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Effect of powder structure on the structure of thermally sprayed WC–Co coatings

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Five representative types of WC–Co powders were selected to clarify the dependence of the structure of sprayed coatings on the structure of powders themselves. The WC–Co coatings were sprayed with the Jet-Kote process and plasma spraying as well. The structure of WC–Co coatings was primarily characterized by X-ray diffraction. The X-ray diffraction patterns of the sprayed coatings were illustrated compared with those of powders, which aims at a better understanding of the structure of thermally sprayed WC–Co coatings. The selected coating was also analysed by differential scanning calorimetry (DSC). The decarburizing process, and the effects of powder structure and spray conditions on the crystal structure of sprayed WC–Co coatings are discussed in detail.

1. Introduction

WC–Co powders constitute the most important spray materials available to produce hard coatings by thermal spraying technologies. There are many kinds of commercially available powders which are usually produced by several different manufacturing methods: e.g. cast-crushed, sintered-crushed, agglomerated, aggregated and coated. Accordingly, the powders are very different in morphology, crystal structure, tungsten carbide grain size in a powder, powder grain size and distribution, and also carbon and cobalt content, depending mainly on manufacturing methods. On the other hand, the structure of a thermally sprayed WC–Co coating is very sensitive to the structure of the starting powder and spraying technique. However, it can be expected that only the coatings, which have a similar structure with cobalt cemented carbide alloy, will give the best mechanical performance.

For cobalt cemented tungsten carbide alloy, the cobalt and carbon content and the carbide grain size are the most important factors which influence the structure and mechanical properties of cemented carbide materials [1]. The carbon content is usually carefully controlled during the sintering of cemented carbide because a small deficiency in carbon content results in the formation of brittle complex carbide, such as eta phase (Co_3W_3C) in the alloy [2]. An alloy with only cobalt and tungsten carbide phases in WC–Co system is desirable [3].

During thermal spraying, WC–Co powders have to be exposed to high temperature flame jet for heating and accelerating. Unsuitable overheating of WC–Co powders results in the decomposition of tungsten carbide [4]. Furthermore, when thermal spraying of WC–Co is carried out in an open air atmosphere where oxygen is usually included into a flame jet [5], the decarburization of tungsten carbide, owing to the oxidation of WC, also occurs. Accordingly, tungsten carbide may decompose to dicarbide (W_2C), and even to metallic tungsten during spraying. Therefore, a lot of workers have attempted to characterize the decomposition of WC during thermal spraying to obtain WC–Co coating with superior mechanical performance. About one decade ago, WC–Co coatings had been mainly sprayed by plasma and detonation gun. During plasma spraying, the decomposition of tungsten carbide becomes severe with an increase in degree of heating of tungsten carbide. It has been found that the decomposition of tungsten carbide increases with an increase in N_2 flow in Ar–N_2 plasma [6] and with the addition of H_2 gas into Ar plasma [7]. As plasma operating gases, H_2 gas promotes the decomposition more than He gas [8, 9]. Low power input to the plasma jet and short spray distance decrease the decomposition of tungsten carbide [9]. It is likely that the decomposition of tungsten carbide during plasma spraying with an internal powder feeder takes place more intensively compared with that sprayed with external powder feeder, because most tungsten carbide decomposed to metallic tungsten after spraying with an internal powder feeder according to the results reported by Arata *et al.* [10] and Detering *et al.* [11].

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It has also been found that the decomposition of tungsten carbide depends greatly on powder type produced by different manufacturing methods [12–14]. All the experimental results suggest that the variation in spraying parameters with increase in rate of heating of tungsten carbide promotes the decomposition of carbide.

High velocity oxy-fuel (HVOF) gas flame spraying, which was firstly commercially developed as the Jet-Kote process about ten years ago [15] and recently has been developed into several different types of commercially available spraying gun but all with similar principles, is characterized as a high velocity and low temperature spray process. It has been found that the wear performance of WC–Co coating sprayed by the HVOF process is better than that of the coating sprayed by plasma and even comparable with that of detonation gun coating [16]. Therefore, it becomes more and more popular to spray WC–Co coatings by the HVOF process. However, with the HVOF process, decomposition of tungsten carbide also occurs, depending on spray conditions such as type of fuel gases, fuel gas pressure and flow rate, length of spray nozzle and powder type [10, 17]. Above all, the structure of the starting powder controlled by manufacturing methods is evidently a key factor to influence the structure of subsequent coatings.

Another problem associated with the structure of WC–Co coating is concerned with the cobalt-related phase in the coating. It has been observed that cobalt phase cannot usually be recognized by X-ray diffraction analysis. Instead, a broad shallow peak in X-ray diffraction pattern is observed. It was considered that such broadening was due to the variation in cobalt matrix composition [14]. Recently, the formation of amorphous phase in WC–Co coating was reported [18], which corresponds to cobalt solid solution with the variation in matrix composition. Besides the decomposition of tungsten carbide during thermal spraying, the formation of complex carbide such as Co_3W_3C, Co_2W_4C, Co_6W_6C, $Co_3W_9C_4$ was also reported. It should be indicated, here, that there are still some unclear points concerning the formation of complex carbides, except Co_3W_3C, because as far as X-ray diffraction patterns were illustrated in the literature, there was no clear evidence for the formation of those complex carbides. This might be also associated with the broad shallow peak in the X-ray diffraction patterns.

The objective of this paper is to examine the effect of structure of powders manufactured by different methods on the structure of WC–Co coatings sprayed by Jet-Kote process and plasma and it aims at a better understanding of the decomposition process of tungsten carbide during thermal spraying and the structure of the coatings.

2. Materials and experimental methods

Five types of representative WC–Co powders were used for thermal spraying produced by different manufacturing methods. Table I shows nominal compositions and manufacturing features.

Spraying of WC–Co coatings was carried out with a Jet-Kote gun. A gas mixture of acetylene (C_2H_2) and 30% propylene (C_3H_6) was used as a fuel gas. Table II shows the spray parameters. During spraying, the sample was held such that the surface of sample was perpendicular to spraying flame of the gun and the gun traversed over the sample with a step of 5 mm after one scan.

For comparison, typical WC–Co powders were also sprayed with just propylene as a fuel gas instead of a gas mixture of C_2H_2–30% C_3H_6. Plasma spraying of WC–Co powders was also performed under the conditions shown in Table III, which was selected so that heating of WC–Co powder by plasma jet was lower in order to minimize the decomposition of tungsten carbide according to previously reported results as mentioned in previous section. Type-1 powder was also sprayed under low pressure argon atmosphere for comparison. Spray conditions are shown in Table III.

