Synergistic effect of ultrasonic cavitation erosion and corrosion of WC–CoCr and FeCrSiBMn coatings prepared by HVOF spraying

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1. Introduction

Cavitation erosion–corrosion is a common mode of material degradation in hydrodynamic systems, which causes reductions in operational efficiency of flow-handling components operated in seawater environment. It is well known that cavitation erosion–corrosion is related to two main effects of mechanical damage and electrochemical corrosion. The synergies or interactions of both effects play important roles in contributing to stress concentration, plastic deformation, crack initiation, crack growth and material deterioration [1–5]. To solve this problem, great attentions have been paid to the selection of appropriate surface treatment techniques, such as cathodic arc plasma ion plating, laser surface melting, plasma enhanced magnetron sputtering, electroless plating, atmospheric pressure plasma spraying, and high-velocity oxygen-fuel (HVOF) spraying [6–13]. Among these techniques, HVOF spraying has attracted much attention in recent years due to its advantages of high flame velocity, low flame temperature and dwell time, with which a dense coating with superior bond strength, high hardness, less decarburization, low porosity and oxide content could be prepared [14,15].

WC-based cermet coatings and Fe-based amorphous/nanocrystalline coatings prepared by HVOF spraying have been widely adopted by hydraulic machinery and coastal installations to enhance the cavitation erosion and corrosion resistance of their mechanical components. Many attempts have been made to investigate the cavitation erosion and corrosion resistance of HVOF sprayed WC-based cermet coatings and Fe-based amorphous/nanocrystalline coatings. Ding et al. [16] prepared conventional, submicron and multimodal WC–12Co cermet coatings by HVOF spraying and the multimodal coating exhibited the best cavitation erosion resistance among three coatings due to its dense nanosstructure, high microhardness and strong cohesive strength. Similar results were also reported in other studies [17,18]. Cavitation erosion resistance for HVOF sprayed FeCrSiBMn amorphous/nanocrystalline coating in distilled water can be 7 times higher than that of ZG06Cr13Ni5Mo martensite stainless steel [19]. Zheng et al. [20] demonstrated that heat treatment on HVOF sprayed FeCrSiBMn coatings improved cavitation erosion resistance. Some publications pointed out that HVOF sprayed WC-based cermet coatings seem to be an alternative to hard chromium coating [21–23]. Our former study also showed that HVOF sprayed FeCrSiBMn amorphous/nanocrystalline coating has superior corrosion resistance to the hard chromium coating in...
3.5 wt.% NaCl solution [24]. Wang et al. [25] reported that HVOF sprayed FeCrMoMnWBCrSi amorphous coatings with a wide passive region exhibit much higher ability to withstand pitting corrosion than that of the 304 stainless steel. Furthermore, the structural changes and the spray parameters in HVOF spray process affected significantly the corrosion resistance of WC-based cermet coatings and Fe-based amorphous/nanocrystalline coatings [26–29]. In earlier studies, we demonstrated that cavitation erosion mainly accelerates the cathodic reaction process of HVOF sprayed near-nanocrystalline WC–10Co–4Cr coating [30]. However, no any detailed description of the synergistic effect of cavitation erosion and corrosion of HVOF sprayed WC-based cermet and Fe-based amorphous/nanocrystalline coating was given. Therefore, in the present research we focus on the cavitation erosion–corrosion behavior, especially the contributions of pure mechanical erosion, pure electrochemical corrosion, and the synergism between cavitation erosion and corrosion to the overall cavitation erosion–corrosion of HVOF sprayed coatings in 3.5 wt.% NaCl solution.

Previously, the present authors investigated the effect of spray parameters on the microstructure and corrosion behavior of HVOF sprayed conventional WC–10Co–4Cr coatings, and obtained the optimal spray parameter [29]. WC–10Co–4Cr coatings and FeCrSiBMe amorphous/nanocrystalline coatings were both synthesized successfully by HVOF spraying process and their microstructures, corrosion and cavitation erosion behavior were reported [19,24,31,32]. This work is an extension of the reported research. The aim of this study was to assess the relative importance of cavitation erosion, pure electrochemical corrosion, and the synergism between cavitation erosion and corrosion in the overall cavitation erosion–corrosion damage of HVOF sprayed conventional WC–10Co–4Cr coatings and FeCrSiBMe amorphous/nanocrystalline coatings in 3.5 wt.% NaCl solution.

