

MICROSTRUCTURE OF INTERFACE BETWEEN HVOF SPRAYED WC-Co COATING AND SPRING STEEL SUBSTRATE^①

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ABSTRACT The microstructure of the interface between the high velocity oxygen-fuel flame (HVOF) sprayed WC-Co coating and spring steel substrate was characterized by electron microscopy. The WC particles embedded in the adhering γ phase of nanometer crystallites were observed in the WC-Co coating. A 2 μm thick diffusive layer of tungsten atoms is present in the spring steel substrate, which implies that atomic movements between the ceramic coating and the metal substrate occur during the HVOF spraying and that may be the main reason of excellent bond between the HVOF sprayed WC-Co coating and the spring steel substrate.

Key words high velocity oxygen-fuel flame spraying microstructure interface

1 INTRODUCTION

Since the thermal spray technique was first present in 1910, it has had a great development and has been widely used to improve the surface properties, such as surface hardness, wear resistance, corrosion resistance, etc of materials, especially of metals and alloys. Along with the requiring of applications and the progressing of materials science, several new flame-spraying techniques have been developed, among them the high velocity oxygen-fuel flame (HVOF) spraying technique developed in 1980s is the most advanced one for getting excellent properties of coating and strong interface bonding between coating layer and substrate of products. The HVOF spraying has got widespread applications^[1] and become an indispensably advanced flame-spraying technique in 1990s. Though the HVOF technique has been used successfully in practice, we are still lacking in understanding of the physical nature of this spraying process, especially the bonding process of the coating materials with the substrate. To further develop the

HVOF technique for meeting the needs of its more widespread uses, it is necessary now to reveal the physical process of HVOF spraying and the causal relationship among spraying process, macroproperties and microstructure of the HVOF sprayed products. Some studies on mechanical and physical properties, structural features, porosities, phase configurations, etc of sprayed coating layers in several HVOF products^[2-4] and also the effects of spraying process on properties and structures of coating layers of HVOF products have been carried out previously^[5-6], but there is a shortage of research work on microstructural characteristics of interface between coating layer and substrate. In this work we have observed the interface microstructure of HVOF sprayed WC-Co coating and spring steel substrate by using an electron microscope equipped with an EDS system. The microstructure characteristics, the amorphous phase grains, the diffusing layer in the bonding area and the nano-crystal in the coating layer are studied. The relationship between the interface

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microstructure and the interface bonding strength is discussed.

2 EXPERIMENTAL

The substrate materials of spring steel (60Si2Mn) were cut into cylinders of $d25\text{ mm} \times 50\text{ mm}$. In one end of each cylinder a female screw socket of $d10\text{ mm} \times 15\text{ mm}$ was made to fix the tensile clamp later. The other end of each cylinder was polished, rinsed, prepared to be sprayed with the WC-Co coating. Before spraying with coating materials, the surface was slightly coarsened with abrasive powder spraying to improve interface bonding. The HVOF spraying was carried out with WC-Co (12%) sintered powder of 300 mesh size by using a Diamant Jet gun produced by American METCO company. The fuel gas was the mixture of oxygen, propane and air, the spray distance was 200~250 mm and the powder supply was 42 g/min. After spraying, the samples of WC-Co coating/spring steel substrate were bound together on the sprayed ends face to face by using a kind of resin with 70 MPa tensile strength and then fixed into a tension machine (AG-50KEN), see Fig. 1. The interface bonding strength of WC-Co coating/spring steel substrate was obtained from this tensile test.

