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Formation of an Amorphous Phase in Thermally Sprayed WC-Co

C.J. Li, A. Ohmori, and Y. Harada

A WC-Co coating was sprayed by the high-velocity oxyfuel process using a feedstock of tungsten carbide clad with cobalt. The structure of the sprayed coating was characterized by x-ray diffraction (XRD), differential scanning calorimetry (DSC), and differential thermal analysis (DTA). It was found that an amorphous phase of Co-W-C ternary alloy observed as a large, broad peak in the XRD pattern can be formed in the as-sprayed WC-Co coating. The DSC, DTA, and XRD analyses revealed that the amorphous phase crystallized at a temperature of around 873 K to metallic cobalt, Co_6W_6C, and tungsten with appreciable precipitation of free carbon. The heat treatment of as-sprayed WC-Co coating at a high temperature of 1173 K suggests that annealing at a temperature higher than about 1104 K will promote the reaction of tungsten and cobalt with carbon to form the complex carbide Co_6W_6C.

1. Introduction

HIGH-VELOCITY OXYFUEL (HVOF) spraying is used to produce dense WC-Co coatings with good wear resistance. One problem encountered during thermal spraying of WC-Co is the decarburization of tungsten carbide, which reduces the material to a dicarbide (W_2C) and metallic tungsten (Ref 1-6). The superior wear resistance of WC-Co cermet is determined by evenly distributed fine tungsten carbide particles bonded to the cobalt matrix (Ref 7); therefore, the reduction of tungsten carbide particles in the coating after spraying will degrade the wear resistance of the coating. Accordingly, the structure of WC-Co coatings is of significant practical interest.

The structure of thermally sprayed WC-Co coatings can be assessed by x-ray diffraction (XRD). It has been observed that a broad, shallow peak appears in the XRD pattern maximized at a 2θ diffraction angle of 40 to 46° (Ref 5). Owing to the shallowness of this broad peak, there is still some uncertainty about the crystallographic structure of the phases. For example, it was considered that such broadening is due to the variation of tungsten and carbon dissolved in the cobalt matrix (Ref 5). A recent transmission electron microscopy (TEM) examination of WC-Co coating structure indicated the formation of an amorphous phase in the coating (Ref 8). However, the phase structure is still unclear because only a small amount of the matrix phase could be identified.

This paper examines the formation of the amorphous phase in WC-Co coatings sprayed by HVOF and investigates the crystallization behavior of the amorphous phase during annealing treatments.

Keywords amorphous phase, HVOF processing, microstructure, phase identification, structure, WC-Co material

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2. Materials and Experiments

The feedstock was a nominal WC-18Co material consisting of tungsten carbide clad with cobalt (Metco 75F). Figure 1 shows the morphology of the powder, and Fig. 2 presents an XRD pattern of the powder. The powder consists of tungsten carbide and cobalt. The feedstocks of other typical powders were also used for comparison.

Tungsten carbide/cobalt was sprayed onto a sandblasted mild steel surface with a Jet-Kote (Osaka University) spray gun under the conditions shown in Table 1. The coating was charac-

Table 1 High-velocity flame spraying conditions

Oxygen	
Pressure, MPa	0.54
Flow rate, L/min	290
Fuel gas (C_2H_2 + 30% C_3H_6)	
Pressure, MPa	0.343
Flow rate, L/min	55
Powder carrier gas (N_2) pressure, MPa	0.196
Length of nozzle, mm	152
Spray distance, mm	150
Traverse speed of gun, mm/s	150

