Journal of the Korea Academia-Industrial cooperation Society
Vol. 21, No. 6 pp. 204-211, 2020

https://doi.org/10.5762/KAIS.2020.21.6.204
ISSN 1975-4701 / eISSN 2288-4688

Wear Behaviors of WC-CoCr and WC-CrC-Ni Coatings Sprayed by HVOF

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고속화염 용사법으로 제조된 WC-CoCr 코팅과 WC-CrC-Ni 코팅의 내마모 거동

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Abstract The high-velocity oxy-fuel (HVOF) thermal spraying coating technique has been considered a promising replacement for traditional electrolytic hard chrome plating (EHC), which caused environmental pollution and lung cancer due to toxic Cr^{6+}. In this paper, two types of cermet coatings were prepared by HVOF spraying: WC-CoCr and WC-CrC-Ni coatings. The produced coatings were analyzed extensively in terms of the micro-hardness, porosity, crystalline phase and microstructure using a hardness tester, optical microscopy, X-ray diffraction, and scanning electron microscopy (including energy dispersed spectroscopy (EDS)), respectively. The wear and friction behaviors of the coatings were evaluated comparatively by reciprocating sliding wear tests at 25 ℃, 250 ℃, and 450 ℃. The results revealed correlations among the microstructures, metallic binder matrixes, porosities, and wear performance of the coatings. For example, WC-CoCr coatings showed better sliding wear resistance than WC-CrC-Ni coatings, regardless of the test temperature due to the more homogeneous microstructure, Co-rich, Cr-rich metallic binder matrix, and lower porosity.

요 약 경질 크롬 도금은 도금과정에서 유독성 물질인 Cr^{+6}을 배출시키기 때문에 환경오염과 폐암을 유발하고 있어 최근 고속화염 용사법 (HVOF)을 이용한 코팅 방법이 대체 방법으로 각광받고 있다. 본 연구에서는 HVOF 방법을 이용하여 경질 크롬 도금 방법을 대체하기 위한 WC-CoCr과 WC-CrC-Ni 서멧 코팅을 제조하였으며, 제조된 코팅층의 물리적/화학적 특성인 미세경도, 기공도, 결정상 및 미세구조를 경도기, 광학현미경, X-선 회절 (XRD), 주사전자현미경 (SEM) 및 EDS를 이용하여 분석하였다. 코팅층의 마모 및 마찰 거동 분석을 위해 왕복 슬라이딩 마모 테스트 방법을 이용하여 25 ℃, 250 ℃, 450 ℃의 온도에서 실시하였으며, 두 코팅층의 마모/마찰 특성을 비교 평가하여, 코팅층의 내마모 성능이 미세구조와 금속기지 결합제 간의 연관성이 있음을 확인하였다. 결과적으로 미세구조가 균일하고, 기공도가 낮을수록 내마모성이 향상되고, 금속기지 결합제가 많을수록 우수한 내마모성을 나타내는 것으로 확인되었다. 즉, 균일한 미세구조와 과량의 Co, Cr 금속기지 결합제, 낮은 기공도로 인해 온도와 테스트 온도와 관계없이 WC-CoCr 코팅이 WC-CrC-Ni 코팅에 비해 내마모성이 우수한 것으로 나타났다.

Keywords : HVOF, Wear Behavior, WC-CoCr Coating, WC-CrC-Ni Coating, Sliding Wear Resistance

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Received March 3, 2020 Revised March 31, 2020
Accepted June 5, 2020 Published June 30, 2020

