Study of alumina sealing of HVOF thermally sprayed WC-Co coatings by sol-gel method

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Abstract
Tungsten carbide (WC) has been known as a hard and wear resistant material. Thermal spray coatings were used widely to deposit Ni and/or Co based WC. The high-velocity oxy-fuel (HVOF) spraying is one of the best methods among thermal spray processes that creates denser coatings with less pores for high corrosive environments applications. In this study, the effect of alumina sealing process on the HVOF WC-12Co coatings by the Sol-Gel method for corrosion and wear properties at high temperature applications was investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were utilized to characterize the morphology and properties of the coatings before and after the sealing process. High temperature wear properties of coatings before and after sealing were tested by ball-on-disk wear tester at 400 °C. The cross-section of the sealed coatings showed that open pores were filled after sol gel. The thickness of the sealed layer was about 14 μm. Results indicated that the sealing process increased the microhardness of coating slightly from 1160 ± 160 to 1250 ± 150 HV. Comparing the results of polarization in 3.5 wt% NaCl solution and wear test showed that the corrosion current density decreased and the wear resistance increased after sealing. A sealed sample with filled open porosity led to recording a higher corrosion resistance (2.9 ± 0.7 μA cm−2) compared to the as sprayed coating (8.90 ± 0.5 μA cm−2). The friction profile of the sealed coating showed reduction of the friction coefficient between 0.25 and 0.5 in comparison to the as-sprayed coating at room temperature (0.4–0.6). Also, the high temperature wear behavior of the sealed coatings was improved. The weight loss was much lower for the sealed coating (5 mg) than that for the as-sprayed coating (13 mg).

1. Introduction
Tungsten carbide has been known as a hard and wear resistant material. The composition of the alloy with soft metals such as Co, Ni, and Cr as a binder, improves the toughness of the brittle fracture of the composite. Coatings of WC-Co by thermal spraying on the surface of substrates are widely used in industries. The WC-Co coatings deposited by high velocity oxygen fuel (HVOF) thermal spray technique possess very dense structure and desired physical properties which make them attractive for a wide range of applications. The WC-Co based thermal spray coatings provide an excellent combination of high hardness, wear resistance and toughness. These special properties make WC-Co coatings as a proper choice to enhance wear resistance of engineering components such as cutting tools, extrusion dies, rollers, etc [1].

Since the pores and cracks negatively affect most properties of sprayed coatings, the sealing of these coatings has been developed. The sealing is a post-spraying treatment which means the filling or closing of near-surface pores and cracks, and a wide variety of methods have been presented. One such method is laser remelting of the top surface, which has been successfully used. However, problems arise when applied to ceramics because of cracking of the remelted zone during cooling, and precipitation of very coarse microstructures. Other methods are infiltration of the coating by molten metals, plastic resins, or aluminum phosphate from which solid materials can be precipitated. Also, the deposition of additional coatings on top of the sprayed layer is a way of
2. Experimental procedure

The substrate material was ST-37 (S355M according to EN 10113-3) carbon steel. Disks with a size of φ50×5 mm were used as substrates. Disks were prepared for spraying by grit blasting with alumina (25 mesh) under 5 bar pressure followed by degreasing in acetone. The mean surface roughness (Ra) of substrates was 8–10 μm.

A commercial agglomerated and sintered WC-12Co (wt%) powder (Amperit 557, H.C. Stark, Goslar, Germany) was sprayed using a HVOF system with K2/GTV, Germany, gun. The HVOF process parameters are listed in table 1.

The sealant solution was prepared by refluxing a mixture of 4 g aluminum triisopropylate (Merck) and 16 g 1,2-Propanediol for 4 h on a heating bath set to 90 °C, followed by cooling to room temperature. The substrates coated with WC-Co were rinsed in acetone, then in ethanol and dried at 120 °C to ensure that the surfaces were free of oil. After cooling, the samples were immersed in the solution with five immersions at a constant speed of 27 mm min⁻¹. The first sample was then cured at 120 °C for 24 h to remove the excess of water and to densify the alumina gel. The second sample was rubbed with 10⁻² M HCl for 20 s to catalyze the gel formation before curing at 120 °C for 24 h.