Fig. 1 Morphology of tungsten carbide clad with cobalt powder

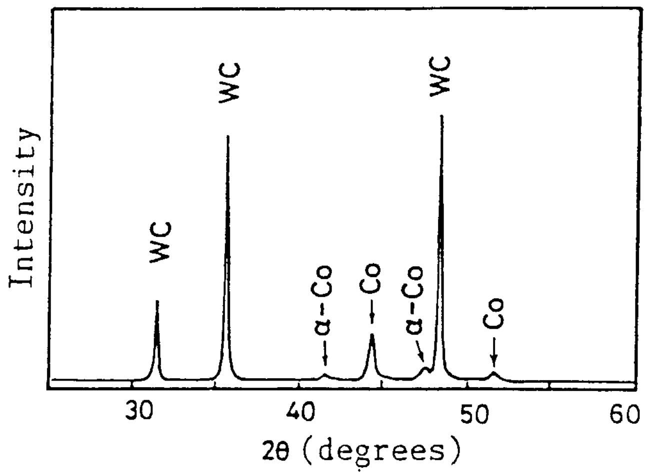

Fig. 2 XRD pattern of tungsten carbide clad with cobalt powder

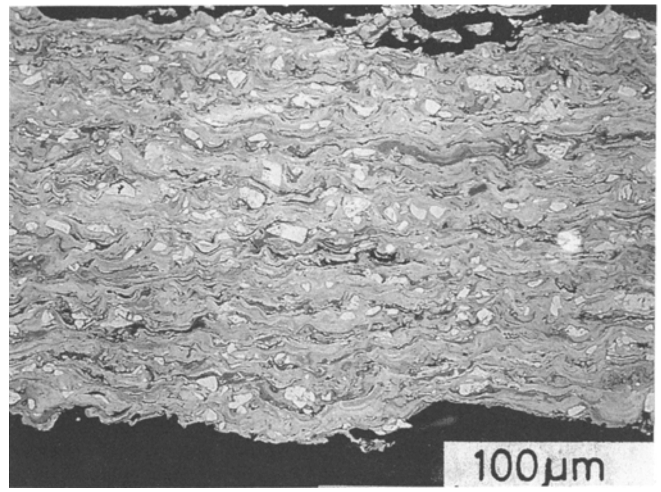

Fig. 3 SEM microstructure of WC-Co coating sprayed by high-velocity flame

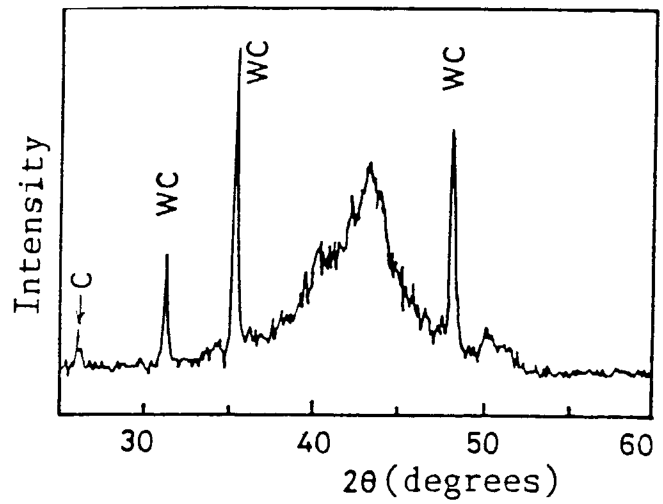

Fig. 4 XRD pattern of WC-Co coating sprayed by high-velocity flame. C, graphite

terized by XRD, differential scanning calorimetry (DSC), and differential thermal analysis (DTA). The XRD analysis was performed with K_α radiation of copper at 40 kV, 20 mA and a 2θ scanning speed of 4°/min. The DSC and DTA analyses were carried out under a N_2 atmosphere at a heating rate of 20 K/min. The coating microstructure was examined by scanning electron microscopy (SEM).

3. Results

3.1 *Structure of As-Sprayed WC-Co Coating*

Figure 3 illustrates the microstructure of the sprayed WC-Co coating, and Fig. 4 shows the XRD pattern. The characteristic peaks of tungsten carbide are superimposed on a broad peak that maximizes at a diffraction angle of approximately 43°, indicating the formation of an amorphous phase. This broad peak is usually more shallow in XRD patterns of thermally sprayed WC-Co coatings; however, the range of diffraction angle in which the broad peak appears is similar. The small magnitude of the broad peak was confirmed from other XRD patterns of WC-Co coatings sprayed with other types of WC-Co powders under the same conditions shown in Table 1.

