High-velocity oxygen-fuel spray parameter optimization of nanostructured WC–10Co–4Cr coatings and sliding wear behavior of the optimized coating

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ABSTRACT

In this paper, the Taguchi method was employed to optimize the spray parameters (spray distance, oxygen flow and kerosene flow) to achieve the highest hardness and, in turn, the best wear resistance of the high-velocity oxygen-fuel (HVOF) sprayed nanostructured WC–10Co–4Cr coating by investigating the correlation between the spray parameters and the hardness. The important sequence of spray parameters on the hardness of the coatings is kerosene flow > oxygen flow > spray distance, and the kerosene flow is the only significant factor. The optimal spray parameter (OSP) for the coating is obtained by optimizing hardness (330 mm for the spray distance, 2000 scfh for the oxygen flow and 6.0 gph for the kerosene flow). The coating deposited under the OSP with low porosity and high microhardness consists predominately of WC and a certain amount of W2C phases. The coating deposited under the OSP exhibits better wear resistance compared with the cold work die steel Cr12MoV. The material removal of the coating is the extrusion of the ductile Co–Cr matrix followed by the crack and the removal of the hard WC particles.

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1. Introduction

WC–Co based thermal spray coatings are well-established as protective barriers in a diverse range of engineering components requiring high abrasive wear resistance due to the combination of high hardness and adequate toughness [1–3]. Recently, a great interest has been taken in nanostructured WC–Co based thermal spray coatings, which possess superior hardness, fracture toughness and correspondingly improved wear resistance compared to the conventional counterparts as a result of the high density of grain boundaries. However, the nanostructured WC–Co based coatings with a greater surface area of WC particles have higher tendency toward decarburization and dissolution during the thermal spraying process that can degrade mechanical properties [4–6]. It is therefore worthwhile to select a proper thermal spraying process for preparing the nanostructured coatings.

High-velocity oxygen-fuel (HVOF) spraying has been proved to be one of the best methods for spraying nanostructured WC–Co based coatings which are well bonded to the substrate with higher fraction of retained WC, lower porosity and a reduced quantity of detrimental reaction products. This is widely attributed to the combination of higher velocity (around 550 m s−1) and relatively lower temperature (1900–3000 K) [7–9]. Therefore, many attempts have been made to investigate the wear resistance of HVOF sprayed nanostructured WC–Co based coatings. Most investigations [4–6,10–12] revealed that HVOF sprayed nanostructured WC–Co based coatings were superior in wear resistance compared to conventional ones, while other authors [13,14] held the opposite opinion. Furthermore, the influence of the spray parameters (e.g., fuel-chemistry, oxygen flow, kerosene flow, spray distance and spray angle) has been studied in relation to the microstructure of HVOF sprayed nanostructured WC–Co coatings and, in turn, the wear resistance [11,15–17]. However, little attention is paid to the effect of variations in the spray parameters on the microstructure and wear property of the HVOF sprayed nanostructured WC–Co–Cr coatings.

The sliding wear mechanism for the HVOF sprayed WC–Co coatings was earlier investigated by Qiao et al. [11], which was consisted of continuous wear of binder and WC grains, removal of entire WC grains and removal of splats. These mechanisms operated in all coatings to different degrees, depending on the coating properties that resulted from the processing parameters. Picas et al. [18] have carried experiment in optimizing the spray parameters using WokaJet 400 HVOF sprayed system. They showed that a WC–Co–Cr coating with the highest microhardness and a relatively
low level of decarburization of WC particles could be produced by HVOF spraying system using kerosene as liquid fuel, which had the highest wear resistance.

In this work, the HVOF spraying conditions are optimized by an alternative approach based on the Taguchi method [19,20] which allows the simultaneous effect of several process parameters from minimum number of experiments. The objective of this work is to optimize the spray parameters (spray distance, oxygen flow and kerosene flow) to achieve the highest hardness and, in turn, the best wear resistance of the HVOF sprayed nanostructured WC–Co–Cr coating by investigating the correlation between the spray parameters and the hardness, as well as to study the microstructure, wear properties and mechanism of the coating deposited under the optimal spray parameter (OSP).

2. Experimental procedure

2.1. Materials and HVOF thermal spraying procedure

A commercially available nanostructured WC–10 wt.% Co–4 wt.% Cr powder with a size distribution of 5–45 μm was agglomerated by the fine particles (100–500 nm). The coatings were deposited on the AISI 1045 steel substrate by HVOF spray system (Praxair Tafa-JP8000, USA). Prior to spraying process, the substrate samples (50 mm × 25 mm × 3 mm) were degreased in acetone and grit blasted with 30 meshes Al2O3.

