Microstructure and Tribocorrosion Properties of Ni-Based Composite Coatings in Artificial Seawater

Bo Li 1,*, Cong Li 1,*, Yimin Gao 1, Hongjian Guo 2, Yunchuan Kang 1 and Siyong Zhao 3

1 State Key Laboratory for Mechanical Behaviour of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China; ymgao@mail.xjtu.edu.cn (Y.G.); kangyc30@stu.xjtu.edu.cn (Y.K.)
2 State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 100864, China; chinaghj2019@hotmail.com
3 Guangxi Great Wall Machineries, Hezhou 542800, China; wei9786@163.com

* Correspondence: libo616@mail.xjtu.edu.cn (B.L.); licong369@stu.xjtu.edu.cn (C.L.)

Received: 6 November 2019; Accepted: 2 December 2019; Published: 4 December 2019

Abstract: NiAl matrix composite coatings were prepared using atmospheric plasma spraying (APS). The mechanical and tribocorrosion properties of the NiAl matrix composite coatings, incorporated with Cr2O3 and Mo, were investigated, and the synergistic effect between corrosion and wear was studied in detail. The microhardness of the composite coating improved from 195.1 to 362.2 HV through the addition of Cr2O3 and Mo. Meanwhile, the Cr2O3 and Mo phases were distributed uniformly in the composite coatings. The X-ray diffraction (XRD) peaks of Ni-based solid solution slightly shifted to the right after adding the Mo. This was probably due to the solid solution of Mo into the matrix. The NiAl–Cr2O3–Mo composite coating had the lowest corrosion current density, wear rate and friction coefficient of 9.487 × 10−6 A/cm2, 3.63 × 10−6 mm3/Nm, and 0.18, in all composite coatings as well as showing excellent tribocorrosion properties.

Keywords: tribocorrosion properties; synergistic effect; corrosion current density; worn surface; tribocorrosion properties

1. Introduction

With the forward depletion of land sources, it is very hard to satisfy the development needs of industry [1,2]. In recent years, the abundance of ocean resources has attracted researchers’ attention [3,4]. Marine equipment has had an important effect on marine exploration, such as ocean wind turbines, vessels and offshore oil platforms. However, ocean equipment easily suffers, not only from direct corrosion, but also the onset of wear, and their combined damage greatly affects the service lives of these kinds of engineering equipment [5–9]. The synergism effect of wear and corrosion is very destructive and usually decided by the reciprocity of chemistry, electrochemistry, mechanics and physics [10,11]. Therefore, corrosion will influence the microstructure, hardness and roughness of worn surfaces, further affecting the wear behavior [12]. In most tribocorrosion situations, the material loss is usually bigger than the simple sum of corrosion and wear [13,14]. The synergetic effects of corrosion and wear reduce the service life, safety and reliability of mechanical parts in seawater environments [15]. Therefore, it is imperative to optimize the corrosion and wear properties of mechanical parts in this environment, and to apply coatings with satisfactory mechanical properties. Tribocorrosion is a promising technology, which may provide good protection in ocean environments.

NiAl intermetallic compounds are considered to be promising materials in marine environments, due to their low density of 5.86 g/cm³, their high thermal conductivity, their high Young’s module of 240 GPa, and their high melting point of 1638 °C, as well as excellent corrosion
and oxidation resistance [16–20]. Nevertheless, the practical application of NiAl has been restricted by its inherent poor ductility at ambient temperatures [21–23]. Acting as a solution-strengthening phase, Mo could improve the strength of materials effectively [24–26]. Meanwhile, Mo could improve the ductility of NiAl intermetallic compounds at ambient temperatures [27,28]. Our previous study on NiAl–Mo2C nanocomposites indicated that the hardness and density of NiAl–Mo2C nanocomposites increased with increasing Mo contents. Meanwhile, the maximum stress and yield strength were all higher than that of NiAl intermetallics [28]. Nevertheless, the NiAl coating has low hardness and suffers severe wear at room temperature [29]. Hence, excellent wear resistant hard phases should be added in the NiAl protective coating [30]. Cr2O3, acting as a strengthening hard phase, could, effectively, improve the wear resistance properties and hardness of materials [31–33].

