Mechanical, Tribological and Microstructure Characteristics of HVOF and Plasma Sprayed Cr3C2-PS.ZrO2 Coatings

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ABSTRACT: The microstructure, mechanical properties and tribological behaviour of Cr3C2 (Chromium carbide) - PS.ZrO2 (Partially stabilized Zirconia) composite coatings prepared with atmospheric plasma spraying and high velocity oxyfuel spraying (HVOF) technologies were systematically investigated. X-ray diffraction and transmission electron microscopy analyses showed that the three kinds of Cr3C2-PS.ZrO2 coatings were mainly consistent with the designed feedstock powders. The three kinds of Cr3C2-PS.ZrO2 coatings have similar and high microhardness. The HVOF Cr3C2-PS.ZrO2 coatings have lower porosity and higher adhesive strength in comparison to the plasma sprayed Cr3C2-PS.ZrO2 coating. The friction coefficients of the HVOF were lower than that of the plasma sprayed coating, and the HVOF coatings displayed better wear resistance. The lower coefficients friction and rate wear of the three coatings at elevated temperatures were attributed to the formation of a compact PS.ZrO2 eutectic lubricating layer on the worn surface.

KEYWORDS: Thermal spray, Hard coating, Solid lubrication, Mechanical properties, Wear

I. INTRODUCTION

Among the existing techniques used for surface engineering, coatings deposited by thermal spraying can provide a cost effective solution for tribological applications in rolling/sliding contact. Some applications include aerospace, turbo engines, heavy machinery, rolls and wear resistant dies, drill bits, wear resistant nozzles and wear components used in the oil exploration and mining industries. However, the properties of coatings deposited by different technologies have significant differences because of the remarkably different flame temperature and the particle’s velocity in the spraying process. It is inferred that high velocity oxyfuel spraying (HVOF) and detonation gun spraying (DS) are superior to plasma spraying for manufacturing wear resistant metallic and cermet coatings.[1,2] Plasma spraying is widely used for ceramics due to its high flame temperature.[3] There were limited studies on the comparison of different coatings deposited by thermal spraying techniques, and most of the studies were concentrated on the comparison of plasma and HVOF coatings.[4–8] The comparison of coatings deposited by three thermal spray technologies (plasma, detonation gun and HVOF spraying) has not been reported,[9–11] especially for thermally sprayed wear resistant solid lubrication coatings. Thermally sprayed Cr3C2 coatings can significantly improve the wear resistance of various sliding components in automotive applications.[12,13] In order to reduce the friction coefficient of Cr3C2 coatings, Ag, CaF2 and BaF2.CaF2 eutectic have been used as solid lubricants to improve their tribological properties.[14–19] Although PS.ZrO2 eutectic is a well known solid lubricant additive and has been used in different antiwear applications, hardly any literature has reported on the comparison of coatings prepared by different thermal spraying technologies using PS.ZrO2eutectic as a solid lubricant. In the present work, an attempt was made to fabricate three kinds of thermally
sprayed Cr3C2-PS.ZrO2 coatings, and the microstructure, mechanical properties and tribological behaviour of three coatings were systematically studied.

