Friction and wear behavior of WC-Ni coatings HVOF sprayed on duplex stainless steel

H S Xu\(^{1,2}\) and Q Dong\(^{1}\)

\(^{1}\)Hitachi (China) Research & Development Corporation, Room 2610, 26F, Rui Jin Building, No. 205 Maoming Road, shanghai, 200020, China

E-mail: hsxu@hitachi.cn

Abstract. The friction and wear behavior of high-velocity oxygen-fuel (HVOF) sprayed WC-Ni coatings was investigated. WC-Co coating was used as reference sample. Pin-on-disc tests were conducted on WC-Ni and WC-Co coatings surface in both pure water and 3.5% (wt.) saline solution, respectively. It was found that WC-Co coatings has superior wear and corrosion resistance in pure water due to their high hardness. However, cracks were observed in the wear scar of WC-Co coating, which wear rate was 2-4 times higher than that of WC-Ni coatings. The corrosion-wear resistance is not only affected by coating hardness, but also by powder composition. So WC-CrNi coating displays an excellent wear- and corrosion-resistance performance in saline solution.

1. Introduction

The application of WC-based thermal spray coatings has been increasing in the industry for raised component lifetime as well as reduced maintenance costs [1]. The coatings sprayed by high-velocity oxygen-fuel (HVOF) were proved to have obvious merits, such as strong adhesion with the substrate, low porosity and high abrasive wear resistance [2-5]. Therefore, they are commonly used as protective barriers in gas turbines, steam turbines, aero-engines, etc. [6, 7].

WC-Co based HVOF coatings are most commonly used due to their high hardness and adequate toughness [2, 8, 9]. Previous studies have indicated that the coating composition, which affected the microstructural integrity and hardness, was a major factor to determine the coating’s wear and corrosion resistance [10, 11]. Previous researches indicated that aggressive environments of saline water had a detrimental effect to lead to degradation of HVOF sprayed WC-Co coatings [1]. However, WC-Ni based coatings, such as WC-Cr$_3$C$_2$-Ni and WC-NiCr [12, 13], were observed to have a moderate wear resistance [14] but superior corrosion resistance than WC-Co coatings [15]. Therefore, these coatings are especially applied for wear-resistant parts working in aqueous environments, such as large-scale water pumps, urban water systems et. al. Although a number of papers involved dry abrasive wear or erosive wear of these coatings, they focused on specific wear rate (or volume wear loss) with their mechanical properties [16, 17], nevertheless ignored the internal relationship between wear-corrosion properties and microstructures of the WC-Ni based coatings.

In this work, WC-Ni based feedstock powders, with a WC-Co based coating as a reference, were HVOF-sprayed to form cermet coatings. The wear and corrosion behavior of coatings was investigated by pin-on-disc tests. In addition, the relationship between wear property in pure water and corrosion property in saline solution were analyzed in depth, to clarify wear mechanisms and practical applications for WC-Ni based coatings.
2. Experimental procedure

2.1. Coating material
Commercially available WC-CrCo (Reference powder), WC-CrNi and WC-C2Cr3-Ni feedstock powders were deposited on the substrate of duplex stainless steel, S32205, by HVOF spray systems (DJ2700 HVOF spray system, Sulzer metco, USA). Hereinafter the coatings would be simplified as coating A, B and C, respectively. The detailed chemical compositions of the powders are listed in table 1, and nominal size distribution of the powders was in range of 20 - 40 um. Before spraying, all the substrate samples were cleaned in acetone and their surfaces for spraying were grit blasted with Al2O3 to a roughened situation, to obtain sufficient bonding ability with the coating. The basic parameters of the coating depositions during HVOF process are shown in table 2.

| No. | Powder designation | Coating designation | Nominal composition (wt%) | Coating density (g/cm3) | Coating porosity (%) |
|-----|--------------------|---------------------|---------------------------|------------------------|----------------------|
| A   | WC-CrCo            | WC-CrCo            | WC–4Cr–10Co               | 14.2                   | 0.15                 |
| B   | WC-CrNi            | WC-CrNi            | WC-20Cr-7Ni               | 13.2                   | 0.23                 |
| C   | WC-Cr3C2-Ni        | WC-(W,Cr)2C-Ni     | WC-20Cr3C2-7Ni            | 13.9                   | 0.12                 |