In this work, the mechanical and tribocorrosion properties of NiAl matrix plasma-sprayed composite coatings, incorporated with Cr2O3 and Mo in artificial seawater, were investigated, and the synergistic effect between corrosion and wear was studied in detail.

2. Materials and Methods

2.1. Material Preparation

The NiAl matrix coatings were produced using atmospheric plasma spraying (APS), and the schematic for the preparation of composite coatings is shown in Figure 1. The spray powders of NiAl, Cr2O3 and Mo were purchased from Sulzer Metco (Winterthur, Switzerland). The mixed feedstock powders were mingled mechanically before spraying. The Inconel 718 substrate was sand-blasted using a sand-blasting machine (Beijing Changkong Sand Blasting Equipment Company Ltd., Beijing, China) with corundum grit before spraying, and then an ultrasonic cleaner (Kunshan Ultrasonic Instruments Company Ltd., Kunshan, China) was used with acetone to clean the residual sand from the composite coating surface. The composition of each composite coating is presented in Table 1. The thickness of the composite coatings was 300 ± 20 μm. The thickness of the composite coatings was measured by the method of microscopically examining the cross-sections. Table 2 presents the spraying parameters. Scanning electron microscopy (FE-SEM, Tescan Mira 3, Bron, Kohoutovice, Czech Republic) was used to characterize the morphologies of the powders and composite coatings. The chemical composition of composite coatings was analyzed using an X’Pert-MRD X-ray diffractometer (Philips, Eindhoven, Netherlands). A microhardness tester (MH-5-VM, Shanghai Hengyi Science and Technology, Shanghai, China) was used to measure the microhardness of composite coatings. The load was 300 g. The dwell time was 5 s.

![Figure 1. Schematic of the preparation of composite coatings.](image-url)

<table>
<thead>
<tr>
<th>Composite Coating</th>
<th>NiAl (wt.%)</th>
<th>Cr2O3 (wt.%)</th>
<th>Mo (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NA1</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>NA2</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>
Table 2. Spraying parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma gas flow Ar, L/min</td>
<td>40</td>
</tr>
<tr>
<td>Secondary gas flow H₂, L/min</td>
<td>5</td>
</tr>
<tr>
<td>Spraying angle</td>
<td>90°</td>
</tr>
<tr>
<td>Powder feed rate, g/min</td>
<td>40</td>
</tr>
<tr>
<td>Current, A</td>
<td>500</td>
</tr>
<tr>
<td>Voltage, V</td>
<td>60</td>
</tr>
<tr>
<td>Spray distance, mm</td>
<td>110</td>
</tr>
</tbody>
</table>

2.2. Tribocorrosion Tests

A reciprocating ball-on-disc tribometer (UMT, Karlsruhe, Germany) was used to measure the tribocorrosion properties of the composite coatings in artificial seawater. The artificial seawater was prepared according the ASTM D114-98 standard [8]. To adjust the artificial seawater pH value to 8.2, 0.1 M NaOH was used. Table 3 presents the artificial seawater’s chemical composition. Figure 2 showed the reciprocating ball-on-disc tribometer’s schematic. The solution cell material was polytetrafluoroethylene (PTFE), which presented excellent corrosion resistance and effectively avoided the environmental effect, according to the experiment results. The Al₂O₃ ceramic ball was used as the counter ball. The diameter of the Al₂O₃ ceramic ball was 5 mm. Firstly, the composite coatings were polished until the composite coating surface roughness was below 0.5 μm. The tribocorrosion tests have been described in detail elsewhere [34].

Table 3. Artificial seawater’s chemical composition.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>24.530</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.090</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>1.160</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>11.110</td>
</tr>
<tr>
<td>KCl</td>
<td>0.695</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.201</td>
</tr>
<tr>
<td>KBr</td>
<td>0.100</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.027</td>
</tr>
<tr>
<td>SrCl₂·6H₂O</td>
<td>0.042</td>
</tr>
<tr>
<td>NaF</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Figure 2. Reciprocating ball-on-disc tribometer’s schematic.

