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Influence of Powder Porous Structure on the Deposition Behavior of Cold-Sprayed WC-12Co Coatings

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The limited deformation of hard cermet particles and impacted coating makes it difficult for conventional thermal spray powders to continuously build up on impact in cold spraying. In this study, three nano-structured WC-12Co powders with different porous structure and apparent hardness were employed to deposit WC-Co coatings on stainless steel substrate by cold spraying. The deposition characteristics of three powders of porosity from 44 to 5% were investigated. It was found that WC-Co coating is easily built-up using porous powders with WC particles bonded loosely and a low hardness. The microhardness of WC-12Co coatings varied from 400 to 1790 Hv with powders and spray conditions, which depends on the densification effects by impacting particles. With porous WC-Co powders, the fracture of particles on impact may occur and low deposition efficiency during cold spraying. The successful building up of coating at high deposition efficiency depends on the design of powder porous structure.

Keywords cold spraying, deposition behavior, hardness, porous structure, WC-12Co

1. Introduction

Carbide cermets are typical wear-resistant coating materials that are widely employed through thermal spraying. The carbide decomposition and dissolution into the binder occurs during thermal spraying of cermets, which deteriorates the performance of cermet materials. The carbide decomposition can be reduced to the minimum through limiting heating of spray powders. Therefore, high-velocity oxy fuel (HVOF) process becomes popular to deposit cermet coatings due to higher flame velocity but lower temperature compared with plasma spraying (Ref 1-10). With using a properly designed WC-Co powder, the decompositions can be reduced to a reasonable low degree (Ref 1). On the other hand, because of the necessity for sufficiently melting the binder alloy to increase the density of the deposit, the carbide dissolution into the molten binder is inevitable during thermal spraying (Ref 1-7). The dissolution becomes severe with the decrease of carbide particles owing to the increased specific surface area of smaller particles. Therefore, despite the limited dissolving time during HVOF, the dissolution can not be significantly avoided, especially when WC carbide particle size decreases to tens of nanometers (Ref 8-12).

With the development of cold spraying, it becomes possible to eliminate completely the decarburization of carbides through decompositions and dissolution because solid spray particles in a much low temperature are employed to deposit the coating (Ref 13-20). However, the limited deformation of both impacting hard cermet particles and the underlying cermet coating makes it difficult for the hard coating to continuously build up on impact in cold spraying using a conventional dense thermal spray powder. In previous papers (Ref 16-20), the deposition of WC-Co particles by cold spraying has been discussed intensively. It was speculated that the successful built-up of WC-Co coating requires the deformation of both the low part of impacting particle near the interface and the underlying WC-Co deposited previously. On the other hand, the upper part of the deposited particle retains its porous structure, which is kept as deformable under the impact of the next particle on its top. Such deformation requirement can easily be fulfilled using a porous powder. However, in such case, it can be considered that several requirements need to be fulfilled to deposit a dense WC-Co coating. The certain cohesion between WC particles bonded by the Co binder is required to avoid the splashing of small WC particles on impact. Then, the impacting particle acquires sufficient kinetic energy to force the

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underlying porous layer to deform sufficiently for full densification. However, excessive energy over that required for full densification may induce intensive cracking and erosion of the deposited layer. Therefore, the matching of porous structure with spray conditions is necessary. With certain porous WC-Co powder, the dense coating can be deposited only in a narrow window of spray conditions. Therefore, the investigations into the influences of porous structure of spray powder and substrate deformability on deposition behavior are essentially important issues to deposit a dense superhard cermet coating.

In this study, three porous WC-12Co powders with different porosity levels were used as feedstocks to deposit nanostructured WC-Co coatings on stainless steel substrate by cold spraying using helium as processing gas. The effect of powder porous structure on deposition characteristics was investigated. The dependence of successful build-up of WC-Co coating with a high deposition efficiency on the design of powder porous structure was discussed.

2. Experimental Materials and Procedures

The powder materials used for this work are three nanostructured WC-12Co powders. They are referred to as HP (high porosity), MP (middle porosity, Zhuzhou Cemented Carbide Group Corporation, Ltd., China), and LP (low porosity, InframatTM S7412, Inframat Corporation, USA) powders.

The cross-sectional microstructures of WC-12Co spray powders were characterized by scanning electron microscopy (SEM, VEGA II-XMU, TESCAN, Czech). The porosities of powders were determined using image processing from the cross section of three powders.

