The Influence of Fuel/Oxygen Ratio in HVOF Spraying on the Deposition of Cr₃C₂ Coatings

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This study was performed to investigate the influence of fuel/oxygen ratio ($F/O = 3.2, 3.0, 2.8$) on the characteristics of the HVOF sprayed Cr₃C₂ (7 mass%NiCr) coatings after heat treatment up to 1000°C. Decomposition and oxidation of the Cr₃C₂ occurred during spraying. The degree of decomposition from Cr₃C₂ to Cr₇C₃ was increased with decreasing the F/O ratio. The micro-structural differences of the as-sprayed coatings with F/O ratio cannot be distinguished. However, large pores were diminished and then the coatings became dense by heat treatment. Micro-hardness of the as-sprayed coating which is sprayed with $F/O = 3.0$ condition was the highest ($Hv_{300} = 1140$) and the hardness was increased to 1660 after heat treatment at 1000°C for 50 h in air. It was supposed that hardness was increased due to the formation of Cr₂O₃ within the Cr₃C₂/Cr₇C₃ matrix and the densification of the coating layer during heat treatment. Mass loss of the as-sprayed coating by erosion varied from 79 to 80.8 mg depending on F/O ratio and varied from 47.2 to 49 mg after heat treatment at 600°C. Erosion resistance of the coating was improved about 40% after heat treatment at 600°C. It is concluded that improvement of erosion resistance of the coatings was due to production of the coatings with a very dense microstructure, high cohesive strength and a very high hardness value by heat treatment.

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1. Introduction

WC-Co and Cr₃C₂-NiCr coatings are used for a wide range of applications.¹⁻³⁾ The hardness of WC-Co coating is higher than that of Cr₃C₂-NiCr coating, but WC-Co coating has low thermal expansion coefficient ($6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), poor oxidation and corrosion resistance.⁴⁾ Therefore, WC-Co coating is not used as a hard-facing coating above 650°C. However, Cr₃C₂ coating serves as protection against wear and erosion such as compressor blades, compressor stator vane and bearing housing at high temperature up to 900°C in spite of the relatively low hardness of coating because it is inexpensive and thermal expansion coefficient ($9.3-11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) of Cr₃C₂ is very similar to that of iron ($12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$).^{5,6)}

Hybrid-HVOF spray system has been developed to apply premium turbine engine coatings.⁷⁾ The hybrid-HVOF gun system does not solely rely on water-cooling but also air assisted, whereas conventional HVOF gun system depends on only water-cooling. Therefore, heat loss of hybrid system is much lower than that of conventional HVOF system. And also hybrid gun system produces gas velocity up to 2100 m/s and produces higher particle velocity.⁷⁾ Accordingly, the sprayed coatings are dense and can get higher hardness than those by plasma spraying method. Generally, combustion fuels used in HVOF thermal spraying include propylene, acetylene, propane, hydrogen and kerosene. Coating properties, such as microstructure, phases and mechanical properties, depend on fuel used for HVOF thermal spraying and fuel/oxygen ratio.^{8,9)}

This study is performed to investigate the influence of hydrogen/oxygen ratio ($F/O = 3.2, 3.0, 2.8$) on the characteristics (microstructure, phases, hardness and erosion resistance) of the hybrid-HVOF sprayed Cr₃C₂ (7 mass%NiCr) and also to investigate characteristics after the heat treatment up to 1000°C.

2. Experimental Procedure

Carbon steel was used as substrate. The specimen size was $\Phi 25 \text{ mm} \times t 5 \text{ mm}$. The surface of substrate was blasted with 80-mesh alumina grit after degreasing at 250°C for 1 h and cleaning with acetone. The average surface roughness (Ra) of substrate was 4.15 μm after blasting. Powder in which Cr₃C₂ and NiCr was mechanically mixed in a ratio of 93 to 7 mass% was used with commercial powder (Metco, Diamalloy 3005). Spraying conditions were shown at Table 1. Gas combination was based on the standard condition recommended by manufacturers of the commercial powder.¹⁰⁾ Hydrogen flow rate was 681 slpm constantly and oxygen flow rate was varied at 215, 229 and 243 slpm. Hydrogen/oxygen ratio was consequently 3.2, 3.0 and 2.8. Characteristics of sprayed coatings were observed after heat treatment at 600°C, 800°C and 1000°C for 50 h in air. Microstructure was observed with SEM (Hitachi S-2350). Pore size and pore size distribution of the coatings were made by mercury intrusion method with Micromeritics Pore Sizer 9305. Phase analysis of the coatings was studied with XRD using monochromatized CuK α radiation at 40 kW and 80 mA. Scanning range was $2\theta = 30-60^\circ$. Micro-hardness of the

Table 1 HVOF spraying conditions.