3. Results and Discussion

3.1. Microstructure and Microhardness of Composite Coatings

Figure 3 shows the SEM morphologies of spray powders. The NiAl and Mo powders were fabricated by gas-atomization and present the spherical shape. The size of the powders was around
50–100 $\mu$m. The feedstock powder of Cr$_2$O$_3$ is fabricated by sintering and crushing and shows an angular shape. The size of the Cr$_2$O$_3$ was 5–53 $\mu$m. All feedstock powders are mingled mechanically before spraying, in order to make sure the powders distribute uniformly [35].

![Figure 3. SEM morphologies of spray powders: (a) NiAl, (b) Cr$_2$O$_3$ and (c) Mo.](image)

Figure 3. SEM morphologies of spray powders: (a) NiAl, (b) Cr$_2$O$_3$ and (c) Mo.

Figure 4 gives SEM images of a polished cross-section of NiAl matrix composite coatings. The composite coatings contain many defects (cracks and pores) (Figure 4a), and present the typical lamellar structure. Combining energy disperse spectroscopy (EDS) and X-ray diffraction (XRD) (Figure 5), the black phase is Cr$_2$O$_3$ and the gray phase is Mo in the composite coatings. The Cr$_2$O$_3$ and Mo phases distribute uniformly, and the interface of these two phases has no evident cracks.

![Figure 4. SEM images of polished cross-section of NiAl matrix composite coatings: (a) NA, (b) NA1 and (c) NA2.](image)

Figure 4. SEM images of polished cross-section of NiAl matrix composite coatings: (a) NA, (b) NA1 and (c) NA2.

Figure 5. presents the XRD patterns of NiAl matrix composite coatings. All composite coatings contain the Ni-based solid solution (JCPDS file no. 04-0850) and NiAl (JCPDS file no. 20-0019). The XRD spectrum of NA1 and NA2 composite coatings contains the diffraction peaks of Cr$_2$O$_3$ (JCPDS file no. 38-1479) and single-phase Mo (JCPDS file no. 42-1120). It is surprising that the diffraction peaks of Ni-based solid solution slightly shift to the right after addition of the Mo, which may be due to the partial solid solution of Mo in the matrix [36].

![Figure 5. XRD patterns of NiAl matrix composite coatings.](image)

Figure 5. XRD patterns of NiAl matrix composite coatings.

Table 4 gives the microhardness of composite coatings. The microhardness of composite coatings increased with the addition of Cr$_2$O$_3$ and Mo. The addition of Cr$_2$O$_3$ makes the
The microhardness of the composite coating increase from 195.1 to 290.5 HV. The Cr₂O₃ often acts as a strengthening hard phase, which could effectively enhance the hardness of materials [37,38]. So, the microhardness of the composite coating is obviously improved. The NA2 composite coating has the highest microhardness, of 362.2 HV in all composite coatings. The Mo could act as the solution-strengthening phase, to greatly increase the microhardness of the composite coatings [39].

### Table 4. Microhardness of composite coatings.

<table>
<thead>
<tr>
<th>Coatings</th>
<th>NA</th>
<th>NA1</th>
<th>NA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vickers hardness (HV)</td>
<td>195.1 ± 13.6</td>
<td>290.5 ± 15.8</td>
<td>362.2 ± 16.9</td>
</tr>
</tbody>
</table>

3.2. Electrochemical Behavior of Composite Coatings

Figure 6 shows the open circuit potential (OCP) evolution before, during and after the tribocorrosion of composite coatings in artificial seawater. During the first half hour, the composite coatings were immersed in artificial seawater before sliding. The initial highest OCP value, before sliding, was for NA1. When the counter ball of Al₂O₃ started sliding on the sample surface, the OCP of all composite coatings shifted rapidly to the negative. The OCP of the NA coating is more negative than that of the NA1 and NA2 coatings. After adding the element Mo, the Mo partially dissolved in the matrix, resulting the effect of solid solution-strengthening in the composite coating. It is very helpful if the coating forms a dense rust layer on the composite coating surface during the first half hour of immersion in artificial seawater [12]. This dense rust layer is very difficult to destroy in the sliding process. So, the OCP of the NA2 coating is the most positive in the process of sliding. The OCP values of all the composite coatings start to gradually increase when the sliding stops, which plays the main role in deciding the OCP value. The addition of Mo makes it easier for NA2 to form a dense, passive film, leading the OCP of this sample having the highest value after sliding.