II. EXPERIMENTAL WORK

For different thermal spraying technologies, preparation methods of feedstock powders and their properties, such as shape, size distribution, density and flowability, have significant influences on the coating’s performances.[20–22] Therefore, it is not easy and suitable to fabricate different thermal spraying coatings with the same powder. In the present work, three kinds of powders were prepared according to the optimisation of particle sizes, distribution and compositions to be suitable for plasma, HVOF and DS technologies respectively. The powder for plasma spraying was prepared with mixture of nichrome clad Cr3C2 and PS.ZrO2 eutectic. The powders for HVOF and DS were prepared by high speed centrifugal and low pressure spray granulating and drying methods respectively. The compositions and part of properties of the three-feedstock powders are shown in Table 1. A Hall flowmeter was used to test the flowability and apparent density of three Cr3C2-PS.ZrO2 feedstock powders. The Cr3C2-PS.ZrO2 coatings were deposited on low carbon steel substrates by atmospheric plasma spraying (APS) 2000K plasma spraying system, JP-5000 HVOF spraying system and Dnepr-III DS system respectively. The plasma spray power was 30–40 kW, and the spraying distance was 110 mm, with a powder feedrate of 30–40 g min⁻¹. Before coating, the substrate was blast cleaned with coarse Al2O3 particles and plasma sprayed with a NiAl bond coat. The HVOF spraying distance was 350 mm, and the oxygen and kerosene fluxes were 50 m³ h⁻¹ and 21 L h⁻¹, with a powder feedrate of 30–40 g min⁻¹. The DS distance was 180 mm, and the acetylene and a oxygen fluxes were 1 m³ h⁻¹ and 1.25 m³ h⁻¹ with a powder feedrate of 25–30 g min⁻¹. of the as The sprayed Cr3C2-PS.ZrO2 coatings Micro structural details was studied using FEI Quanta 200 FEG scanning electron microscope (SEM), equipped dispersive X-ray analysis system (EDX). The porosity of the sprayed Cr3C2-PS.ZrO2 coatings was derived by image analysis. The constituents of the Cr3C2-PS.ZrO2 powders and derived coatings were studied by X-ray diffraction (XRD) using filtered Cu Ka radiation. Transmission electron microscopy was used to study the details of the phases in the as sprayed Cr3C2-PS.ZrO2 coatings. A Vickers hardness tester with 1.96 N test load and a dwell time of 15 s on polished cross-sections was used to test the Cr3C2-PS.ZrO2 coating’s microhardness. The tensile strength of Cr3C2-PS.ZrO2 was tested WDW-100E microcomputer controlled material testing machine. The friction and wear tests were found out using a HT-1000 ball on disc high temperature tribometer (Ducom Instruments), as shown in Fig.6. [25] The friction and wear tests were carried out with a load of 9.8 N and a sliding speed of 0.188 m s⁻¹, from room temperature to 800°C and 20 min test duration. The coupled balls are Si3N4 ceramic balls with a surface roughness of 0.02 mm (Ra). Before the wear test, the composite Cr3C2-PS.ZrO2 coatings were carefully polished to obtain a surface roughness of 0.2 mm (Ra). The wear volumes of coatings were measured using the Rank Taylor Hobson Talysurf 5P-120 surface profilometer. The wear rates of specimens were calculated as k5W/FS, where W is the wear volume in cubic millimeters, F is the normal load in newtons and S is the total sliding distance in meters. Tests were performed repeated for each frictional pair, and the averaged results of the three repeat tests are reported in this article. The wear volume of Si3N4 removed from the coupled balls was acquired by using a geometric technique, measuring the diameter of the wear scar formed on the ball with an optical microscope and assuming that the wear scar is perfectly circular and flat in order to simplify the calculations. SEM with EDX to identify the lubrication mechanism examined the morphology and chemical compositions of the worn surfaces on the composite Cr3C2-PS.ZrO2 coatings and the counter faces.

III. RESULTS AND DISCUSSION

Characteristics of feedstock powders and as sprayed coatings Figure 1 presents the typical morphologies of three spraying powders. From Fig. 1a, it can be seen that the plasma spraying powder is fine and uniform, with a size range from 38 to 90 mm. The powder is clearly seen to be irregular in shape and possesses sharp edges. From Fig. 1b, the size ranges of detonation gun obtain spheric and round shape particles and HVOF spraying are mainly 38–75 and 15–45 mm respectively.
The three powders contain high nichrome alloy matrix, Cr3C2 reinforced phase and PS.ZrO2 eutectic solid lubricant. The nickel alloy 80Ni–20Cr offers excellent high temperature oxidation/corrosion resistance and mechanical strength. The high temperature strength is further enhanced by chromium carbide particles, which function as a hardener to enhance the antiwear performance of the coating. The PS.ZrO2 eutectic functions as a solid lubricant.

Table 1: Composition and properties of Cr3C2–PS.ZrO2 powders

<table>
<thead>
<tr>
<th>Properties</th>
<th>APS (mass-%)</th>
<th>HVOF (mass-%)</th>
</tr>
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<tbody>
<tr>
<td>PS.ZrO2</td>
<td>8-12</td>
<td>5-9</td>
</tr>
<tr>
<td>Cr3C2</td>
<td>25:75</td>
<td>25:75</td>
</tr>
<tr>
<td>Apparent density / g cm−3</td>
<td>2.3-2.5</td>
<td>1.8-2.0</td>
</tr>
<tr>
<td>Flowability / s/50 g</td>
<td>30-35</td>
<td>55-60</td>
</tr>
<tr>
<td>Particle size /µm</td>
<td>-90+38</td>
<td>-45+15</td>
</tr>
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</table>

Table 1 shows the nominal compositions and some properties of the three-feedstock powders. It can be seen that all the powders show excellent flowability and apparent density, which can guarantee uniform powder feeding in the spraying process to avoid nozzle clogging and ensure the powder to feed into the flame centre to maintain well melting characteristics.

