Designs and preparation of advanced HVOF-PVD duplex coating by combination of
HVOF and arc ion plating

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Abstract: Advanced HVOF-PVD duplex coatings were produced on the medium carbon steel by combinations of High Velocity Oxygen-Fuel (HVOF) and arc ion plating. The microstructures and mechanical properties were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) in association with mechanical property measurement. The results show that the duplex coating are composed of an inner NiCr-Cr₃C₂-based HVOF-sprayed layer mainly consisted of γ -NiCr and Cr₃C₂ phases, and an outmost PVD-AlCrN layer containing fcc-AlCrN phase. Duplex coatings reveal more excellent wear resistance when compared to the HVOF-sprayed coating. The improved wear resistance is mainly related to the outmost AlCrN layer with more excellent wear resistance in comparison to the

HVOF-sprayed coating against WC ball. The AlCrN layer deposited on NiCr-75 wt.% Cr₃C₂ duplex coating reveals higher wear resistance than that of the AlCrN layer deposited NiCr-30 wt.% Cr₃C₂ duplex coating. The improvement of wear resistance is mainly associated to its higher surface hardness, load capacity and bond strength. The main wear mechanisms of the duplex coatings are adhesive and oxidation wear, whereas the ones of the single HVOF-sprayed NiCr-Cr₃C₂-based coating are adhesive wear as well as spalling and chipping wear.

Key words: HVOF-PVD duplex coating; NiCr-Cr₃C₂-based coating; AlCrN coating; Microstructure; Mechanical property

1 Introduction

High Velocity Oxygen-Fuel (HVOF) spraying has been widely carried out to improve surface wear resistance of steel parts for industrial applications, which is due to the formation of carbide composites with high hardness, bond strength of coatings to substrate, load capacity and wear resistance, such as WC-Co-based [1-3] or NiCr-Cr₃C₂-based coatings [4-5]. The composite coatings are commonly composed of hard metal phases embedded in soft bonding matrix. However, some micro-pores are commonly observed within the HVOF-sprayed coatings, which interrupt material continuity and further deteriorate its mechanical properties such as surface hardness and wear resistance. Furthermore, soft bonding phases are commonly extruded and removed by its plastic deformation during the severe sliding wear process, resulting in pulling-out of the hard particles [6]. As a result, the applications in some engineering fields such as under more intensive loading conditions are restricted.

Compared with the HVOF-sprayed coatings, the coatings produced by physical vapor deposition (PVD) reveal much higher surface hardness, compact structure and more excellent wear resistance [7-10]. However, due to its intrinsically brittle characteristic, thin thickness and high hardness differences between PVD coating and substrate, the PVD coatings reveal low load-bearing capacity and limit bond strength of coatings to substrate, which restrict PVD applications in some fields of more intensive loading conditions due to the plastic deformation of soft substrate [11]. Therefore, in order to obtain higher load-bearing capacity and more excellent tribological properties, a duplex surface treatment combined with nitriding and PVD

for steels has been widely investigated.

Nitriding-PVD duplex coatings, consisting of an outmost PVD hard coating and an inner nitrided layer, have been carried out to significantly improve lifetime of tool components compared to single PVD-coated or nitrided tools [10, 12-14]. In relative to the substrate, the nitrided layers reveal higher load-bearing capacity and diffusion-type hardness profile that eliminates the danger of stress concentration at the layer-core interface [11-12, 15-16]. In addition, hard nitrided layers provide a stronger supporting effect for the outmost PVD. As a result, the nitriding-PVD duplex coatings show higher load capacity and excellent wear resistance, especially under extensive loads. The similar strengthening mechanisms will occur for the HVOF-PVD duplex coatings in which a thick HVOF-sprayed coating replaces the nitrided layer. In addition, the micro-pores within the HVOF-sprayed coatings will be directly blocked by the outmost smooth PVD coatings, which avoids the soft bonding phases to be removed as the PVD coatings effectively separate the slider and HVOF-sprayed coatings. A few investigations of the advanced HVOF-PVD duplex coatings deposited on the Ti-6Al-4V alloy have been reported yet [17-19], and the duplex coatings shows improved structural integrity and high load capacity. However, the investigations of HVOF-PVD duplex coatings produced on the steels are limit. In the present work, a NiCr-Cr₃C₂-based coating was first produced on medium carbon steel, and then a PVD AlCrN coating was deposited. The microstructure an mechanical properties were systematically investigated, as well as tribological properties against WC counter-ball.

2 Material and methods

2.1 Spray powders

Pure commercially sintered NiCr (Tianjin casting gold surface engineering material technology development co., LTD, particle size: $-45/+15\mu\text{m}$) and commercially sintered NiCr-75 wt.% Cr_3C_2 powders (Tianjin casting gold surface engineering material technology development co., LTD, particle size: $-45/+15\mu\text{m}$) were combined to prepare NiCr-30 wt.% Cr_3C_2 blended powders by a mechanical ball milling tester (Retsch PM 100). The ball milling process parameters are following: chromium-hardened steel containers, GCr15 steel balls with a diameter of 10mm, rotational speed of 200rpm, the ball to powder ratio of 20:1 and milling time of about 2h. Then the NiCr-30 wt.% Cr_3C_2 coating was produced on the substrate by the blended powders. Meanwhile, the NiCr-75wt.% Cr_3C_2 coating was also produced by NiCr-75wt.% Cr_3C_2 powders.