2. Experimental procedure

Commercially available WC–CoCr and FeCrSiBMe powders with the particle size of 15–45 μm were used in the present study and their nominal compositions were 4 wt.% Cr–10 wt.% Co–5.3 wt.% C–80.7 wt.% W and 44.7 wt.% Cr–1.98 wt.% Si–2.97 wt.% B–0.08 wt. % Mn–50.27 wt.% Fe, respectively. These powders were deposited on the 1Cr18Ni9Ti stainless steel substrate by using commercial HVOF thermal spray system (Praxair Tafa-JP8000, USA). Details of HVOF spraying process parameters were given in Table 1. The substrate samples were cooled with compressed air jets during and after spraying. Prior to coating deposition, the substrate samples were pre-cleaned in acetone, dried in hot air, and then grit blasted with 30 mesh Al2O3 to provide a fresh and rough surface for better adhesion.

The cavitation erosion–corrosion experiments were carried out using a magnetostrictive-driven cavitation facility with electrochemical test system, according to the ASTM G32-10 standard [33]. A detailed description of the cavitation erosion–corrosion test apparatus and its screw specimen’s dimension was shown in Fig. 1. Prior to the cavitation erosion–corrosion tests, the specimens were ground and polished to mirror finish with an average surface roughness Ra = 0.02 μm, cleaned with acetone in an ultrasonic bath, and dried in hot air. Then, the specimen used to transfer the energy of ultrasonic cavitation was attached to the free end of the horn. The specimens used to assess the relative importance of cavitation erosion, corrosion and the synergism between them in the overall cavitation erosion–corrosion damage were placed co-axially with the horn and were held quiescent at a distance of 0.5 mm from the horn tip.

In the testing process, distilled water and 3.5 wt.% NaCl solution were used as the test liquid, respectively. The horn was immersed at a depth of 15 mm in the test liquid held in a 1000 mL beaker and the system kept in a resonant condition by controlling the output power of the ultrasonic generator. The vibratory frequency and double vibratory amplitude were 19 ± 1 kHz and 60 ± 5 μm, respectively. The beaker was surrounded by the flowing cooling water to keep the test liquid inside it at 25–30 °C. The specimen was degreased, rinsed, dried and weighed periodically by an analytical balance with an accuracy of 0.1 mg to determine mass loss. Mass loss was converted to volume loss after the density of the tested specimen was considered. The densities adopted for the WC–10Co–4Cr coating and the FeCrSiBMe coating were 12500 kg m⁻³ [34] and 7850 kg m⁻³ [35], respectively. The eroded surfaces of the coatings were observed by scanning electron microscope (SEM, Hitachi S-3400N, Japan).

EC & G Princeton Applied Research Potentiostat/Galvanostat Model 263 A & 5210 lock-in-amplifier with software M398 was applied to collect electrochemical data under static and cavitating conditions. A three-electrode electrochemical cell composed of a specimen as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode was used. After cavitation for 15 min, potentiodynamic polarization curves were swept from −250 mV relative to corrosion potential at a fixed rate of 1 mV s⁻¹. The corrosion current density (icorr) and corrosion potential (Ecorr) were obtained as the intersection point of linear fits to the anodic and cathodic polarization curves, according to the Tafel extrapolation technique. Each test was repeated at least thrice to make sure a good repeatability of the experiment result.

3. Results and discussion

3.1. Cumulative volume loss rates of the coatings

Fig. 2 shows the relationship between cumulative volume loss rate and cavitation erosion time for the WC–10Co–4Cr coating and the FeCrSiBMe coating in distilled water and 3.5 wt.% NaCl solution. Initially, the volume loss rate of the coatings increased rapidly until reaching a peak value. Then a gradual decrease was followed to a steady-state value. After eroded for 30 h, the volume loss rates of the WC–10Co–4Cr coating in distilled water and 3.5 wt.% NaCl solution were 0.00744 and 0.00984 mm³ h⁻¹ respectively, whereas the volume loss rates of the FeCrSiBMe coating in distilled water and 3.5 wt.% NaCl solution were 0.0217 and 0.0243 mm³ h⁻¹ respectively. This indicated that corrosion would accelerate the cavitation erosion damage of the coatings. Moreover, the WC–10Co–4Cr coating exhibited a superior cavitation erosion–corrosion resistance compared to the FeCrSiBMe coating. Firstly, this could be explained that there were more inclusions at the interface between the FeCrSiBMe coating and the substrate (Fig. 1(a) in [24]) than that in the WC–10Co–4Cr coating (Fig. 2(c) in [32]). Secondly, the porosities of both coatings were less than 1%, whereas the hardness of the WC–10Co–4Cr coating (1423 HV0.1) was much higher than that of the FeCrSiBMe coating (1082 HV0.1) since the hardness had a great influence on the cavi-

