

Article The Corrosion and Wear-Corrosion of the Iron-Base Amorphous Coating Prepared by the HVOF Spraying

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Abstract: In this work, the corrosion behaviors of an iron-based amorphous coating produced by high-velocity oxy-fuel (HVOF) spraying were investigated. Potentiodynamic and potentiostatic polarization and corrosion pin-on-ring (corrosion-wear) tests were conducted to evaluate the corrosive properties of the coating as compared with the 316L substrate. The corrosion behaviors of the 316L substrate and coated sample were tested in 3.5 wt.% NaCl, 1 M HCl, and 0.5 M H₂SO₄ solutions. In the 3.5 wt.% NaCl and 1 M HCl solutions, the corrosion resistance of the coating was a little inferior or equivalent to that of the 316L substrate after potentiodynamic polarization tests. In the 0.5 M H₂SO₄ solution, the two tested samples exhibited wide passivated zones in the polarization curves. In such a mild acid, the corrosion resistance of the 316 substrate was superior to that of the amorphous coating, possibly due to the presence of defects in the coating. After potentiodynamic polarization tests, the linkage of initial fine pits into large, deep pores was seen in the corroded 316L substrate. By contrast, extensive corrosion along with preferentially corroded defective sites was seen in the coating. Moreover, the coating exhibited a much higher resistance to corrosion-wear, or low weight loss, in 3.5 wt.% NaCl solution. After the corrosion-wear tests, deep furrows were present in the 316L substrate, whereas a rubbed smooth surface and a corroded zone were seen in the coating. The greater weight loss of the 316L substrate confirmed its poor resistance to corrosion-wear relative to the amorphous coating in 3.5 wt.% NaCl solution.

Keywords: 316L; Fe-based amorphous; HVOF; Potentiodynamic polarization; corrosion-wear

1. Introduction

High-velocity oxy-fuel (HVOF) spraying can produce a coating of distinctive surface properties for industrial structures and components in aggressive environments [1–3]. The feedstock powders are heated and accelerated to extremely high speed by the spraying gun, and then they constantly impact with and are deposited onto the substrate surface to form a dense, low-defect coating [4,5]. It is reported that high compressive residual stress is induced inside the HVOF coating [1]. In addition, HVOF can be used to prepare different coatings, including metallic [6,7], cermet [8], and ceramic [9,10] materials.

During the past few decades, bulk glassy metals have been developed in different alloy systems [11–16]. Among the different amorphous alloys, iron-based ones have been attracting much attention because of their inherent excellent mechanical and chemical properties, as well as their cost-effectiveness [17–20]. However, the high cooling rates required after solidification to form the amorphous phase limit their applicability as prospective structural materials. A good alternative is to use an iron-based amorphous alloy as the feedstock powder for a thermal spray coating [21–29]. Moreover, HVOF is advantageous for forming an amorphous coating because the high cooling rate of the deposits enhances the formation of the amorphous phase [30,31]. With an increase in spraying power, the microhardness and wear resistance of the amorphous Fe-10W-4Cr-3Ni-2Mo-4B-4Si-1C coating increases [32]. The bonding strength of the Fe₄₈Cr₁₅Mo₁₄C₁₅B₆Y₂ amorphous coating



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increases with increasing substrate roughness but decreases with coating thickness [33]. Moreover, an amorphous coating produced from fine powder is more likely to have a dense structure, while one from coarse powder will have superior corrosion resistance [34]. The low wear rate of the $Fe_{52}Cr_{15}Mo_{25}C_3B_2Y_3$ amorphous coating is associated with the decreased porosity in the coating [35], which can be affected by the fuel and oxygen flow rate of HVOF spraying [36]. In both 3.5% NaCl and 0.5 M H₂SO₄ solutions, the corrosion resistance of the $Fe_{43}Cr_{16}Mo_{16}C_{15}B_{10}$ coating in the amorphous form is superior to that in the crystalline form [37]. It is reported that an amorphous coating has been successfully applied to extend the service life of marine pumps [25,27].