2.2 Sample preparation

The initial material was a commercial medium carbon steel with the carbon chemical composition of 0.42 wt.%, and its hardness was about 220HV. The samples were machined to be plates with a 10mm×60mm×100mm in dimension, and an average surface roughness of the plates was about 0.8 μm . Prior to the HVOF spraying, the TR7500 sand-blasting machine was carried out to blast-cleaned the plates with Al_2O_3 particles to increase the surface roughness (about 3.5 μm) to enhance the bond strength of HVOF-sprayed coatings to substrate. Blasting pressure, blasting distance, nozzle level movement speed and blasting angle were 0.3 MPa,

250mm, 6 mm/sec and 80°, respectively. Then the Sulzer WorkStar-610 HVOF system based on liquid fuel (Kerosene of aviation grade) was carried out to produce HVOF-coated samples. The powders were axial feed by nitrogen. In brief, the main HVOF spraying parameters are listed in Table 1. Then coatings were air-cooled after the HVOF spraying. In order to investigate the effects of HVOF-sprayed layers with different microstructures and hardness values on mechanical properties of the HVOF-PVD duplex coatings, the NiCr-30 wt.% Cr₃C₂ and NiCr-75 wt.% Cr₃C₂ coatings were produced.

Prior to the PVD deposition, the HVOF-coated samples were machined to obtain cubic samples with a 12mm×12mm×3mm in dimension. The cubic samples were polished to be an average surface roughness of about 0.1μm, and then ultrasonically cleaned in alcohol for 15min. Finally, the AlCrN coating was deposited on the HVOF coated samples by arc ion plating (Model AS700). The detailed parameters of the AlCrN coating were shown in Table 2. For convenience, the NiCr-30wt.% Cr₃C₂ and NiCr-75wt.% Cr₃C₂ coatings are labeled as NiCr-30 and NiCr-75, respectively. The NiCr-30wt.% Cr₃C₂-PVD AlCrN duplex coating and NiCr-75wt.% Cr₃C₂-PVD AlCrN duplex coating are labeled as NiCr-30-AlCrN and NiCr-75-AlCrN, respectively.

2.3 Microstructure characterization

All HVOF-PVD duplex coated and HVOF-sprayed samples were ultrasonically cleaned in alcohol before characterization. Cross-sectional microstructures of the HVOF-sprayed coated samples were observed by a Phenom XL scanning electron

microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS). A large angle XRD (Bruker D8 advance X-ray diffractometer) operating with Cu K α radiation at 50kV and 150 mA was performed to identify the phase structure of the NiCr and NiCr-Cr₃C₂ powders, as well as the HVOF-PVD duplex coatings. The scans recorded in the range of 30-100° with a step size of 0.02° and a 0.5s dwelling time.

2.4 Mechanical property measurement

A standard Rockwell-C indentation tester (Wilson/Rockwell B503-R) with a load of 150 kgf and a dwelling time of 15 s was performed to measure the bond property of the HVOF-PVD duplex coatings to substrate, and three Rockwell indent points were measured for each tested samples. The indentation impresses were observed by an optical microscope (OM). In addition, the bond strength of the PVD coatings to substrate was further quantificationally measured by a multifunctional scratch tester (HT-3001) with a load of range of 10-100N. Scratches were made using a diamond Rockwell indenter at a constant of 2 mm/min, and the load speed and distance were 20N/min and 9.0mm respectively. The tester equipped with an acoustic sensor was used to detect the critical load which corresponds to the creation of the first cracks. After the scratch generation, the details in the tracks were observed by SEM. A ball-on-disk tribometer (HT-2005) with WC counter-balls were carried out to measure the friction coefficients under a relative humidity of 15% at room temperature. The hardness of the counter-ball is about 950HV. The applied normal load was 10N, and wear time was 3500s. The diameter of counter-ball and rotational speed were 6mm

and 318 rpm respectively, and tracking diameter and the total sliding distance are about 6mm and 350m respectively. Follow-up wear surface was cleaned by compressed Ar gas. Cleaned wear surface morphologies were observed by SEM, and the volume loss from wear surface of the HVOF-PVD duplex coated samples was measured by a KLA-Tencor AlphaStep P-7 tester. The load capacity of the duplex coatings was measured by a standard Vickers hardness tester with different loads of 50-1000g, and each hardness value is an average of the five test points. The loading, dwelling and unloading times for all Vickers hardness tests are 15 s.