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<th>Table 1</th>
<th>Process parameters employed for HVOF spraying process.</th>
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<tr>
<td>Spray parameters</td>
<td>Coating</td>
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<tr>
<td>Oxygen flow rate (L min⁻¹)</td>
<td>897</td>
</tr>
<tr>
<td>Kerosene flow rate (L min⁻¹)</td>
<td>0.38</td>
</tr>
<tr>
<td>Carrier gas flow rate (L min⁻¹)</td>
<td>10.86</td>
</tr>
<tr>
<td>Spray distance (mm)</td>
<td>300</td>
</tr>
<tr>
<td>Powder feed rate (g min⁻¹)</td>
<td>50</td>
</tr>
<tr>
<td>Spray gun speed (mm s⁻¹)</td>
<td>280</td>
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tation erosion resistance [36]. It can also be seen that there was no evidence of incubation period for both coatings. The reason is that pores and microcracks on the surface of the coating acted as the prefabricated cavitation erosion pits and preferential corrosion initiation sites would raise the volume loss rate at the beginning of test, although the coated samples has been ground and polished with the same surface roughness before the cavitation erosion–corrosion tests [37,38].

3.2 Cavitation erosion–corrosion morphology observations

To gain further information about the difference in the cavitation erosion–corrosion resistance of the WC–10Co–4Cr coating and the FeCrSiBMn coating, SEM was taken to obtain detailed cavitation erosion–corrosion damage from the cavitation erosion region of the eroded specimen, which had been introduced in our previous work [39]. Fig. 3 illustrates typical morphological features of the coatings after cavitation erosion–corrosion for different time in 3.5 wt.% NaCl solution. For the WC–10Co–4Cr coating, the surface after eroded for 10 h was relatively smooth (Fig. 3(a)). As shown in Fig. 3(b), craters were detected on the surface of the coating after eroded for 30 h. It can also be noticed from the inset of Fig. 3(b) that the volume loss began at the edge of pores and propagated along the carbide-binder interface. As compared with the surface of the WC–10Co–4Cr coating after eroded for 10 h, the surface of the FeCrSiBMn coating (Fig. 3(c)) was roughened with many big craters. The volume loss of the FeCrSiBMn coating began at the edge of pre-existing pores and the interfaces between the unmelted particles and the matrix when exposed to the electrolyte and under repetitive impacts of microjet and shock waves (as shown in the inset of Fig. 3(c)), which was in accord with our previous study [19]. The surface morphology of the FeCrSiBMn coating eroded 30 h (Fig. 3(d)) presented similar features to the WC–10Co–4Cr coating, although the craters were much larger and deeper compared to Fig. 3(b). This is consistent with the volume loss rate result, where the cavitation erosion–corrosion volume loss rate of the FeCrSiBMn coating (0.0243 mm³ h⁻¹) was about 2.5 times to that of the WC–10Co–4Cr coating (0.00984 mm³ h⁻¹) after eroded for 30 h.

Fig. 4 shows the cross-sectional morphologies of the coatings after cavitation erosion–corrosion for 30 h in 3.5 wt.% NaCl solution. Some cracks and voids could be observed. These cracks, initiated from surface, were diffusion channels for chloride ions to corrode the interior of the coating. There was obvious difference in crack profile for the WC–10Co–4Cr coating and the FeCrSiBMn coating, which is consistent with the result of surface morphologies of the coatings. Furthermore, considering the fact that the voids in the FeCrSiBMn coating (Fig. 4(b)) were much more and bigger than that in the WC–10Co–4Cr coating (Fig. 4(a)), it is easy to understand that the cavitation erosion–corrosion resistance of the FeCrSiBMn coating was worse than that of the WC–10Co–4Cr coating in 3.5 wt.% NaCl solution.

