Corrosion Behavior of High Velocity Oxy-Fuel Sprayed Composite Ni-/Fe-Based Self-Fluxing Alloy – Cermet Coatings

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Abstract: The paper focuses on the corrosion behavior of Ni-/Fe-based self-fluxing alloy – WC-Co/Cr₂C₃-Ni cermet composite coatings manufactured by high velocity oxy-fuel spraying (HVOFS). Microstructure and phase composition of the coatings were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The potentiodynamic tests were conducted in the 3.5 wt.% NaCl solutions under room temperature using a three-electrode cell setup (sample was applied as the working electrode, Pt as the counterelectrode, and Ag/AgCl – as the reference electrode) after 10 min and 24 h of immersion. Stainless steel AISI 316L was used as a reference. Tafel polarization plots were obtained, and corrosion potential Ecorr and corrosion current density icorr were determined. All the studied coatings exhibited more negative Ecorr values than the reference steel, both under short and long immersion time, whereas in the latter case, the difference in the corrosion potentials increased remarkably. The reason was the expansion of corrosion products at the self-fluxing alloy–cermet interface that led to cracking and penetration of electrolyte deeper into the coating. Ni-alloy based coatings demonstrated better resistance to corrosion during short immersion time due to a nobler matrix; Fe-based coatings, vice-versa, exhibited better corrosion resistance during long immersion time due to a larger amount of amorphous phase. No influence of porosity and cermet reinforcement type on the corrosion resistance of the HVOFS coatings was observed. The principal corrosion mechanism of the coatings was crevice corrosion, accompanied with binder depletion in the cermet reinforcement.

Keywords: HVOFS spraying, Ni-based alloy, Fe-based alloy, cermet, corrosion resistance, corrosion mechanism.

1. INTRODUCTION

According to different sources, corrosion damage causes losses of 3.1–4.2% of the gross domestic product (GDP) of a country [1–3]. Approximately 80% of corrosion damage is related to aqueous corrosion [4]; therefore, protection against it is of utmost importance. For this purpose, various organic and metallic coatings are commonly applied, whereas the latter are more advantageous in terms of hardness and wear resistance [5]. For decades, electrolytic hard chrome (EHC) coatings were recognized as the industrial standard of a wear and corrosion resistant coating [6–8], but due to government restrictions driven by environmental and health concerns [9,10], its usage is being limited in developed countries.

One of the widely proposed alternatives to EHC coatings is high velocity oxy-fuel sprayed (HVOFS) coatings [11–14]. Among commonly sprayed materials, Ni-based self-fluxing (Ni-Cr-Si-B) alloys have proved to be in the capacity of providing the highest resistance to corrosion [15], which exceeds that of EHC coating [16]. Ni-Cr-Si-B HVOFS coatings have also been reported to have better corrosion resistance than, for example, stainless steels AISI 304 [17,18] and AISI 309 [18], what makes them attractive from the point of view of corrosion protection.

In recent years, Fe-based self-fluxing (Fe-Cr-Si-B) alloys were proposed as an alternative to those of Ni-based, owing to their higher mechanical properties and lower price [19–21]. However, there is still a lack of information about comparative corrosion resistance of these groups of alloys. Also, despite numerous studies of wear resistance of thermal sprayed composite coatings prepared from self-fluxing alloys, reinforced by cermet particles [20–29], to authors’ best knowledge, no reports of the influence of different cermet reinforcement on the corrosion performance of such coatings have been published. Therefore, this paper focuses on a comparative corrosion study of WC-Co and Cr₃C₂-Ni particles reinforced NiCrSiB and FeCrSiB HVOFS coatings in the NaCl solution. The results are compared with the stainless steel AISI 316L, and the corrosion mechanisms are explored.

2. EXPERIMENTAL

2.1. Spraying Process

The chemical composition and the range of particle size of the feedstock powders are presented in Table 1.
Prior to spraying, four composite powder mixtures were prepared by mechanical blending – NiCrSiB+WC-Co, NiCrSiB+Cr<sub>3</sub>C<sub>2</sub>-Ni, FeCrSiB+WC-Co, and FeCrSiB+Cr<sub>3</sub>C<sub>2</sub>-Ni. The content of the self-fluxing alloy and the cermet was 60 vol.% to 40 vol.%, respectively, in all the cases. The shape and size distribution of the constituents of the composite powder mixtures is described in [20].