To analyze the influence of spray parameters on the hardness of the coatings, the experiments were conducted with three controllable three-level spray parameters: spray distance, oxygen flow and kerosene flow. Other spray parameters, such as argon carrier gas flow rate (23 scfh), powder feed rate (5 rpm), and spray gun speed (280 mm s⁻¹), were kept constant during the experimentation. The experimental parameters and their values used in the study were determined in the light of preliminary experiments, and are given in Table 1.

In this study, the Taguchi method based on a L9 orthogonal array with four columns and nine rows was used to reduce number of the experiments. Each parameter was assigned to a column and nine spray parameter combinations were available. Therefore, only nine experiments are required to study the entire parameter space using the L9 orthogonal array, which had four columns, one column of the array was left empty for the error of experiments. Orthogonality was not lost by letting one column of the array remain empty. The experimental layout for the three spray parameters using the L9 orthogonal array is shown in Table 2.

2.2. Characterization of the as-sprayed coating deposited under the OSP

In order to identify the phases composition, X-ray diffraction (XRD, Bruker D8-Advanced, Germany) was performed on the as-sprayed coatings with Cu Kα radiation and step 0.02°. Microstructures of the as-sprayed coatings were observed by using a scanning electron microscope (SEM, Hitachi S-3400N, Japan). An image analyzer was done to measure porosity. The cross-sectional SEM images of the coating with magnification of 1000 from different positions were used for the porosity measurement. Microhardness measurements were performed on the transverse section of the coating under a load of 2.94 N for 15 s using a Vickers microhardness tester (HXD-1000TC). At least 10 measurements were done for each specimen to ensure the data repeatability.

2.3. Sliding wear test

The sliding wear tests were conducted on a MG-2000 pin-on-disk tribometer (Beilun Balancing Machinery Co. Ltd., Zhangjiakou, China). The test was performed in accordance with the standard ASTM: G99-05. In the test, the upper pin of Al2O3 ball (Ø 6 mm) was stationary, while the counterface disk (Ø 45 mm × 7 mm) was rotated. Mating materials were the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP and the cold work die steel Cr12MoV.

Prior to the test, specimens were prepared by sequential grinding with 240–2000 mesh grade SiC abrasive papers, polished by 2.5 and 0.5 μm diamond pastes, then degreased in acetone in an ultrasonic bath and dried in warm air. Each test was carried out for up to a sliding distance of 1500 m under a load of 70 N without lubrication. The sliding velocity was set to a constant value of 0.9 m s⁻¹. The temperature and the relative humidity varied between 20 and 25 °C and between 40% and 50%, respectively. Mass loss of the specimens was determined by using an analytical balance with an accuracy of 0.1 mg before and after the test. The frictional moments were recorded by a computer consistently. The worn surface morphologies were observed by optical microscope (OM, OLYMPUS BX51M, Japan) and SEM.

3. Results and discussion

3.1. Analysis of the signal-to-noise (S/N) ratio

In Taguchi method, the experimental results are transformed into a S/N ratio, which can be divided into three categories, i.e., the nominal-the-better, the higher-the-better, and the lower-the-better [21,22]. In this work, the higher-the-better performance characteristic for hardness should be taken for obtaining optimal wear resistance performance. The S/N ratio (η) is defined as:

$$\eta = -10 \log(M.S.D.)$$

(1)

where M.S.D. is the mean-square deviation for the output characteristic. The M.S.D. for the higher-the-better performance characteristic can be expressed as:

$$M.S.D. = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{H_i^2}$$

(2)

where n is the number of the test and H_i is the value of hardness for the ith test.

Table 3 shows the orthogonal array and associated experimental results for hardness with calculated S/N ratios. The S/N ratio is calculated based on Eqs. (1) and (2). The optimal spraying condition was found as 62.97 S/N ratio for hardness in L9 orthogonal array in Table 3.

Table 4 shows the S/N response table for hardness, including the mean S/N ratio for each level of the spray parameters and the total mean S/N ratio for the nine experiments. The effect of each spray parameter is separated out at different levels, mainly attributed to the orthogonality of experimental design. The kerosene flow has the highest difference among the values of the three levels, 2.31 dB. Based on the Taguchi prediction, the larger difference between value of S/N ratio, the more influential is the spray parameter. Thus, it can be seen in Table 4 that the kerosene flow appeared the strongest influential factor for hardness.