Hydrogen flow rate (SLPM)	Oxygen flow rate (SLPM)	H ₂ /O ₂ ratio	Air flow rate (SLPM)
681	215	3.2	361
	229	3.0	
	243	2.8	
Other conditions: Gun-to-work distance		:200 mm	
Rotating speed		:221 m/min	
Gun traverse rate		:7.8 m/min	

coatings was obtained from cross-sectional specimens by the micro-Vickers hardness tester (Digital Micro Hardness Tester MXT- α 7; Matsuzawa) with a load 300 g for 10 s. In order to compare a relative erosion rate of the coatings depending on fuel/oxygen ratio, erosion was tested at room temperature, an erodent velocity of 60 m/s, an impingement angel of 30°, erodent feeding of 10 g/min and duration time of 30 min after heat treatment up to 800°C for 50 h in air. Erosion rate was determined by sample mass loss divided by the mass of the erodent. The erodent was an angular 80-mesh alumina. The nozzle for the erosion tester was made from 304 stainless steel tube of 6.35 mm outside diameter and 4.72 mm internal diameter. Eroder particles were placed in the air-floating particle hopper that feeds the particles into a nozzle, 500 mm in length, directed vertically downward at the specimen. More detailed description of the erosion apparatus is given in reference.¹¹⁾

3. Results and Discussion

Figure 1 shows the SEM micrograph (a) and particle size distribution (b) of the Cr_3C_2 (7 mass%NiCr) powder. The powder consists of irregular shaped Cr_3C_2 and NiCr mixed mechanically. The average particle size was 15.9 μm and particle size distribution ranges from 5 to 50 μm .

Fig. 1 SEM morphology (a) particle size distribution (b) of the Cr_3C_2 (7 mass%NiCr) powder.

Figure 2 shows the SEM micrograph and pore size distribution of the as-sprayed coatings depending on hydrogen/oxygen ratio (indicate as F/O ratio). The micro-structural differences of the as-sprayed coatings according to F/O ratio cannot be externally distinguished. However, the pore size and pore size distribution were different according to the F/O ratio. The micro-pores under 1 μm and large pores over 10 μm were also observed in coating at F/O = 3.2 condition. And at the F/O = 3.0 condition, the mezzo-pores below 10 μm was distributed. And also, a lot of pores over 1 μm and large-pores over 10 μm were observed at the F/O = 2.8 condition.

Figure 3 is a plot showing the porosity change of the coatings depending on the F/O ratio. The porosity of the coating was varied from 0.69 to 0.99% depending on the F/O ratio. And the porosity of the coating, as shown in Fig. 3, was the highest at F/O = 2.8 condition and was the lowest at the F/O = 3.0 condition. Accordingly, we found that the porosity of the coating was influenced by F/O ratio. The reason is that F/O ratio has an effect on the lamellae structure of the coating because flame temperature and gas velocity were directly controlled by F/O ratio.^{10,12)} Typically the flame temperature increases as the fuel/oxygen ratio decreases and the gas velocity increases as the fuel/oxygen ratio increases, and also high flame temperature is produced when the fuel/oxygen ratio comes closer to stoichiometric ratio (2 in terms of volume).¹³⁾ Consequently, by investigating the effect of the F/O ratio on porosity of the coating, we found that the F/O = 3.0 condition was the optimal condition for hybrid-HVOF thermal spraying of Cr_3C_2 (7 mass%NiCr) powder in the range of this study. Indeed, F/O = 3.0 condition was superior to other conditions not only in porosity but also in hardness and erosion resistance of the coating.