The phase configuration of the coating layer

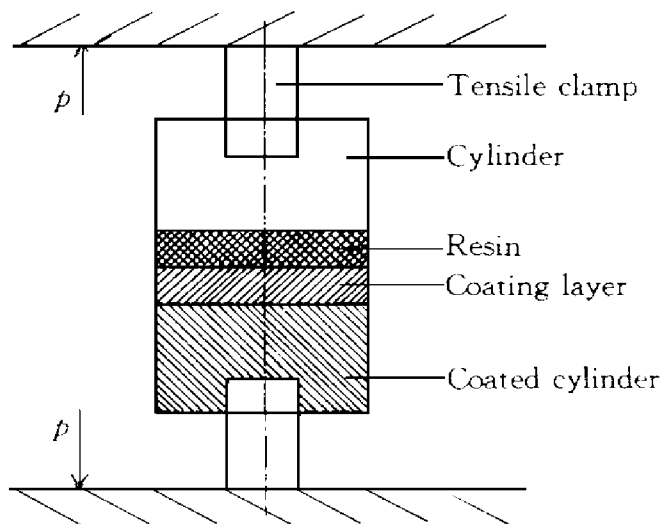


Fig. 1 Schematic diagram of tensile testing for an HVOF coated spring steel cylinder

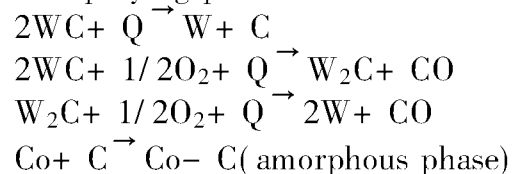
was studied with X-ray diffraction analyses. Some samples of WC-Co coating/spring steel substrate were cut and sliced along axial section of cylinders to prepare the cross-section specimens of coating/substrate interface. A scanning electron microscope (JEM-840) was used to observe and analyze the coating/substrate interfaces. The slices of the coating/substrate cross-section specimens were mechanically ground, polished, dimpled and ion-milled with Ar⁺ by a Gaten Due-Mill machine to prepare the foils for observing with a transmission electron microscope. An analytical transmission electron microscope (JEM-2000FX with LINK EDS system) was used to investigate the microstructure and micro-compositions of the coating/substrate interface.

3 RESULTS AND DISCUSSION

3.1 Bonding strength of coating/substrate interface and phase configuration of coating layer

The tensile test results show that all the samples break up in the resin positions, which means a bonding strength of coating/substrate interfaces higher than 70 MPa as consistent with the previous work^[7].

The X-ray diffraction analyses of the spray powder and the coating layer are shown in Fig. 2 (a) and (b). The coating layer mainly has the same phases as the sintered spray powder, that is WC and W₂C phases. This result implies that the phase transformation of spray materials does not occur obviously in HVOF spraying process. From other work^[6] it is known that some chemical reactions (presented as follows) often occur in flame spraying processes:



Those reactions, especially the formation of brittle Co-C amorphous phase, will deteriorate the properties of coating layer and should be restrained completely. HVOF spraying process has shown its superiority in this respect.