1. Introduction

Electrolytic hard chrome (EHC) has been extensively used for many years in applications that require wear and corrosion resistance, such as hydraulic cylinders, rotating shafts, aircraft landing gears, valves, rolls and machines tools. However, the toxicity of the galvanic bath and the hexa-valent chromium ion (Cr6+) are environmental problems leading to high waste-disposal costs. Because of these problems, many researchers have investigated alternatives to EHC such as physical vapor deposition, chemical vapor deposition, plasma nitriding, high velocity oxy-fuel (HVOF), and laser cladding [1]. Recently, HVOF thermal spraying technique was considered as a promising candidate for the replacement of EHC. HVOF sprayed cermet coatings are dense, have high bond strength and retain a high level of carbide. HVOF sprayed cermets like WC-Co, WC-10Co-4Cr (WC-CoCr), Cr_3C_2-NiCr, WC-NiCr and WC-Ni are being investigated to replace hard chrome plating for applications that include ball valves, corrugating rolls, printing rolls and aircraft landing gear. The WC-CoCr coating showed similar properties for friction coefficient to the hard chrome plating, while exhibiting better resistance to abrasive wear [2]. The WC-CrC-Ni coating has better wear resistance than EHC [3]. Therefore, in this work, studies on cermet coatings such as WC-CoCr and WC-CrC-Ni coatings prepared by HVOF spraying have been carried out [4]. The coating properties like micro-hardness, microstructure, porosity, crystalline phase have been analyzed. The sliding wear behaviors such as friction coefficient, volume loss and wear mechanism of coatings at 25 ℃, 250 ℃ and 450 ℃ have been investigated comparatively. Finally, the correlations between microstructures, metallic binder matrixes, porosities and sliding wear resistances of coatings have been established.

2. Experiment

2.1 HVOF coatings preparing and characterizing

In this study, Inconel 718 (IN718) nickel-based superalloy was used as the base material. Grit blasting treatment was performed to allow convenient coating layer formation on the surface of the IN718 by using alumina powder. The commercial WC-CoCr (TAFA 1350VM) and WC-CrC-Ni powder (TAFA 1356VM) were used to form the HVOF coatings on substrate of IN718 with coating processes which have been optimized. Fig. 1 shows the fabrication process and analysis method for WC-CoCr and WC-CrC-Ni coatings. Table 1 and Table 2 list the chemical compositions of the powders and IN718 and optimal coating processes, respectively. The details about the optimization can be found elsewhere [4]. The powder particles were accelerated and heated as they travel through the hot flame of temperature up to 3,500℃ and velocity upto 1,000 m/s [5, 6]. They are molten or partially molten, and a small portion of the particles decomposes during the flight. Particles and droplets impact the surface forming bond with the surface and subsequently building coating by piling up and rapid cooling.

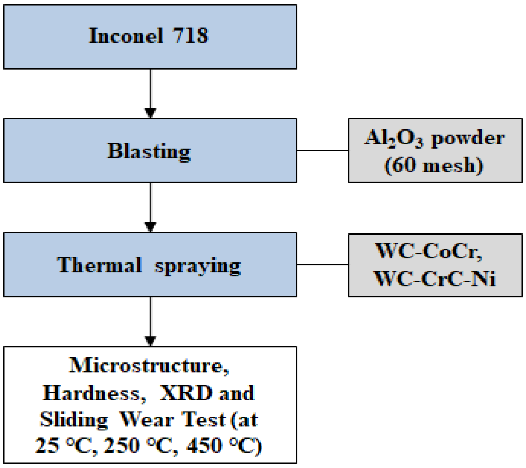

Fig. 1. Schematic diagram of fabrication process and analysis method for WC-CoCr and WC-CrC-Ni coatings

Table 1. Chemical compositions of substrate (IN718) and coating powders (WC-CoCr and WC-CrC-Ni) (wt %)

Element	W		C		Cr	Co		Ni
WC-CoCr	81.3		5.2		4	9.5		
WC-CrC-Ni	68		5		21	-		6
IN 718	C	Cr	Ni	Fe		Nb	Mo	
	0.08	17-21	Bal.	11.16-22.15		4.75-5.5	2.8-3.3	

Table 2. The optimal coating process of HVOF sprayed WC-CoCr and WC-CrC-Ni powder

Parameter / Powder	Oxygen flow rate (FMR)	Hydrogen flow rate (FMR)	Spray distance (inch)	Feed rate (g/min)
WC-CoCr	38	53	7	35
WC-CrC-Ni	38	53	7	25

The microstructure of the as-sprayed WC-CoCr and WC-CrC-Ni coating layers was observed using a scanning electron microscope (SEM), and the hardness of the coating layer was measured through Vickers hardness experiment.