The Fe-(Cr,Mo)-(C,B) system has been noted to have a high glass-forming ability [38–43], and minor elements can be added to it to further improve that ability. In fact, the amorphous feedstock for a coating need not have the same high glass-forming ability as for large glassy structural components. A lean alloy composition (Fe-2.5Cr-6.7Si-2.5B-0.7C wt%) has been developed for an amorphous thermal coating [44]. In this work, to reduce the high cost of the Mo, Co, and Y elements, the Mo content was lowered but other elements were added to the FeCrMoCB system to maintain the glass-forming ability. Moreover, such a modified alloy powder can be used to form an amorphous coating for conventional thermal spraying. Herein, a seven-element alloy system, FeCrNiMoCBSi, is proposed as an alternative to a thermal spray coating. In the open literature, the application of an iron-based amorphous coating to improve the corrosion and wear resistance of structural components is an important issue and has received much attention in the past few years [45-47]. In this study, the corrosion behaviors of the coated samples were studied in three distinct solutions using potentio-polarization tests and the results were compared with those of the 316L substrate. The microstructures of the investigated samples were examined using a scanning electron microscope (SEM). The corrosion-wear properties of distinct samples were determined with a pin-on-ring corrosion abrasion instrument.

2. Materials and Experimental Procedures

2.1. Thermal Spray and Microstructural Investigations

The amorphous feedstock powder (7 elements) used in this work was fabricated by Ar-gas atomization and provided by Chung Yo Materials Co., Ltd. (Kaohsiung City, Taiwan). The chemical composition of the feedstock powder in weight percent (wt%) was as follows: 21.53 Cr, 13.65 Ni, 14.41 Mo, 2.07 C, 2.73 Si, 2.30 B, and the balance Fe. The amorphous powder ranged from +15 to $-45 \,\mu\text{m}$ in size. HVOF was applied to perform the amorphous coating onto the 316L plates of 6 mm thickness and the 316 round bars with a diameter of 20 mm. The process parameters of HVOF spraying were as follows: a kerosine flow rate of 5 GPH, an oxygen flow rate of 1700 SCFH, a gun moving speed of 600 mm/s, a spraying distance of 380 mm, and a powder feeding rate of 30 g/min. The total thickness of the coating was about $150 \ \mu m$. The phases of the powder and coating were analyzed with a D2 X-ray diffractometer (XRD, Bruker, Billerica, MA, USA) using Cu Kα radiation. A 404 F3 high-temperature differential scanning calorimeter (HT-DSC, Netzsch, Selb, Germany) was applied to determine the transformation temperature of the powder. The samples were heated to about 1400 °C at a heating rate of 10 °C/min, followed by cooling to room temperature. The samples for metallographic examinations were ground with SiC papers up to 1500 grit, then polished with a colloidal silica suspension. The microstructures of the prepared specimens were inspected with a 4800 SEM (Hitachi, Tokyo, Japan). The micro-hardnesses of the distinct samples were determined using an MVK-G1500 Vickers hardness tester (Mitutoyo, Kanagawa, Japan) loaded at 50 gf and a dwell time of 15 s.

2.2. Corrosion and Corrosion-Wear Resistance Determinations

The potentiodynamic polarization curves of the coating were determined in a standard three-electrode cell system with a Zahner-Elektrik potentiostate (Zahner-Elektrik, Landkreis Kronach, Germany) and compared with those of the 316L substrate. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate acted as the counter

electrode. The potentiodynamic polarization tests were carried out at room temperature in three solutions within a potential range from -1.0 V to +2.0 V and at a scanning rate of 1 mV/sec. Three testing solutions including 3.5 wt.% NaCl, 1 M HCl, and 0.5 M H₂SO₄ were applied in this work. Corrosion-wear tests were performed using coated cylindrical samples with dimensions of about 20.3 mm diameter \times 10 mm. An alumina cube (21 mm \times 21 mm \times 21 mm) with a hardness of about Hv 1450 was used as the wear counter. For the corrosion-wear test, the applied load was 29.4 N, the rotating speed was 200 rpm, and the duration was 30 min.