3.2 *Crystallization Behavior of the Sprayed Coating during Annealing Treatments*

3.2.1 Effect of Annealing Treatments on the Phase Structure of the Sprayed Coating

Figure 5 shows XRD patterns of annealed WC-Co coating under conditions of 673 K/3 h and 873 K/6 h in ambient atmosphere. At 673 K, the phase structure is quite similar to that of the as-sprayed coating, except for the precipitation of graphite as indicated by "C" in Fig. 5(a) (at about 2θ = 26.6°). At 873 K, however, the amorphous phase crystallizes to metallic cobalt, the complex carbide Co_6W_6C, and tungsten. A doublet is observed near the cobalt main peak (at about 2θ = 44.2°), which might arise from a partially oversaturated solution of the cobalt matrix.

Figure 6 shows the XRD pattern of the WC-Co coating after vacuum annealing at 1173 K for 0.5 h. The amorphous phase in the as-sprayed coating has crystallized to cobalt and Co_6W_6C, with little trace of metallic tungsten.

3.2.2 Characterization of the Coating by DSC and DTA

The DTA and DSC results for the coating are shown in Fig. 7 and 8, respectively. Figure 7 also shows the results obtained after reheating the sample. Two exothermic reactions occur at about 944 and 1104 K during initial heating of separated coating films. From DSC data, a crystallization temperature, T_x, of 898 K can be recognized, with a peak crystallization at 934 K. According to DSC, DTA, and XRD data, the amorphous phase in as-sprayed WC-Co coating will crystallize at around 873 K to form the complex carbide Co_6W_6C and metallic cobalt with precipitation of free carbon. The lack of tungsten in the WC-Co coating annealed at 1173 K suggests that the other reaction, which occurred at about 1104 K as indicated by DTA data, was the reaction forming Co_6W_6C with the consumption of crystallized cobalt and tungsten with carbon or carbide.

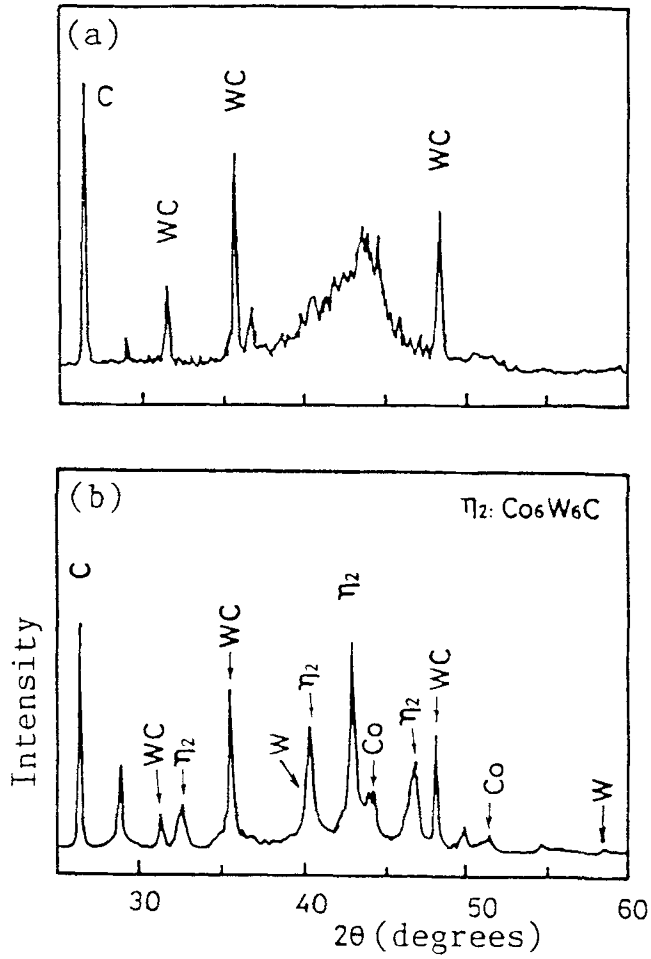

Fig. 5 XRD patterns of annealed WC-Co coating at different conditions C, graphite. (a) 673 K for 3 h. (b) 873 K for 6 h

