to relative atomic mass of the sample material, \( F \) denotes the Faraday constant, \( i_{corr} \) is the average current density during the sample process, and \( W_{fc} \) can be calculated by Equations (2)–(4).

3. Results and Discussion

3.1. Microstructures of Coating

Figure 2 shows the macroscopic morphology of the TCN coating. It can be seen that the thickness of the coating is about 1.85 mm, there are no obvious cracks, pores, or other defects on the surface, and the cross-section is lenticular. After cladding materials melted with the matrix, an arc-shaped fusion line was formed at the bonding area, which showed good metallurgical bonding.

![Figure 2. Macroscopic morphology of the TCN coating.](image-url)
Figure 3 shows the interface of the TCN coating and the microstructure in the middle of the coating. It can be seen that the transition between the fusion coating layer and the substrate is smooth, and there are no defects such as pores or cracks. The reinforced particles in the melted coating layer were densely and evenly distributed. The dendrites and a small amount of particle crystals were mainly distributed on the substrate at the bottom of the coating, while the dendrites in the middle of the melted coating layer gradually increased and tended to be developed. The characteristics of rapid melting and solidification of laser cladding made the ceramic phase precipitating in the Ti-Al-C-N melt, and grow mainly in the form of dendritic crystals. During the solidification process, the movement of the solid–liquid interface gradually reduced the temperature gradient, and the dendritic crystals in the middle of the coating gradually tended to be developed. Figure 4 shows the XRD pattern of the coating. It shows that TCN is composed of intermetallic compounds TiAl and Ti3Al, ceramic phase TiC and TiN, ceramic solid solution phase TiC0.3N0.7, and MAX phase Ti2AlC and Ti2AlN.

![Figure 3. Microstructure of the TCN coating. (a) Interface of TCN and (b) media zone of TCN.](image1)

![Figure 4. XRD patterns of the TCN coating.](image2)

Figure 5 shows the microhardness distribution of the cross-section of the TCN coating, and the average hardness is 673.56 HV, which is 2.04 times that of the substrate TC4 alloy (330 HV). It can be seen from Figure 5 that from the bottom to the surface, the hardness...
of TCN continuously increased, and the hardness of the bonding zone greatly increased, which is because during the solidification process, the extremely fast cooling rate made the coating layer fine and produced martensite with high hardness inside the matrix. In addition, hard particles such as dispersed ceramic solid solution phase TiC$_x$N$_{1-x}$ and MAX phase Ti$_2$AlC and Ti$_2$AlN were in situ generated on the substrate of the coating. During the solidification process, with the mutual restriction of the growth of TiC and TiN, the microstructure of strengthening phases in the coating presented a fine and dense state. At this time, the internal hardness of the coating was high and evenly distributed.

![Figure 5. Vickers hardness of the TCN coating.](image)

### 3.2. Electrochemical Response to Sliding

The open-circuit potential curves of TCN composite coatings before, during, and after friction under different load conditions are gathered in Figure 6. It shows that before friction, as the soaking time rose, the open-circuit potential slowly increased, indicating a dense and stable passive film gradually formed on the surface of the TCN coating. As wear started, the open-circuit potential represented the mixed potential between the worn area and the unworn area, and reflected the corrosion trend of the whole surface. Under various load conditions, the open-circuit potential of TCN dropped sharply by about 0.5 V because the ploughing action of the grinding ball on the sample surface led to removal of the passive film and some surface materials, thereby exposing the fresh surface to corrosive medium. The galvanic cell was formed in both worn and unworn areas due to potential differences, and the fresh surface can be used as the anode of the cell due to the low potential, which made corrosion reactions accelerate [19]. As the applied load rose, the exposed fresh surface of the damaged area increased, resulting in an enhanced corrosion area and deteriorated corrosion in the wear area. As a result, the open-circuit potential drop of the sample also increased [17]. By stopping wear, the open-circuit potentials of samples started to slowly rise, indicating that a passive film was regenerated on the surface of the samples which had good re-passivation ability.

The polarization curves of TCN during static and dynamic corrosion friction processes are depicted in Figure 7. The parameters related to static corrosion and friction corrosion are listed in Table 2. Without friction, the self-corrosion potential of TCN was $-0.405$ V, and the corrosion current density was $0.2 \mu$A·cm$^2$. During friction and wear, the polarization curves showed obvious oscillations due to the dynamic process of removal and formation of the passive film on the sample surface. As the load rose, the friction became more intense, resulting in the enhancement of plastic flow of the material surface. Additionally, the density of defects, such as dislocations and vacancies in the local deformation area, increased. The wear area with more defects and gathered residual stress became the anode of electrochemical battery due to its high corrosion activity, which aggravated its corrosion
reaction. As a result, the self-corrosion potential of TCN decreased by about 0.3 V, while the corrosion current increased by two orders of magnitude. Under 30 N, the self-corrosion potential decreased to $-0.89$ V, and the corrosion current density increased to $24.5 \, \mu A \cdot cm^2$.