![Figure 6. OCP evolution before, during and after tribocorrosion of composite coatings in artificial seawater.](image)

Figure 7 presents the potentiodynamic polarization curves of composite coatings sliding in artificial seawater. Basic parameters (corrosion current density (\(i_{\text{corr}}\)), corrosion potential (\(E_{\text{corr}}\)), anodic and cathodic Tafel slopes (\(\beta_a\) and \(\beta_c\)) of the composite coatings are listed in Table 5, measured from Figure 7, using the Tafel extrapolation method. The polarization resistance value (\(R_p\)) is calculated using the Stern–Geary equation:

\[
R_p = \frac{\beta_a \times \beta_c}{2.303i_{\text{corr}}(\beta_a + \beta_c)}
\]  

(1)

The results show that the corrosion potential (\(E_{\text{corr}}\)) of the NA2 composite coating is −0.490 V (vs. saturated calomel electrode (SCE)) and obviously higher than that of the NA and NA1 composite coatings.
coatings of −0.583 V (vs. SCE) and −0.552 V (vs. SCE). The NA2 composite coating has the highest corrosion potential value of all composite coatings. Still, the corrosion current density \(i_{\text{corr}}\) of the NA2 composite coating, at 9.487 \(\times\) \(10^{-6}\) A/cm\(^2\), is lower than that of NA and NA1 composite coatings, at 8.896 \(\times\) \(10^{-5}\) and 4.624 \(\times\) \(10^{-5}\) A/cm\(^2\), respectively, indicating that the NA2 composite coating presents the best corrosion resistance and is very difficult to corrode. Generally speaking, corrosion current density is an important criterion in valuing the corrosion resistance of materials [8,40]. So, the NA2 composite coating presents lower corrosion rates than those of the NA and NA1 composite coatings, and may be very hard to corrode. At the same time, the NA2 composite coating has the highest \(R_p\) of 9.003 \(\times\) \(10^2\) \(\Omega\), which further illustrates that the NA2 composite coating presents very strong corrosion resistance under artificial seawater. In general, the \(\beta_a\) is higher than \(\beta_c\) of the material [4,7,11,41]. In this test result, the \(\beta_a\) of all composite coatings are higher than the \(\beta_c\). This kind of phenomenon is related to the fact that the cathodic part exchange-current density value is higher than that of the anodic part. The entire kinetics of the corrosion of all composite coatings are decided by the anodic part [11]. That is to say, the anodic dissolution rate is slower than that of the cathodic reaction.

Figure 7. Potentiodynamic polarization curves of composite coatings sliding in artificial seawater.

Table 5. Corrosion parameters of composite coatings from potentiodynamic polarization curves.

<table>
<thead>
<tr>
<th>Coatings</th>
<th>(E_{\text{corr}}) (V, vs. SCE)</th>
<th>(i_{\text{corr}}) (A/cm(^2))</th>
<th>(\beta_a) (V/dec)</th>
<th>(-\beta_c) (V/dec)</th>
<th>(R_p) ((\Omega))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>−0.583</td>
<td>8.896 (\times) (10^{-5})</td>
<td>0.059</td>
<td>0.046</td>
<td>1.262 (\times) (10^2)</td>
</tr>
<tr>
<td>NA1</td>
<td>−0.552</td>
<td>4.624 (\times) (10^{-5})</td>
<td>0.050</td>
<td>0.042</td>
<td>2.143 (\times) (10^2)</td>
</tr>
<tr>
<td>NA2</td>
<td>−0.490</td>
<td>9.487 (\times) (10^{-6})</td>
<td>0.042</td>
<td>0.037</td>
<td>9.003 (\times) (10^2)</td>
</tr>
</tbody>
</table>