2.2 Sliding wear test

Reciprocating sliding tests (tester: TE77AUTO, Plint & Partners) for WC-CoCr and WC-CrC-Ni coatings were carried out at 25 ℃, 250 ℃ and 450℃ in order to study the effects of temperature on friction, wear behaviors of the coatings comparatively. The sliding distance, frequency, speed, load and time were 16 mm, 2.5 Hz, 0.161 m/s, 10 N and 10 minutes, respectively. The SUS 304 steel balls (diameter 9.53 mm and hardness 227) were selected as counter balls without lubricants. Before tests, the surfaces were polished to Ra 1 ~ 1.4 μm by silicon carbide abrasive paper and diamond paste because of sensitivity to the effect of the initial surface roughness of the coating layer. The friction coefficients were recorded consecutively by the automatic apparatus when tests are carrying out. The morphology and chemical compositions of wear traces had been characterized by SEM and EDS. The depth profiles and volume loss of coatings had been investigated by surface profiler Tencor P-11.

3. Results and discussion

3.1 Characteristic of coatings

Fig. 2 shows the hardness and porosity of WC-CoCr and WC-CrC-Ni coatings coated by HVOF. The micro-hardness values of WC-CoCr and WC-CrC-Ni coatings are 1180 Hv and 1150 Hv, respectively. The difference between the two coatings is negligible although WC-CoCr powder contains more tungsten and less metallic matrix.

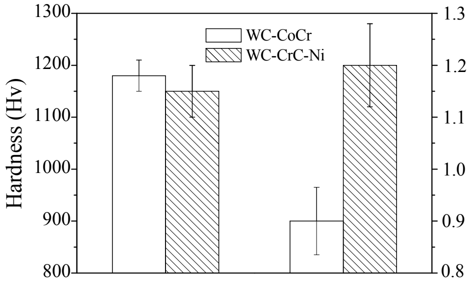

Fig. 2. Hardness and porosity of WC-CoCr and WC-CrC-Ni coatings

The porosities of HVOF coatings are around or less than 1% as reported [5, 7]. In this work, the porosity is 0.9% for WC-CoCr coating and 1.2% for WC-CrC-Ni coating. WC-CrC-Ni coating possesses more 33% pores than WC-CoCr coating.

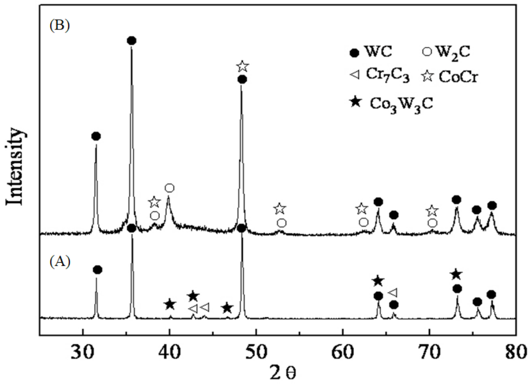

Fig. 3. XRD patternss of HVOF sprayed WC-CoCr feedstock powder (A) and coating (B)

Fig. 3 and 4 show the XRD results of WC-CoCr and WC-CrC-Ni including initial powders and formed coatings. In the powder spectrums, it can be seen that intense peaks are related to WC regardless of powder. Additionally, other weaker peaks such as Co_3W_3C, Cr_7C_3 in WC-CoCr powder and Cr_2O_3, Cr_3Ni_2, Cr_7C_3, Ni_3C in WC-CrC-Ni powder can also be observed. However, in the coating spectrums W_2C peaks have appeared although WC phases remain dominant in both coatings, which reveals that the decarburization of WC has taken place because of the high temperature (upto 3000 ℃) and high velocity flame (upto 1000 m/s) during HVOF spraying when the decomposition temperature of 1250 ℃ for WC is considered [5]. It is well known that W_2C is harmful because it is harder but more brittle than WC. Besides, other carbides such as Co_3W_3C and Cr_7C_3 in WC-CoCr powder and Cr_7C_3 and Ni_3C in WC-CrC-Ni powder can be decomposed in the severe spraying condition. A portion of the free carbon resulting from decomposition of carbides and the excess reagent oxygen forms carbon oxide gases which produce pores inside the coating. It is clear that Cr_2O_3 and Cr_3Ni_2 show excellent stability in WC-CrC-Ni initial powders.