3. Results

3.1. Transformation Temperature of the Feedstock Powders and Phase Identification

Figure 1 shows the morphology of the feedstock powder and its differential scanning calorimeter (DSC) curve, which was used to identify the phase transformation temperature. Figure 1a displays the amorphous powder in a round shape with diameters of 15–45 μ m for HVOF spraying. It was noticed that the external surfaces of the powders were very smooth and lacked any sign of dendritic structure. As shown in Figure 1b, the cross-sectional view of the powder with micro-hardness indentation revealed that the powder hardness could be as high as Hv 1400, which was much harder than the conventional alloys in the market. It was expected that the amorphous coating would have a very high hardness. Figure 1c presents the DSC curve of the feedstock powder; the red line and the blue line are the temperature-rising and the temperature-cooling curves, respectively. The DSC curves of the amorphous powder displayed the glass transition temperature (T_{g} , 554 °C), crystallization temperature (T_x , 625 °C), peak crystallization temperature (T_p , 659 °C), solidus temperature (T_S , 1116 °C), and liquidus temperature (T_L , 1196 °C). The results indicated that the addition of certain amounts of C, B, and Si into the Fe-based amorphous alloy had caused a drop of about 250 $^\circ$ C in the liquidus temperature as compared with that of the conventional alloy steels.



Figure 1. (**a**) The external morphology of the feedstock powder, (**b**) the cross-sectional view with hardness indentation of the powder and (**c**) the differential scanning calorimeter (DSC) curves of the feedstock powder.

Figure 2 shows the X-ray diffractometer (XRD) patterns of the powder and coating. The results indicated broad halo peaks in both samples, indicating very high amorphous

contents. It was noticed that a few sharp peaks were present in the XRD pattern of the powder, indicating the formation of second phases or fine precipitates inside the powder. Those precipitates in the feedstock powders could be the complex alloy carbides, borides, and intermetallics, as shown in Figure 2a. By contrast, no such precipitates were found in the coating; their absence could be associated with the high cooling rate of the coating after HVOF spraying. Overall, the glass-forming ability of this developed FeCrNiMoCBSi powder could meet the requirements of thermal spray coating. Moreover, the high cooling rate of HVOF spraying also contributed to forming an amorphous phase in the coating, as compared with the feedstock powder.



Figure 2. X-ray diffractometer (XRD) spectra of (a) the feedstock powder and (b) the coating.

3.2. SEM Images of the Coating

Figure 3 shows the SEM images of the top and cross-sectional views of the amorphous coating. Figure 3a shows the surface appearance of the amorphous coating; it reveals the partially molten zone mixed with residual powders. The partially molten powder could be accelerated to extremely high speed in the HVOF combustion chamber. The crosssectional images (Figure 3b,c) of the coating indicated that it was a dense layer showing the HVOF deposits, and only very fine voids were visible. As shown in Figure 3b, the coating had a thickness of about 150 µm and there was a ripple-like interface between the coating and the 316L substrate. It was noticed that fine porosities (indicated by the arrows) were trapped along the coating interface (Figure 3b). It is reported that large voids located between flattened droplets are due to the loosely packed layer, while pinholes are the cause of shrinkage porosity [48]. Those pinholes in the coating could be related to the shrinkage of the molten amorphous layer. Moreover, the use of a fine powder for HVOF spraying can reduce porosity [34]. The micro-hardness of the as-deposited coating was above Hv 1120 (Figure 3c), indicating that it was obviously harder than conventional alloy steels and precipitation-hardening alloys. This hardness could be attributed to the influence of minute defects in the coating, which would lower its hardness to less than that of the feedstock powder. A nano-indenter loaded at 2000 μ N was used to measure the hardness and elastic modulus of the amorphous coating (indicated by the circle in Figure 3d) and the 316L substrate. Detracting those data highly deviated from the average, the nano-hardness of the coating fell in the range of 11-14 GPa and had an elastic modulus of 200–220 GPa. Moreover, the nano-hardness of the 316L substrate was within the range of 2.5–4.6 GPa and had an elastic modulus of 180–200 GPa. It was obvious that the Fe-based amorphous coating had about the same elastic modulus as that of commercial alloy steels, but was much harder than the alloy steels. In fact, the elastic modulus of the metals is strongly dependent on the atomic attraction force between atoms, therefore, the Fe-based amorphous coating had the similar elastic property as the commercial steels. Overall, the results of nano-indentation were roughly consistent with the micro-hardness measurement. Nevertheless, the amorphous coating provided by HVOF spraying was expected to have a high wear resistance to external loading, as compared with the conventional alloys.