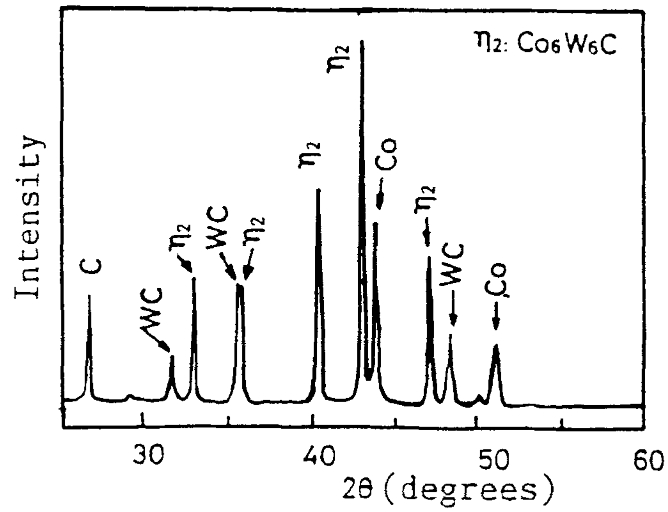

Fig. 6 XRD pattern of WC-Co coating annealed at 1173 K for 0.5 h in vacuum C, graphite

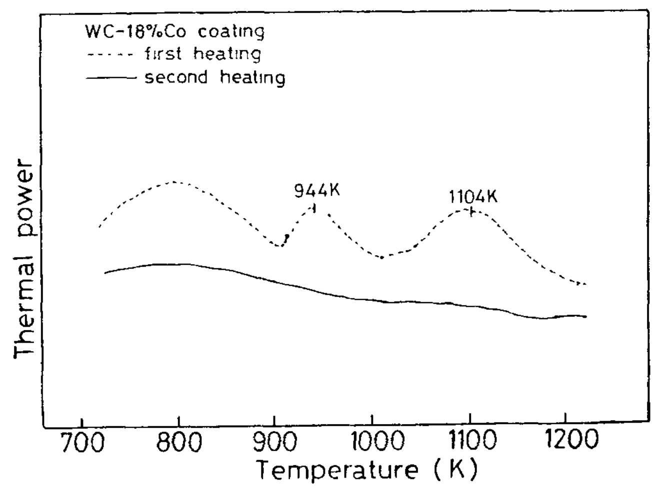

Fig. 7 DTA curve of WC-Co coating Heating rate 20 K/min, in N_2 atmosphere

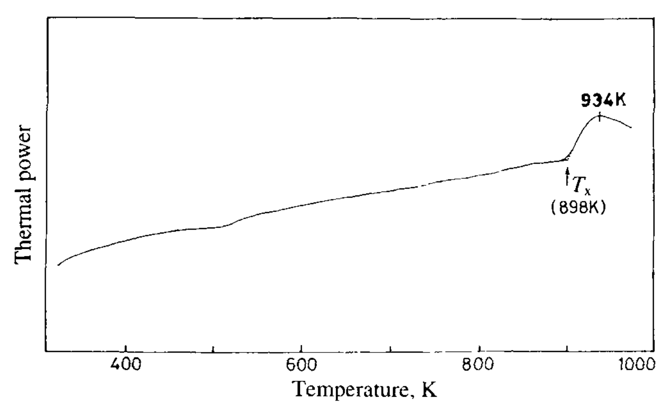

Fig. 8 DSC curve of WC-Co coating Heating rate 20 K/min, in N_2 atmosphere

3.2.3 Effect of Powder Type

Figures 9(a) to (c) illustrate the XRD patterns of agglomerated WC-17Co powder (Metco 73F), the subsequent coating sprayed under the conditions shown in Table 1, and the coating after annealing at 873 K in ambient atmosphere, respectively. Figure 9(b) shows a broad peak similar to that observed in Fig. 4, although of smaller magnitude, which indicates amorphous phase formation. Furthermore, it was also found that annealing leads to the formation of the complex carbide Co_6W_6C through crystallization of the amorphous phase at 873 K for 6 h. Investigation into the effect of several kinds of typical commercially available WC-Co powders yielded results similar to those for the agglomerated powder.