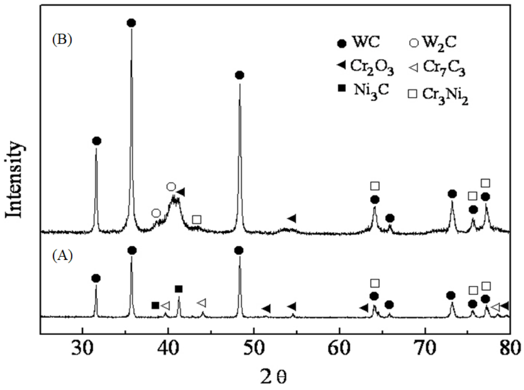

Fig. 4. XRD patterns of HVOF sprayed WC-CrC-Ni feedstock powder (A) and coating (B)

SEM and EDS indicate that the hard ceramic phase WC particles and metallic matrix play different roles in both coatings. WC particles are dominant and compact whereas the metallic matrixes only take a little space in WC-CoCr powder resulting in the homogeneous microstructure between the two phases. In contrast, the content of metallic matrix included in WC-Cr-Ni coating are much more than that in WC-CoCr coating which leads to the relative inhomogeneous microstructure between WC phase and metallic matrix which is considered to influence the wear and friction properties intensively.

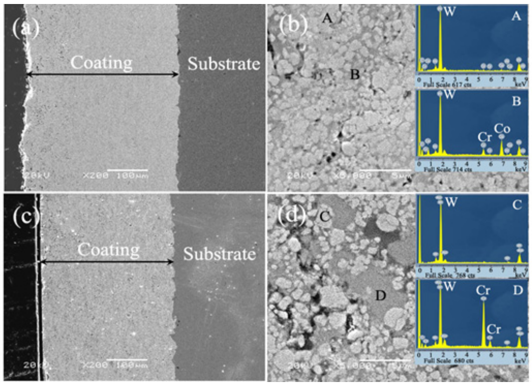

Fig. 5. A comparison of the microstructure between WC-CoCr and WC-CrC-Ni HVOF sprayed coatings. a) SEM profile image of WC-CoCr coating, b) high magnified cross-section of WC-CoCr coating and the EDS analysis of special portion, c) SEM profile image of WC-CrC-Ni coating and d) high magnified cross-section of WC-CrC-Ni coating and the EDS analysis of special portion.

3.2 Wear behaviors

Fig. 6 shows the SEM images of wear traces. The traces on WC-CrC-Ni coating are wider than WC-CoCr regardless of temperature indicating that more surface areas on WC-CrC-Ni have been involved in the sliding wear tests. It seems that the load applied to the counter-balls cause the abrasive effect on the surfaces of coatings, hence some local plastic deformation like wear tracks and scratches can be seen on worn surface. It is also noticeable some cracks which are perpendicular to sliding direction appear on WC-CrC-Ni trace at 450 ℃ in terms of shear stress during reciprocating sliding contact [10, 11].