Figure 3. SEM images showing (a) the top and (b,c) cross-sectional views of the amorphous coating, and (d) the nano-indentation sites of the coating.

3.3. Corrosion Resistance of the 316L Substrate and the Coated Samples

The potentiodynamic polarization curves of the 316L substrate and an amorphous coated sample in distinct solutions are shown in Figures 4–6. The corrosion potential (E_{Corr}), corrosion current density (i_{Corr}), and pitting potential (E_{Pit}) are listed in Table 1. Figure 4 shows the results of the potentiodynamic polarization tests for the samples tested in 3.5 wt.% NaCl solution. It indicated that the E_{Corr} of both samples was about -0.55 V. The i_{Corr} of the 316L substrate and the coating were about 3.96 and 4.70 μ A/cm², respectively. There was not much difference in E_{Corr} and i_{Corr} between the two samples tested in 3.5 wt.% NaCl solution. The pitting potential was determined at the inflection point of the polarization curve in the anodic side. As shown in Figure 4, the limited passive regions of the two tested samples implied a low ability to resist pitting corrosion in 3.5% NaCl solution. The E_{Pit} of the 316L substrate was about +0.10 V, with a value of -0.12 V for the coating. In addition, the passive current density of the 316L substrate was about one order smaller than that of the amorphous coating.



Figure 4. The potentiodynamic polarization curves of the 316L substrate and the amorphous coating in 3.5 wt.% NaCl solution.



Figure 5. The potentiodynamic polarization curves of the 316L substrate and the amorphous coating in 1M HCl solution.



Figure 6. The potentiodynamic polarization curves of the 316L substrate and the amorphous coating in 0.5M H₂SO₄ solution.

Sample	Corrosion Propertiesy	Testing Solution		
Sample		3.5% NaCl	1M HCl	$0.5M H_2SO_4$
316L	E _{Corr} (V)	-0.55	-0.34	-0.35
	i _{Corr} (μA/cm ²)	3.96	58.2	55.0
	E _{Pit} (V)	+0.10	-0.08	+0.80
Coating	E _{Corr} (V)	-0.55	-0.29	-0.32
	i _{Corr} (µA/cm ²)	4.70	39.2	62.0
	E _{Pit} (V)	-0.12	-0.20	+0.88

Table 1. The E_{Corr}, i_{Corr}, and E_{Pit} of the coating and the 316L substrate tested in distinct solutions.

Figure 5 shows the potentiodynamic polarization curves of the samples tested in 1M HCl solution. The corrosion current densities of the tested samples in 1M HCl solution were much higher than those of the counterpart samples tested in 3.5 wt.% NaCl. The E_{Corr} and i_{Corr} of the 316L substrate were about -0.34 V and 58.2 μ A/cm², respectively. By contrast, those of the coating were about -0.29 V and 39.2 μ A/cm², accordingly. In harsh HCl solution, both samples showed lowered resistance to pitting corrosion and uniform corrosion. No passive zones in the polarization curves were found in both samples tested in 1M HCl solution. As shown in Figure 5, the E_{Pit} of the 316L substrate and the coating was about -0.08 V and -0.20 V, respectively. In addition, the corrosion current density of the coated sample was found to be smaller than that of the 316L substrate at an applied

potential of -200 mV, which meant that the corrosion resistance of the coated sample would be higher than that of the 316L substrate.