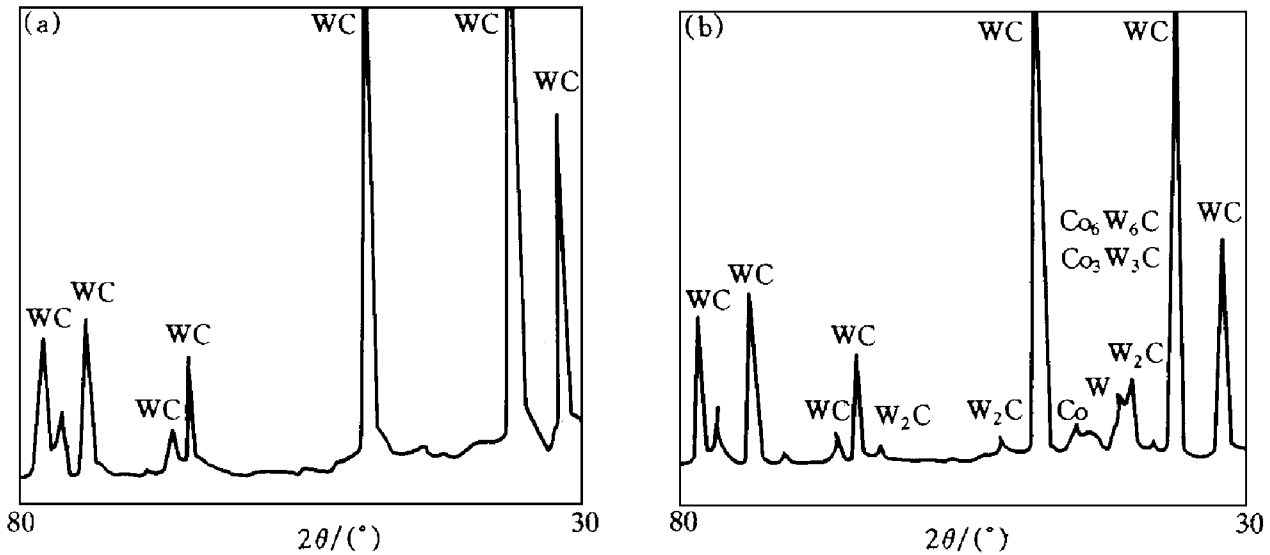


Fig. 2 X-ray diffraction spectra of (a) spray powder, (b) coating layer

3. 2 Composition distribution and diffusive layer in coating/ substrate bonding area

Fig. 3 is a secondary electron image of the HVOF sprayed coating/substrate interface. The boundary is mainly straight, and even well bonded. The composition analysis results for coating layer and substrate are listed in Table 1. The mean compositions of coating layer and substrate are WC-Co (12%) and 60Si2Mn respectively, but there is a few of W being detected in the substrate adjacent to the interface.

Table 2 shows the depth of W atoms diffusing into substrate detected by line-scanning

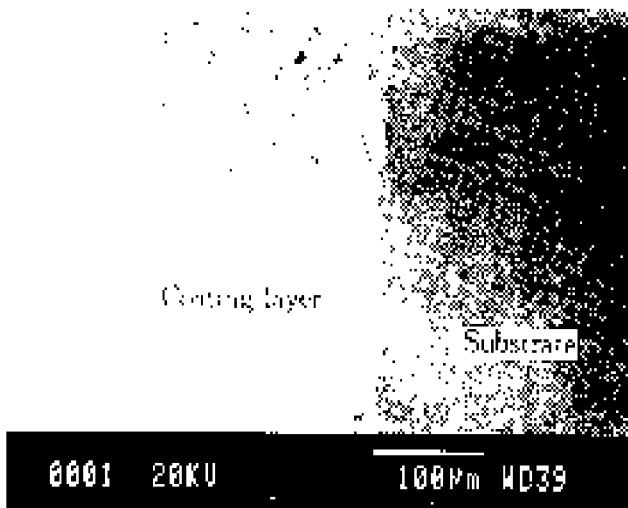


Fig. 3 Secondary electron image of an interface between the HVOF sprayed WC-Co coating and spring steel substrate

Table 1 Compositions of the spring steel substrate and the coating layer(%)

	Substrate				Coating	
	Si	Cr	Mn	Fe	W	Co
1	1.79	0.14	0.68	97.39	87.20	12.80
2	1.55	0.00	0.59	97.86	87.23	12.77
3	1.67	0.17	0.59	97.57	87.17	12.83
average	1.67	0.11	0.62	97.61	87.20	12.80

Table 2 Depth of W atom diffusing to spring steel substrate

Sample	Depth of diffusion/µm
1	1.99
2	2.49
3	1.75
average	2.08

of SEM (scanning electron microscope). The formation of the diffusing layer will greatly increase the bonding strength of interface and must be a main reason of stronger interface bonding produced by HVOF than by other flame spraying processes.

3. 3 Microstructure characteristics of coating/ substrate bonding area

Using a TEM and an EDS (X-ray energy dispersive spectrum) system, we have observed the microstructure and analyzed the micro-com-

positions of the HVOF sprayed WC-Co coating/spring steel substrate interface. Fig. 4 shows the common microstructure of taped crystals in spring steel substrate. Fig. 5 is a microstructure image of coating layer, WC crystal particles are