The results of XRD analyses, as shown in Fig. 2, indicate that the major constitutional phases of the three thermally sprayed composite Cr3C2-PS.ZrO2 coatings are nearly the same as that in the feedstock powders

![Fig.2](image)  
**Fig.2:** X-ray diffraction analyses of Cr3C2-PS.ZrO2 powders and their derived coatings: (a) APS; (b) HVOF

This demonstrated that no significant decomposition and oxidation of materials occurred during the spraying and resolidification process. From Fig. 2a, it can be found that compared with feedstock powder, only a small number of
oxide (Cr2O3 and NiO) peaks appeared in the coating, and no obvious Cr7C3 and Cr23C6 peaks were found. The analyses of detonation gun and HVOF coating showed that no obvious oxide and other carbide were found. From Fig. 2, it can also be seen that some diffraction peaks of the coatings became broad, which were related to the grain refinement in the spraying process. However, as pointed out by Zimmermann, the presence of Cr7C3 and Cr23C6 in the as sprayed Cr3C2 coating cannot be proven solely by the XRD approach because their main diffraction peaks coincide with the lines referring to Cr3C2. [26]

The TEM observation shown in Fig. 3 was conducted in order to reveal all the phases in the plasma sprayed Cr3C2-PS.ZrO2 coating.

It was found that, except the obvious phases appearing in XRD analysis, trace amounts of Cr7C3, Cr23C6, NiCrO4, BaCrO4 and CaCrO4 phases were also seen. Further examination showed that Cr7C3 was observed in the area just around the big block of Cr3C2 carbide particles, and Cr23C6 was found within the NiCr alloy matrix. This fact suggests that Cr7C3 resulted from the decarburisation of Cr3C2 owing to the overheating of the particles in the spraying process, and Cr23C6 in the plasma sprayed coating was precipitated during the coating deposition process.

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It can be seen that the coatings and substrates had a very good mechanical bonding, which indicated the coatings high bonding strength. From Fig. 4, it can also be seen that the plasma sprayed Cr3C2-PS.ZrO2 coating had more porosity and less compact microstructure in comparison to detonation gun and HVOF sprayed Cr3C2-PS.ZrO2 coatings. The detonation gun and HVOF sprayed Cr3C2-PS.ZrO2 coatings were more compact and lamellar than the plasma sprayed coating and had no obvious delamination, crack and big pores. Table 2 shows the porosity of three thermally sprayed Cr3C2-PS.ZrO2 coatings. The HVOF sprayed coating showed the lowest porosity, which was 1%. The average porosities of HVOF and detonation gun coatings were 0.98 and 1.4% respectively, which were significantly lower than the porosity in plasma sprayed coating (average 6.8%). Owing to the higher jet velocity, the particles will have more
sufficient deformation during impacting on the substrate in the HVOF and DS processes, leading to a more compact coating microstructure. Figure 5 shows the cross-sectional backscattered electron (BSE) images of the three as sprayed Cr3C2–PS.ZrO2 coatings.

From Fig. 5, it can be found that the three composite coatings exhibited a typical thermal sprayed lamellar structure. The main defect structures in the composite coatings were pores and internal boundaries. The morphology and distribution of different constituents in three Cr3C2–PS.ZrO2 coatings can be clearly found in Fig. 5. Cr3C2 (grey regions), PS.ZrO2 eutectic and little oxide (dark regions) constituents are evident and can be easily identified, mainly as fine, typical lamellar structures with different grey levels in BSE mode. X-ray dot mapping analysis showed that the elements of Ba, Ca and F were in the same splat, which indicated that the eutectic was not decomposed and oxidized during the thermal spraying process. From Fig. 5, it can also be concluded that the detonation gun and the HVOF sprayed Cr3C2–PS.ZrO2 coatings had a more compact and fine microstructure than the plasma sprayed Cr3C2–PS.ZrO2 coating. The microhardness and tensile strength of three as sprayed Cr3C2–PS.ZrO2 coatings are shown in Table 2.