The structure of powders and coatings were primarily characterized with X-ray diffraction (Rigaku)

TABLE I Powder compositions

Powder type	Description of manufacturing method	Composition
Type-1	sintered–crushed	WC–12% Co
Type-2	aggregated[a]	WC–12% Co
Type-3	agglomerated	WC–17% Co
Type-4	clad	WC–18% Co
Type-5	casted-crushed and fused	WC–12% Co

[a]Manufactured through sintering and crushing.

TABLE III Plasma spraying conditions

		APS[a]	LPPS[b]
Spray gun		METCO 9MB	
Plasma gas (Ar)	pressure	0.7 MPa	0.7 MPa
	flow rate	$47\,\mathrm{l\,min^{-1}}$	$47\,\mathrm{l\,min^{-1}}$
Auxiliary gas (H_2)	pressure		0.49 MPa
	flow rate		$6.6\,\mathrm{l\,min^{-1}}$
Powder carrier gas		Ar	Ar
Plasma current		900 A	600 A
Plasma power		32 kW	33 kW
Spray distance		100 mm	250 mm

[a]APS, Atmospheric plasma spraying.
[b]LPPS, Low pressure plasma spraying.

TABLE II Jet-Kote spraying conditions

Oxygen pressure	Flow rate	Fuel gas pressure	Flow rate	Powder carrier gas pressure	Length of nozzle	Spray distance	Traverse speed of gun
0.54 MPa	$290\,\mathrm{l\,min^{-1}}$	0.343 MPa	$55\,\mathrm{l\,min^{-1}}$	0.196 MPa	152 mm	150 mm	$150\,\mathrm{mm\,s^{-1}}$

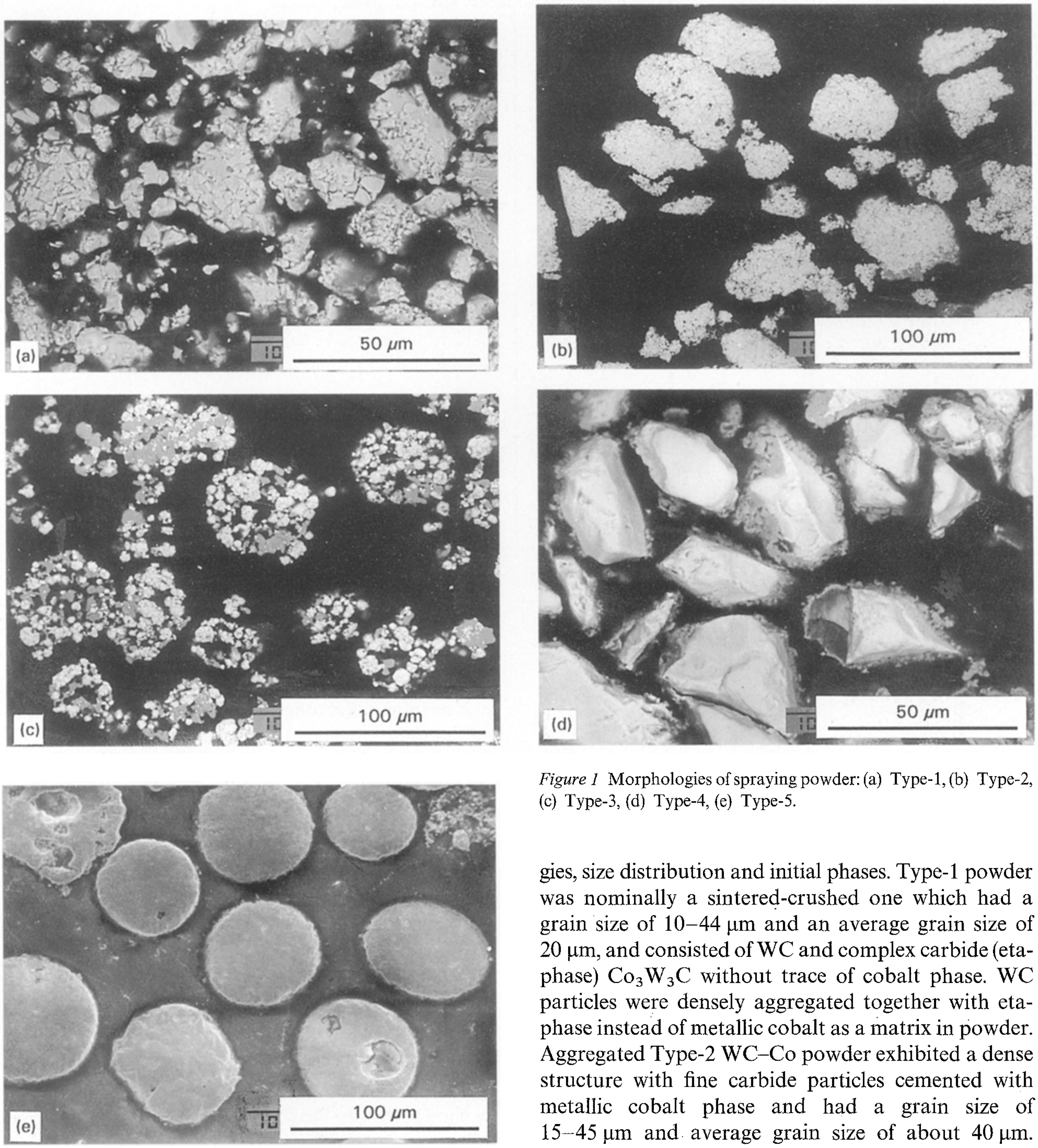


Figure 1 Morphologies of spraying powder: (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4, (e) Type-5.

using a copper X-ray tube operated at 40 kV and 20 mA. The scanning speed of 2θ was 4° min^{-1} during measurement. The selected WC–Co coating was also analysed by differential scanning calorimetry (DSC). DSC was carried out with a Shimadzu DSC-50 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 20 K min^{-1}.

The microstructure of powders and sprayed coatings was characterized with scanning electron microscopy (SEM).