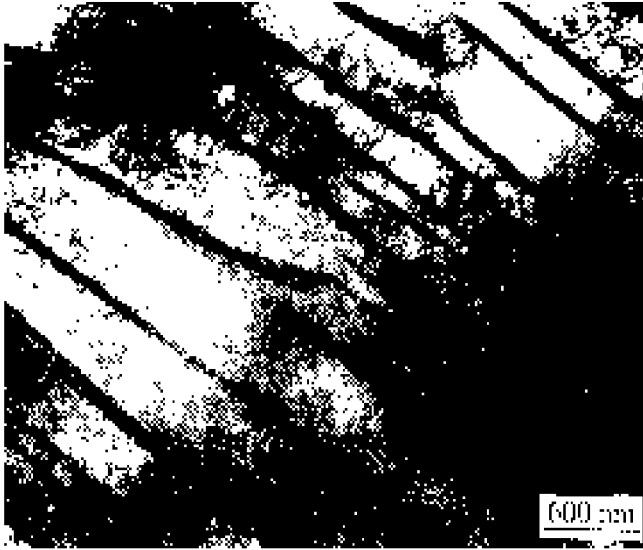


Fig. 4 TEM image from the interior of substrate

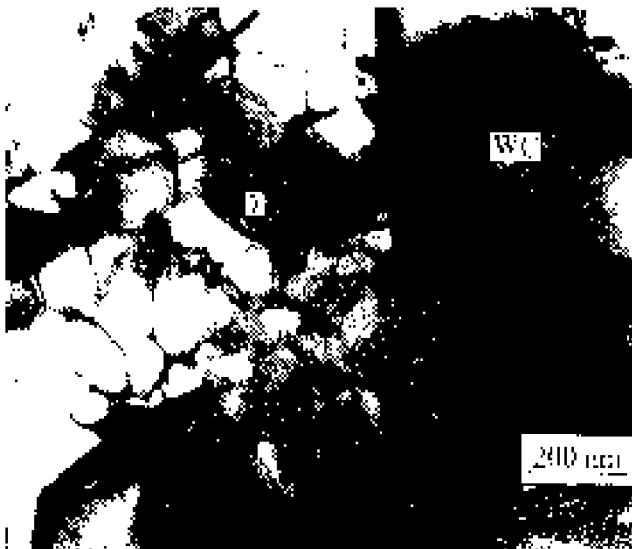


Fig. 5 TEM image of coating layer with WC particles embedded in nano-crystal γ adhering phase

embedded in the adhering phase. An EDS analysis, Fig. 6, showing the composition of the adhering phase in Fig. 5, tells us the adhering phase in coating layer is γ phase, a solid solution phase of WC in Co. The grains of γ phase in the region near coating interface take a nano-crystalline structure and the average grain size is 50 nm. It is obvious that this nano-crystalline struc-

ture can not be inherited from the spray powder, because the powder has been sintered and no nano-crystalline grains can keep antigrowing at a high sintered temperature. It can be deduced, therefore, the nano-crystalline structure of the γ adhering phase in the region near coating interface is formed in a rapid solidification process, which occurs at the moment that the semi-molten spray powder with a very high speed bumps into the cold surface of the spring steel substrate. From this explanation, the grain size of the adhering phase in coating layer should increase with the distance from coating interface and it is exactly proved from our observations about grain size distribution. The nano-crystal grains will make the WC particles well embedded and increase the strength and toughness of the coating greatly.