Right after the sealing and curing process and prior to the corrosion and wear tests, all samples were ground by using SiC paper (1000 grit) in order to remove any excess of sol-gel material from the surface of the thermal spray coating. All corrosion and wear tests were performed at least twice for reproducibility. Only one plot of each test is shown. Corrosion tests were performed in 50 ml aerated and unstirred 3.5 wt% NaCl solution under 5 bar pressure followed by degreasing in acetone. The mean surface roughness (Ra) of substrates was 8–10 μm.

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| Deposition parameter       | Value |
|---------------------------|-------|
| Spraying distance (mm)    | 380   |
| Oxygen (Lit min⁻¹)        | 900   |
| Liquid fuel (Lit min⁻¹)   | 0.43  |
| Powder feed rate (g min⁻¹)| 80    |
3. Results and discussion

3.1. Characterization of WC-12Co powders and HVOF-sprayed coatings

Figure 1(a) shows the SEM micrographs of WC-12Co powders. The agglomerated powder particles of WC-12Co have spherical morphology and porous structure. The particle size distribution of the WC-12Co powders is shown in figure 1(b). The particle size is in the range of 35 ± 10 μm. The scanning electron microscopy image in figure 2 shows the distribution of tungsten carbide particles in cobalt as a matrix in each individual powder. The powder particles consist of tungsten particles of mono-carbide, which is located inside the cobalt metal substrate.

Figure 3 shows the SEM micrographs of the as-sprayed coating. The coating microstructure is relatively dense. Moreover, the coating contains some pores and microcracks resulting from the high velocity impact of semi-molten in-flight particles to the substrate followed by severe plastic deformation and rapid solidification [14]. The porosity percentage in terms of the area fraction of pores, thickness and average surface roughness (Ra) of the coatings are tabulated in table 2.

The XRD patterns of the as-received powders and corresponding coatings are shown in figure 4. The x-ray pattern of the WC-12Co coating shows the presence of WC, W2C phases and η(Co6W6C) in the structure of the coating. Also, No sharp free cobalt peak was detected suggesting that cobalt partially reacted with carbon and tungsten to form η(Co6W6C) phase. The high temperature of the flame causes the dissolution of WC in liquid cobalt followed by carbon oxidizing to form CO/CO2. Then, the W2C phase precipitates from the W-rich liquid phase binder during cooling [14, 15].
3.2. Sealing of WC-12Co coating

Figure 5 shows the cross-sectional SEM micrograph of the sealed coating by sol-gel after 24 h aging and calcination at 500 °C. The coating thickness was around 14 μm. Also, the decrease in porosity throughout all thickness of the specimen is obvious. The average microhardness of each condition is presented in table 3 and

![Figure 3](image)

**Figure 3.** (a), (b) SEM micrograph from the cross-sectional microstructure of WC-12Co coating, (c) BSE image of WC-12Co coating.

**Table 2.** Porosity, thickness and average surface roughness Ra of as-sprayed coatings.

| Coating          | Porosity (%) | Thickness (μm) | Surface roughness Ra(μm) |
|------------------|--------------|----------------|--------------------------|
| WC-12Co coating  | 1–3%         | 583 ± 10       | 5 ± 0/5                  |

![Figure 4](image)

**Figure 4.** The XRD patterns of WC-12Co initial powders and the as sprayed coating.

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The hardness of the coatings is more than that of the composite coating due to the closure of the porosities in the near-surface layers by alumina precipitants.