3. Results

3.1. Characterization of spray powders

Figs 1 and 2 show the morphologies and X-ray diffraction patterns of five, types of spray powders, respectively. It can be seen that all powders were significantly different from each other in morphologies, size distribution and initial phases. Type-1 powder was nominally a sintered-crushed one which had a grain size of 10–44 μm and an average grain size of 20 μm, and consisted of WC and complex carbide (eta-phase) Co_3W_3C without trace of cobalt phase. WC particles were densely aggregated together with eta-phase instead of metallic cobalt as a matrix in powder. Aggregated Type-2 WC–Co powder exhibited a dense structure with fine carbide particles cemented with metallic cobalt phase and had a grain size of 15–45 μm and average grain size of about 40 μm. Although Type-2 powder was also said to be manufactured by the sintered–crushed method, this powder had a very different structure from Type-1 powder. Accordingly, this powder is referred to as aggregated powder in the present paper. Agglomerated Type-3 WC–Co powder showed a loose structure with WC cluster cemented by cobalt phase which was clearly identified from X-ray diffraction patterns and had a similar grain structure with that of aggregated Type-2 powder. Clad Type-4 powder showed a morphology of large WC particles with their surfaces coated by metallic cobalt and had a grain size of 5–44 μm and an average size of 27 μm. Measurement of carbide size showed that clad powders contained carbide particles of average grain size of about 18 μm [19]. Casted–crushed and fused Type-5 powder used in the present study had the largest average grain size of 69 μm with a range of 45–75 μm. X-ray diffraction analysis revealed that the powder consisted of dicarbide W_2C,

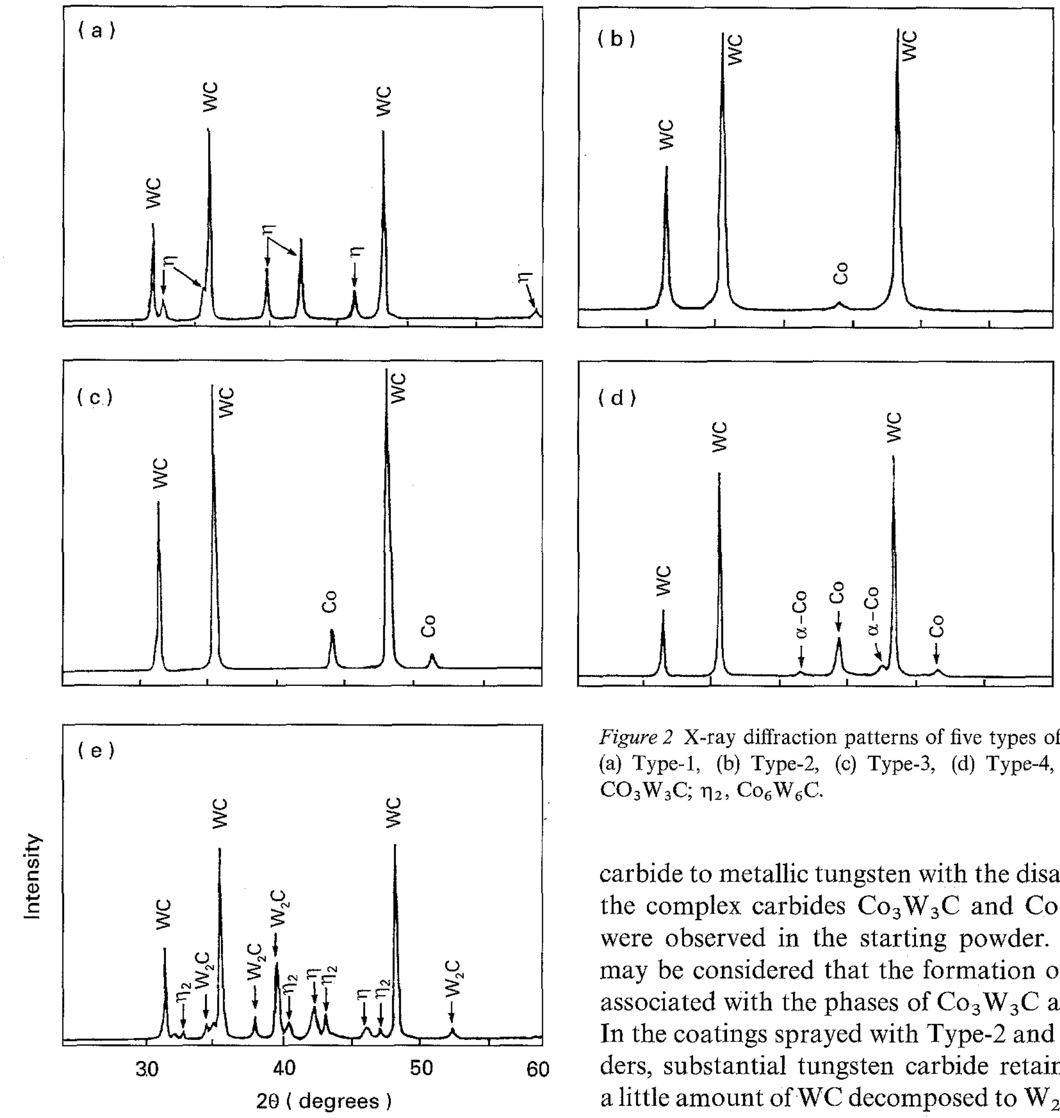


Figure 2 X-ray diffraction patterns of five types of spray powders: (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4, (e) Type-5. η, CO_3W_3C; η_2, Co_6W_6C.

complex carbide Co_3W_3C and Co_6W_6C besides the main phase of WC.

X-ray diffraction analysis clearly showed that Type-2, Type-3 and Type-4 powders contained only two phases of tungsten carbide and metallic cobalt, and Type-1 and Type-5 powders contained tungsten carbide and complex carbide instead of metallic cobalt phase.

3.2. Structure of Jet-Kote sprayed WC–Co coatings

Fig. 3 shows X-ray diffraction patterns of WC–Co coatings sprayed by the Jet-Kote process under the conditions given in Table II with five types of powders. It can be found that the decomposition of tungsten carbide occurred during Jet-Kote spraying with all types of powders, which is evidently shown by the peak of free carbon in the X-ray diffraction patterns. However, the degree of the decomposition of carbide evidently depended largely on powder type. Clearly, most tungsten carbide has decomposed to metallic tungsten in the case of Type-1 powder after spraying. In the WC–Co coating sprayed with Type-5 powder, the formation of the complex carbide Co_2W_4C was observed as well as the decomposition of tungsten carbide to metallic tungsten with the disappearance of the complex carbides Co_3W_3C and Co_6W_6C which were observed in the starting powder. Therefore, it may be considered that the formation of Co_2W_4C is associated with the phases of Co_3W_3C and Co_6W_6C. In the coatings sprayed with Type-2 and Type-3 powders, substantial tungsten carbide retained and only a little amount of WC decomposed to W_2C and metallic tungsten. On the contrary, metallic cobalt phase cannot be identified in the X-ray diffraction patterns of all coatings and a broad shallow peak was observed at 2θ of around 43° instead. Furthermore, X-ray diffraction pattern of the coating sprayed with clad WC–Co powder was significantly different from those of the coatings sprayed with all other types of powder, as shown in Fig. 3(d). Clearly, as well as some WC being retained, a very large broad peak at around 2θ of 43° was observed. This suggests the formation of a non-crystalline phase in the coating as a matrix.