3.3. Tribological Behavior of NiAl Matrix Composite Coatings

Figure 8 shows the friction curves and wear rate of the NiAl matrix composite coatings in artificial seawater. Obviously, the friction coefficient and wear rate of the NA2 composite coating, of 0.18 and 3.63 \(\times\) \(10^{-6}\) mm\(^3\)/Nm, respectively, are the lowest of all the composite coatings. This result is probably due to the way CrO\(_3\) acts as a strengthening hard phase, to enhance the hardness and wear resistance properties of composite coatings effectively. Meanwhile, the Mo could dissolve in the matrix and has a solid solution-strengthening effect in the NA2 composite coating. These are very useful in helping form the dense rust layer on the worn surface of the NA2 composite coating, which effectively reduces the corrosion rate, friction coefficient and wear rate of the NA2 composite coating.
In order to further investigate the tribocorrosion behavior of NiAl matrix composite coatings in artificial seawater, a color 3D laser scanning microscope was used. Figure 9 gives the 3D profiles of worn surfaces of NiAl matrix composite coatings after being tested in artificial seawater. The NA2 composite coating worn track is, at 118.9 μm, narrower than the NA and NA1 composite coatings, at 189.6 and 136.3 μm, respectively. This observation is in accordance with the friction coefficient and wear rate results of NiAl matrix composite coatings (Figure 8). Meanwhile, the worn surface of the NA coating suffered very severe corrosion. However, the worn surfaces of NA1 and NA2 composite coatings display slight corrosion. This result is similar with that of the corrosion current densities of the composite coatings (Table 5). Corrosion could aggravate the wear rate of the NiAl matrix composite coatings. So, the NA coating presents the highest wear rate and the NA2 coating has the lowest wear rate (Figure 8). It further illustrates that, in artificial seawater, the NA2 composite coating presents excellent tribocorrosion properties.

Figure 9. 3D profiles of worn surfaces of NiAl matrix composite coatings: (a) NA, (b) NA1 and (c) NA2.

Figure 10 presents the SEM morphologies of composite coating worn surfaces during sliding. The NA coating displayed poor corrosion performance at cracks and pores (Figure 10a). The coating with the addition of Cr2O3 and Mo had visibly less corrosion than those of any other coatings (Figure...
It is probably due to the way Mo acts as a solution-strengthening phase, which could enhance the strength of materials [24–26].

**Figure 10.** SEM morphologies of composite coating worn surfaces: (a) NA, (b) NA1 and (c) NA2.

### 4. Conclusions

In this study, composite coatings were fabricated using APS. The mechanical and tribocorrosion properties of composite coatings incorporated with Cr₂O₃ and Mo in artificial seawater were investigated, and the synergistic effect between corrosion and wear were investigated in detail. The main conclusions are given as follows:

- Upon adding Cr₂O₃ and Mo, the microhardness of the composite coatings improves from 195.1 to 362.2 HV. Meanwhile, the Cr₂O₃ and Mo phases distribute uniformly and the interface of these two phases has no evident cracks.
- The Ni-based solid solution diffraction peaks slightly shift to the right after the addition of Mo, which is maybe due to the partial solid solution of the element Mo into the matrix.
- The NiAl–Cr₂O₃–Mo composite coating has the lowest corrosion current density, friction coefficient and wear rate of 9.487 × 10⁻⁶ A/cm², 0.18 and 3.63 × 10⁻⁶ mm³/Nm in all composite coatings.
- The NiAl–Cr₂O₃–Mo composite coating shows excellent tribocorrosion properties in artificial seawater.

**Author Contributions:** Writing—original draft preparation, B.L.; writing—review and editing, C.L.; project administration, Y.G.; visualization, H.G.; data curation, Y.K.; formal analysis, S.Z.

**Funding:** This research was funded by the National Natural Science Foundation of China (Grant Nos. 51805408, 51665026), the Natural Science Foundation of Shaanxi Province (Grant No. 2019JQ-283), the China Postdoctoral Science Foundation (Grant No. 2019M653597), the Shaanxi Province Postdoctoral Science Foundation, the Fundamental Research Funds for Central Universities (Grant Nos. xzy012019010, xtr0118008), the Guangxi Innovation Driven Development Project (Grant No. GUIKEA18242001) and the Guangdong Province Key Area R&D Program (Grant No. 2019B010942001).

**Conflicts of Interest:** The authors declare no conflict of interest.

**Reference**


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).