3.3 Corrosion potential responses during cavitation erosion–corrosion

Fig. 5 reveals $E_{corr}$ vs. time under quiescence and cavitation conditions for the WC–10Co–4Cr coating and the FeCrSiBMn coating in 3.5 wt.% NaCl solution. Fig. 5(a) indicates that the corrosion potential for the WC–10Co–4Cr coating tended to shift in noble direction for about 15 mV SCE when cavitation started, shifted gradually in anodic direction during the cavitation of 30 min, and shifted back to $-340$ mV SCE after cavitation was stopped. Such shifts were attributed to the increase of mass transfer of oxygen [30,40]. The characteristic in potential shift for the FeCrSiBMn coating (Fig. 5(b)) was similar to that of the WC–10Co–4Cr coating, although the variation of the corrosion potential was much larger compared to Fig. 5(a). These results reflected that the mass transfer of oxygen on the surface of the FeCrSiBMn coating was more pronounced.
under repetitive impacts of the collapsing bubble compared to the WC–10Co–4Cr coating.

3.4. Potentiodynamic polarization tests

Fig. 6 presents potentiodynamic polarization curves under quiescence and cavitation conditions for the WC–10Co–4Cr coating and the FeCrSiB Mn coating in 3.5 wt.% NaCl solution. Some important electrochemical parameters, such as the corrosion potential \( E_{\text{corr}} \) and corrosion current density \( i_{\text{corr}} \) of the coatings tested are summarized in Table 2. It can be observed from Fig. 6 that both coatings exhibited similar polarization behavior. The \( i_{\text{corr}} \) values of the WC–10Co–4Cr coating under quiescence and cavitation conditions were 1.56 and 5.69 \( \mu\text{A cm}^{-2} \) respectively, whereas the \( i_{\text{corr}} \) values of the FeCrSiB Mn coating under quiescence and cavitation conditions were 2.33 and 6.45 \( \mu\text{A cm}^{-2} \) respectively. It is apparent that cavitation erosion had a strong influence on the cathodic reaction process of both coatings. The result was consistent with the results in our previous study that cavitation erosion–corrosion process of the coating in 3.5 wt.% NaCl solution was controlled by accelerated cathodic reaction and mechanical impact [30]. It also reflected that the corrosion current density of the FeCrSiB Mn coating was less affected by cavitation erosion than that of the WC–10Co–4Cr coating.

3.5. Synergistic effects of cavitation erosion and corrosion

When the cavitating liquid is corrosive, both mechanical erosion and electrochemical corrosion may accelerate the removal of material from the surface and increase the amount of material degradation. Besides cavitation erosion and corrosion, cavitation erosion–corrosion consists of the synergistic effect of both factors that we should not neglect. In general, the synergism between cavitation erosion and corrosion is related to the erosion-induced cor-

![Fig. 3. Cavitation erosion characteristics of the WC–10Co–4Cr coating (a, b) and the FeCrSiB Mn coating (c, d) in 3.5 wt.% NaCl solution: (a, c) eroded 10 h; (b, d) eroded 30 h.](image1)

![Fig. 4. Cross-sectional SEM morphologies of the WC–10Co–4Cr coating (a) and the FeCrSiB Mn coating (b) after eroded for 30 h in 3.5 wt.% NaCl solution.](image2)
erosion component and the corrosion-induced erosion component \[41\]. The volume loss rates of total cavitation erosion (\(V_T\)) for the coatings in 3.5 wt.% NaCl solution can be described by the following equation:

\[
V_T = V_E + V_C + V_S = V_E + V_C + (V_{EIC} + V_{CIE})
\]

(1)

where \(V_C\) is volume loss rate of pure corrosion, \(V_E\) is volume loss rate of pure erosion, \(V_S\) is volume loss rate of synergism, \(V_{EIC}\) is volume loss rate of erosion-induced corrosion, and \(V_{CIE}\) is volume loss rate of corrosion-induced erosion.