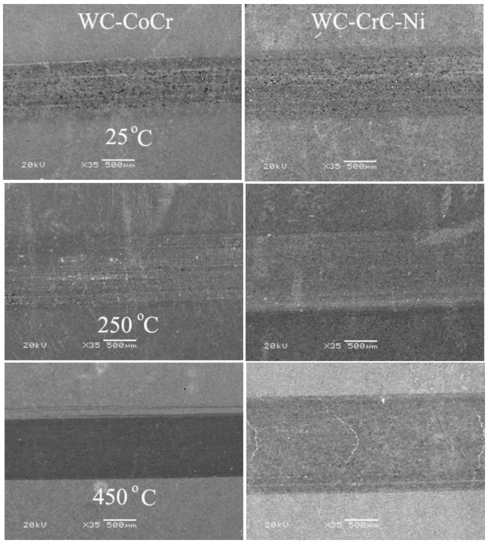

Fig. 6. SEM images of wear trace after sliding wear test

Fig. 7 presents wear traces by the magnified SEM images at 25 ℃. Some white particles with diameter of several micrometers (indicated by black arrow) distribute disorderly on the worn surfaces. The EDS depicts that they are WC particles mixed with some metallic matrix and oxides. These hard particles may work as third-body particles between worn surfaces and counter-balls which scratch the surface and increase the amount of wear loss [10]. It can be also observed that the higher the applied temperature, the less the white particles and the smoother the worn surface.

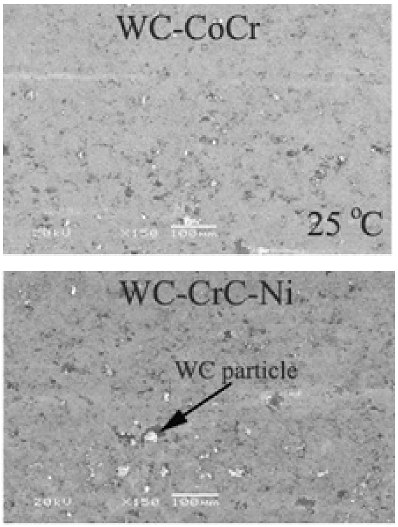

Fig. 7. SEM images of high magnified wear trace after sliding wear test

As shown in Fig. 8, the cross-sections of wear traces are presented. At 25 ℃ and 250 ℃, the wear traces on WC-CoCr are shallow compared with WC-CrC-Ni. And it can be observed that there is evidence of deep detachment and significant damage on both coatings probably due to the abrasive hard particles. However, there is no distinct difference of depth between both coatings at 450 ℃.

Moreover, these worn surfaces without deep detachment or serious damage at 450 ℃ are smoother than that at 25 ℃ and 250 ℃, which is consistent to the SEM images shown in Fig. 6.

Table 3 gives the average friction coefficients for coatings. For the given coating, the values for WC-CrC-Ni coatings decrease with increased

Table 3. The optimal coating process of HVOF sprayed WC-CoCr and WC-CrC-Ni powder

Temp \ Properties	Friction Coefficient		Wear loss (mm^3/N·min)	
	WC-CoCr	WC-CrC-Ni	WC-CoCr	WC-CrC-Ni
25 ℃	0.332	0.359	0.039	0.206
250 ℃	0.420	0.340	0.329	0.438
450 ℃	0.259	0.227	0.726	0.842

temperature, but there is no obvious relation between friction coefficients and temperature for WC-CoCr coating. For the given temperature, the WC-CoCr and WC-CrC-Ni coatings have the similar friction coefficients (with the difference ≦ 0.08) regardless of temperature.

Table 3 also lists the wear rates of coatings which are calculated basing on the profiles of wear traces. On the one hand, it can be seen that the temperature has the same effect on wear rates for both coatings, that is, the wear rates increase when the temperature is raised. On the other hand, WC-CoCr coatings has less wear rates than WC-CrC-Ni coatings at 25 ℃, 250 ℃ and 450 ℃ which means that WC-CoCr coating has better sliding wear resistance than WC-CrC-Ni coating regardless of temperature.

In present paper, the wear mechanism which is called third-body mechanism during sliding wear test has been proposed: when the coatings and counter-balls are taking into sliding contact at the beginning, the soft ductile metallic binder matrix between WC particles undergoes severe deformation by the compression produced by the sliding counter-balls. When the support of the matrix are no longer present, the WC particles are pull-out due to the exhausting of adhesion to matrix, leading to the original formation of wear debris which are called the third-body particles. The third-body particles are entrapped between the worn surfaces and counter-ball to work as the abrasive materials to scratch the surface and increase the amount of wear loss. Therefore the ternary wear mechanism takes place on the combination of third-body particles, coatings and counter-balls [10-11, 13-17].