Normalized carbon steel C45E (wt.%: 0.42–0.50 C, 0.50–0.80 Mn, 0.035 P, 0.035 S, ≤0.40 Cr, ≤0.10 Mo, ≤0.40 Ni, bal. Fe) was used as the substrate. Prior to spraying, specimens with dimensions of 100 × 25 × 5 mm were grit-blasted with corundum (mesh size 36). High velocity oxy-fuel spraying was carried out, using Diamond Jet Hybrid 2700 system equipped with propane-fuelled spray gun (Oerlicon Metco, Switzerland). The optimized spraying process parameters, which were the same for all the coatings, are shown in Table 2. The resultant coatings had a thickness of 0.3–0.4 mm.

Table 2: Spraying Parameters [20]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane flow, m&lt;sup&gt;3&lt;/sup&gt;/s</td>
<td>1.13×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Oxygen flow, m&lt;sup&gt;3&lt;/sup&gt;/s</td>
<td>4.0×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Air flow, m&lt;sup&gt;3&lt;/sup&gt;/s</td>
<td>6.25×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Spraying distance, m</td>
<td>2.5×10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Speed of gun movement, m/s</td>
<td>2.0×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Powder feed rate, kg/s</td>
<td>6.7×10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

2.2. Microstructure Studies

Microstructure of the obtained coatings was studied under the scanning electron microscope (SEM) EVO MA-15 (Carl Zeiss, Germany). Porosity of the coatings was estimated according to the standard ISO/TR 26946:2011, using the Buehler<sup>®</sup> Omnimet<sup>®</sup> software.

Phase composition of the obtained coatings was studied, using the X-ray diffractometer (XRD) AXS D5005 (Bruker, Germany) equipped with a CuK<sub>α</sub> radiation source, with a step of 0.04°.

2.3. Corrosion Tests

Prior to corrosion testing, the obtained coatings were manually wet polished at the abrasive diamond ring with an average grain size of 40 µm. After polishing, specimens were ultrasonically rinsed in acetone and dried with compressed air. Surfaces not subjected to corrosion were sealed with hot glue, leaving an area of approximately 1 cm<sup>2</sup>. The potentiodynamic polarization tests were conducted in the 3.5 wt.% NaCl aqueous solution at the room temperature, applying the three-electrode cell setup (specimen as the working electrode, Pt wire as the counter electrode and Ag/AgCl wire as the reference electrode), using an electrochemical worksation CHI660C (CH Instruments, USA). The Tafel plots were recorded for the coated specimens and the reference steel AISI 316L (wt.%: ≤0.030 C, ≤1.00 Si, ≤2.00 Mn, 0.045 P, 0.030 ßS, 16.5–18.5 Cr, 10.5–13.0 Ni, 2.50–3.00 Mo, ≤0.11 Ni, bal. Fe) at the potential sweep rate of 5.0×10<sup>-3</sup> V in the range from −1.0 to 0.5 V with a rate of 10<sup>3</sup> V/s after 10 min and 24 h of immersion. The obtained Tafel curves were extrapolated to find the corrosion potential E<sub>corr</sub> (V) and corrosion current density i<sub>corr</sub> (A/cm<sup>2</sup>). The corroded surfaces were studied under SEM after the 24 h test to determine the corrosion mechanisms.

3. RESULTS AND DISCUSSION

3.1. Microstructure Studies

The sprayed coatings had a lamellar microstructure with low porosity, typical for HVOFS coatings (Figure 1). The formation of a negligible amount of
pores, mostly located at the reinforcement-matrix boundary, may be explained by the different shrinkage of molten self-fluxing alloy and cermet particles during coating deposition [21, 27]. Both WC-Co and Cr₃C₂-Ni particles fractured and became elongated at the impact with the substrate. As a result of a higher fracture toughness of the WC-Co cermets (29.4 MPa·m⁰.⁵ [31]) than that of Cr₃C₂-Ni (13.4 MPa·m⁰.⁵ [31]), WC-Co particles fractured to a lesser extent; therefore, the average size of the embedded WC-Co fragments was larger.