![Figure 6](image_url)  
**Figure 6.** Open-circuit potential measurement curve of the TCN coating in artificial seawater.

![Figure 7](image_url)  
**Figure 7.** Polarization curve of the TCN coating in static corrosion and tribocorrosion in artificial seawater.

**Table 2.** Electrochemical parameters of TCN in static corrosion and friction corrosion.

| Load/N | 0   | 10  | 20  | 30  |
|--------|-----|-----|-----|-----|
| $E_{corr} / V$ | -0.41 | -0.78 | -0.80 | -0.89 |
| $I_{corr} / (\mu A \times cm^2)$ | 0.2 | 13.2 | 19.9 | 24.5 |

3.3. Friction and Wear

The variation curves of the friction coefficient in artificial seawater are illustrated in Figure 8. It can be seen from Figure 8 that when the time reached 100 s, the friction coefficient curve had basically reached stability. It is shown that with the increase of load from 10 to 30 N, the friction coefficient curve showed a small fluctuation and the average friction coefficient decreased from $0.30 \pm 0.06$ to $0.28 \pm 0.05$. On the one hand, in the
artificial seawater environment, seawater played a cooling and lubrication role (Figure 8). On the other hand, Ca$^{2+}$ and Mg$^{2+}$ ions in artificial seawater generated friction chemical products with a boundary lubrication effect, such as CaCO$_3$ and MgCO$_3$ on the friction surface with acid radical ions such as CO$_3^{2-}$ during friction. The corrosion of seawater also made the TCN surface prone to the formation of a passive film composed of oxides or hydroxides with a certain lubricating effect [20,21]. The surface material became loose and easy to remove because of corrosion. Under the action of friction, there was a continuous alternation between the generation and discharge of wear debris between the friction pairs, which caused the friction coefficient curve to regularly fluctuate with time. Hence, the friction coefficient remained at a low level and decreased slightly when the load increased from 10 to 30 N.

![Friction curves of the TCN coating under different load conditions in artificial seawater: (a) 10 N, (b) 20 N, and (c) 30 N.](image)

**Figure 8.** Friction curves of the TCN coating under different load conditions in artificial seawater: (a) 10 N, (b) 20 N, and (c) 30 N.

The existence of elements in the wear scar of the composite coating TCN surface was further analyzed by XPS testing. Figure 9 presents the 3D XPS spectra of Si 2p, Al 2p, Ti 2p, and O 1s. As shown in Figure 9a, Si 2p displayed two pairs of obvious peaks, with one pair near 101.9 and 102.4 eV corresponding to Si$_3$N$_4$ phase. It shows that, due to the fatigue effect caused by the reciprocating motion between the grinding pairs, adhesives wear occurred there, and the surface material of dual-sphere Si$_3$N$_4$ fell off and adhered to the composite coating surface during friction. The other pair was located near 103.6 and 104.2 eV, corresponding to SiO$_2$ phase. It shows that, due to the corrosion of seawater, some lubricating hydroxides were generated due to frictional chemical reactions during friction. Additionally, some lubricating hydroxides were generated due to frictional chemical reactions during friction.

![3D XPS spectra of Si 2p, Al 2p, Ti 2p, and O 1s.](image)

**Figure 9.** 3D XPS spectra of Si 2p, Al 2p, Ti 2p, and O 1s.
well as 73.24 and 73.65 eV, corresponded to Al_2O_3, indicating the oxidation of Al on the coating surface. The peaks at 74.20 and 74.63 eV were attributed to Al(OH)_3, suggesting the generation of Al(OH)_3 with a boundary lubricating effect by tribochemical reaction of Al_2O_3 during friction. In Figure 9c, TiO_2 was recorded at 458.3 and 464.0 eV, and TiN was observed at 457.70 and 463.00 eV in the Ti 2p map. These data revealed the oxidation of Ti on the coating surface. As shown in Figure 9d, the spectra of O 1s corresponding to TiO_2, Al_2O_3, O_2, and SiO_2 were observed at 529.9, 531.4, 532.3, and 533.7 eV, respectively. In summary, the passive film on the composite coating surface was composed of TiO_2 and Al_2O_3. Additionally, some lubricating hydroxides were generated due to frictional chemical reactions during friction.