4. Discussion

4.1 *Phase Analysis by XRD*

The phases in a thermally sprayed WC-Co coating are generally characterized using XRD analysis. A broad, shallow peak, present at 2θ from 40 to 46° (Fig. 9b), is usually observed. It has been reported that this broad XRD peak is associated with the content of tungsten and carbon dissolved in cobalt matrix (Ref 5). Recently, based on TEM observations of the WC-Co coating structure, it was reported that the broad, shallow peak is associ-

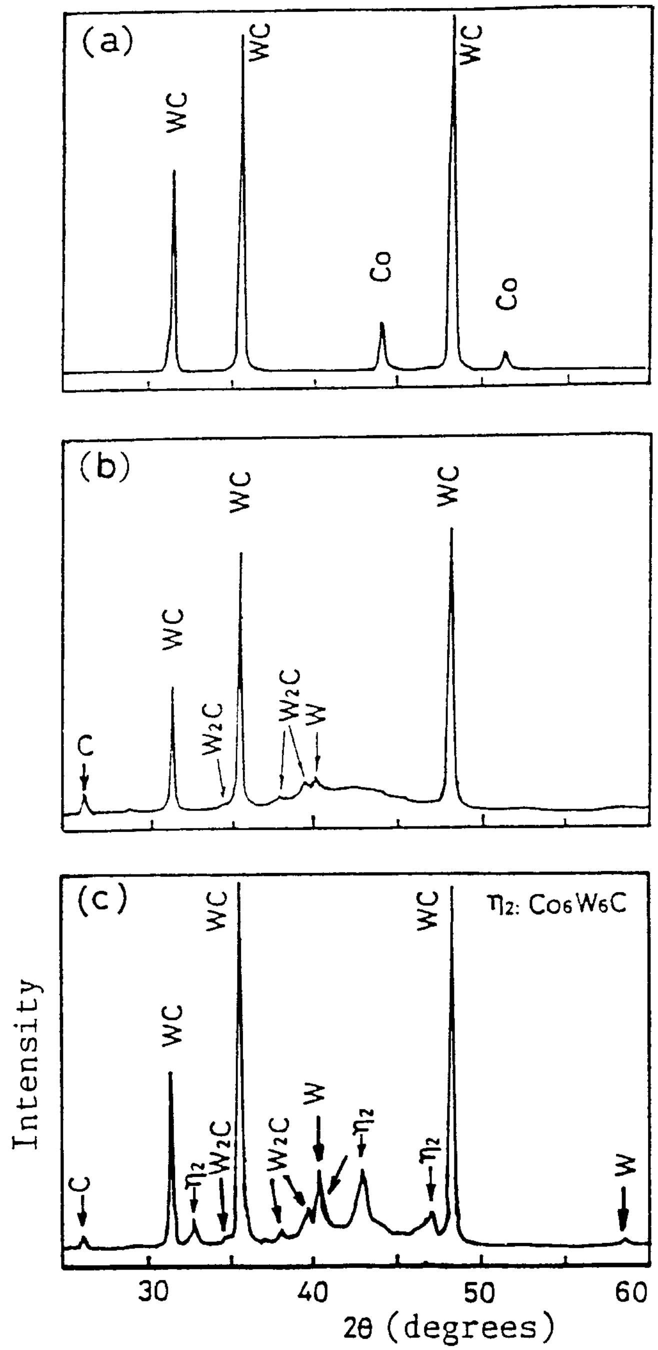

Fig. 9 XRD patterns of agglomerated WC-Co powder (a), as-sprayed WC-Co coating (b), and WC-Co coating after annealing at 873 K for 6 h (c). C, graphite

ated with the formation of an amorphous phase in the coating (Ref 8).

Using the feedstock of tungsten carbide clad with cobalt and the HVOF spray process in the present study, a large, broad peak was recognized in the XRD pattern of the sprayed coating at the same 2θ range as those reported. This peak revealed the formation of an amorphous phase in the coating, confirming that such peaks are associated with the formation of an amorphous phase in thermally sprayed WC-Co coatings.

The HVOF-sprayed coating with the feedstock of cobalt-clad WC contained a large amount of amorphous phase compared with other WC-Co powders. This result is due to preferential deposition of cobalt-based matrix phase during HVOF spraying (Ref 9). Annealing treatment shows that the amorphous phase formed in the coating is a Co-W-C ternary alloy.