WC-Co particles reinforced coatings exhibited slightly higher porosity than those of the Cr₃C₂-Ni particles reinforced (Table 3). The most probable reason for that was the lower value of the coefficient of thermal expansion (CTE) of the WC-Co cermet (ca. 4.8×10⁻⁶ K [32]) as compared with the CTE value of Cr₃C₂-Ni (ca. 10.1×10⁻⁶ K [33]).

The Ni-based matrix mainly comprised Cr(Ni) or Ni(Cr) solid solutions with minor content of Ni- and Cr-based borides and silicides (Figure 2a,b). A tiny amount (0.8 wt.%) of NiW₆ (not shown), indicating negligible dissolution of the WC-Co reinforcement in the molten matrix, was also observed. The dissolution extent of the Cr₃C₂-Ni reinforcement could not be reliably estimated in the coatings, as it comprised the same chemical elements as the matrix alloy.
The Fe-based matrix of the FeCrSiB+WC-Co coating consisted mostly of pure Fe and Fe(Co) and Fe(Cr) solid solutions, as well as the (Cr\textsubscript{19}W\textsubscript{4})C\textsubscript{6} carbide (Figure 2c). The relatively large amount of the last is a sign of a higher dissolution of the WC-Co reinforcement as compared with the Ni-based matrix coating. Apart from these phases, chromium boride CrB and various Cr- and Ni-based silicides (not shown), and the amorphous phase were present in the matrix. The principal phase in the matrix of the FeCrSiB+Cr\textsubscript{3}C\textsubscript{2}-Ni coating was boron carbide BC\textsubscript{7} (Figure 2d). The amount of the amorphous phase was also significant. In addition, different Cr-, Ni- and Fe-based borides, carbides and silicides (not shown) were discovered; however, the content of each individual phase was negligible.

### 3.2. Corrosion Resistance

The corrosion potential ($E_{\text{corr}}$) values of all the investigated materials became more negative with long immersion time (24 h), and corrosion current density ($i_{\text{corr}}$) became higher (Table 4). The $E_{\text{corr}}$ values of all

<table>
<thead>
<tr>
<th>Material</th>
<th>Immersion Time</th>
<th>$E_{\text{corr}}$, V</th>
<th>$i_{\text{corr}}$, $10^{-6}$ A/cm\textsuperscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCrSiB+WC-Co</td>
<td>10 min</td>
<td>-0.532</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.878</td>
<td>1.00</td>
</tr>
<tr>
<td>NiCrSiB+Cr\textsubscript{3}C\textsubscript{2}-Ni</td>
<td>10 min</td>
<td>-0.468</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.859</td>
<td>5.51</td>
</tr>
<tr>
<td>FeCrSiB+WC-Co</td>
<td>10 min</td>
<td>-0.558</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.786</td>
<td>3.18</td>
</tr>
<tr>
<td>FeCrSiB+Cr\textsubscript{3}C\textsubscript{2}-NiC</td>
<td>10 min</td>
<td>-0.533</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.797</td>
<td>0.66</td>
</tr>
<tr>
<td>AIS-Ni I 316L (reference)</td>
<td>10 min</td>
<td>-0.416</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>24 h</td>
<td>-0.434</td>
<td>0.48</td>
</tr>
</tbody>
</table>
the coatings were lower as compared with the reference steel AISI 316L, what indicates their generally lower corrosion resistance. Ni-based coatings exhibited a slightly more positive $E_{\text{corr}}$ values than Fe-based coatings, after short immersion time (10 min), probably due to the more positive potential of Ni/Ni$^{2+}$ than with Fe/Fe$^{2+}$ (respectively, $-0.25$ V and $-0.44$ V against standard hydrogen electrode (SHE) [4]); however, after long immersion time, the Fe-based coatings exhibited more positive $E_{\text{corr}}$ values. At the same time, neither definite influence of the reinforcement type nor porosity on the corrosion performance of the studied coatings was revealed.

Study of the Tafel polarization plots (Figure 3) showed that after short immersion time, all the coatings exhibited a negligible passivation at around $-0.23$ V (Figure 3a), which is associated with the passive Cr oxide film formation [34]. However, after long immersion time, no passivation behavior of the coatings was observed, while the steel AISI 316L underwent transpassivation, associated with pitting corrosion [35] at the $E_{\text{corr}}$ value of approximately $+0.10$ V (Figure 3b).