The potentiodynamic polarization curves of the samples tested in 0.5 M H₂SO₄ solution are shown in Figure 6. The results showed marked passive regions in the two samples tested in such a mild acid. The E_{Corr} and i_{Corr} of the 316L substrate were -0.35 V and 55.0 μ A/cm², respectively. The E_{Corr} and i_{Corr} of the coated sample were -0.32 V and 62.0 μ A/cm². Moreover, the E_{pit} of both samples was about 0.8 V, but the current density of the 316L substrate was obviously lower than that of the coating. The presence of a passive region in the polarization curve of the coating meant the formation of a protective film in 0.5M H₂SO₄ solution, but the high corrosion current density implied the occurrence of local corrosion.

Potentiostatic polarization tests at a constant applied potential were performed to confirm the change in corrosion current density with time, and the results are shown in Figures 7 and 8. The chosen potentials were based on the potentiodynamic polarization curves shown in Figures 4 and 6. In the 3.5% NaCl solution, the applied potential would be the open circuit potential (-500 mV), in the passivated zone (-200 mV), or near the transpassive dissolution range (+300 mV). As shown in Figure 7a, the coating had about the same current density (or corrosion rate) as the 316L substrate in 3.5% NaCl solution at -500 mV. Figure 7b showed that a drop in current density with increasing time occurred for the coated sample, which could be due to the gradual formation of protective film in the passivated zone (-200 mV). In 3.5% NaCl solution at +300 mV (Figure 7c), pitting corrosion resulted in an increase in the current densities of the tested samples with increasing time. It was noticed that the coating displayed slightly higher corrosion resistance than the 316L substrate in 3.5% NaCl solution at the applied potentials of -200 and +300 mV. By contrast, the 316L substrate had better corrosion resistance than the coating in the passivated (+500 mV) and transpassive dissolution (+1000 mV) states in 0.5 M H_2SO_4 solution (Figure 8). The results revealed that in 0.5 M H₂SO₄ solution, i.e., in mild acid, the corrosion resistance of the 316L substrate was superior to that of the amorphous coating, possibly due to the presence of defects in the latter.



Figure 7. The change in corrosion current density with time in 3.5% NaCl solution at a constant potential: (**a**) -500 mV, (**b**) -200 mV and (**c**) +300 mV.



Figure 8. The change in corrosion current density with time in $0.5M H_2SO_4$ solution at a constant potential: (**a**) +500 mV and (**b**) +1000 mV.

3.4. Surface Morphology of the Samples after Potentiodynamic Polarization Tests

The surface morphologies of the 316L substrate and the coating after potentiodynamic polarization tests are shown in Figure 9. After testing in 3.5% NaCl and 1 M HCl solutions, the 316L substrate exhibited clear corrosion damage due to the linkage of fine corrosion pits into large elongated pores (Figure 9a,b). The severe corrosion in 1 M HCl solution resulted in the formation of deep ditches and pores in the 316L substrate (Figure 9b). By contrast, only a few fine, shallow pits formed in the 316L substrate tested in $0.5M H_2SO_4$ solution (Figure 9c). The potentiodynamic polarization curve of the 316L substrate also confirmed that the 0.5 M H₂SO₄ solution was a mild acid relative to the 3.5% NaCl and 1 M HCl solutions. The 316L substrate displayed high corrosion resistance in the $0.5 \text{ M H}_2\text{SO}_4$ solution. The corroded appearances of the coatings after potentiodynamic polarization tests are shown in Figure 9d–f. Overall, the corrosion features of the coatings in distinct solutions were quite different from those of the 316L substrate under the same testing conditions. Predominantly fine pits, which formed initially at the interface of residual powders and the molten zone, connected into fine ditches around the residual powders. Large corrosion pits or pores were not seen in the corroded coating, regardless of the testing solution. The results revealed that the amorphous coating had more capacity to resist uniform/pitting corrosion than the 316L substrate.