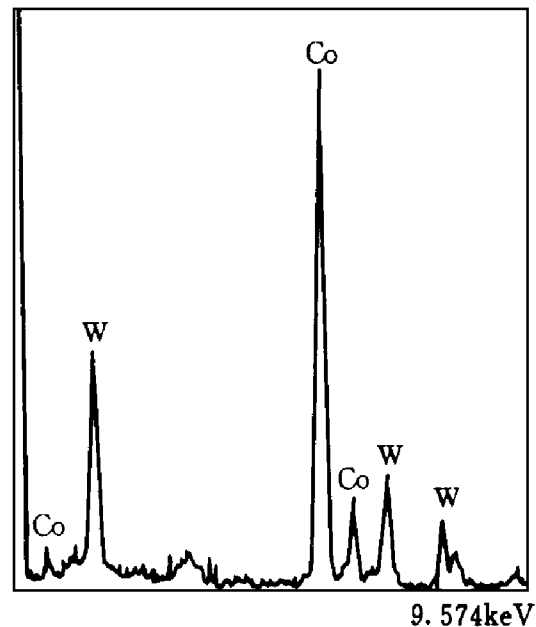


Fig. 6 EDS composition spectrum of the γ adhering phase

Fig. 7 is a TEM image of the coating/substrate interface, the boundary between coating layer and 60Si2Mn substrate seems to be no longer even and straight in such a high magnification, but still well bonded. From TEM observations we have found that there is almost no WC particle located rightly adjacent to the substrate and a layer of adhering phase, thicker or thinner, is there between the WC particles and the nearest substrate grains at the interface. That may be reasonable. The melt point of the γ

adhering phase is much lower than that of the WC particles and, therefore, the adhering phase, but WC particles, becomes molten and shows a better mobility when the spray powder bumps into the substrate, this molten adhering phase will be attached and bonded to the substrate surface more easily and forms a thin layer separating WC particles and substrate grains.

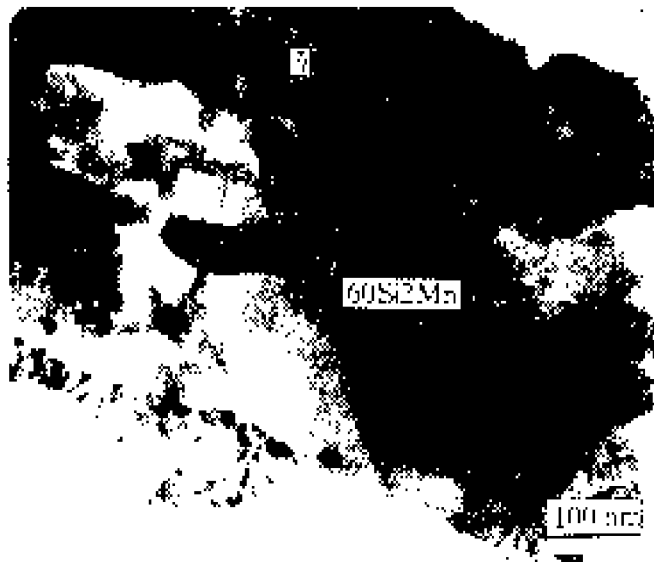


Fig. 7 TEM image of an interface between the HVOF sprayed WC-Co coating and spring steel substrate

The electron diffraction patterns from the substrate and the adjacent coating layer in Fig. 7 are shown in Fig. 8 (a) and (b) respectively, which tells that the substrate grains next to the interface keep the same crystal structure with the interior and that the coating layer rightly next to the substrate grains has an amorphous structure. EDS analyses to this amorphous layer, see Fig. 9, indicate that the Co/W composition of this amorphous phase is different from that of γ phase (comparing Fig. 9 with Fig. 6) and close to η phase. From W-C α -C phase diagram^[8] it is known that the η phase ($\text{Co}_3\text{W}_6\text{C}$, $\text{Co}_2\text{W}_8\text{C}_3$, etc) usually forms in the atom sphere of C deficiency. In our case, it seems that when molten γ phase rapidly bumps into and stops on the substrate surface, a rapid solidification process and a decarbonisation process take place. The former causes a formation of the amorphous phase in the coating interface, and the nano-crystals in coating layer as well, and the latter makes γ phase

transform to η phase. The effect of this thin layer of amorphous η phase on interface bonding strength is not clear now, and a further study is needed. Generally, an amorphous phase layer in an interface of crystal materials is harmful to interface strength. In this respect, the amorphous η phase should be restrained with effort. To increase substrate temperature and decrease spray powder speed may be a way to depress the formation of amorphous phase, but in consideration of the advantage of nano-crystal structure in coating layer, a proper control of the substrate temperature and the spray powder speed is necessary.