A slight negative shift in the potential of the reference steel AISI 316L during long immersion time is most probably caused by the more extensive dissolution of the passive film due to the action of Cl$^-$ ions [4]. The Cr depletion could also contribute to the negative shift of the corrosion potentials of the investigated coatings [36]. However, the relatively higher increase of the $E_{\text{corr}}$ values of the studied coatings in comparison with the reference steel can hardly be explained by this phenomenon alone.

In metal matrix composites, corrosion process is usually initiated at the matrix-hardphase interface [37, 38]. Thus, at the start of the corrosion, it occurs at the few sites where reinforcement particles are instantly exposed to the electrolyte at the coating surface. As the corrosion progresses, the corrosion products will accumulate at the matrix-reinforcement interface. In [39], it was suggested that these corrosion products may cause tensile stresses in the coating and lead to formation of cracks. Assuming that cracks mainly develop through the pores in the coating [40] and that the majority of pores are situated at the matrix-reinforcement border, cracking would lead to the increase of the number of galvanic couples 'matrix-reinforcement'. On the other hand, cracks would prevent the formation of a continuous passive layer. All this would accelerate the corrosion process [41] that is reflected in a negative shift of the corrosion potential values of the studied coatings. This suggestion is supported by the observations of the corrosion current density $i_{\text{corr}}$, the values of which were lower than those of the reference steel after short immersion time; it occurred despite the more negative $E_{\text{corr}}$ values of the coatings owing to a relatively small number of sites where corrosion occurs. However, after long immersion time, $i_{\text{corr}}$ values of the coatings became larger than those of the reference steel AISI 316L as a result of an
increased number of galvanic couples and, consequently, higher general corrosion current.

3.3. Corrosion Mechanisms

The corroded surfaces of the investigated materials are shown in Figure 4. Crevice corrosion was the principal corrosion mechanism and localized corrosion of the binder inside the cermet reinforcement – an accompanying corrosion mechanism of all the investigated HVOFS coatings (Figure 4a-d), while pitting corrosion occurred in the case of the reference steel AISI 316L (Figure 4e). The corrosion in the
coatings occurred both at the matrix-reinforcement boundary and at the boundary of separate splats, whereas it was much more severe in Ni-based coatings (Figure 4a,b) than in Fe-based (Figure 3c,d). The reason may be a larger amount of the reinforcement phase in the latter [42-44].

CONCLUSIONS

1. The corrosion resistance of both Ni- and Fe-based self-fluxing alloy-cermet high velocity oxy-fuel (HVOFS) sprayed coatings was lower than that of the stainless steel AISI 316L, whereas it deteriorated with immersion time due to the cracking of the coatings and subsequent in-depth penetration of electrolyte.

2. Cermet reinforcement (WC-Co/Cr3C2-Ni) had no influence on the corrosion resistance of the HVOFS coatings.

3. The Ni-based self-fluxing alloy-cermet coatings exhibited higher corrosion resistance after short immersion time (10 min) due to a nobler matrix and the Fe-based self-fluxing alloy-cermet coatings – after long immersion time (24 h) due to a larger amount of the amorphous phase.

4. The principal corrosion mechanism of all the HVOFS coatings was crevice corrosion, accompanied by binder depletion in the cermet reinforcement.

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HIGHLIGHTS

a. Corrosion resistance and mechanisms of high velocity oxy-fuel sprayed (HVOFS) composite Fe-Ni-based self-fluxing alloy–WC-Co/Cr3C2-Ni cermet coatings were studied and compared to the stainless steel AISI 316L.

b. All the studied HVOFS coatings exhibited lower corrosion resistance than the stainless steel AISI 316L, whereas after long immersion time (24 h), the difference became more remarkable.

c. The coatings with the Ni-based matrix had higher corrosion resistance after short immersion time (10 min); coatings with the Fe-based matrix had higher corrosion resistance after long immersion time.

d. The corrosion mechanism of the coatings was the crevice corrosion, accompanied by the depletion of the binder in the cermet reinforcement.

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