3.5. Corrosion-Wear in 3.5% NaCl Solution

With the applied potential and loading, corrosion-wear tests were performed to determine the wear resistance in 3.5% NaCl solution for the coating and the 316L substrate. Weight loss was the index used to evaluate the corrosion-wear resistance of the tested samples. Figure 10 shows the change in corrosion current density vs. time at a fixed load of 29.4 N at different potentials. Despite the different applied potentials, it was found that the corrosion current density of the coating was about the same as that of the 316L substrate and changed little with time. As compared with the potentiostatic polarization tests (Figure 7), the corrosion current density of the corrosion-wear samples was much higher than that of the samples without loading. At a potential of -500 mV, the corrosion current density would change from 6×10^{-6} A/cm² to about 3×10^{-4} A/cm² if an external load was applied. The same situation occurred when the potential was increased to -200 or +300 mV. Even at the passivated potential (-200 mV), the corrosion-wear current density could be as high as 3×10^{-3} A/cm², which implied the disappearance of passivation or a high corrosion rate (Figure 10b). The rupture of the passivated film during contact wear was responsible for the increased corrosion rate. Increasing the potential also caused an increase in current density or corrosion rate in the corrosion-wear test (Figure 10c). Table 2 lists the weight loss of the corrosion-wear samples at distinct potentials. Increasing the potential caused increases in the weight loss of the tested samples. Moreover, the wear-corrosion tests showed that the samples with the amorphous coating had obviously low wear loss in 3.5%NaCl solution, as compared with the 316L substrate under the same testing conditions.



Figure 9. The typical surface morphologies of $(\mathbf{a}-\mathbf{c})$ the 316L substrate and $(\mathbf{d}-\mathbf{f})$ the coating after potentiodynamic polarization tests. (\mathbf{a},\mathbf{d}) in 3.5% NaCl; (\mathbf{b},\mathbf{e}) in 1M HCl; (\mathbf{c},\mathbf{f}) in 0.5M H₂SO₄ solutions.

 Table 2. The weight loss of the corrosion-wear samples in 3.5% NaCl solution at distinct potentials.

Weight Loss (mg) Sample	-500 mV	-200 mV	+300 mV
316L	52	92	106
Coating	8	16	22



Figure 10. The change in the corrosion current density vs. time at a fixed load of 29.4 N at (**a**) -500 mV, (**b**) -200 mV, and (**c**) +300 mV.

3.6. SEM Observations of the Samples after Corrosion-Wear Tests

Figure 11 exhibits the worn surface morphologies of the 316L substrate and amorphous coating after the wear-corrosion tests in 3.5%NaCl solution. It was found that the surface features of the tested sample changed little with increasing potential after the corrosion-wear test. Parallel plastic furrows were seen on the contact surface of the 316L substrate after the corrosion-wear tests (Figure 11a). This morphology was related to the micro-cutting mechanism. In addition, adhesive wear occurred in combination with micro-cutting. In contrast, no plastic furrows or adhesive wear were found on the contact surface of the amorphous coating after the tests (Figure 11b). A rubbed smooth surface and a corroded zone on the worn surface of the coating (Figure 11b) implied that corrosion-wear dominated the failure of the amorphous coating in the tests. In addition, the corrosion was more likely to initiate at and propagate along the defective sites such as fine voids and interfaces in the coating. According to the damaged surface morphology, the deep furrows were responsible for the greater weight loss of the 316L substrate in the corrosion-wear test. Undoubtedly, the amorphous coating was more resistant to corrosion-wear than the 316L substrate in 3.5%NaCl solution.



Figure 11. The worn surface morphologies of the (**a**) 316 substrate and (**b**) amorphous coating after the corrosion-wear tests.