![Figure 9](image-url)

Figure 9. XPS spectra acquired on the wear scar. (a) Si 2p, (b) Al 2p, (c) Ti 2p, and (d) O 1s.

The three-dimensional morphologies of the wear scar of the TCN coating in artificial seawater under different loading conditions are provided in Figure 10. Figure 11 shows a cross-sectional view of the center position of the wear trace morphology of the sample in the three-dimensional morphologies in Figure 10. Obvious furrows were seen on the surface of wear marks, mainly presenting typical abrasive wear morphologies. As load increased from 10 to 30 N, the width and depth of the wear scars enhanced, and average widths were estimated to be 601.6, 656.7, and 909.1 µm, respectively. The maximum wear scar depths were 17.92, 25.90, and 29.51 µm, respectively. In addition, the increase in load led to increments in surface roughness of the wear scars from 4.649 to 8.418 µm. Meanwhile, the number of furrows in wear scars gradually increased, indicating enhanced material loss between the friction pairs during friction that aggravated abrasive wear.
Figure 10. 3D topographies of the wear tracks of the TCN coating under different load conditions in artificial seawater: (a) 10 N, (b) 20 N, and (c) 30 N.

Figure 11. Cross-section profiles of the wear scars of the TCN coating under different load conditions in artificial seawater.

The wear morphologies of TCN composite coatings in artificial seawater are gathered in Figure 12. The friction surface became smooth and flat under 10 N due to the continuous shearing and dragging of peeled wear debris between the grinding pairs, mainly manifested as abrasive wear and a small amount of adhesive wear, according to Figure 12. As load increased to 20 N, the wear scar gradually widened and furrows parallel to the friction direction appeared with large numbers of debris particles on the sample surface. In this case, the surface passive film was destroyed during the friction process. Moreover, the material surface of the friction pair could not be discharged in time after falling off under friction, leading to a three-body friction phenomenon between the friction pairs that aggravated the wear. When the load increased to 30 N, there was a small amount of adhesion and transfer of wear debris which related to the multiple failure mechanism of abrasive wear and adhesive wear. Due to the continuous shearing and dragging of wear debris between the grinding
pairs, some cracks initiated and propagated at the peeling wear debris (Figure 12f). During friction and wear, debris shedding from friction pairs can be regarded as low-cycle fatigue failure, and the surface of the material was prone to microcrack formation. When seawater penetrates into these microcracks, the static wedge effect will occur, making the crack expand and a small amount of material fall off. In addition, due to the small area of cracks and shedding pits, it was easy to form a ‘small anode and large cathode’ crevice corrosion battery with the nearby area under the action of oxygen concentration polarization. The material in the crevice was used as the anode of the battery because of the higher oxygen consumption rate than the outside world, which accelerated the corrosion reaction rate in the crevice. Combined with the electrochemical parameters in Figure 7, it can be concluded that after friction and wear, the repeated removal and formation of the passive film led to the transfer and diffusion of corrosive medium into the specimen through defects such as surface cracks and shedding pits, which promoted the corrosion reaction and aggravated the effect of galvanic corrosion and crevice corrosion. Due to its relatively dense structure, the composite coating prevented further infiltration of the corrosive medium into bulk, and hard reinforcement on its surface showed a certain resistance to damage. Therefore, the wear mechanism of TCN in the seawater environment was mainly made of abrasive wear and adhesive wear caused by corrosion.

Figure 12. Wear scar morphology of the TCN coating in artificial seawater: (a,b) 10 N, (c,d) 20 N, and (e,f) 30 N.
3.4. Corrosion–Wear Synergism Mechanism

The volume losses of friction and wear of the TCN composite coating in artificial seawater with and without cathodic protection are shown in Figure 13. Under cathodic protection, the volume loss of the material increased with the load, and the wear amount enhanced from $1.28 \times 10^{-2}$ to $2.85 \times 10^{-2}$ mm$^3$. In the corrosion state, the friction loss under the same load condition was further increased due to the synergism of corrosion and wear, and the wear amount of TCN enhanced from $1.46 \times 10^{-2}$ to $3.24 \times 10^{-2}$ mm$^3$. Combined with Figure 12, it can be concluded that the passive film on the specimen’s surface produced microcracks under the fatigue effect of contact stress. In corrosive medium, active anions such as $\text{Cl}^-$ were often adsorbed and gathered in the local area of the passive film, which destroyed the equilibrium state of dissolution-repair of the passive film, resulting in the dissolution rate of the passive film on the surface of the sample being higher than its repair rate, leading to the active dissolution of the passive film. The surface material became loose and easy to remove because of corrosion, and a passive film quickly formed on the exposed fresh surface [22]. In this way, the continuous cycle process of passivation–de-passivation further consumed the material on the sample surface, making TCN more easily worn under corrosion conditions under the same load.