The home-made cold spraying system (CS2000) was employed to deposit the coatings in this study (Ref 21). A spray gun with a converging-diverging de Laval-type nozzle with a throat diameter of 2 mm was adopted. Helium gas was employed as both accelerating gas and powder feeding gas at a pressure of 2.0 and 2.5 MPa, respectively. The gas temperature in the prechamber was 640 °C. The standoff distance from the nozzle exit to the substrate surface was 20 mm. During deposition, the spray gun was manipulated by a robot at a traverse speed of 20 mm/s relative to the substrate for coating deposition and 800 mm/s for single particle deposition, respectively. Stainless steel with the surface sand-blasted was used as a substrate for coating deposition and the polished stainless steel was prepared for single particle deposition.

The microhardness of the powder was tested by a microhardness tester under a 20 g load for a loading time of 10 s owing to small size of the powders, while the microhardness of the coating was tested under a 300 g load for a loading time of 30 s.

The deposition efficiency was measured through the weight gain of the test specimen after spray torch traversed over the specimen and the weight of powders fed into the spray gun at a time interval that the gun took to traverse over the specimen. The deposition efficiency is defined as:

$$D_{\mathrm{E}} = \frac{\Delta m_{\mathrm{c}}}{\Delta m_{\mathrm{p}}}$$

where D_{E} is the deposition efficiency of powders, Δm_{c} is the weight increment of the substrate resulting from WC-Co deposition at a time interval that the spray gun traverses over the substrate, and Δm_{p} is the weight of WC-Co powders fed into the gun at the same time intervals.

3. Results

3.1 Characterization of the Feedstock

Figure 1 shows the cross-sectional microstructure of three WC-12Co powders. All powders exhibited a spherical morphology and porous microstructure. The measurement results showed that the porosity of the three powders changed from 44, 30 to 5%, and the microhardness of the three powders changed from 78, 548 to 1317 Hv, as shown in Table. 1.

3.2 Deposition Test of the Isolated Particles

Figure 2 shows typical particles deposited on stainless steel substrate by three powders, exhibiting the deformation degree on impact, for comparison. It can be clearly recognized that with the increase of powder porosity the powder particles deform more greatly and, however, the substrate deforms less. It was evident that the powder porosity influences significantly the deformation of particles on impact. Moreover, the deformation of the substrate under impact of particles is also influenced by the powder porosity. Therefore, using a porous WC-Co powder of certain porosity and cohesive strength would easily fulfill the requirements for the deposition of hard cermet coating by cold spraying.

3.3 Deposition Behavior and Microstructure of the WC-Co Coatings

Figure 3 shows the cross-sectional microstructure of the coatings prepared with HP, MP, and LP powders. Three coatings were deposited with the same spray parameters except spray passes. The coatings shown in Fig. 3(a) and (c), in the form of the free standing, were deposited by 2 passes using the HP and MP powders, respectively, while the coating in Fig. 3(e) was deposited by LP powder by five passes. Although the coatings deposited by HP and MP powders exhibited a dense microstructure, the lateral cracks were observed in the coating, especially in the region near the coating surface as shown in Fig. 3(d). With LP powder, only a thin coating was present on the stainless substrate surface with lateral cracks distributed on cross section as shown in Fig. 3(f). The lamellar structure was characterized by the lateral cracks in the coating. Compared with the much limited deformation of single particles as shown in Fig. 2(c), the particles in the coating evidently experienced remarkable deformation. Such effect