Fig. 4 shows the microstructure of WC–Co coatings sprayed with five types of powder. Except for the coating sprayed with Type-5 powder, dense coatings were obtained with all other types of powders. However, it was observed that only a small amount of WC particles retained in the coatings sprayed with Type-1 and Type-4 powders compared with the coatings sprayed with Type-2 and Type-3 powders. The lack of WC particles in the coating of Type-1 powder is consistent with the fact that WC substantially decomposed to metallic tungsten, as revealed by X-ray diffraction. On the other hand, a small number of WC particles retained in the coating sprayed with cobalt clad powder were only small compared with the WC particle size in the powders. Such a lack of large WC particles is evidently due to the rebound of large solid tungsten carbide particles which are wrapped with liquid

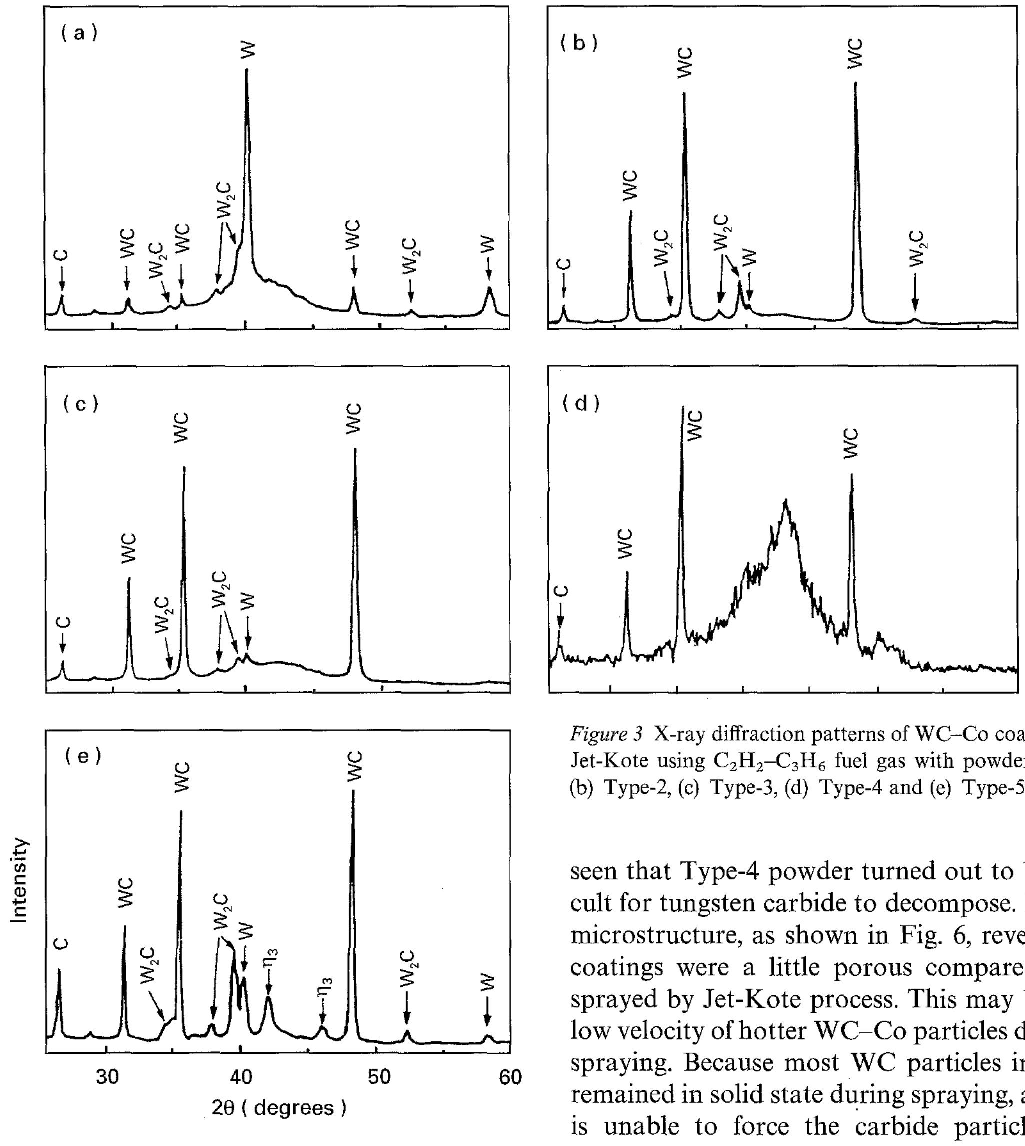


Figure 3 X-ray diffraction patterns of WC–Co coatings sprayed by Jet-Kote using C_2H_2–C_3H_6 fuel gas with powders of (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4 and (e) Type-5. η_3, Co_2W_4C.

cobalt deposited after impacting on the surface of the coating deposited already, which has been discussed in detail elsewhere [19].

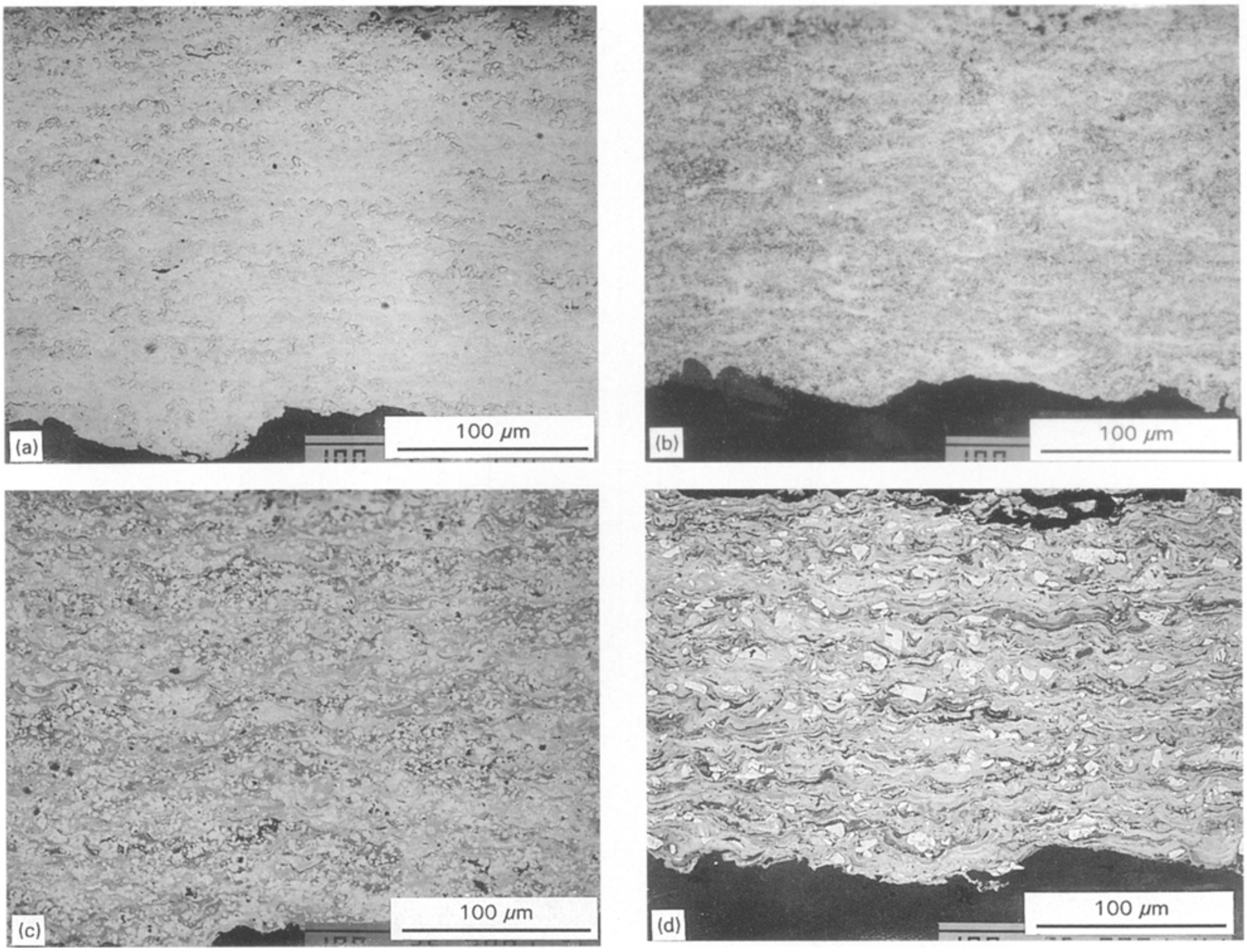
3.3. Structure of plasma-sprayed WC–Co coatings

