Properties of Cr$_3$C$_2$-NiCr Cermet Coating Sprayed by High Power Plasma and HVOF Processes

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Abstract

The structure, hardness and shear adhesion strength have been investigated in Cr₃C₂-NiCr cermet coatings sprayed onto a mild steel substrate by 200 kW high power plasma spraying (HPS) and high velocity oxy-fuel (HVOF) processes. Amorphous and supersaturated nickel phases form in both as-sprayed coatings. The hardness of the HVOF coating is higher than that of the HPS coating because the HVOF coating contains more non-melted Cr₃C₂ carbide particles. On heat-treating at 873 K, the amorphous phase decomposes and the supersaturated nickel phase precipitates Cr₃C₂ carbides so that the hardness increases in the HPS coating. The hardness measured with a large load exhibits lower values compared with that measured with a small load because of cracks generated from the indentation. The ratio of the hardesses measured with different loads can be regarded as an index indicating the coating ductility. The ductility of the HVOF coating is higher than that of the HPS coating. Adhesion strength of the HVOF coating was high compared with the HPS coating. The adhesion of the coatings is enhanced by heat-treating at 1073K and that of the HVOF coating was over 350 MPa.
1. Introduction

Chromium carbide, Cr$_3$C$_2$ with NiCr, coatings exhibit heat-resistance and wear-resistance and are applied for heat-treatment rolls [1,2] and coal burning boiler tubes because of the superior heat-resistance and erosion-resistance against fly ash [3]. It is also expected in future that such cermet coatings will be used for structural parts in high-temperature environments.

High-quality coatings have been obtained through the extensive development of thermal spraying apparatus, such as high velocity flame spraying (HVOF and HVAF) and high power plasma spraying (HPS). In the former process, the decomposition of the spray material is retarded due to the high flame speed and the low flame temperature. In the latter process, although materials of high melting point can be sprayed and a dense coating is obtained, it has a disadvantage due to decomposition of hard materials [4] because of the high temperature.

It is known that the properties of cermet coatings markedly depend on the structure of the coatings [5,6]. Though there are some investigations concerning the properties of Cr$_3$C$_2$ cermet coating [3,6-9], most of them do not evaluate the characteristics of coatings but measured only a property of the coating, such as wear-resistance. The aim of this work is to
characterize the structure and properties of Cr$_3$C$_2$ cermet coatings thermal sprayed by HVOF and HPS processes.

2. Experimental Procedure

The cermet powder (75 mass% Cr$_3$C$_2$ - 25mass% NiCr, SHOWA DENKO SHOCOAT KC-21E; Showa Denko, Minato, Tokyo, Japan, +53·16 μm particle size range) used in this study was manufactured by sintering. Figure 1 shows a SEM image of the powder used. The powder was thermal sprayed onto a mild steel substrate (JIS-SS400) using 200 kW HPS and HVOF processes. The coating thickness was about 350 μm. The spraying conditions of the HPS (PLAZJET III-250) and HVOF (HOBART TAFA JP-5000 HP/HVOF Spray System) processes were shown in Tables 1 and 2, respectively.

The structure and phases in the as-sprayed and heat-treated coatings were examined by means of electron microprobe analysis (EPMA) and X-ray diffraction (XRD) with Cu-K$_\alpha$ radiation. The heat-treatment was carried out in vacuum at temperatures up to 1273 K for 3.6 ks. The hardness of the coatings was measured more than 15 randomly located positions on the cross section for each specimen by a Vickers microhardness tester and adhesion strength of the coating was evaluated for 10 specimens on each condition by a shear test. Shear test pieces used in this study have a semicircular notch of 0.4 mm in radius proposed by
the authors as shown in Fig. 2 in order to reduce the stress concentration at the corner of the protruded step [10].

3. Results and Discussion

3.1 Structure and Phases

Figure 3 shows back scattered electron (BSE) images of the as-sprayed coatings by the HPS and HVOF processes. The granular dark particles as shown by arrows are Cr$_3$C$_2$ carbides which are deposited without melting. More granular Cr$_3$C$_2$ particles remained in the HVOF coating compared with the HPS coating and the lamellar structure of the HVOF coating is finer than that of the HPS coating. Thus the spray powders are melted more by the HPS process than the HVOF process because of the temperature difference between the plasma and HVOF flame.

Figure 4 shows XRD patterns of the original powder and the as-sprayed coatings. Peaks of nickel solid solution and Cr$_3$C$_2$ carbide are observed in the pattern of the powder. The XRD patterns of both sprayed coatings are similar. All peaks of nickel solid solution and Cr$_3$C$_2$ become broad and a very broad peak centered around 43 degrees appears in the as-sprayed condition of both coatings. The very broad peak indicates formation of an amorphous phase. Therefore, it is considered that nickel-chromium alloy and some Cr$_3$C$_2$ carbide are melted and some amorphous phase forms.
Phase changes of the coatings by heat-treatment at various temperatures were investigated by XRD. The XRD patterns of the coatings heat-treated at 673 K were similar to those of the as-sprayed coatings. The very broad peaks of HPS and HVOF disappear on heat-treating at 873K as shown in Fig.5, and peaks of nickel solid solution and Cr$_3$C$_2$ carbide become sharp compared with those of the as-sprayed coatings. It is seen that the amorphous phase decomposed on heat-treating at 873K. Figure 6 shows XRD patterns of the coatings heat-treated at 1073K. Peaks of nickel solid solution and Cr$_3$C$_2$ carbide become more clear.