Figure 4 is SEM images showing fracture morphologies and pore size distribution of the as-sprayed coating sprayed with F/O = 3.0 after heat treatment at 600°C and 800°C for 50 h in air. The splats in as-sprayed coating were clearly distinguished but the splats became gradually indistinct with increasing heat-treating temperature from 600 to 800°C. And also the pores ranging from 0.03 to 0.8 μm perfectly disappeared after heat treatment at 600°C. Furthermore, the pores under 5 μm were conspicuously increased but the pores over 8 μm were not observed after heat treatment at 800°C.

Figure 5 is a plot showing the porosity of the coating depending on heat-treating temperature. The porosity of the coating was linearly decreased with increasing heat-treating temperature. It was believed that a conspicuous reduction of the porosity was due to densification of the coating resulting from a sintering effect by heat treatment.

Figure 6 shows XRD patterns of the powder and the coatings sprayed with F/O = 3.0 after heat treatment at 600, 800 and 1000°C for 50 h. Main phases of the powder consisted of Cr_3C_2 and NiCr binder and also Fe_2O_3 was observed. After HVOF-spraying, main phase of the coating, as shown in Fig. 6, was Cr_7C_3 phase. And also a small amount of Cr_2O_3 was observed but NiO was not observed. Generally, phases in the as-sprayed coating consist of Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 and Cr_2O_3 but it is difficult to exactly distinguish Cr_{23}C_6 from the XRD pattern because of overlapping of diffraction line of several carbide phases and NiCr binder.^{12,14)} Cr_7C_3 and Cr_{23}C_6

Fig. 2 SEM microstructure and pore size distribution of the coatings depending on F/O ratio.

Fig. 3 Porosity change of the as-sprayed coatings depending on F/O ratio.

phase may occur by decomposition of the Cr_3C_2 during spraying. However, Cr_{23}C_6 phase seems not to be present in this study. The amount of decomposition is influenced by flame temperature and local oxidation potential. After heat treatment at 600°C , intensity of Cr_7C_3 (151) plane was abruptly increased whereas intensity of Cr_7C_3 (112) plane was decreased. NiO was observed at a nearby 37 and 43.5° and also a complex NiCr_2O_4 oxide was observed nearby 30° after heat treatment at 800°C .

Figure 7 is a plot showing the relative intensity ratio obtained from Cr_3C_2 (121) and Cr_7C_3 (222) after Gaussian fitting with Cr_3C_2 (121) and Cr_7C_3 (222) plane in order to investigate decomposition rate of the coatings depending on F/O ratio and heat treatment. Decomposition rate from Cr_3C_2 to Cr_7C_3 was the lowest at $\text{F/O} = 3.2$, whereas it was the highest at $\text{F/O} = 2.8$. It means that flame temperature at $\text{F/O} = 3.2$ (approximately 2070°C) was relatively lower than flame temperature at $\text{F/O} = 3.0$ (approximately 2097°C) and $\text{F/O} = 2.8$ (approximately 2180°C).¹³ And decomposition of Cr_3C_2 was

Fig. 4 SEM microstructure and pore size distribution of the coating at F/O = 3.0 depending on heat-treating temperature.

Fig. 5 Porosity change of the coating (F/O = 3.0) depending on heat-treating temperature.

accelerated with decreasing F/O ratio. Generally, decomposition rate increases when flame temperature increases and the fuel/oxygen ratio comes closer to stoichiometric ratio.¹³⁾ And after heat treatment up to 800°C, decomposition of the coating gently occurred at F/O = 3.2 but linearly occurred at F/O = 3.0 and F/O = 2.8 by oxidation reaction. However, after heat treatment at 1000°C, as shown in Fig. 7, the fraction of Cr_3C_2 phase at F/O = 3.0 and F/O = 2.8 was similar to that of 800°C, whereas the fraction of Cr_3C_2 phase at F/O = 3.2 was decreased below 10%. From these results, we found that the F/O ratio had an important effect on oxidation behavior of the sprayed Cr_3C_2 coating. And oxidation behavior of the Cr_3C_2 coating depending on F/O ratio is going to be reported.