Fig. 1 shows the mean S/N response graph for hardness. As shown in Fig. 1, kerosene flow exhibits the largest variations. It also
can be seen from Fig. 1 that the mean S/N ratio rises to the top of the curve as the kerosene flow increases to 6.0 gph from 5.0 gph. When the kerosene flow increases to 7.0 gph, the mean S/N ratio bounces back downward. The response of the S/N ratio to the oxygen flow is similar to that for the kerosene flow. However, the mean S/N ratio decreases at first, then increases as the spray distance increases. It is seen that an interaction among the three spray parameters on hardness, and the greater the S/N ratio, the higher the hardness around the desired value. A similar correlation has been also documented by others [18,23]. It has been demonstrated that the hardness of WC–Co–Cr coating increases with increasing the particle temperature and particle velocity [24]. When the kerosene flow and the oxygen flow reach a maximum value, the oxygen content is enough for the complete combustion of the kerosene producing the highest flame temperature, lead to the highest content of the harder W2C phase that from the decarburization of WC particles during the HVOF spraying process and, in turn, the highest hardness of the as-sprayed coating. This view is similar to that proposed by Picas et al. [25]. However, for higher kerosene flow and oxygen flow, the particle temperature decreases due to the excess oxygen (which often acts as cooling gas) and the shorter residence time of the particle into the flame [23,25]. It can be seen that more appropriate values of kerosene flow and oxygen flow are provided under the spray condition of No. 2.

3.2. Analysis of variance (ANOVA)

A statistical analysis of variance (ANOVA) was employed to investigate the significance of the spray parameters towards the hardness, which is critically important for the control of the final response. The ANOVA is performed by separating the total variability of the S/N ratios, which is measured by the sum of the squared deviations from the total mean S/N ratio, into contributions by each of the spray parameters and the errors. The Fisher's values (F) were calculated for each spray parameters. If $F > 4$, the corresponding spray parameter has a significant influence on the quality characteristic [26].

Table 5 shows the results of ANOVA for hardness. As seen in Table 5, it can be concluded that the kerosene flow has the greatest influence on the hardness of the coatings with the 83.92% contribution, while the oxygen flow and the spray distance are the insignificant factors with the 10.62% and 2.05% contributions, respectively. As a result, based on the S/N and ANOVA analyses, the optimal condition is A1, B2, and C2. In another word, the OSP under the same conditions for the experiments to be conducted will be 330 mm for the spray distance, 2000 scfh for the oxygen flow and 6.0 gph for the kerosene flow.
3.3. Phase and microstructure

Fig. 2 shows the XRD pattern for the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP. It can be identified from Fig. 2 that the coating consisted predominately of WC (JCPDS 89-2727) and a certain amount of W2C (JCPDS 35-776), which is in accord with those reported by other researchers for this kind of coating [7,27]. The W2C phase was detected because of the decarburization of WC particles during the HVOF spraying process.

Fig. 3 shows the polished cross-sectional microstructure of the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP. Overall view of the coating, shown in Fig. 3(a), reveals that the coating is very dense and well-bonded to the substrate, which is mainly due to the higher velocity of HVOF thermal spraying. The average thickness of the coating is around 200 μm. A similar morphology has been observed in our previous investigations [8,28–31]. The average porosity value of the coating (measured at a magnification of 1000x) is less than 1% (Fig. 3(b)), which is in agreement with the results of other HVOF sprayed coatings [4,18,23,30].

3.4. Sliding wear behavior

Fig. 4 shows the variation of the friction coefficients with the sliding distance for the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP and cold work die steel Cr12MoV at room temperature. It is shown that there is a short running-in stage at the beginning of the test, then the friction coefficients reach relatively steady-state period with some fluctuation. The sliding distance before the steady-state period is short, which is possibly due to the high contact pressure of 70 N. Yang et al. [32] has shown that the higher the contact pressure, the shorter the sliding distance before the steady state. It is evident that the as-sprayed coating deposited under the OSP exhibited a lower friction coefficient than that of the cold work die steel Cr12MoV over the entire testing time. After reaching the steady-state period, the average friction coefficient of the coating was 0.45, only 66% that of the cold work die steel Cr12MoV (0.68).