**Table 2 : Properties of three as sprayed Cr3C2–PS.ZrO2 coating**

<table>
<thead>
<tr>
<th>Properties</th>
<th>APS</th>
<th>HVOF</th>
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<tr>
<td>Porosity %</td>
<td>6.8 ± 0.8</td>
<td>0.98 ± 0.1</td>
</tr>
<tr>
<td>Micro Hardness /</td>
<td>410–1001</td>
<td>680 ± 33</td>
</tr>
<tr>
<td>Tensile strength /MPa</td>
<td>28±4</td>
<td>50 ± 5</td>
</tr>
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It can be seen that all three coatings have high microhardness. The tensile strengths of detonation gun and HVOF sprayed Cr3C2–PS.ZrO2 coatings are close to each other, but notably higher than that of the plasma sprayed Cr3C2–PS.ZrO2 coating. This can be attributed to the higher particle velocity in the HVOF and DS processes, which make the particles have more sufficient deformation during impacting on the substrate, leading to a more compact microstructure. The more uniform phase distribution of detonation gun and HVOF sprayed Cr3C2–PS.ZrO2 coatings also play an important role on higher microhardness and cohesive strength. However, for the plasma sprayed Cr3C2–PS.ZrO2 coating, microhardness has a higher variation due to the bigger particle size and the broader size distribution in the feedstock powder and relatively insufficient particle deformation during impacting on the substrate. The microhardness of hard carbide and the soft eutectic phase area in the plasma sprayed Cr3C2–PS.ZrO2 coating are about 930 and 450 respectively. Because of the protection of NiCr layer on particle surface, the decarburization and oxidation of carbide were restricted, which lead to high microhardness for the plasma sprayed coating. The average microhardness values of detonation gun and HVOF sprayed Cr3C2–PS.ZrO2 coatings are 628.6 and 680.7 respectively. The average microhardness of the DS Cr3C2–PS.ZrO2 coating is little lower than that of the HVOF coating. This may be due to the slightly higher PS.ZrO2 content in the DS coating. Generally speaking, the wear resistance of a material
increases with its hardness. Therefore, the high microhardness of three coatings is very helpful to improve their wear resistance.

Sliding friction and wear behaviours of three kinds of coatings Figure 6 presents the friction coefficients of three Cr3C2-PS.ZrO2 coatings sliding against Si3N4 balls from room temperature to 800uC. The plasma sprayed 25NiCr–75Cr3C2 coating was used for comparison. It can be seen that the friction coefficients of the Cr3C2 coating are always higher than three Cr3C2-PS.ZrO2 coatings at all test temperatures. At room temperature, the friction coefficients of three kinds of Cr3C2-PS.ZrO2 coatings are close to that of NiCr/Cr3C2 coating and decrease with increasing ambient temperatures. When the temperature is up to 500uC, the friction coefficients of three Cr3C2-PS.ZrO2 coatings were all significantly lower than that of the NiCr/Cr3C2 coating, which indicates that only when the ambient temperature is sufficiently high can PS.ZrO2 supply effective solid lubrication due to plastic transformation. It can also be seen that the friction coefficients of detonation gun and HVOF Cr3C2-PS.ZrO2 coatings are generally lower than that of plasma sprayed Cr3C2-PS.ZrO2 coating. However, they are almost the same at 700uC. The lowest friction coefficients of plasma, detonation gun and HVOF Cr3C2-PS.ZrO2 coatings appear at 800uC, which are 0.38, 0.29 and 0.23 respectively. From 500 to 650uC, the friction coefficients of detonation gun and HVOF Cr3C2-PS.ZrO2 coatings showed a slight increase, which may be due to the strong friction adhesion between NiCr and Si3N4. As the...
ambient temperature is up to 800uC, the plastic deformation of NiCr increases, resulting in a reduced surface tension, which can weaken the adhesion between NiCr and Si3N4. This phenomenon can also be found in the NiCr/Cr3C2 coating.

However, from Fig-7 it was found that the friction coefficient of the plasma sprayed Cr3C2-PS.ZrO2 coating continuously decreases from 500 to 800uC, which is different from the other test coatings.

That is because the porosity of the plasma sprayed Cr3C2-PS.ZrO2 coating is much higher than the detonation gun and HVOF Cr3C2-PS.ZrO2 coatings. The rough worn surface of the plasma sprayed Cr3C2-PS.ZrO2 coating can effectively cut the adhesion between NiCr and Si3N4. Obviously, the PS.ZrO2 eutectic has been shown to be an effective solid lubricant above 400uC and plays an important role in the variation of friction coefficients. The friction reduction with temperature may also be affected by the presence of Cr2O3, which is an intrinsic solid lubricant above 500uC. [26,27] However, Cr3C2 and NiCr alloy are stable below 700uC, and mild oxidation may happen only when the temperature is above 800uC.