3. Results and discussion

3.1 Powder characterization

Morphologies of the coating powders are shown in Fig.1. It can be seen that the NiCr powders (Fig.1a) reveal spherical particles with smooth surface, and the particle sizes are in the range of 10-50 μ m. EDS analysis shows that the NiCr powders contain about 21.2 wt.% Cr and 78.8 wt.% Ni. XRD certifies (Fig.2a) that the phase structure of the NiCr powder is entirely of γ -NiCr phase with a face-centered cubic (fcc) structure, without Cr phase with a body-centered cubic (bcc) structure. As shown in Fig.1b, the NiCr-75 wt.% Cr₃C₂ powders reveal granular particles with coarse surface, and the particle sizes range from 10 μ m to 50 μ m. The phase structure of the NiCr-75.wt.% Cr₃C₂ powders consist of γ -NiCr and Cr₃C₂ phases as shown in Fig.2a. Magnified image (Fig.1c) shows that the NiCr-75.wt.% Cr₃C₂ powders are composed of numerous cellular sub-particles with about 1-6 μ m in diameter. Morphologies of the blended powders are shown in Fig.1d, and it can be seen that the distribution of the NiCr and NiCr-75 wt.% Cr₃C₂ powders is relative uniform. The phase structure of the blended powders also consists of γ -NiCr and Cr₃C₂ phases.

3.2 HVOF-PVD duplex coating characterization

In previous work [13], the AlCrN coating is entirely composed of alternatively fcc-AlCrN layers with an ultra-high hardness of about 42 GPa and about 3 μ m in thickness, without the appearance of Cr. Details of microstructures of the AlCrN layer can be shown in literature [13]. Due to strong probing depth of X-ray, the phase structure of both the HVOF and PVD layers of the duplex coated samples are

identified as shown in Fig.2b. For the NiCr-30-AlCrN duplex coated sample, in addition to the fcc-AlCrN phase, the diffraction peaks of γ -NiCr, Cr_3C_2 and Cr phases are clearly observed, indicating that the NiCr-30 layer is composed of the γ -NiCr, Cr_3C_2 and Cr phases. It has been reported that decarburization of Cr_3C_2 to Cr_7C_3 or Cr_{23}C_6 occurs for the plasma sprayed Cr_3C_2 -NiCr-based coatings due to high deposition temperature [20-21], whereas the decarburization reaction is commonly not observed for the HVOF Cr_3C_2 -NiCr-based coatings, which is due to the very high spraying speed of the HVOF spraying and powder particles staying shortly in flame stream. However, in some cases the decarburization reaction maybe occurs for the HVOF sprayed coatings [22], but the decarburization almost does not have a detrimental effect on coating wear resistance [23]. Careful observation shows that no diffraction peaks of Cr_7C_3 or Cr_{23}C_6 phase are observed, indicating that the decarburization of the Cr_3C_2 to Cr_7C_3 or Cr_{23}C_6 does not occur. Based on the thermodynamic data [24], the decomposition of the Cr_7C_3 or Cr_{26}C_6 to Cr cannot occur due to it high positive Gibbs free energy at above room temperature. In fact, the phase transformations of Cr_7C_3 or Cr_{26}C_6 to Cr are not observed in reported works [25-26]. In addition, according to Ni-Cr binary alloy equilibrium phase diagram [27], at 21.2 wt.% Cr and 78.8 wt.% Ni chemical point, only γ -NiCr phase occurs, indicating that no Cr phase precipitates from γ -NiCr phase. Therefore, it can be concluded that the Cr should precipitate from γ -NiCr induced by the ion bombardment during the PVD deposition. For the NiCr-70-AlCrN duplex coated sample, the phase structure of the NiCr-70 layer is mainly composed of γ -NiCr and

Cr₃C₂ phases, probably with a few Cr. The Cr precipitation will be carefully investigated in future work.

In the back scatter electron (BSE) imaging mode, the images shows a Z-contrast proportional to $Z^{1.7\sim 2.0}$ [28-29]. Hence, the BSE image contrast is relatively easy to interpret in terms of composition and the structure. In the present work, the BSE image was used to identify the Cr₃C₂ particles due to its low Z-contrast among the γ -NiCr, Cr and Cr₃C₂ phases. As shown in Fig.3a and b, it can be clearly seen that both the HVOF-sprayed coatings with about 400 μ m in thickness reveal dense structure and well bond performance with the substrate. Besides, some micro-pores within the HVOF-sprayed coatings are observed. Careful observation shows that the microstructures of both the NiCr-30 and NiCr-75 coatings are mainly composed of gray and black zones. EDS analysis shows that the gray zones are rich in Ni and Cr atoms, and the black zones primarily contain Cr and C atoms, indicating that the gray and black zones indeed correspond to the γ -NiCr and Cr₃C₂ phases, respectively. For the NiCr-30 coating (Fig.3a), the distributions of both the γ -NiCr and Cr₃C₂ phases are relatively nonuniform, and some typical imperfect boundaries of lamellar appear. The morphologies of the γ -NiCr grains are elongated in the direction parallel to coating surface, which is due to the accumulation of the high speed molten or semi-molten NiCr particles on the substrate [30]. For the NiCr-75 coating (Fig.3b), the Cr₃C₂ particles with irregular shape distribute uniformly in γ -NiCr substrate.