Figure 8 is a plot showing the average micro-hardness values of the coating depending on F/O after heat treatment up to 1000°C. The micro-hardness value of as-sprayed coatings was from 1099 to 1140 with F/O ratio. Micro-hardness of the as-sprayed coating sprayed with F/O = 3.0 condition

Fig. 6 XRD patterns of the powder and the coating ($F/O = 3.0$) depending on heat-treating temperature.

Fig. 7 XRD intensity ratio of Cr_3C_2 to Cr_7C_3 depending on heat-treating temperature.

was the highest, which was $Hv_{300} = 1140$. And also the micro-hardness value was increased by 300–400 depending on F/O ratio after heat treatment at 600°C . In the case of $F/O = 3.0$ condition, the micro-hardness value was significantly increased up to 1500. It was supposed that hardness was increased due to the densification of the coating layer by sintering effect during heat treatment 600°C .¹¹⁾ And also after heat treatment at 800°C , the hardness was not greatly different from that at 600°C but after heat treatment at 1000°C , though it was somewhat different with F/O ratio, hardness of $F/O = 3.0$, as shown in Fig. 8, was increased up to 1660. It is believed that the coating formed oxide/carbide composite due to the formation of Cr_2O_3 within $\text{Cr}_3\text{C}_2/\text{Cr}_7\text{C}_3$ matrix by

Fig. 8 Micro-Vickers hardness of the coatings depending on F/O ratio.

Fig. 9 Mass loss of the coatings depending on F/O ratio.

internal oxidation of the coating layer.⁵⁾

Figure 9 is a plot showing mass loss of the coating with impingement angle of 30° and Al_2O_3 erodent velocity of 60 m/s in order to study erosion resistance of the coating depending on F/O after heat treatment to 800°C . Mass loss of the as-sprayed coating at $F/O = 3.2$ was 83 mg and also mass loss at $F/O = 3.0$ and $F/O = 2.8$ was 79 and 80.8 mg, respectively. Accordingly, mass loss of the coating seems to be directly related to hardness value of the as-sprayed coating but to be of no relevance to the pore size and pore size distribution of the coating. And also mass loss of the coating was greatly decreased with increasing heat-treating temperature. Erosion resistance of the coating was improved about 40% after heat treatment at 600°C regardless of F/O ratio. And erosion resistance after heat treatment at 800°C was slightly decreased than that after heat treatment at 600°C . In conclusion, it is concluded that improvement of erosion resistance of the coatings was due to production of the coating with a very dense microstructure, high cohesive strength and a very high hardness value by heat treatment. Regrettably, because the speci-

men was not able to be attached to erosion tester by the severe oxidation of the substrate after heat treatment at 1000°C for 50 h, the erosion resistance at 1000°C could not be compared with other temperature conditions.

4. Conclusion

The characteristics of HVOF sprayed Cr_3C_2 (7 mass%NiCr) coatings depending on hydrogen/oxygen ratio are summarized as follows.

(1) The porosity of the coating was the lowest at F/O = 3.0 ratio and linearly decreased with increasing heat-treating temperature.

(2) The decomposition in as-sprayed coating, regardless of the F/O ratio, occurred from $\delta\text{-Cr}_3\text{C}_2$ phase to $\beta\text{-Cr}_7\text{C}_3$ phase but Cr_{23}C_6 phase was clearly not distinguished. And decomposition rate was the highest at the F/O = 2.8 ratio.

(3) The micro-hardness value of as-sprayed coatings was varied from 1099 to 1140 with F/O ratio. Micro-hardness of the as-sprayed coating sprayed with F/O = 3.0 condition was the highest, which was $\text{Hv}_{300} = 1140$. After heat treatment at 1000°C, though it was somewhat different with F/O ratio, hardness of F/O = 3.0 was increased up to 1660.

(4) Mass loss of the as-sprayed coating at F/O = 3.2 was 83 mg and also mass loss at F/O = 3.0 and F/O = 2.8 were 79 and 80.8 mg, respectively. And erosion resistance of the coating was improved about 40% after heat treatment at 600°C. It is concluded that improvement of erosion resistance of the

coatings was due to production of the coatings with a very dense microstructure, high cohesive strength and a very high hardness value by heat treatment.

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