Depending on this established wear mechanism, it is well known that the sliding wear behaviors of WC-based coatings are affected by the amount, size and distribution of WC particles, the type of metallic binder matrix and porosity. More, finer and more homogeneously dispersed WC particles, the metallic binder matrix with

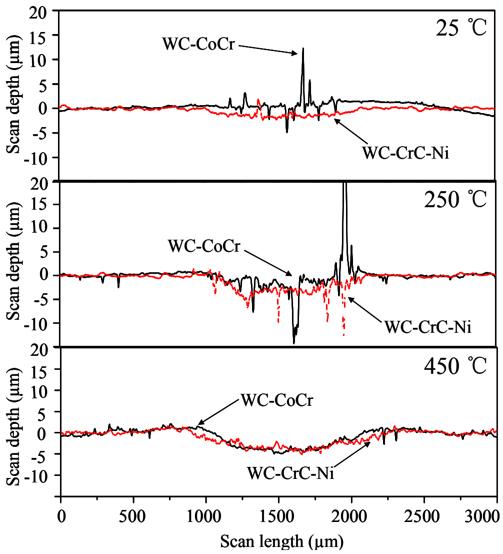

Fig. 8. Depth profiles of wear trace after wear test at 25 ℃, 250 ℃ and 450 ℃

high hardness and toughness and low porosity in coating are benefit to enhance the sliding wear resistance [16-17].

Therefore it can be concluded WC-CoCr coating has better sliding wear resistance mainly due to the following: (1) There are more, compact and homogeneously distributed WC particles in WC-CoCr coating. As shown in Fig. 2, WC particles which are distributed homogeneously and connected with each other are the dominant phase in WC-CoCr coating whereas the amount of WC particles is almost equal to metallic binder matrix in WC-CrC-Ni coating. The WC particles in WC-CrC-Ni coatings are isolated loosely by matrix resulting in the inhomogeneous structure to aggravate the wear on matrix preferentially during the sliding tests. Consequently more abrasive third-body particles can be pull-out and increase the wear loss in WC-CrC-Ni coatings. (2) Co, Cr rich metallic binder matrix in WC-CoCr coatings have higher fracture strength and better adhesive strength with WC particles than Ni, Cr rich metallic binder matrix in WC-CrC-Ni coatings [14, 18]. (3) The WC-CoCr coatings have lower porosity than WC-CrC-Ni. It has been reported the presence of pores on the surface perhaps has the effect of increasing the contact pressure, since there is less materials to support a given load. Finally the rate of r/emoval of materials can be accelerated resulting in the inferiors sliding wear resistance [18].

4. Conclusions

In this work, from the experimental results and discussions of WC-CoCr and WC-CrC-Ni HVOF spraying coatings, the followings can be concluded:

1) The properties of coatings include: the difference of hardness between WC-CoCr coatings (1180 Hv) and WC-CrC-Ni coating (1150 Hv) is negligible, but WC-CoCr coating (0.9%) has less porosity than WC-CrC-Ni coating (1.2%); XRD shows that carbides such as WC, Co_3W_3C, Cr_7C_3 in WC-CoCr powder and WC, Cr_7C_3, Ni_3C in WC-CrC-Ni powder have decomposed during HVOF spraying; WC-CoCr coating has the homogeneous structure whereas WC-CrC-Ni coating has the relative inhomogeneous structure.
2) The wear behaviors of coatings include: the friction coefficients of both coatings are similar at 25 ℃, 250 ℃ and 450 ℃; but WC-CoCr coatings possess better sliding wear resistance than WC-CrC-Ni coatings regardless of temperature due to more homogeneous microstructure to limit the formation of third-body particles, Co, Cr rich metallic binder matrix with high fracture strength and better adhesive strength with WC particles and lower porosity.

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〈Research Interests〉
Thermal barrier coatings, Li-ion batteries