In present work, \(V_E\) and \(V_T\) were measured under cavitation erosion condition for 30 h in distilled water and 3.5 wt.% NaCl solution respectively. \(V_C\) was calculated from the \(i_{corr}\) in the polarization curve under quiescence condition according to the Faraday’s law. \(V_{EIC}\) was calculated from the \(i_{corr}\) in the polarization curve under cavitation condition (\(V_C\) was deducted to work out) and \(V_{CIE}\) could be obtained from Eq. (1). Table 3 lists the parameters described above for the WC–10Co–4Cr coating and the FeCrSiBMn coating. Obviously, WC–10Co–4Cr coating possessed much higher cavitation erosion resistance than FeCrSiBMn coating in both distilled water and 3.5 wt.% NaCl solution by the values of \(V_E\) and \(V_T\).

To analyze the components of cavitation erosion–corrosion, contributions of cavitation erosion, corrosion and synergism to total cavitation erosion–corrosion for the WC–10Co–4Cr coating and the FeCrSiBMn coating are given in Table 4. It indicated that the contribution of erosion component (\(V_E\) and \(V_{CIE}\)) to \(V_T\) was more than 90% and \(V_E\) occupied the largest proportion for \(V_T\), which meant that mechanical effect was the main factor for cavitation–corrosion behavior of both coatings. Therefore, how to improve the cavitation erosion resistance rather than corrosion resistance of both coatings is the key to prolong their service lifetime. It can also be seen that the contribution of corrosion component (\(V_C\) and \(V_{EIC}\)) to \(V_T\) was different for the WC–10Co–4Cr coating and the FeCrSiBMn coating. In this work, compared to the WC–10Co–4Cr coating, the higher content of Cr in the

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**Table 2**

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<th>Material</th>
<th>Quiescence</th>
<th>Cavitation</th>
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<tbody>
<tr>
<td></td>
<td>(E_{corr}) (mV)</td>
<td>(i_{corr}) ((\mu)A cm(^{-2}))</td>
</tr>
<tr>
<td>WC–10Co–4Cr coating</td>
<td>–305</td>
<td>1.56</td>
</tr>
<tr>
<td>FeCrSiBMn coating</td>
<td>–241</td>
<td>2.33</td>
</tr>
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</table>

**Table 3**

<table>
<thead>
<tr>
<th>Material</th>
<th>Volume loss rates (10(^{-3}) mm(^3) h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V_T)</td>
</tr>
<tr>
<td>WC–10Co–4Cr coating</td>
<td>9.84</td>
</tr>
<tr>
<td>FeCrSiBMn coating</td>
<td>24.33</td>
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**Fig. 5.** \(E_{corr}\) vs. time for the WC–10Co–4Cr coating (a) and the FeCrSiBMn coating (b) in 3.5 wt.% NaCl solution under quiescence and cavitation conditions.

**Fig. 6.** Potentiodynamic polarization curves for the WC–10Co–4Cr coating (a) and the FeCrSiBMn coating (b) in 3.5 wt.% NaCl solution under quiescence and cavitation conditions.
FeCrSiBmN coating resulted in the formation of more continuous and compact passive film on the surface of the coating, which acted as a barrier for anodic dissolution and contributed to the relatively low percentage values of the volume loss rate for pure corrosion and erosion-induced corrosion [42, 43]. In terms of testing results, it can be inferred that HVOF sprayed WC–10Co–4Cr coating could provide better protection to the substrate from cavitation erosion–corrosion in 3.5 wt.% NaCl solution, compared with the FeCrSiBmN coating.

4. Conclusions

Conventional WC–10Co–4Cr coatings and FeCrSiBmN amorphous/nanocrystalline coatings were fabricated by HVOF spraying process. WC–10Co–4Cr coatings exhibited good resistance to cavitation erosion–corrosion. After eroded for 30 h, the volume loss rate of the WC–10Co–4Cr coating was about 2/5 that of the FeCrSiBmN coating in 3.5 wt.% NaCl solution. The superior cavitation erosion–corrosion resistance of the WC–10Co–4Cr coating was attributed to its fewer inclusions at the interface between the coating and the substrate. The percentage of corrosion component of the WC–10Co–4Cr coating was larger than that of the FeCrSiBmN coating. The main damages of both coatings under cavitation erosion–corrosion were caused by the effect of pure cavitation erosion.

Acknowledgments

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