3.3. Corrosion resistance

The corrosion behavior of the as sprayed and sealed coatings was investigated under different conditions. In relation to the tribological behavior, it should be noted that factors such as porosity, cracks, and phase transformations in the thermal spraying process can have a complex influence on the mechanical properties of coatings. From the point of view of corrosion properties, it has been suggested that the presence of porosity and cracks can decrease the corrosion resistance of the coating. On the other hand, based on the results of XRD from the initial powders and coatings, it was found that the amount of tungsten carbide (WC) phase was reduced due to the decomposition and changing to W2C and some other oxide phases such as C6WO6 (W (CO)6) during the coating process. These amorphous regions could increase the corrosion resistance of the coating. Since the

| Coating          | Microhardness (HV0.3) |
|------------------|-----------------------|
| WC-12Co coating  | 1160 ± 160            |
| Sealed coating   | 1250 ± 150            |

**Figure 5.** SEM micrograph from the cross-sectional microstructure of the sealed coating.

**Figure 6.** Microhardness profiles of the coatings.
amount of these amorphous-nano-crystalline phases are the same in all coatings, the porosity percentage is a controlling factor in the corrosion behavior of the coatings. Corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) were calculated using the Tafel extrapolation method [16]. The potentiodynamic curves (figure 7) and their analyses (table 4) indicated that the sealed coating significantly improved the corrosion resistance of the substrate. According to the results of polarization, the potential evolution of the samples and the extrapolation of the Tafel specimen showed that the sealed samples exhibited the lowest corrosion current density ($2.9 \pm 0.7 \, \mu A \, cm^{-2}$) and the most positive corrosion potential ($-13.4 \pm 366 \, mV$), and thus the highest corrosion resistance. The positive shift of $E_{corr}$ and decrease of $I_{corr}$, as compared to the steel substrate, indicated a significant corrosion inhibition. In general, it can be said that the inhibition mechanism for the sealed coatings could be due to filling the open pores on the surface. Moreover, the corrosive media was exposed to a very low portion of the real coating surface which is in contact with the aggressive solution and also, the shift of $E_{corr}$ toward positive values [17]. Thus, It could be stated that the porosity percentage is the main factor in the corrosion behavior in this study.

### 3.4. Wear measurements

The variations of the coefficient of friction of the sealed and unsealed coatings during wear test at room temperature and under the vertical load of 20 N are shown in figure 8. The coefficient of friction and its fluctuation of the sealed coating were lower than those for the as-sprayed coating.

The SEM micrographs of the worn surfaces after sliding tests are shown in figures 9 and 10. The worn track on the as-sprayed coating exhibited significant sub-surface cracks (figure 9(a)) and showed large amounts of material loss from the surface. It was stated that cracks preferentially propagated through the W$_2$C phase and W-rich binder regions [18, 19] and also spread on the boundary of splats and created a network of sub-surface cracks. This phenomenon is accompanied by a considerable separation of the material from the surface of the coatings with delamination. According to SEM images, some dark regions on the worn surface of the coating can be observed. EDS analysis (table 5) verified that these tribofilms ($A_1$) possess a relatively dense structure.
containing W, Co, Si, C and O. The high percentage of Si in the worn layer (22.85 atomic%) indicated that this layer is formed by the mixing of the materials separated from the coating surface and the SiC ball during the wear test. Also, a porous phase with a sponge-like morphology (B1) can be detected at the underlying surface [20]. The wear mechanisms in the as-sprayed and sealed coatings were abrasive and adhesive wear. The dominant wear mechanism could be adhesive wear followed by delamination.

The tribofilm formation and delamination repeatedly occur all through the sliding test causing severe fluctuation of the friction coefficient.

The SEM-EDS analysis from the wear track of sealed coatings (figure 10) demonstrated a fairly smooth surface. The mechanism of the sub-surface cracks formation and delamination is similar to the as-sprayed coating. Also, it is obvious the width of the sliding film is far less than the as-sprayed coating and decreased the materials transfer from the sliding counterface through adhesive wear. Thus, the friction coefficient of the sealed coatings was noticeably decreased.