The wear volume loss curves of the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP and cold work

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Spray parameter</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>F</th>
<th>Contribution (Pct)</th>
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<tr>
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<td>10.62</td>
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<tr>
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<td>8</td>
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<td>100</td>
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</tr>
</tbody>
</table>

Table 5

Results of the ANOVA for hardness.

Fig. 2. XRD pattern of the as-sprayed coating deposited under the OSP.

Fig. 3. SEM images of a transverse section of the as-sprayed coating deposited under the OSP: (a) a lamellar morphology; (b) pores.

Fig. 4. Friction coefficients of the as-sprayed coating deposited under the OSP and cold work die steel Cr12MoV varied with sliding distance (counterface Al2O3, load 70 N, sliding velocity 0.9 m s⁻¹).
die steel Cr12MoV are shown in Fig. 5. It can be seen that the wear volume loss increases more or less linearly with the sliding distance, which shows that the wear volume loss rate is constant. After sliding for 1500 m, the wear volume losses of the coating and cold work die steel Cr12MoV were 102.4 mm$^3$ and 230.4 mm$^3$, respectively. A simple comparison of volume loss indicates that the wear volume loss of the cold work die steel Cr12MoV was 2.3 times to that of the coating. However, the evaluation of wear properties of the coating and cold work die steel Cr12MoV are not only based on the friction coefficient and volume loss data, but also need further observation of the wear morphology.

Fig. 6 shows the representative OM images of worn morphology for the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP and cold work die steel Cr12MoV against Al$_2$O$_3$ ball at room temperature under a load of 70 N. After sliding for 1500 m, the worn surface of cold work die steel Cr12MoV (Fig. 6(a)) is smoother than that of the coating (Fig. 6(b)). The friction coefficients in Fig. 4 also show that steel Cr12MoV is more stable may mainly due to smoother surface. Fig. 6(a) shows that a lot of ploughed grooves existed on the worn surface of the cold work die steel Cr12MoV, which formed as a result of abrasive wear on the cold work die steel disk. The debris wearing the surfaces as a three-body abrasive was obtained after the fragmentation of wear particle under sliding process, which is due to the relatively low hardness of the cold work die steel Cr12MoV (about 58 HRC) [33]. From Fig. 6(b), it can be noticed that the dimple-like features are covered along the sliding direction, which may trap wear particles and relieve the damage of lubricating film, such as the oxide film of chromium, cobalt and tungsten on the surface. This phenomenon was similar to the results reported by other researchers [34,35].

SEM investigation of the worn morphology of the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP is shown in Fig. 7. A low magnification plan view image of the wear track (Fig. 7(a)) shows that some features associated with the exclusion of the hard WC particles and ductile Co–Cr matrix. The worn surface at a higher magnification (Fig. 7(b)) reveals that the cracks initiate at the carbide–binder interface. Moreover, some scratches form as a result of the abrasion process at the surface. For the nanostructured WC–Co–Cr coating, the ductile Co–Cr matrix undergoes severe deformation at the beginning of the test, and then the matrix is removed under the contact pressure (i.e. 70 N), which will result in the crack being generated and the hard WC particles being pulled out. This phenomenon was similar to the results reported by other researchers [32,36–38]. It is supposed
that the Co and W oxides, which caused by the high temperatures achieved during the sliding process, could decrease the friction coefficient due to their good lubricant properties [37–39].

4. Conclusions

The spray parameters of nanostructured WC–10Co–4Cr coatings prepared by JP8000 HVOF spray system are optimized by the Taguchi method based on a L9 orthogonal array. The main conclusions are as follows:

(1) The optimal spray parameter for HVOF sprayed nanostructured WC–10Co–4Cr coating is obtained by optimizing hardness (330 mm for the spray distance, 2000 scfh for the oxygen flow and 6.0 gph for the kerosene flow). The important sequence of spray parameters on the hardness of the coatings is kerosene flow > oxygen flow > spray distance, and the kerosene flow is the only significant factor.

(2) The HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP has a dense structure and well-bonded to the substrate. The phases of the coating consist of predominately of WC and a certain amount of W2C.

(3) The friction coefficients and wear volume losses of the HVOF sprayed nanostructured WC–Co–Cr coating deposited under the OSP are lower than that of the hard cold steel Cr12MoV. The material removal of the coating is the extrusion of the ductile Co–Cr matrix followed by the crack and the removal of the hard WC particles.

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