4.2 *Influence of the HVOF Process*

During plasma spraying of WC-Co feedstocks, tungsten carbide clad with cobalt is most difficult to decompose to W_2C and metallic tungsten (Ref 3). Due to the characteristics of low heating ability and high velocity during HVOF spraying, it can be surmised that the decomposition of tungsten carbide clad with cobalt is further limited during spraying. When the powder is injected into the flame, clad cobalt will first melt and dissolve some tungsten and carbon to form a liquid phase that covers the tungsten carbide particle in flight. Upon impact, owing to the high velocity of the particle, the "droplet" prefers to deposit this liquid covering and the large tungsten carbide solid core rebounds from the substrate or the surface of the coating formed previously (Ref 9). As a result of the rapid cooling inherent to thermal spraying, spraying yields an amorphous matrix controlled coating (Fig. 4). Such massive deposition of the amorphous phase during thermal spraying of WC-Co powders may be the result of using both a cobalt-clad tungsten carbide feedstock and the HVOF process.

4.3 *DSC Analysis*

Data obtained by DSC revealed a crystallization temperature (T_x) of the amorphous phase of about 898 K, consistent with the results of the annealing treatment. Data obtained by DTA presented two exothermic reactions, occurring at temperatures of 944 and 1104 K. The former exothermic reaction agrees with the T_x obtained by DSC. Annealing at 873 K shows that the amorphous phase of Co-W-C formed in the coating crystallizes at around 873 K to metallic cobalt, the complex carbide Co_6W_6C, and tungsten, with substantial precipitation of graphite. The second exothermic reaction that appeared in the DTA curve likely is associated with the reaction of crystallized tungsten and cobalt with carbon to form Co_6W_6C. This result is inferred because the XRD pattern of the WC-Co coating annealed at 1173 K exhibited the formation of crystallized phases of Co_6W_6C and cobalt besides free carbon, with little trace of tungsten. The crystallization of the amorphous phase to Co_6W_6C was recognized in all typical WC-Co coatings annealed at 873 K for 6 h. Therefore, it is suggested that the crystallization temperature of 1133 K reported by Nerz et al. (Ref 8) corresponds to the second reaction rather than to the crystallization of amorphous phase in thermally sprayed WC-Co coatings. Only the Co_6W_6C phase was clearly recognized in the present study; in particular, a well-crystallized Co_6W_6C phase was detected from the XRD pattern of coating annealed at 1173 K. Therefore, there is also a discrepancy between the crystallized carbide phase of Co_6W_6C in the present study and that of Co_2W_4C reported by Nerz et al. (Ref 8).

4.4 *Formation of Complex Carbides*

The formation of the complex carbide Co_6W_6C progresses during annealing at high temperatures. Therefore, either (1) the cobalt or tungsten crystallized from Co-W-C amorphous alloy at a relatively low temperature range or (2) tungsten resulting from decarburization of tungsten carbide during spraying will be completely consumed by annealing. Thus, a well-crystallized WC-Co coating will exhibit carbide phase and only one metallic phase, depending on the relative tungsten and cobalt contents in the coating. In the present experiment, with annealing at 1173 K, the residual metallic phase was cobalt rather than tungsten. If substantial metallic tungsten from decomposition of tungsten carbide was observed in the coating, then it can be considered that an annealed WC-Co coating would not contain metallic cobalt.

5. Conclusions

The structure of a WC-Co coating sprayed by HVOF with a cobalt-clad powder was characterized by XRD, DSC, and DTA. The XRD pattern of the as-sprayed coating showed the presence of a large, broad peak at a 2θ angle of 40 to 46°. This broad peak occurs as a less intense response in other thermally sprayed WC-Co coatings. Annealing of the as-sprayed WC-Co coating has indicated the formation of Co-W-C ternary amorphous phase. Such an amorphous phase will crystallize to the complex carbide Co_6W_6C and metallic phases such as cobalt and tungsten with precipitation of free carbon at a temperature of approximately 873 K.

Acknowledgments

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