Table 2. HVOF process parameters for coating depositions.

| Powder carrier gas (Ar) flow rate (L/min) | 9 |
| Powder feed rate (g/min)                | 120 |
| Oxygen flow rate (L/min)               | 900 |
| Spray distance (mm)                     | 400 |

2.2. Coating characterization
The phased compositions were identified by X-ray diffraction (XRD, Ultima IV, Rigaku, Japan), with Cu Kα radiation. The basic settings for XRD were: scanning angle from 20º to 90º; tube voltage 35 kV; tube current 30 mA; step 0.02º (speed 2º/min, DHL slit 5mm, DS slit 1/2º). Microstructure of the coatings was observed by optical microscope (OM, Scope A1, Zeiss, Germany) and scanning electron microscope (SEM, SU-70, Hitachi, Japan) with an energy dispersive X-ray (EDX) detector. The average porosities were calculated by Image J with 5 SEM images at magnification of 1000 x. The microhardness was measured with a Vickers micro-hardness tester (DM2D, AFFRI, Italy), under a 3 N load. Hardness values represent the average of 5 individual indentations made on a coating.

2.3. Sliding wear test
The sliding wear tests were conducted using a vertical type pin-on-disc tribometer (MMW-1A, Jinan Yihua, China), and the test conditions are listed in Table 3. The coatings on the pins (surface area: 49 mm²) were ground to obtain an initial Ra 0.8 μm. During the sliding wear test, 3 upper pins were mounted against an Al2O3 disc (Ф 56 mm) with a load of 100 N (initial contact pressure: 0.68 MPa), at room temperature. The lubricated environment for the test was under pure water and 3.5% NaCl saline solution. The disc was stationary and the pins rotated at 200 rpm against it. The test was performed over a period of 30 hours for a total sliding distance of ~ 52 km. The weight loss measurement was conducted at every 10 hours by an analytical balance (CAV264C, OHAUS, U.S.).

The weight loss was unified into wear rate according to [18]:

$$\omega_s = \frac{M_{\text{loss}}}{(W \cdot s \cdot \rho)},$$

(1)
where $M_{\text{loss}}$ is weight loss, $w$ is the normal load, $s$ is the sliding distance, and $\rho$ is the density of the coating. To evaluate wear and corrosion behavior, the friction coefficient of coatings was measured and the worn surface was observed by SEM.

### Table 3 Pin-on-disc test conditions.

| Environment                      | Wet (pure water, 3.5% saline solution) |
|----------------------------------|----------------------------------------|
| Temperature                      | Room temperature                       |
| Load (N)                         | 100                                    |
| Rotation speed (rpm)             | 200                                    |
| Sliding time (h)                 | 30                                     |

3. Results and discussion

Figure 1 (a), (b) and (c) shows polished cross-sectional microstructures of the HVOF-sprayed coating A, B and C, respectively, among which (a) - (c) are images at low magnification indicating the general view of the coatings, whereas (d) - (f) are ones for detailed microstructures and porosity investigation. According to technical requirements, the coating thickness after polishing was thicker than 200 μm, and the porosity (table 1) was less than 1% [5,19,20]. The coatings showed similar dense microstructure, however, coating A was observed to have more uniform microstructure than B and C.

![Cross-sectional SEM images](image1)

**Figure 1.** Cross-sectional SEM images ×200 (a-c) and × 1000 (d-f) of HVOF-sprayed coatings for coating A, B and C, respectively; (g) XRD patterns of the HVOF-sprayed coatings A, B and C (Ra < 0.8 μm).

The X-ray diffraction patterns of the HVOF-sprayed coatings A, B, and C are shown in Figure 1(g). The result was identified that all the coatings consist predominately of WC (JCPDS 89-2727), and no noted W$_2$C (JCPDS 35-776), Co-, Ni- or Cr-containing contents were identified in the coatings. The peaks of Cr$_3$C$_2$ are less obvious while those of (W, Cr)$_2$C became intense and broad. For coating B, broad band in the $37^\circ$<2θ<$46^\circ$ range is probably belonging to an amorphous phase of finely dispersed crystals [2]. In coating C, a small quantity of oxide of Cr$_2$O$_3$ was observed, and the oxide was speculated to form during HVOF process.