It has been reported that the mechanical properties, especially tribological properties, are significantly affected by surface macroparticles (MPs) [7, 31]. Because

the AlCrN layer of the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coated samples are deposited under the same parameters, indicating that the surface morphologies and roughness of the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coated samples are almost the same, which have been indeed certified by SEM observations and roughness measurements. As shown in Fig.3c, it shows that the MPs, mainly consisted of solid droplets and a few shallow craters, are induced by arc ion plating, which is considered commonly as coating defects. Generally, these MPs emits from the arc spots of the targets, and the collision between atoms or ions arises due to the high applied pressure, for which, atoms or ions can agglomerate into MPs before arriving at the surface coating [32]. It has been reported that the numerous micro-pores are formed within the HVOF-sprayed coatings [1-5]. However, the micro-pores are subsequently blocked by the AlCrN coating. The average surface roughness is measured as shown in Fig.3d, and it is about 0.086 μm .

3.3 Property measurement

Surface hardness tested under different indentation loads commonly reflects a comprehensive hardness of both surface hard coating and the inward soft substrate [10, 12, 16, 33-34]. Fig.4 reveals the surface hardness profiles with respect to the different loads employed to indent the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coated samples. It can be clearly found that the surface hardness of the duplex coated samples is closely dependent on the indentation loads. The surface hardness of the NiCr-75-AlCrN duplex coated sample gradually decreases with the indentation loads, whereas the surface hardness of the NiCr-30-AlCrN duplex coated sample rapidly

lowers (especially before 300g). At the same loads, the surface hardness of the NiCr-75-AlCrN duplex coated sample is always higher than that of NiCr-30-AlCrN duplex coated sample. To qualitatively hint about the load capacity of our HVOF-PVD duplex coatings, the morphological features of the indented surface under different loads were observed by OM. For the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coatings, cracks first appear under the loads of 100 and 150g respectively (as shown the insets in Fig.4). This means that the latter shows much higher load capacity relative to the former. The improved load capacity is mainly related to the HVOF-sprayed NiCr-75 layer with a higher hardness of about 950HV, which provides a much stronger supporting effect for the outmost AlCrN layer when compared with the NiCr-30-AlCrN duplex coating as the hardness value of the HVOF-sprayed NiCr-30 is about 470HV.

Bond strength of the duplex coatings is a notably important property and can directly affect the service lifetime of duplex coated products. Up to now, Rockwell indentation and scratch tests are performed to obtain the bond strength [12,16]. As shown in Fig.5, it can be clearly seen that there are not coating peeling off around indentation impresses, indicating that the bond strength of the AlCrN coatings to substrate is relative high for the NiCr-30-AlCrN and NiCr-75-AlCrN samples. However, some coarse circle and radial cracks are observed at around indentation impress for the NiCr-30-AlCrN duplex coated sample, whereas no cracks are observed for the NiCr-75-AlCrN duplex coated sample. It has been reported that a higher load capacity can be obtained for the hardened supporting layer with a

diffusion-type hardness profile that can lower the danger of stress concentration at the layer/core interface [15-16]. While in our present work, the thickness of HVOF-sprayed layers is thick, and load capacity is mainly related to the hardness of supporting layer. So, some cracks are observed for the NiCr-30-AlCrN sample due to lower load capacity of the NiCr-30 layer.

Quantitative measurements of bond strength of the AlCrN layer to substrate for the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coated samples were carried out by scratch tester, and corresponding measured results are shown in Fig.6. It has been reported that the whole scratch process is divided into three stages: the first cracks stage (LC1), the peeling off stage (LC2) and the complete peeling off stage (LC3) [16, 35-36]. LC2 is commonly used to be considered as bond strength, which is defined as a sign of coating failure. In this work, the LC2 is obtained by combination of A.E. signal and OM image. As shown in Fig.6a, the bond strength of the AlCrN layer to substrate for the NiCr-30-AlCrN duplex coated sample is about 37N, whereas the bond strength of the NiCr-75-AlCrN duplex coated sample is about 55N (Fig.6b). It has been reported that the improved bond strength for the nitriding-PVD duplex coatings is mainly associated with higher load capacity and lower danger of stress concentration at coating/substrate interfaces [15-16]. For the HVOF-PVD duplex coated samples, HVOF-sprayed coatings act a similar effect the same as the nitrided layer. Therefore, it can be claimed that the improved bond strength is mainly related to the higher load capacity and lower danger of stress concentration at interfaces between the AlCrN layer and NiCr-Cr₃C₂-based layer.

Fig.7 reveals the changes in the friction coefficient as a function of the wear time for the NiCr-30, NiCr-75, NiCr-30-AlCrN and NiCr-75-AlCrN coated samples at 10N load force to ball-on-disc. It can be found that the friction coefficients of the NiCr-30 and NiCr-75 coatings with high fluctuations are in the range of 0.7-0.8 and 0.6-0.7 respectively. Measured wear rates show that the wear rates of the NiCr-30 and NiCr-75 coatings are $8.67 \times 10^{-14} \text{ m}^3/\text{Nm}$ and $2.57 \times 10^{-14} \text{ m}^3/\text{Nm}$ respectively. For the duplex coated samples, the wear processes can be divided into three wear stages as follows: before 300s (initial wear stage), the friction coefficients of the two duplex coated samples almost overlap mainly due to almost the same surface morphologies and surface roughness; in the range of 300-2000s (intermediate wear stage), both of the duplex coated samples undergo rapidly wear; and after 2000s (stable wear stage), the friction coefficient of the NiCr-30-AlCrN duplex coated sample exhibits a relatively low fluctuations along the wear time, and its friction coefficient ranges from 0.44 to 0.5, whereas the friction coefficient of the NiCr-75-AlCrN duplex coated sample is relative stable and remains 0.45. The wear rates of the NiCr-30-AlCrN and NiCr-75-AlCrN duplex coated samples are $7.12 \times 10^{-15} \text{ m}^3/\text{Nm}$ and $4.67 \times 10^{-15} \text{ m}^3/\text{Nm}$, respectively. Compared with the NiCr-30 (or NiCr-75) coating, NiCr-30-AlCrN (or NiCr-75-AlCrN) coating shows lower friction coefficient and wear rate, indicating that the duplex coatings reveals much better wear resistance against WC balls. Improved wear resistance is mainly related to the stronger supporting effect of HVOF-sprayed layers (NiCr-30 and NiCr-74) and higher bond strength. The higher the surface hardness of the HVOF-sprayed layer is, the better the wear resistance of