In order to confirm the dependence of tungsten carbide decomposition on the powder structure, plasma spraying of five types of powders was performed and the structure of the sprayed WC–Co coatings was investigated. As for the spraying conditions, spray parameters were selected so that the decomposition could be minimized according to the results reported up to now, as mentioned in the introduction. Fig. 5 shows X-ray diffraction patterns of the WC–Co coatings. Consistently, a similar tendency on the dependency of carbide decomposition during plasma spraying upon powder type was clearly recognized with that observed in Jet-Kote spraying, as shown previously. Obviously, tungsten carbide in Type-1 powder was most apt to decompose after passing through a flame jet. Furthermore, there was substantial retention of WC, although the decomposition of WC to dicarbide for Type-2 and Type-5 powders, and to metallic tungsten for Type-3 could be recognized. It can also be seen that Type-4 powder turned out to be most difficult for tungsten carbide to decompose. However, the microstructure, as shown in Fig. 6, revealed that the coatings were a little porous compared with those sprayed by Jet-Kote process. This may be due to the low velocity of hotter WC–Co particles during plasma spraying. Because most WC particles in the powder remained in solid state during spraying, a low velocity is unable to force the carbide particles to flatten laterally sufficiently with the liquid phase to consolidate a dense coating.

4. Discussion

The present experimental results clearly showed that the decarburization of tungsten carbide occurs after a powder passed through spray flame, as revealed by others. Moreover, the degree of the decarburization depends strongly on the structure of spray powder. Generally, it can be considered that the decarburization of tungsten carbide occurs in two ways: namely, classical thermal decomposition and oxidation assisted decarburization. The fact that free carbon appeared in sprayed coatings as far as substantial dicarbide W_2C and metallic tungsten was observed at present experiment suggests that thermal decomposition is mainly responsible for the decarburization of tungsten carbide. This is consistent with previous findings that more heat is transferred to a powder from a flame, the more tungsten carbide decomposes.

For most easily decarburizing Type-1 WC–Co powder, plasma spraying was carried out at low pressure conditions under argon atmosphere to examine the decarburization of tungsten carbide to the exclusion of the effect of oxidation. The result, as shown in Fig. 7, revealed that thermal decomposition of tungsten



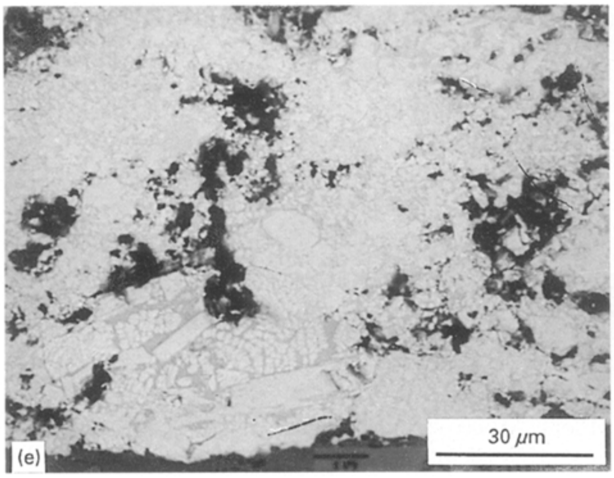


Figure 4 Microstructure of WC–Co coatings sprayed by Jet-Kote using C_2H_2–C_3H_6 fuel gas with powders of (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4 and (e) Type-5.

carbide occurred, but the decomposition was mainly limited to W_2C rather than to metallic tungsten as observed under air atmosphere. It may be argued that this is because a plasma jet under low pressure has a lower heating ability to spray powder than a plasma jet under air atmospheric pressure [20]. However, this fact implies that thermal decomposition is mainly responsible for the stage of the decomposition of WC to W_2C and that oxidation during thermal spraying may be mainly responsible for further decarburization from W_2C to metallic tungsten, regarding the high temperature of a plasma jet.

Recently, laser remelting treatment applied to WC-based coatings revealed that substantial WC was converted to W_2C after irradiation but without metallic tungsten [21]. Regarding the intensive melting of the coating during laser irradiating which was obvious from the microstructure of the remelted zone of the coating and the negligible effect of oxygen, this result clearly supports the theory that thermal decomposition of WC is mainly responsible for the occurrence of W_2C and that the thermal decomposition of WC to W and C, and W_2C to W and C, can be negligible. This was also confirmed using a CO_2 laser to remelt, under inert argon atmosphere, a WC–Co coating Jet-Kote sprayed with Type-3 powder as in this study [22]. Therefore, oxidation of tungsten carbide must be responsible for the decarburization of WC to W during spraying. Accordingly, under an atmosphere without oxygen, the decarburization of WC to metallic W hardly ever occurs. This is evident from the above mentioned result of WC–Co coating sprayed under low pressure atmosphere.

According to above results, it can be considered that the decomposition of tungsten carbide occurs following two steps: WC to W_2C and then W_2C to W. The first step is controlled by thermal decomposition as follows

$$2WC \rightarrow W_2C + C \qquad (1)$$

Therefore, this reaction will become more intensive with an increase in the heating ability of a flame to spray powder.