4. Discussion

The XRD pattern of the powder (Figure 2) consisted of a few sharp peaks, which could be associated with the complex alloy carbides, borides, and intermetallics, whereas no such precipitates or nanostructures were found in the amorphous coating (Figure 2). Therefore, the high cooling rate of the HVOF spraying enforced the formation of the amorphous phase in the coating. This developed FeCrNiMoCBSi powder had a sufficiently high glass-forming ability for thermal spray coating. In this work, the HVOF coating contained only very fine pinholes and microcracks/interfaces between the molten zone and partially melted powders (Figure 3). The micro-hardness of the as-deposited coating was above Hv 1120, which was obviously harder than conventional alloys. Therefore, the coating was expected to be able to provide high resistance to wear. In addition, the amorphous coating possessed a similar elastic constant as the conventional steel alloy.

In prior studies, the 316 coating fabricated by HVOF in seawater has shown corrosion resistance inferior to the 316 substrate [49,50]. The corrosion behavior of the 316 coating is affected by the porosity, unmelted particles, and micro- and macro-cracks [49,50]. Therefore, the defects present in the coating are expected to obviously deteriorate its corrosion resistance. The high uniform and pitting corrosion resistance of the amorphous alloys is attributed to their homogeneous structure, which lacks grain boundaries. The addition of Cr and Mo into the Fe-based amorphous coating assists in the formation of a passive surface film to increase corrosion resistance and passivity. [51]. Moreover, the corrosion resistance of a Fe-based amorphous coating in 3.5% NaCl solution is affected by the powder size [34], spraying power [52], and kerosene/oxygen flow rate [23]. The defective sites and interfaces between the unmelted powders and the molten zone in the amorphous coating are the preferential sites for corrosion [23,34]. It has been pointed out that the influence of porosities on the corrosion resistance of the coating has a long-lasting effect [53].

The potentiodynamic polarization curves showed that the coating had about the same corrosion rate as the 316L substrate in the 3.5% NaCl and 1 M HCl solutions. In $0.5M H_2SO_4$ solution, the passive current density of the 316L substrate was lower and the passive range of the 316L substrate was wider than those of the coating. The results of potentiostatic polarization at a constant applied potential confirmed that the coating and the 316L substrate had about the same corrosion rate in the 3.5% NaCl solution, but that it was inferior to the 316L substrate in the 0.5 M H₂SO₄ solution. However, the corroded features of the coating were clearly different from those of the 316L substrate under the same testing conditions. Predominantly fine pits, which formed initially at the interface between partially melted powders and the molten zone, connected to form fine ditches around the residual powders. By contrast, large pores and deep ditches were observed in the corroded 316L substrate exposed to the 3.5% NaCl and 1M HCl solutions. It was obvious that the amorphous coating had higher resistance to uniform/pitting corrosion than the 316L substrate.

With applied potential and loading, the pin-on-ring tests were carried out to determine the corrosion-wear resistances of the coated sample and the 316L substrate in 3.5% NaCl solution. Despite different applied potentials, the corrosion current density of the coating was about the same as that of the 316L and changed little with time (Figure 10). When the potentiostatic polarization test was conducted with a constant applied potential, a great increase in current density at the same applied potential during the corrosion-wear test implied an obvious increase in the corrosion rate. Such events could be attributed to the continuous removal of passive film during contact wear. As listed in Table 2, the amorphous coating had an obviously low wear loss in 3.5%NaCl solution, as compared with the 316L counterpart tested under the same conditions. The worn surface morphology of the 316L substrate contained parallel plastic furrows formed on the contact surface of the 316L after the corrosion-wear tests (Figure 11a). By contrast, a rubbed smooth surface and a corroded zone were found on the worn surface of the coating (Figure 11b). The less damaged surface also confirmed that the coating had greater corrosion-wear resistance than the 316L substrate in 3.5%NaCl solution.