the HVOF-PVD duplex coated samples is. The strength mechanisms of the HVOF layer for the HVOF-PVD duplex coatings are similar with those of the nitrided or nitrocarburized layer for the nitriding-PVD duplex coatings [11-12, 15-16].

Differences in the friction coefficients are closely related to surface morphologies of wear surface. Therefore, SEM observation and element mapping analysis were carried out to further investigate wear behaviors and wear mechanisms of the single-HVOF and duplex coated samples, and corresponding results are shown in Fig.8 through Fig11. As shown in Fig.8, numerous cracks and debris are observed. It is claimed that the soft bonding NiCr phases preferentially extruded and removed by its plastic deformation during the severe sliding wear process, resulting in the hard carbide particles directly contacting with WC ball. Therefore, a greater shear stress occurs at the edges of the carbide particles. When the shear stress exceed bond strength of carbide particles to bonding NiCr substrate, the carbide particles crack or spall and then form spalling pits. Spalling carbide particles act as abrasive particle for abrasive wear, accelerating the failure of coatings [6]. Therefore, the main wear mechanisms of the NiCr-30 and NiCr-75 coatings are adhesion and abrasive wear, as well as spalling and chipping wear.

For the duplex coatings, the wear surface is notably different from the one of the single HVOF-sprayed coatings. As shown in Fig.9a, it can be clearly seen that the wear surface is mainly composed of gray zones and bright zones. Elemental mapping analysis (Figs.9b~f) shows that the bright zones are rich in W and O atoms, whereas the gray zones rich contain Al, Cr and N atoms. This means that the bright zones are

containing-W oxidation films, and the gray zones correspond to the AlCrN layer. The appearances of W and O atoms demonstrate that the adhesive and oxidation wear occur. Fig.10 shows another zone of surface wear of the NiCr-30-AlCrN duplex coated sample. It can be seen that some bright zones are rich in Cr and Ni atoms, which indicates that the spalling and chipping wear also occur for the NiCr-30-AlCrN duplex coated sample. Similar observations were also carried out for the NiCr-75-AlCrN duplex coated sample as shown in Fig.11. It can be found that the wear surface is almost completely covered by bright zones (Fig.11a), and elemental mapping analysis (Fig.11b and c) demonstrates that the bright zones are indeed containing-W oxidation films, without the appearance of the coating spalling and chipping wear. This means that the main wear mechanisms of the NiCr-75-AlCrN duplex coated sample are adhesive and oxidation wear.

Our previous investigations have shown that the wear mechanisms of the AlCrN coatings deposited on the as-received T10 steel substrate are spalling and chipping wear, whereas the ones of the AlCrN deposited on nitrocarburized T10 steel substrate were oxidation wear [10]. The wear mechanisms of duplex coatings are closely dependent on substrate hardness. Higher hardness of substrate can provide a much stronger supporting effect for the outmost PVD coatings, and simultaneously improve interfacial hardness distributions and further enhance bond strength of PVD coatings to substrate. Therefore, the HVOF-PVD duplex coatings shows relative friction coefficients when compared with the single PVD coatings, which is due to the formation of tribochemical films which act as lubrication actions.

Different wear surface morphologies occur for the duplex coated samples as shown in Fig.9a and Fig.11a. For the NiCr-30-AlCrN duplex coated sample, the containing-W oxidation films are discontinuous (Fig.9a), whereas the ones are continuous for the NiCr-75-AlCrN duplex coated sample (Fig.11a). The differences in oxidation films are mainly related to the supporting effect of the HVOF-sprayed layer. For the NiCr-30 layer, it contains too much coarse and soft γ -NiC phases, indicating that the plastic deformation more easily occurs under intensive loads. In addition, the containing-W oxidation films are relatively hard but brittle. Therefore, the containing-W oxidation films are more easily scraped away by WC ball for the NiCr-30-AlCrN duplex coated sample. The broken debris acts as abrasive materials and accelerates coating failure. While for the NiCr-75-AlCrN duplex coated sample, the plastic deformation of the NiCr-75 layer is relative difficultly due to its higher hardness. Therefore, the relative compact containing-W oxidation films are formed on the NiCr-75-AlCrN duplex coated sample. During the wear testing, the following reactions among the fcc-AlCrN, WC ball and oxygen gas, thermodynamically feasible, occur [24,37]:

$$\Delta G_f^T = \Delta G_f^\theta + nRT \ln K$$

$$\Delta G_f^{298} = -861.642 \text{ kJ/mol}$$

$$\Delta G_f^{298} = -1120.04 \text{ kJ/mol}$$

where ΔG_f^T and ΔG_f^{298} are Gibbs free energy of formation at T K and 298 K

respectively; n is molar fraction; R is molar gas constant ($8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); T is reaction temperature (K); and K is equilibrium constant at T K. According to above data, it is concluded that the tribochemical reaction between the WC and oxygen gas more easily occurs than that between the AlCrN and oxygen gas. Generally, the oxidation films effectively separate the real contact between the slider and the coating, and result in considerably enhancing of the wear resistance [38-39]. However, the spalling and chipping wear plays an opposite effect for the coating wear resistance. As a result, the NiCr-75-AlCrN duplex coated sample show lower friction coefficient when compared with the NiCr-30-AlCrN duplex coated sample. In addition, the improved wear resistance is also related to its higher surface hardness, load capacity and bond strength of the NiCr-75-AlCrN duplex coated sample in comparison to the NiCr-30-AlCrN duplex coated sample.

4. Conclusions

In the present work, the NiCr-30 and NiCr-75 coatings were first produced on the surface of medium carbon steel by HVOF system, and then the AlCrN coating was deposited on the HVOF coated samples. The microstructure and mechanical properties were systematically studied by means of XRD, SEM and mechanical property measurement. From the results obtained, the following can be concluded.

(1) An advanced HVOF-PVD duplex coating consisted of an inner thick NiCr-Cr₃C₂-based layer with high hardness and an outmost AlCrN layer with excellent wear resistance was produced on the medium carbon steel by combination of HVOF and arc ion plating.

(2) The HVOF-sprayed layer notably enhances surface hardness, load capacity and bond strength of the HVOF-PVD duplex coatings as a result of the thick HVOF-sprayed layer with higher hardness in comparison to substrate. Hence, the HVOF-PVD duplex coated samples show lower friction coefficients and higher wear resistance against WC ball when compared with the single HVOF-sprayed coatings. The main wear mechanisms of the HVOF-sprayed coatings are adhesive wear as well as spalling and chipping wear, whereas the ones of the duplex coatings are adhesive and oxidation wear. Therefore, the HVOF-PVD duplex treatment is a suitable candidate for improving the mechanical and tribological properties of the medium carbon steels.

(3) For the duplex coatings, the higher the hardness of HVOF-sprayed layer is, the higher the load capacity and bond strength are, and the better the wear resistance

is.

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References:

- [1] Y.C. Zhu, C.X. Ding, K. Yukimura, T.D. Xiao, P.R. Strutt, Deposition and characterization of nanostructured WC-Co coating, *Ceram. Int.* 27(2001)669-674.
- [2] L. Jacobs, M.M. Hyland, M. De Bonte, Comparative study of WC-Cermet coatings sprayed via the HVOF and the HVOF process, *J. Therm. Spray Technol.* 7(1998)213-218.
- [3] V. Bonache, M.D. Salvador, V.D. Rocha, A. Borrell, Microstructural control of ultrafine and nanocrystalline WC-12Co-VC/Cr₃C₂ mixture by spark plasma sintering, *Ceram. Int.* 37(2011)1139-1142.
- [4] M.X. Xie, S.H. Zhang, M.X. Li, Comparative investigation on HVOF sprayed carbide-based coatings, *Appl. Surf. Sci.* 273(2013) 799-805.
- [5] M.A. Zavareh, A.A.D.M. Sarhan, B.B. Razak, W.J. Basirun, The tribological and electrochemical behavior of HVOF-sprayed Cr₃C₂-NiCr coating on carbon steel. *Ceram. Int.* 41(2015) 5387-5396.
- [6] J.K.N. Murty, B. Venkataraman, Abrasive wear behavior of WC-CoCr and Cr₃C₂-20(NiCr) deposited by HVOF and detonation spray processes, *Surf. Coat. Technol.* 200(2006) 2642-2652.
- [7] W.L. Chen, Y. Lin, J. Zheng, S.H. Zhang, S.Y. Liu. S.C. Kwon, Preparation and characterization of CrAlN/TiAlSiN nano-multilayers by cathodic vacuum arc, *Surf. Coat. Technol.* 265(2015) 205-211.
- [8] S.L. Ma, D.Y. Ma, Y. Guo, B. Xu, G.Z. Wu, K.W. Xu, P.K. Chu, Synthesis and characterization of super hard, self-lubrication Ti-Si-C-N nanocomposite coatings, *Acta Mater.* 55(2007)6350-6355.
- [9] D. Tytko, P.P. Choi, D. Raabe, Thermal dissolution mechanisms of AlN/CrN hard coating superlattices studied by atom probe tomography and transmission electron microscopy, *Acta Mater.* 85(2015)32-41.
- [10] W.L. Chen, J. Zheng, Y. Lin, S.C. Kwon, S.H. Zhang, Comparison of AlCrN and AlCrTiSiN coatings deposited on the surface of plasma nitrocarburized high carbon steels, *Appl. Surf. Sci.* 332(2015) 525-532.
- [11] Y. Sun, T. Bell, Drying sliding wear resistance of low temperature plasma carburized austenitic stainless steel, *Wear* 253(2002)698-693