Figure 2 shows the EDX element analysis for coating A, B and C, respectively. Bright regions, marked spot 1, show similar atomic percent of C and W element with the ratio of about 1:1. They were verified as clusters of micrometric WC grains, dominating carbides that compose the coatings. It was observed that coating A contained more WC than that in B and C, which corresponded to the nominal compositions and XRD patterns. Dark regions were investigated as mixture of carbide and binder of matrix. In coating A, possible composition at dark region of spot 2 was (W, Cr)$_2$C and Co. Similarly, in coating B, spot 2 was evaluated as (W, Cr)$_2$C and Ni mixture; in coating C it was WC, Cr$_3$C$_2$ and Ni.
mixture. We observed black regions, marked spot 3, which were composed of Ni matrix in coatings B and C.

![Image](a) Coating A (b) Coating B (c) Coating C

| Element (Atomic %) | (a) Coating A | (b) Coating B | (c) Coating C |
|--------------------|---------------|---------------|---------------|
|                    | Spot 1 (bright) | Spot 2 (dark) | Spot 1 (bright) | Spot 2 (dark) | Spot 3 (black) | Spot 1 (bright) | Spot 2 (dark) | Spot 3 (black) |
| C K                | 51.21          | 19.02         | 57.97          | 30.13         | 32.26          | 50.7           | 31.81         | 30.43          |
| W M                | 48.79          | 26.13         | 42.03          | 19.29         | 1.62           | 49.3           | 15            | 1.93           |
| Ni L               | -              | -             | 12.83          | 66.12         | -              | -              | 3.94          | 6.53           |
| Cr K               | 15.05          | -             | 37.75          | -             | -              | -              | 49.25         | 61.11          |
| Co L               | -              | 39.8          | -              | -             | -              | -              | -             | -              |

**Figure 2.** EDX analysis of the regions labelled in coating A-(a), B-(b) and C-(c).

Figure 3(a) shows the friction coefficient for A, B and C coatings, respectively, in pure water. Short run-in stages were observed at the beginning of the test and then the friction coefficients reached for relatively steady stages. The friction coefficient of C coating was obviously higher than the others over the entire testing time. The friction coefficient at steady stage for A, B and C coatings are 0.15, 0.13 and 0.24, respectively. Coating C exhibits obviously higher friction coefficient than other coatings during the steady stage.

![Image](a) Friction coefficients of the HVOF-sprayed coatings varied with sliding time; (b) Volume losses of the HVOF-sprayed coatings varied with sliding time.

The coating volume loss varied with sliding time is shown in figure 3(b), in which hollow and solid marks represent the test environment of pure water and saline solution, respectively. The results indicated that the volume loss increased linearly with the sliding time in both pure water and saline solution, meaning a constant wear volume loss for each coating. The average wear rates, calculated from equation (1), for coating A, B and C are listed in table 4. Coating A had a lowest wear rates, which was 2.5 and 3.6 times in pure water and 1.9 and 3.6 times in saline solution lower than coating B and C.
respectively. The probable reason for its superior wear resistance is attribute to higher hardness of Co-based coating. Coating C, which contains Cr$_2$O$_3$, shows relative higher wear rate, as cohesiveness of oxidation on the coating is relatively weak and trends to generate oxide debris [14]. The comparison of wear rates in pure water and in saline, as shown in table 4, demonstrated that coating B had nearly the same behavior in pure water and saline solution. Thus, coating B indicated excellent resistance with the synergic wear-corrosion effect.

| Parameter                                      | A        | B        | C        |
|------------------------------------------------|----------|----------|----------|
| Wear rate (mm$^3$/Nm) in Pure water            | 9.7      | 24.0     | 34.9     |
| Wear rate variation ($\omega_s-\omega_p$ / $\omega_p$ (%)) | 37.1     | 4.6      | 35.8     |

Table 4. Comparison of wear rates in pure water and saline solution.