![Figure 13. Volume loss of the TCN coating in different conditions.](image)

In order to further evaluate the contribution of mechanical wear and electrochemical corrosion to the total volume loss of the sample, one set of data was selected to calculate the wear components of the composite coating in simulated seawater under different load conditions (Table 3). In each component of the corrosion–wear interaction, $W_{fc}$ and $W_{cf}$ of TCN, increased simultaneously with load. This meant that the increment caused by corrosion, as well as the corrosion increment caused by wear, both rose simultaneously. Therefore, corrosion and wear presented positive synergism, promoting each other. The proportion of each component in the total loss was expressed by plotting each component in Figure 14. Note that the contribution of pure corrosion loss, $W_{c0}$, of TCN to the total loss, $W$, was very small, and thereby can be ignored. As shown in Figure 14, the increase in load led to a decline in pure friction volume loss, $W_{f0}$, of TCN from 89.89% to 87.83%, while the synergistic effect, $\Delta W$, increased from 10.11% to 12.17%. The proportion of wear increment, $W_{f0}$, in the synergistic effect, $\Delta W$, rose from 61.92% to 71.08%, indicating that the synergism between corrosion and wear cannot be ignored. Since the corrosion reaction would preferentially occur at the grain boundaries with many defects and large confusion, the actual area of the corrosion reaction decreased after the precipitation of reinforcement phase with higher hardness and stable physical and chemical properties in the composite coating, which extended the path of corrosive ion diffusion into the material, thereby maintaining a low corrosion effect. As a result, the volume loss caused by abrasion of the composite coating in simulated seawater was still mainly determined by the friction behavior.
Table 3. Corrosion and wear components of TCN in artificial seawater under different loads.

| Load/N | Corrosion and Wear Components |
|--------|-------------------------------|
|        | $W_{f0}$/mm³ | $W_{ce}$/mm³ | $W_{cf}$/mm³ | $W_{cf}$/mm³ |
| 10     | $1.45 \times 10^{-2}$ | $1.28 \times 10^{-2}$ | $9.48 \times 10^{-6}$ | $1.06 \times 10^{-3}$ | $6.16 \times 10^{-4}$ |
| 20     | $2.41 \times 10^{-2}$ | $2.17 \times 10^{-2}$ | $9.48 \times 10^{-6}$ | $1.51 \times 10^{-3}$ | $9.29 \times 10^{-4}$ |
| 30     | $3.24 \times 10^{-2}$ | $2.85 \times 10^{-2}$ | $9.48 \times 10^{-6}$ | $2.80 \times 10^{-3}$ | $1.14 \times 10^{-3}$ |

Figure 14. Proportion of each volume loss component of the TCN coating under different load conditions.

4. Conclusions

The tribocorrosion properties of MAX phase containing Ti-Al-(C, N) composite coatings were studied under different loads in artificial seawater. The influences of applied loads on corrosion and wear behaviors of the composite coatings were investigated and the mechanism of corrosion–wear synergism was clarified. The following conclusions could be drawn:

1. During friction, as load rose from 10 to 30 N, the dynamic behavior of passive film removal–formation led to diffusion of the corrosive medium to the bulk of the material through material surface defects. Under the galvanic corrosion and crevice corrosion, the self-corrosion potential decreased from $-0.405$ to $-0.886$ V, and corrosion current density increased from 0.20 to 24.5 $\mu$A cm$^{-2}$.

2. The lubrication effect of self-lubricating phases Ti$_2$AlC and Ti$_2$AlN, as well as the lubrication of corrosion products generated during the friction process, resulted in smooth changes in the friction coefficient curve of the composite coating. The friction coefficient decreased from 0.30 to 0.28 as load increased from 10 to 30 N. The wear mechanism of the composite coating in the seawater environment was mainly abrasive wear and adhesive wear caused by corrosion, and the total wear increased from $1.45 \times 10^{-2}$ to $3.24 \times 10^{-2}$ mm$^3$.

3. As load increased from 10 to 30 N, the pure friction volume loss, $W_{f0}$, in TCN decreased from 89.89% to 87.83%, and the proportion of corrosion-induced wear increment, $W_{cf}$, in the synergistic effect, $\Delta W$, enhanced from 61.92% to 71.08%. Hence, the wear resistance of TCN in artificial seawater was mainly determined by its surface wear resistance. In summary, the laser-cladded MAX phase containing composite coatings looks promising for marine engineering equipment applications.

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