During the sliding wear test, the soft and ductile (Co) matrix, which is more prone to plastic deformation, forms a thin layer at the sliding interface in which the carbides are embedded with relatively strong bonding (see figure 8(b)). Therefore, carbide particles are supported by the metallic matrix to perform their wear resistance function against SiC ball, resulting in the substantial decrease in the sliding wear rate. In addition, the presence of the metallic layer containing WC particles on the wear track reduces the actual area of surface contact between the coating and SiC ball [15, 21], causing the lower friction coefficient with insignificant oscillation. This is also confirmed by EDS analysis that shows extremely low Si content in the worn surface of the sealed coating (table 5). Thus, The wear mechanisms in both coatings were not changed significantly.

3.5. High temperature (HT) sliding test results

Variation of the high temperature friction coefficient of coatings at 400 °C is depicted in figure 11. The HT-friction profile of the as-sprayed coating shows an initial rise to 0.5 followed by a sudden decrease to 0.4 and, then, a fluctuating growth to the range of about 0.4–0.65. Also, there is a different behavior between the sealed coating and as-sprayed coating. The coefficient of friction for the sealed is almost constant and varies between 0.6 and 0.3.

The significant differences observed in the HT-wear rate and friction coefficient of the coatings can be interpreted with the aid of morphological and chemical analyses of the worn surfaces. High temperature wear track of WC-12Co (figure 12) revealed the formation of a tribofilm with plastic deformation, induced by high temperature sliding conditions, cracks formation mainly at the interface and delamination [22]. Over time, the

Figure 8. Variations of the friction coefficient of (a) as-sprayed and (b) sealed WC-12Co coating at room temperature.
tribofilm was broken and disconnected from the surface that helps to increase the wear rate. Therefore, the formation and separation of tribofilm that occurs alternately during high temperature can lead to severe fluctuations in the friction coefficient of the WC-12Co coating. During the plastic deformation process, the slip in some areas of the surface that have a different phase in the areas of accumulation of tungsten particles monocarbide remains or porous oxide stopped and by creating stress concentration points, conditions provide for cracking and creating a cavity. In addition to some areas of high wear levels, traces of cracks are observed occasionally.

Figure 13 shows the weight loss of different coatings at room temperatures and 400 °C. The as-sprayed coating exhibited lower wear resistance compared to the sealed coatings. As the test temperature increased to 400 °C, the friction coefficient of the coating was comparatively lower than that measured at room temperature. The reason is that the worn surfaces at high temperature significantly influences the sliding wear behavior after a long-term high temperature contact. It could cause the oxidation of wear debris and create oxide layers that can avoid the adhesion between the coating and the SiC ball and possess self-lubricant function. The wear rate of coatings increased with increasing the substrate temperature. Increasing the substrate temperature promoted the formation of oxides on the coating surface and reduced the coating hardness, resulting in coating delamination. In summary, it can be concluded that the sealed coatings exhibited better wear resistance under room and high temperature operating conditions [23].

Figure 9. (a)–(c) SEM images from the worn surface of the as-sprayed WC-12Co coating at different magnifications. (d), (e) EDS results obtained for worn surfaces of the as-sprayed WC-12Co coating.
4. Conclusions

The sealing process by the sol-gel method to form alumina precipitation was performed on WC/12Co coatings deposited by HVOF. The thickness of the sealed layer was around 14 μm. The results showed that the corrosion barrier properties and wear resistance of the sealed coating were improved by using aluminum triisopropylate as a sealing agent. Compared to the as-sprayed WC-12Co coating, the sealed coating exhibited lower corrosion...
current density \((2.9 \pm 0.9 \mu \text{A cm}^{-2})\) versus \((8.90 \pm 0.5 \mu \text{A cm}^{-2})\), higher corrosion potential \((-366 \pm 13.4 \text{ mv})\) versus \((-4.34 \pm 33 \text{ mv})\) and made acceptable improvement of corrosion resistance in 3.5 wt\% NaCl solution. The dominant wear mechanism for the as-sprayed and sealed coatings was adhesive
wear such as sub-surface crack formation induced delamination, while it was proposed that the presence of the metallic layer containing WC particles on the wear track caused the lower friction coefficient with insignificant oscillation. Results of temperature effect on wear properties exhibited that the wear resistance of the sealed coating was improved at room and high temperature.

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