Figure 7 shows BSE images of the heat-treated HVOF coatings. The coating heat-treated at 673 K were similar to the as-sprayed coatings. Fine precipitates in the lamellar structure can be seen in the coatings heat-treated at 873 K (Fig.7a). The fine precipitates in the lamellar structure, which are not granular dark particles as shown in Fig.3 but are indicated by arrow as the example, grow when heat-treated at 1073 K and 1273 K (Fig.7b and c). This fine precipitates are considered from the XRD patterns to be Cr$_3$C$_2$ carbides formed by decomposition of the amorphous phase and those precipitated from supersaturated nickel solid solution. The same change in structure of the coating by heat-treatment was also seen in HPS coatings.

3.2 Hardness and Adhesion strength

Figure 8 shows change in hardness of the coatings measured with different loads of 9.8 N and 49 N as a function of heat-treatment
temperature. It is clear that the scatter of hardness is larger and the value of hardness is higher when measured with a low load of 9.8 N compared to the measurement with a high load of 49 N. The hardness of the as-sprayed HVOF coating is higher than that of the HPS coatings at both of these loads measurements. Therefore, the HVOF coating is more dense and contains more retained Cr$_3$C$_2$ carbide compared to the HPS coating. The hardness of the HPS coating measured at a load of 9.8 N is enhanced appreciably with the heat-treatment temperature up to 1073 K and nearly attains the hardness of the HVOF coating.

The enhancement of hardness may have resulted from the decomposition of the amorphous phase and the precipitation of Cr$_3$C$_2$ carbide in nickel solid solution. The melted part is less in the HVOF coating so that the increase of hardness is less compared to the HPS coating. The hardness of the HVOF coating increases slightly with the heat-treatment temperature. The hardness of the coatings heat-treated at 1273 K decreases due to coarsening of the structure (Fig.7c). The hardness measured with a load of 49 N is lower than that measured with a load of 9.8 N and the difference in hardness of the HPS coating is larger than that of the HVOF coating. Lin et al. investigated the hardness of the plasma sprayed materials of metals, intermetallics, and ceramics by different loads on Vicker indentation tests [11]. They reported that the hardness enhances and the data variation become large with decreasing load. The tendency is consistent with present work.

Both coatings of the HVOF and HPS process have no cracks around the hardness indentation when indented with a small load of 9.8 N. The
indentation of the HVOF coating also has no visible cracks even when indented with a large load of 49 N. However, cracks developing from an indentation are clearly observed in the HPS coating when indented with a large load of 49 N as shown by arrows in Fig.9. This means that the HPS coatings are more brittle than the HVOF coating.

The difference of the hardness measured with different loads may be the result of cracks that develop from the indentation when measured with a large load and the hardness is evaluated to be low. Thus, the difference of the hardness becomes more significant when the coating is more brittle. Therefore, the ratio is regarded as an index indicating the ductility of the coating. Figure 10 shows the ratio of the Vickers microhardness measured with a load of 49 N to that measured with a load of 9.8 N as a function of heat-treatment temperature. The ratio of the HVOF coatings is about 0.94 for the as-sprayed and heat-treated coatings. On the other hand, the ratio of the HPS coatings is about 0.84 for the as-sprayed and heat-treated coatings up to 1073 K and increases to 0.87 for the coating heat-treated at 1273 K. Accordingly, it is considered that the ductility of the HVOF coatings is appreciably higher compared to the HPS coatings.

The adhesion strength of the coatings were evaluated by the shear test using a specimen having a semi-circular notch as shown in Fig.2. Figure 11 shows the measured shear adhesion strength of the coatings. The adhesion shear strength of the as-sprayed HVOF coating is about 300 MPa which is about three times of the HPS coating. The adhesion shear strength of the as-sprayed HVOF coating was about 200 MPa when
measured with the test pieces having no semi-circular notch [10]. The difference is caused by the stress concentration at the step of the test piece. Therefore, the adhesion shear strength using test pieces having no semi-circular notch would be evaluated lower than that measurement in this work. On heat-treatment at 1073 K for 3.6 ks, the adhesion strength of the HPS coating increased by about 1.5 times of the as-sprayed coating. The adhesion strength of the HVOF coating also increased a little. This is caused by the diffusion between the coating and the substrate by heat-treatment as seen in Fig.7b and c. It is known that the coating of significantly high adhesion strength is obtained by HVOF process.

4. Summary

The properties of the Cr$_3$C$_2$ cermet coatings obtained by the HPS and HVOF processes were investigated by using SEM, EPMA, XRD and the shear test.

The results obtained are summarized as follows:

1. An amorphous phase forms in the as-sprayed HPS and HVOF coatings and decomposes on heat-treatment up to 873 K.
2. The hardness of the as-sprayed HVOF coating is higher than the hardness of the as-sprayed HPS coating. The hardness of the HPS coating increases appreciably with heat-treatment temperature due to the decomposition of the amorphous phase and the precipitation of Cr$_3$C$_2$ carbide.
3. The ratio of the hardness measured with a large load to that measured with a small load can be used as an index to indicate the ductility of the coatings.

4. Shear adhesion strength of the as-sprayed HVOF coating is 300 MPa which is three times of the adhesion strength of the HPS coating. The adhesion strength of the HPS coating increases by 1.5 times and that of the HVOF coating increases a little by heat-treatment at 1073 K.

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References