The effect of temperature on the wear rates of three Cr3C2-PS.ZrO2 coatings are shown in Figures 8 and 9.
It can be seen that the wear rates of NiCr/Cr3C2 coatings at elevated temperatures are significantly higher than that at low temperatures. From room temperature to 800°C, the wear rates of detonation gun and HVOF sprayed Cr3C2–PS.ZrO2 coatings are lower than that of plasma sprayed Cr3C2–PS.ZrO2 coating at all times. Below 600°C, the wear rate of HVOF sprayed Cr3C2–PS.ZrO2 coating is notably lower than the DS coating but becomes similar when the temperature is above 600°C. The wear rates of detonation gun and plasma sprayed Cr3C2–PS.ZrO2 coatings decrease sharply when the temperature is above 400°C, which is attributed to the lubrication effect of the PS.ZrO2 eutectic. However, the wear rate of HVOF sprayed Cr3C2–PS.ZrO2 coating just has a slight change and keeps a low value from room temperature to 800°C. As the microstructures of detonation gun and HVOF Cr3C2–PS.ZrO2 sprayed coatings are more dense and compact and have a lower porosity than the plasma sprayed coating, the extent of cracking and delamination of lamellar splats will be lower when exposed to continuous stress. This is the main reason why the wear rates of detonation gun and HVOF sprayed Cr3C2–PS.ZrO2 coatings are lower than that of plasma sprayed Cr3C2–PS.ZrO2 coating. On the other hand, from Fig.9, it can be found the wear rates of Si3N4 balls have significantly decrease when sliding against three Cr3C2–PS.ZrO2 coatings at elevated temperatures.

The wear rates of Si3N4 balls sliding against with three Cr3C2–PS.ZrO2 sprayed coatings are always lower in comparison to sliding against with Cr3C2 coating. This can be attributed to that the soft PS.ZrO2 lubrication film releases the direct contact among hard particles.

For more information about the wear mechanism, the worn surface morphology was analysed by SEM with EDX. Worn surface morphology analysis Figure 10 shows the SEM morphologies of the worn surfaces of three thermal sprayed Cr3C2–PS.ZrO2 coatings at room temperature, 500 and 600°C. [25] For the as sprayed Cr3C2–PS.ZrO2 coatings, pores, intersplat boundaries and other low-density areas pre-existed.
On further deformation during wear tests carried out at room temperature, all these voids elongated and formed long cracks on the wear surface. At room temperature, typical brittle fractures were observed on the worn surface without obvious evidence of plastic deformation. Large wear debris and fine wear particles on the tribocontact surfaces were considered to result from microcracking, crack propagation and delamination. The plasma sprayed Cr3C2–PS.ZrO2 coating has relatively lower intersplat and lamellar cohesive strength with higher porosity, resulting in higher wear rates when compared to detonation gun and HVOF sprayed coatings. At 500 and 600uC, the worn surfaces were covered with smooth PS.ZrO2 eutectic material transfer films for all three coatings. The EDX exhibited that the film surface contained large amounts of Ba, Ca and F, indicating that fluoride particles were ejected out of the reservoirs due to plastic deformation. The higher superficial temperature rise at the contacting surface effectively activated the selflubrication property of the PS.ZrO2 phase and subsequently significantly enhanced the wear resistance and reduced the friction coefficient of the coating. Plastic deformation and continuous formation of PS.ZrO2 transfer films became the dominant wear mechanism at 500 and 600uC. Uniform dispersion of the PS.ZrO2 solid lubricating phase is definitely beneficial for a more efficient exploitation of both the self-lubrication properties of PS.ZrO2 and the wear resisting properties of Cr3C2–PS.ZrO2 under dry sliding wear conditions.

Fig.10: Morphologies (SEM) of worn surfaces of three Cr3C2–PS.ZrO2 coatings: (a) PS, at room temperature; (b) PS, at 600uC; (c) HVOF, at room temperature; (d) HVOF, at 500uC
Using three kinds of composite powders, high performance Cr3C2-PS.ZrO2 coatings were successfully fabricated by plasma, detonation gun and HVOF spraying technologies. The Cr3C2-PS.ZrO2 coatings deposited by HVOF and DS show lower porosity and higher bond strength and microhardness in comparison to the plasma sprayed coating. The friction coefficients of the three kinds of Cr3C2–PS.ZrO2 coatings decreases with increasing temperatures, and the high temperature friction coefficients were significantly lower than that at room temperature. The friction coefficients of HVOF and DS coatings were lower than plasma spraying coating and showed better wear resistance. The friction coefficients and the wear rates of three coatings as well as the wear rates of coupled Si3N4 balls were reduced due to the formation of PS.ZrO2 lubrication films at elevated temperatures.

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