The micro-hardness (HV$_{0.3}$) values of coatings A, B, and C are depicted in figure 4(a). Their initial values are 1831, 1214 and 1286, respectively. Coating A had the highest hardness, insofar as Co-matrix is much harder than that of Ni. Besides, coating A had brighter WC than coatings B and C, and its hardness was sensitive to the amount of WC in the coating, since it was harder than (W, Cr)$_2$C [21,22]. Coating B was relatively softer than coating C due to a higher content of Ni and absence of Cr$_3$C$_2$ in its microstructure. Figure 4(b) shows a linear decreasing trend between wear rate and coating hardness in pure water.

![Micro-hardness of the HVOF-sprayed coatings](image1.png)

![Relationship of wear rate and average hardness of HVOF coatings in pure water](image2.png)

Figure 4. (a) Micro-hardness of the HVOF-sprayed coatings; (b) Relationship of wear rate and average hardness of HVOF coatings in pure water.

Wear rate variations of coatings in saline solution and pure water after 30 h of wear tests are shown in figure 5. Linear fits with the slope of 3.42, 0.85, and 1.72 are obtained for coating A, B and C, respectively. Although the wear rate of coating A was the lowest, it rose fastest with the sliding time. This implies that WC-Co coatings are more prone to dissolving in the saline solution than WC-Ni ones, and one can forecast that WC-Ni coatings, especially coating B with higher content of Ni and lower of Cr$_3$C$_2$ in the matrix, will be more durable than WC-Co ones.

The representative worn morphologies of surfaces (figure 6 a), b,c)) and cross-sections (figure 6 d), e), f)) for coatings A, B, and C in pure water illustrate that cracks grew deepest into coating A. It means that dominant wear mechanism in coatings were different, and the brittle bonding of Co matrix resulted in cracking of coating A only [23]. The brittle bonding makes the coating structure fragile with the sliding time, resulting in a fast increase of wear rate. In coatings B and C, pitting on the matrix with pulling out of carbide was observed at the wear scars. As it was earlier mentioned WC and (W, Cr)$_2$C carbide particles are wear-resistant and retain in the binder even when they are partially exposed by wear. However, when the microstructure distribution was non-homogeneous, carbide particles peeled
off the boundary with a higher Ni concentration, forming debris and enhancing wear. Therefore, the wear rate was relatively high for Ni-based coatings.

Figure 5. Increase in HVOF coatings’ wear rate in saline water, as compared to that in pure water.

Figure 6. Representative worn morphologies of surfaces (a) A, (b) B, (c) C and cross-sections (d) A, (e) B, (f) C tested in pure water.

Figure 7. Representative worn morphologies of surfaces (a) A, (b) B, (c) C and cross-sections (d) A, (e) B, (f) C tested in saline solution.

The similar wear morphologies are displayed for coating surfaces (figure 7 (a), (b), (c)) and cross-sections (figure 7 (d), (e), (f)) of coatings A, B, C in saline solution. It is noteworthy that some severe
cracks grew inside coating A, and more pits were produced on the rougher surface of coatings B and C, as compared to their wear morphology in pure water. Since aggressive ions Cl⁻ in saline water damage the passivity of Ni and Co, the corrosion-wear synergic effect accelerates the cracks and pits propagation in brittle coating A and Ni contained coating B, C, respectively. However, from coating B and C, no obvious propagated worn features were observed in depth direction. The wear mechanisms of coating A can be reduced to crack initiation and propagation for coating A, and to three-body abrasive wear for coatings B and C.

4. Conclusions
WC–Co and WC-Ni coatings have been deposited by HVOF spraying to investigate their friction and corrosion behavior. It was revealed that initially the WC-Co coating has superior wear and corrosion resistance due to its high hardness. However, cracks were observed in its wear scar, and its wear rate exceeded that of WC-Ni coatings by 2–4 times. The corrosion-wear resistance was found to be controlled not only by coating hardness, but also its powder composition. The WC-CrNi coating under study exhibited excellent wear and corrosion resistance under long-term conditions.

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