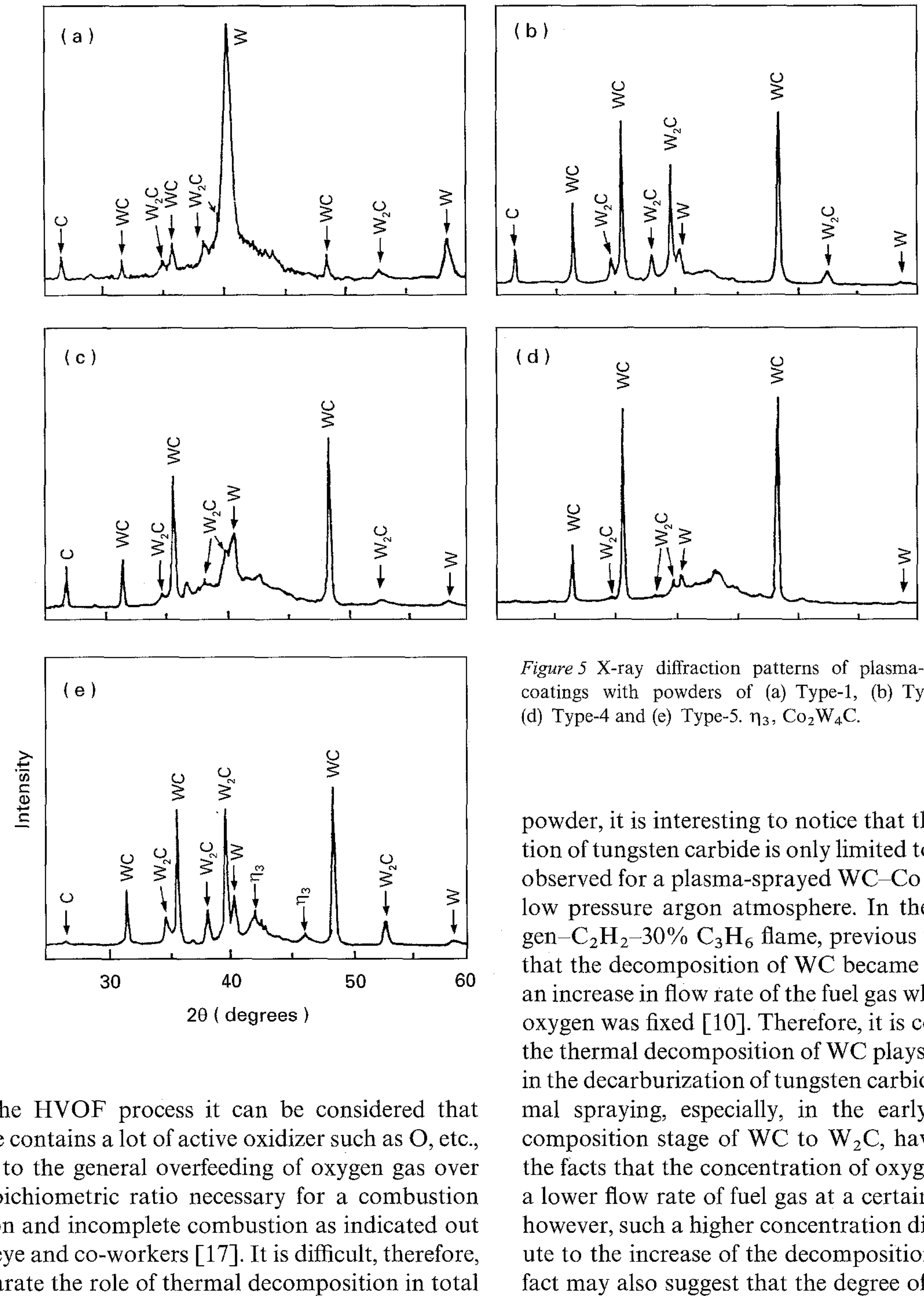
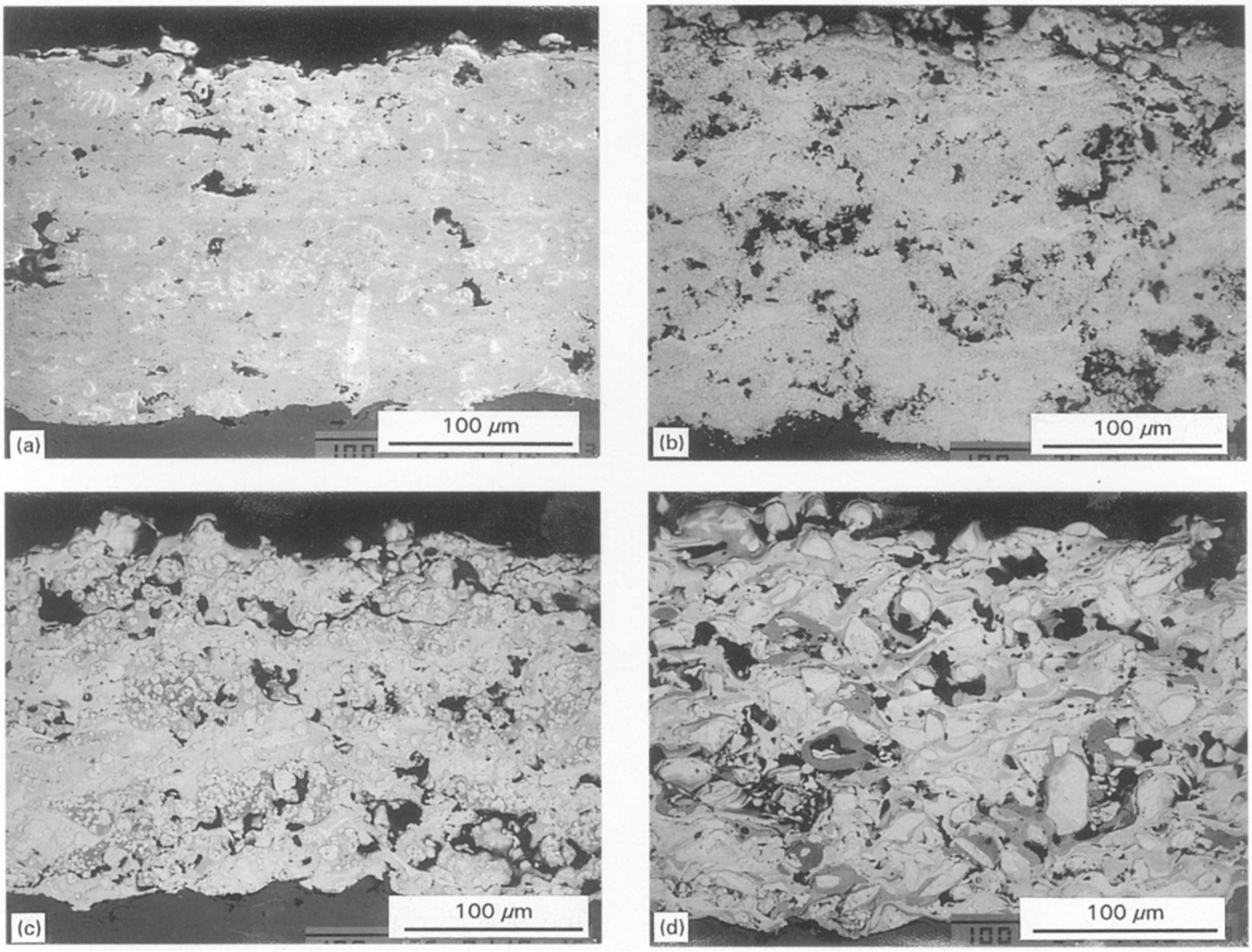


Figure 5 X-ray diffraction patterns of plasma-sprayed WC–Co coatings with powders of (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4 and (e) Type-5. η_3, Co_2W_4C.