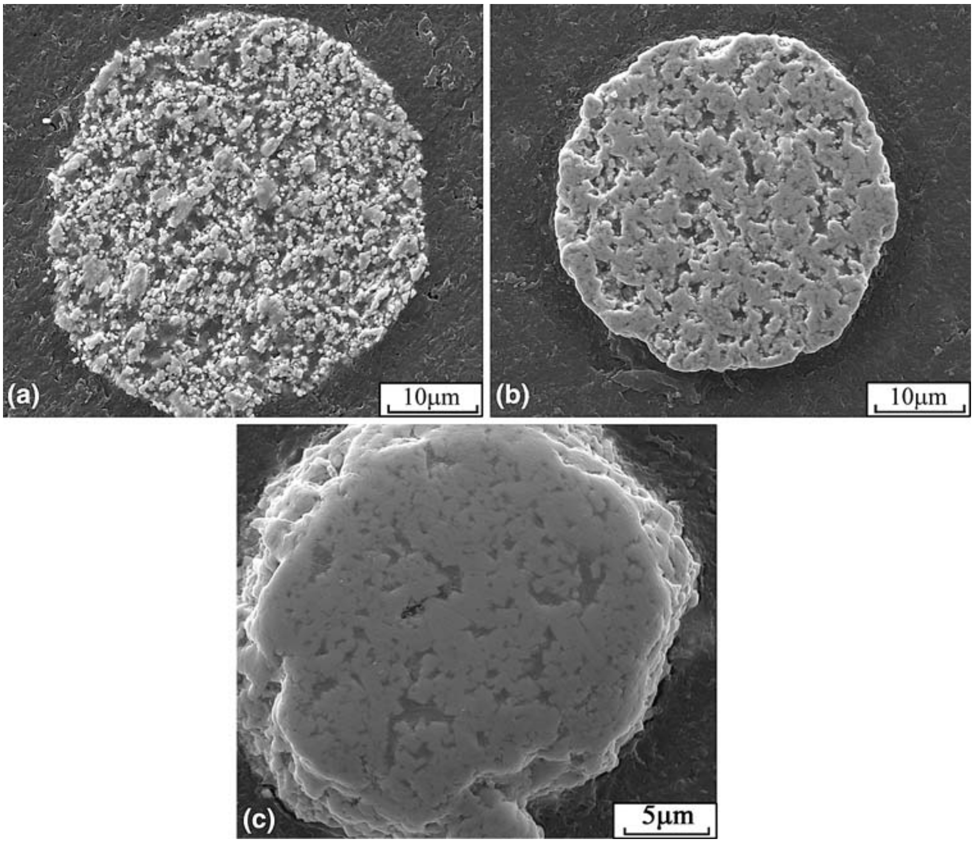

Fig. 1 Cross-sectional microstructure of three powders: (a) HP, (b) MP, and (c) LP

Table 1 Porosity and hardness of three powders

Powder type	HP	MP	LP
Porosity, %	44 ± 1	30 ± 1	5 ± 1
Microhardness, Hv	77.6 ± 2.3	548 ± 46	1317 ± 247

may be attributed to the forced deformation by multi-impacts by spray particles.

Figure 4 shows the microstructure of the coatings deposited by the MP powder by 1 and 10 passes. The coating deposited by 2 passes is shown in Fig. 3(c) and (d). The measurements yielded a thickness of 200, 330, and 350 μm for the coatings deposited by 1, 2, and 10 passes, respectively. It was clearly observed that although the coating thickness increased with the increase of spray pass, the thickness increment of each pass tended to decrease with the increase of spray pass. Moreover, cracks were observed in the coatings, as shown in Fig. 3(d), Fig. 4(b) and (d). The detailed examination revealed that the apparent crack density decreased with the increase of spray pass. The possible reason for crack density reduction with increasing spray pass is the densification through successive impacts of spray particles. With the cracks near the surface region, the spalling by peening effect of hard particle may eliminate the cracks and is also responsible for the reduction of the deposition efficiency.

The deposition efficiency measurements yielded 18.1, 19.2, and 7.1% at spray passes 1, 2, and 10 for the MP powder, respectively, as shown in Fig. 5. It is clear that the deposition efficiency till 2 passes changed less significantly, while it tended decrease with the increase of overlaying spray pass. These results are consistent with those observed from the coating thickness change with spray pass. During cold spraying, the densification through successive impacts of spray particles would make the hardness of the deposited WC-Co to increase gradually. Therefore, the deformability of the previously deposited WC-12Co layer would be decreased comparably. The spray particles would impact on the hard surface of the deposited layer. As a result, the DE value of MP powder decreased enormously with the increase of the spray pass, which was consistent with the thickness increment tendency. LP powder had the highest microhardness and the lowest deformability among the three powders. Once a layer of LP powders embedded into the stainless steel substrate and a thin layer of WC-Co coating covered over the substrate, the hardness of the newly formed substrate, i.e., WC-Co coating, would increase intensively. The further deposition of LP powders, behaviors just like that of MP powder deposition, experienced many spray passes. Both the LP powder and newly formed substrate were hard to deform, which led to a much low DE value. On the other hand, the HP powder had higher porosity and deformability than the MP powder.