- [12] J. Zheng, S.H. Zhang, P. Wu, S.C. Kwon, M.X. Li, S.Y. Liu, W.L. Chen, Microstructures and mechanical properties of duplex-treated composite s coatings with and without compound layer, *Ceram. Int.* 41(2015) 2519-2526.
- [13] W.L. Chen, J. Zheng, X.N. Meng, S.C. Kwon, S.H. Zhang, Investigation on microstructures and mechanical properties of AlCrN coatings deposited on the surface of plasma nitrocarburized cool-work tool steels, *Vaccum*, 121(2015) 194-201.
- [14] W.S. Baek, S.C. Kwon, S.R. Lee, J.J. Rha, K.S. Nam, J.Y. Lee, A study of the interfacial structure between the TiN film and the iron nitride layer in a duplex plasma surface treatment, *Surf. Coat. Technol.* 114(1999)94-100.
- [15] Y.M. Lin, J. Lu, L.P. Wang, T. Xu, Q.J. Xue, Surface nanocrystallization by surface mechanical attrition treatment and its effect on structure and properties of plasma nitrided AISI 321 stainless steel, *Acta Mater.* 54(2006) 5599-5605.
- [16] W.L. Chen, C.L. Wu, Z.R. Liu, S. Ni, Y. Hong, Y. Zhang, J.H. Chen, Phase transformations in the nitrocarburizing surface of carbon steels revisited by microstructure and property characterizations, *Acta Mater.* 61(2013) 3963-3972.
- [17] E. Bemporad, M. Sebastiani, M.H. Staia, E. Puchi Cahrera, Tribological studies on PVD/HVOF duplex coatings on Ti6Al4V substrate, *Surf. Coat. Technol.* 203(2008) 566-571.
- [18] E. Bemporad, M. Sebastiani, D. De Felicis, F. Carassiti, R. Valle, F. Casadei, Production and characterization of duplex coatings (HVOF and PVD) on Ti-6Al-4V substrate, *Thin Solid Films.* 515(2006)186-194.
- [19] E. Bemporad, M. Sebastiani, F. Casadei, F. Carassiti, Production and characterization of duplex coatings (HVOF and PVD) on Ti-6Al-4V substrate for specific mechanical applications, *Surf Coat Technol.* 201(2007)7652-7662.
- [20] Z. Marcano, J. Lesage, D. Chicot, G. Mesmacque, E.S. Puchi-Cabrera, M.H. Staia, Microstructure and adhesion of Cr₃C₂-NiCr vacuum plasma sprayed coatings, *Surf. Coat. Technol.* 202(2008) 4406-4410.
- [21] M.H. Staia, T. Valente, C. Bartuli, D.B. Lewis, C.P. Constable, Part I: characterization of Cr₃C₂-25% NiCr reactive plasma sprayed coatings produced at different pressures, *Surf. Coat. Technol.* 146-147(2001)553-562.
- [22] S. Hong, Y.P. Wu, Q. Wang, G.B. Ying, G.Y. Li, W.W. Gao, B. Wang, W.M. Guo, Microstructure and cavitation-silt erosion behavior of high-velocity oxygen-fuel (HVOF) sprayed Cr₃C₂-NiCr coating, *Surf. Coat. Technol.* 225(2013) 85-91.

- [23] P. Vuoristo, K. Niemi, A. Makela, T. Mantyla, Proceedings of the 7th National Thermal Spray Conference, 20-24 June 1994. Boston, Massachusetts, 1994, p.121.
- [24] Thermochemical data of pure substances. VCH Verlagsgesellschaft mbH. D-69451 Weinheim, Third Edition, 1995.
- [25] J.K.N. Murthy, K. Satya Prasad, K. Gopinath, B. Venkataraman, Characterisation of HVOF sprayed Cr₃C₂-50(Ni20Cr) coating and the influence of binder properties on solid particle erosion behaviour, Surf. Coat. Technol. 204(2010) 3975-3985.
- [26] L. Janka, J. Norpoth, R. Trache, L.M. Berger, Influence of heat treatment on the abrasive wear resistance of a Cr₃C₂-NiCr coating deposited by an ethane-fuelled HVOF spray process, Surf. Coat. Technol. 291(2016) 444-451.
- [27] ASM Handbook, Alloy Phase Diagrams, vol.3, ASM, Materials Park, OH, 1993.
- [28] L.A. Giannuzzi, M. Utlaut, Non-monotonic material contrast in scanning ion and scanning electron images, Ultramicroscopy. 111(2011) 1564-1573.
- [29] S.B. Wang, J.H. Chen, M.J. Yin, Z.R. Liu, D.W. Yuan, J.Z. Liu, C.H. Liu, C.L. Wu, Double-atomic-wall-based dynamic precipitations of the early-stage S-phase in AlCuMg alloys, Acta Mater. 60(2012) 6573-6580.
- [30] C.W. Lee, J.H. Han, J. Yoon, M.C. Shin, S.I. Kwun, A study on powder mixing for high fracture toughness and wear resistance of WC-Co-Cr coatings sprayed by HVOF, Surf. Coat. Technol. 204 (2010) 2223-2229.
- [31] L. Wang, S.H. Zhang, Z. Chen, J.L. Li, M.X. Li, Influence of deposition parameters on hard Cr-Al-N coatings deposited by multi-arc ion plating, Appl. Surf. Sci. 258(2012) 3629-3636.
- [32] X.S. Wan, S.S. Zhao, Y. Yang, J. Gong, C. Sun, Effects of nitrogen pressure and pulse bias voltage on the properties of Cr-N coatings deposited by arc ion plating, Surf. Coat. Technol. 204(2010) 1800-1810.
- [33] H. Ichimura, Y. Ishii, A. Rodrigo, Hardness analysis of duplex coating, Surf. Coat. Technol. 169-170(2003) 735-741.
- [34] M. Raoufia, Sh. Mirdamadi, F. Mahboubi, Sh. Ahangarani, M.S. Mahdipoor, H. Elmkhah, Effect of active screen plasma nitriding pretreatment on wear behavior of TiN coating deposited by PACVD technique, Appl. Surf. Sci. 258(2012)7820-7825.
- [35] D.B. Lee, T.D. Nguyen, S.K. Kim, Air-oxidation of nano-multilayered CrAlSiN thin films between 800°C and 1000°C, Surf. Coat. Technol. 203(2009) 1199-1204.