In the HVOF process it can be considered that a flame contains a lot of active oxidizer such as O, etc., owing to the general overfeeding of oxygen gas over the stoichiometric ratio necessary for a combustion reaction and incomplete combustion as indicated out by Kreye and co-workers [17]. It is difficult, therefore, to separate the role of thermal decomposition in total decarburization from that of oxidizing decarburization. However, as far as thermal decomposition is mainly concerned, decreasing the heat of a flame to a powder will decrease effectively the decomposition of tungsten carbide. Kreye and colleagues reported that a flame using acetylene as a fuel gas in the Jet-Kote process has a higher heating ability than other hydrocarbon fuels available, such as ethylene, propylene and propane [23]. It can be expected that when propylene or ethylene is used as a fuel gas in HVOF process, the decomposition of WC can be decreased with respect to the use of acetylene. Fig. 8 illustrates X-ray diffraction patterns of WC–Co coatings Jet-Kote sprayed with Type-1 and Type-2 powders using propylene as a fuel gas. Clearly, in the coating sprayed with Type-2 powder substantial tungsten carbide was retained just as in the case using acetylene–30% propylene gas. Moreover, even for Type-1 powder, it is interesting to notice that the decomposition of tungsten carbide is only limited to W_2C, as that observed for a plasma-sprayed WC–Co coating under low pressure argon atmosphere. In the case of oxygen–C_2H_2–30% C_3H_6 flame, previous work revealed that the decomposition of WC became intensive with an increase in flow rate of the fuel gas while the flow of oxygen was fixed [10]. Therefore, it is considered that the thermal decomposition of WC plays a leading role in the decarburization of tungsten carbide during thermal spraying, especially, in the early thermal decomposition stage of WC to W_2C, having regard to the facts that the concentration of oxygen is higher at a lower flow rate of fuel gas at a certain oxygen flow; however, such a higher concentration did not contribute to the increase of the decomposition of WC. This fact may also suggest that the degree of direct oxidization of WC to W is negligible under thermal spray conditions. Therefore, it becomes obvious that a powder which is sensitive to thermal decomposition such as the Type-1 powder used in the present study should be sprayed using fuel gas with lower combustion intensity, such as propylene or ethylene, instead of acetylene-rich fuel gases in the HVOF process to suppress the decomposition of WC.

As for the decomposition temperature of tungsten carbide to W_2C, Orton reported thermodynamically a temperature of 2030 K for W–C binary system [24]. On the other hand, according to Sara's phase diagram for W–C binary system established experimentally, a decomposition reaction (Equation 1) occurs at a temperature of about 3000 K but without indication of further decomposition [4]. Based on the results in the present study, Sara's result would be more feasible for thermal spraying.



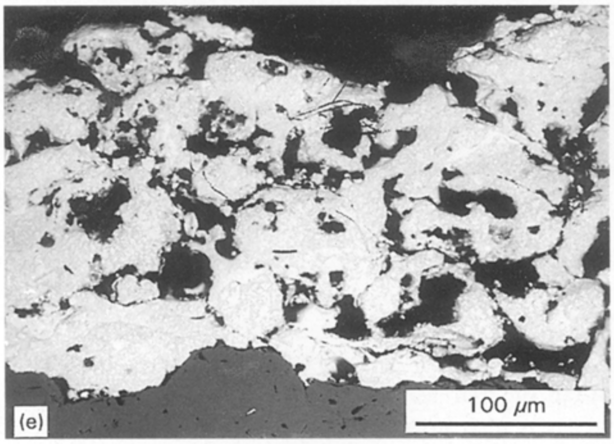


Figure 6 Microstructure of plasma-sprayed WC–Co coatings with powder of (a) Type-1, (b) Type-2, (c) Type-3, (d) Type-4 and (e) Type-5.

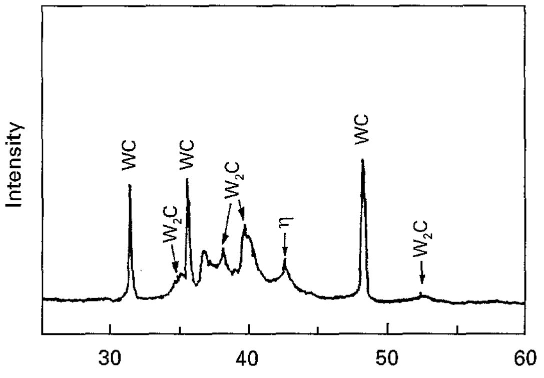


Figure 7 X-ray diffraction patterns of a WC–Co coating plasma-sprayed under low pressure argon atmosphere with Type-1 powder. η, Co_3W_3C.

A simple fusing test with the insertion of molybdenum and tungsten wire into the HVOF flame jet outside the gun exit estimated that two flames have a temperature between 2883 K (melting point of Mo) and 3683 K (melting point of tungsten) [25]. Such a flame temperature is comparable with the thermal decomposition temperature of tungsten carbide reported by Sara [4]. Although the mean temperature of a powder may be lower, the surface layer of a powder can almost reach to flame temperature. Accordingly, it is reasonable that the thermal decomposition of WC–Co powder occurs during the HVOF process. The calculation of theoretical flame temperature of combustion of hydrocarbon fuel with air suggests that the temperature of an acetylene flame would be 400 K higher than a propylene flame [26]. Such a temperature difference in flame jet may be responsible for the degree of the decomposition of tungsten powder during spraying with two flames, especially using two-phase WC and Co_3W_3C powder, and to the sensitivity of decomposition to the type of flames.