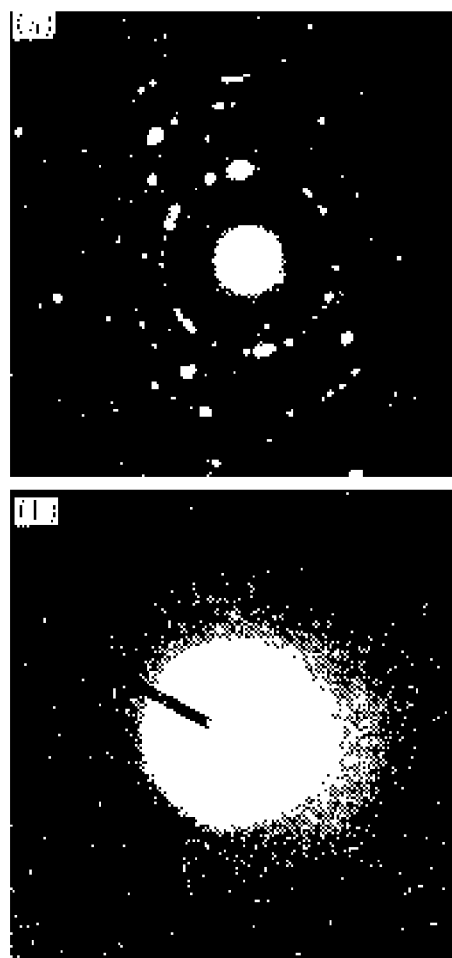


Fig. 8 Electron diffraction patterns of (a) the substrate and (b) the amorphous coating phase in Fig. 7

In order to further verify the diffusive layer in the interface region detected by SEM line scanning mentioned above, we use TEM and EDS to analyze the micro-compositions of the substrate in the bonding region and the interior

region as well. In the interior of substrate, shown in Fig. 4, no W and Co peaks are found in EDS spectra, but in all substrate region (about 0.5 μm in width) shown in Fig. 7, W and Co elements can be detected anywhere by EDS. W and Co distribute in this region inhomogeneously and compositions of W, Co are changed from grain to grain and grain boundary. These results prove that there is a diffusing process of W and Co atoms from coating layer to substrate in the HVOF spraying process and this diffusing is affected by the microstructure characteristics of the substrate, such as the crystal orientation of grains, the grain boundary structure etc.

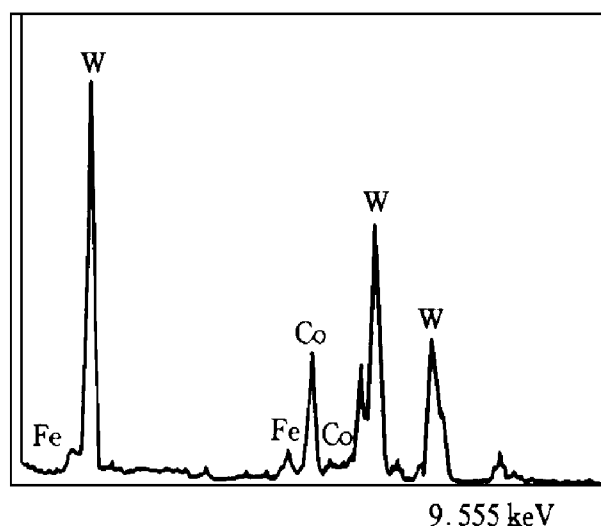


Fig. 9 EDS composition spectrum of the amorphous coating phase in Fig. 7

To sum up, we can tell that the nano-crystal structure of the coating layer and the atom diffusion from coating to substrate may be the main reasons of high strength, toughness and good interface bonding properties of the HVOF sprayed WC-Co coating/spring steel substrate products.

4 CONCLUSIONS

In difference from other flame spraying processes, there is no phase transformation occurred during the HVOF spraying. The HVOF sprayed WC-Co coating layer consists of WC particles embedded in γ adhering phase, which shows a nano-crystal structure with an average grain size of 50 nm. A diffusing layer of about 2 μm in depth is observed in the interface region and this proves the diffusion of W and Co atoms from coating to the spring steel substrate. A thin layer of amorphous phase presents at the coating interface and its composition is close to η phase.

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