- [36] L. Hultman, H.T.G. Hentzell, J.E. Sundgren, B.O. Johansson, U. Helmersson, Initial growth of TiN on different phases of high speed steel, *Thin Solid Films*. 124(1985) 163-170.
- [37] E.A. Lee, K.H. Kim, Deposition and mechanical properties of Ti-Si-N coated layer on WC-Co by RF inductively coupled plasma-enhanced chemical vapor deposition, *Thin Solid Films* 420–421 (2002) 371–376.
- [38] T. Bell, K. Mao, Y. Sun, Surface engineering design: modelling surface engineering systems for improved tribological performance, *Surf. Coat. Technol.* 108–109 (1998) 360–368.
- [39] S.C. Lee, W.Y. Ho, W.L. Pao, Process and properties of CrN coating deposited on plasma nitrided high-speed steel, *Surf. Coat. Technol.* 73 (1995) 34–38.

Figure captions:

Fig.1 SEM images of coating powders. (a) NiCr; (b) NiCr-75 wt.% Cr_3C_2 ; (c) a magnified image of a NiCr- Cr_3C_2 powder in (b); (d) NiCr-30 wt.% Cr_3C_2 .

Fig.2 XRD spectra of coating powders and HVOF-PVD duplex coatings. (a) powders; (b) NiCr-30 and NiCr-75 coating.

Fig. 3 (a-b) Typical cross-sectional observations for (a) BSE, NiCr-30 coating; and (b) SEM, NiCr-75, with a magnified BSE inset; (c) Typical SEM surface morphologies for NiCr-75-AlCrN sample magnified BSE image; (d) Surface roughness of (c).

Fig. 4. Surface hardness of the duplex coatings under various testing loads.

Fig.5 Typical micrographs of Rockwell indentation on the tested coatings. (a) NiCr-30-AlCrN; (b) NiCr-75-AlCrN.

Fig. 6 Micrographs of scratch tests for the duplex coatings. (a) NiCr-30-AlCrN; (a) NiCr-75-AlCrN.

Fig. 7 The friction coefficients of the NiCr-30-AlCrN and NiCr-75-AlCrN coatings at a load of 10N against a 6mm WC counter-ball.

Fig.8 Wear surface morphologies for the NiCr-30 and NiCr-75 samples.

Fig.9 Wear surface morphology for the NiCr-30-AlCrN coating and its elemental mapping analysis. (a) Back scatter electron (BSE)image; (b) Al; (c) Cr; (d) N; (e) W; (f) O.

Fig.10 Wear surface morphology for the NiCr-30-AlCrN coating and its elemental mapping analysis. (a) SEM; (b) Cr; (c) Ni.

Fig.11 Wear surface morphology for the NiCr-75-AlCrN coating and its elemental

mapping analysis. (a) SEM; (b) W; (c) O.

Table:

Table 1 Main spray parameters

Parameter	Oxygen	Fuel	Combustion	Powder	Spray	Kerosene	Spray	Carrier
	(NLPM)	(l/h)	pressure	feed rate	distance	back	angle	gas flow
			(bar)	(g/min)	(mm)	pressure	(°)	rate
						(bar)		(NLPM)
NiCr-30	790	21.6	10.3	45×2	320	13.6	90	10
NiCr-75	880	23.1	10.3	45×2	320	13.6	90	10

Table 2 The parameters of the AlCrN coating processes

Parameters	CrN interlayer	AlCrN work layer
Nitrogen partial pressure (Pa)	2	3
Deposition time (min)	25	180
Arc current (A)	65	75
Bias voltage (V)	-80	-80
	350	350
Temperature (°C)	400	400
	450	450
Targets	Cr	Al ₇₀ Cr ₃₀