The corrosion resistance of Fe-based amorphous coatings is reported to be better than that of 304 but not far from that of 316 stainless steel [47]. Lee et al. [47] pointed out that the Fe40-Cr19-Mo18-C15-B8 alloy's amorphous coating has a corrosion resistance equivalent to that of the 316 and is better than that of the 304. As mentioned previously in this work, the corrosion resistance of the coating will be affected by the alloy compositions and the original defects in the coating or the coating quality. It is reported that Ni-based coatings are also widely used in marine environments [53–61]. Referring to the open literature, the corrosion resistance and hardness of the investigated amorphous coating are compared to those of the Ni-based coatings, as listed in Table 3. The coating hardness of NiCr or NiCrBSi was in the range of Hv 570–Hv 660, which was lower than that of the Fe-based amorphous coating. In 3.5% NaCl solution or seawater, the potentiodynamic polarization tests of NiCr or NiCrBSi coatings show that the E_{Corr} of the coating is in the range of -350to -580 mV. However, a great variation in i_{Corr} from 0.11 to 30 μ A/cm² is found for the distinct coatings, which can be attributed to the difference in compositions and the original defects in the as-deposited coating. Therefore, reducing the defects in the coating definitely improved the corrosion resistance of the coating.

Samulas		Properties		
Samples –	E _{Corr} (mV)	i _{Corr} (µA/cm ²)	Hardness (Hv)	
NiCr [54]	-397	1.08	574	
NiCr-Cr ₃ C ₂ [55]	-515	18.98	-	*
NiCrBSi [53]	-350	6.95	-	
NiCrBSi [56]	-499	0.11	-	
NiCrBSi [57]	-565	4.31	600	
NiCrBSi [58]	-390	0.91	-	*
NiCrBSi [59]	-580	30	650	**
NiCrBSiFeMoCo [60]	-490	18	660	**
Fe-amorphous	-550	4.70	1120	

Table 3. The E_{Corr} (vs. SCE), i_{Corr}, and micro-vickers hardness of different coatings.

* polarization test after 1 day immersion in 3.5% NaCl solution. ** polarization test in seawater, other referenced results are tested in 3.5% NaCl solution.

Overall, the newly developed FeCrNiMoCBSi alloy system possessed a sufficiently high glass-forming ability and met the requirement as the feedstock for HVOF coating. The results of corrosion and corrosion-wear tests showed that the defective sites present in the amorphous coating obviously deteriorated its properties. To improve the resistance to wear and corrosion, the number of defects in the coating had to be reduced by optimizing the spray process parameters, remelting the coating to densify the surface layer [61], or applying other advanced spraying technologies. Therefore, the use of Fe-based glassy metals for coating will be an effective way to enhance the surface properties of structural components.

5. Summary

- 1. The FeCrNiMoCBSi alloy system has been developed and proposed as the feedstock for HVOF coating. The XRD spectra revealed that the feedstock powder possessed few carbides and borides, and no such precipitates were found in the amorphous coating. The micro-hardness of the as-deposited coating was above Hv 1120, and it was expected to provide high wear resistance.
- 2. In potentiodynamic and potentiostatic polarization tests, the coating and the 316L substrate had roughly the same corrosion rates in 3.5% NaCl and 1M HCl solutions. The corrosion resistance of the coating in the 0.5M H₂SO₄ solution was inferior to that of the 316L, which could be attributed to the presence of defects in the former. SEM features of the corroded samples revealed large pores and deep ditches in the 316L corroded in the 3.5% NaCl and 1 M HCl solutions, whereas predominantly fine ditches around the residual powders were observed in the corroded coating.
- 3. The corrosion-wear tests of the coating and the 316L substrate in 3.5% NaCl solution showed that the corrosion current densities of the two were about the same. For comparison with the counterpart samples in potentiostatic polarization tests, a large increase in corrosion current density during corrosion-wear tests at the same applied potential implied an obvious increase in corrosion rate. Such results were due to the continuous removal of the passive film of the samples during contact wear. The worn surface morphology of the 316L SS displayed parallel plastic furrows. In contrast, a rubbed smooth surface and corroded zone were found on the worn surface of the coating. The less damaged surface confirmed that the coating had greater corrosion-wear resistance than the 316L substrate in 3.5% NaCl solution.

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