Regarding the structure of a laser-remelted WC–Co coating, it is reasonable to consider that the second step of decarburization of WC to metallic tungsten is due to the oxidation of W_2C as follows

$$W_2C + O_2 \rightarrow 2W + CO_2 \qquad (2)$$

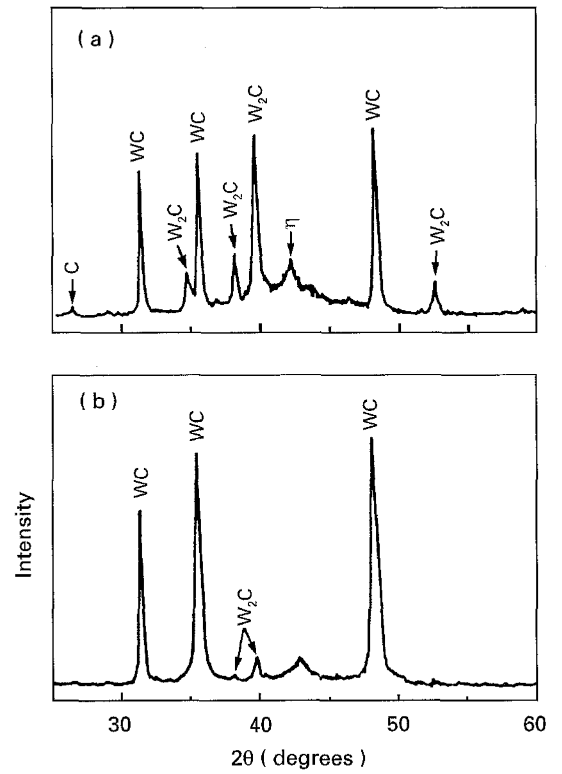


Figure 8 X-ray diffraction patterns of WC–Co coatings sprayed by Jet-Kote using propylene as a fuel gas with Type-1 (a) and Type-2 (b) powders. η, Co_3W_3C.

Based on the above processes of decarburization of tungsten carbide, it can be speculated that a powder with pre-existence of W_2C phase is apt to decarburize to metallic tungsten. Kreye *et al.* showed that during Jet-Kote spraying of WC–Co using propylene as a fuel gas and a 15-cm nozzle, the relative intensity of tungsten to retained WC in X-ray diffraction pattern of the coating was reported to be 60% for a WC–Co powder containing 15% W_2C and 25% eta-phase (main peak ratio with respect to WC) and 15% for a powder of WC and Co two phase [17]. According to the results reported by Arata *et al.* [10], it can be also seen that a WC–Co powder containing W_2C was more apt to decarburize to metallic tungsten even than WC and Co_3W_3C two phase powder. This is also evident in Vinayo and colleagues' results [13]. Those results support the above suggested two-step decarburizing processes. The present results of coating Jet-Kote sprayed with Type-5 powder, which contained W_2C phase, clearly presented a relatively high peak of metallic tungsten compared with Type-2 and Type-3 powder, although substantial WC was retained. This is because the powder had a large grain size.

The present results also evidently revealed that the eta-phase (Co_3W_3C) in WC–Co powder can accelerate the decomposition of tungsten carbide and is sensitive to spray conditions. This may possibly be due to the thermal property difference between eta-phase and metallic cobalt.

On the other hand, it is interesting to find that the coating sprayed with Type-4 powder clearly showed an X-ray diffraction pattern with a large broad peak around $2\theta = 43°$. This broad peak corresponds to a very shallow broad one at the same diffraction angle observed for the coatings sprayed with other types of powders. This result provided clear evidence of the formation of an amorphous phase in the coatings. As the behaviour of formed Co–W–C ternary amorphous phase has been discussed in detail elsewhere [27], annealing at 673 K for 3 h (in ambient atmosphere) only caused appreciable precipitation of free carbon, while after annealing at 873 K for 6 h the amorphous phase crystallized to metallic cobalt, tungsten and Co_6W_6C complex carbide. The same annealing treatment to other WC–Co coatings showed the disappearance of the broad shallow peak in the X-ray diffraction pattern and the crystallization of metallic tungsten and Co_6W_6C carbide instead. The DSC data of Jet-Kote sprayed Type-4 WC–Co coating clearly presented a glass crystallization temperature T_x of about 896 K and confirmed the formation of amorphous phase in the coating.

Concerning the structure of thermally sprayed WC–Co coatings, the formation of complex carbides such as Co_3W_3C, Co_2W_4C, $Co_3W_9C_4$, $Co_6W_6C_6$, [12] and $W_2(C,O)$ [13] in plasma-sprayed WC–Co coatings and $Co_3W_9C_4$ [28] in HVOF sprayed coatings were also reported as well as the decomposition of WC. However, the present results evidently confirm the formation of Co_3W_3C and Co_2W_4C in as-sprayed WC–Co coatings. The evidence of the formation of $W_2(C,O)$, the main diffraction peak appears at 2θ of 36.8° in X-ray diffraction pattern, was only observed in some of plasma-sprayed WC–Co coatings, especially, in WC–Co coating plasma-sprayed under argon low pressure (Fig. 7). The formation of Co_3W_3C in the coating is associated with the pre-existence of Co_3W_3C in the powder and the formation of Co_2W_4C was accompanied by the disappearance of Co_3W_3C and Co_6W_6C observed in powder. On the other hand, it is clear that the annealing treatment of the coating contributes greatly to the formation of Co_6W_6C. Regarding the formation of Co–W–C amorphous phase in WC–Co coating as a matrix, which appears typically broad but shallow in the X-ray diffraction pattern, and the fact that the main diffraction peaks of most complex carbides drop into the diffraction angle range $2\theta = 40\text{–}46°$ of the broad peak of Co–W–C amorphous phase, it is worth indicating that Co–W–C amorphous phase in WC–Co coatings may result in an uncertainty on the formation of complex carbide in a thermally sprayed WC–Co coating.

5. Conclusions

Five representative types of WC–Co powders were sprayed with the Jet-Kote process and plasma spraying. The structure of sprayed coatings was characterized by X-ray diffraction. The decomposition of tungsten carbide in spray powder after passing through flame depends greatly on the structure of powder, in particular, the pre-existence of complex carbides Co_3W_3C and W_2C as well in the powder. The powder with tungsten carbide particles aggregated with Co_3W_3C instead of metallic cobalt is more preferable for tungsten carbide to decompose to dicarbide W_2C or metallic tungsten and is very sensitive to spray conditions. The powder with WC particles densely aggregated with cobalt is most difficult for WC to decompose thermally in the Jet-Kote process. It was evident that decarburization of tungsten carbide occurs through two steps: firstly thermal decomposition of WC to W_2C and then oxidation-assisted decarburization of W_2C to metallic tungsten. The structure of the coating sprayed with cobalt-clad WC type of powder clearly illustrated that an amorphous phase of Co–W–C can be formed in a thermally sprayed WC–Co coating. The crystallization of the amorphous phase occurs at a temperature lower than 873 K to tungsten, cobalt and Co_6W_6C.

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