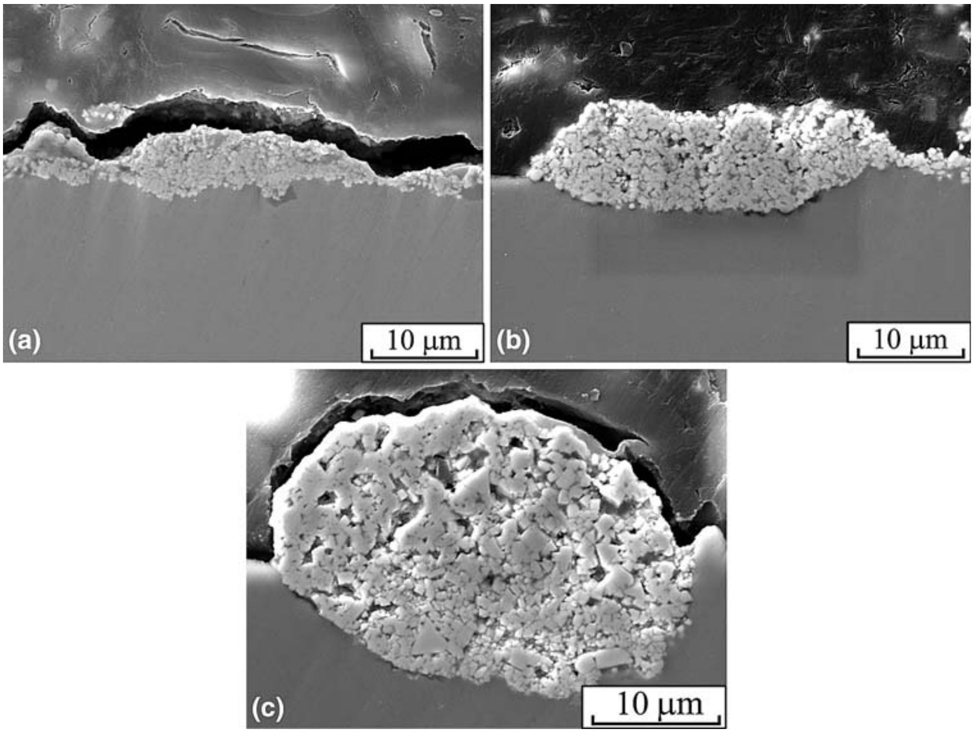

Fig. 2 Cross-sectional microstructure of the deposited single particles using different powders: (a) HP, (b) MP, and (c) LP

During deposition of the HP powder, even though the deposited WC-Co layer exhibited high hardness and poor deformability, the HP powder could deform intensively and flatten onto the deposited layer to build up a layer of coating. However, due to the relatively weak cohesion, the HP powder deformed intensively on impact and partially disintegrated, which resulted in rebounding off of a fraction of powder material as shown in Fig. 2(a). Accordingly, the deposition using the HP powder yielded a lower DE value than the MP powder.

3.4 Microhardness of the Coating

The microhardness of WC-Co coating deposited by the HP powder is 1790 ± 23 Hv. It can be seen from Table 2 that the microhardness of the WC-Co coatings deposited by MP powders increased with the increase of the spray pass. The microhardness of the coatings deposited at 1, 2, and 10 passes were 400, 670, and 1340 Hv, respectively. Such increase is possibly attributed to the densification effect caused by tamping of particle jet impacting on the coating surface. Taking account of the high coating hardness and low deposition efficiency using the HP powder compared with that of the MP powder, it is evident that the densification effect through tamping of impacting hard particle is essential to deposit a dense nanostructured coating using porous powder.

3.5 Deposition Test at a Fixed Position

It is clear that under the same spray conditions the nanostructured WC-Co coatings were deposited using HP and MP powders. The spalling of the deposited layer makes it difficult to deposit a well-cohered WC-Co coating using the LP powder. However, it was found that the dense deposit can be obtained when spray gun was held stationary during deposition using all three powders. Figure 6 shows the microhardness of WC-Co deposits obtained using three powders for 5 s. The microhardness of the cold-sprayed three nanostructured WC-Co deposits is comparable despite initial hardness of starting powders. This fact suggests that some other factors such as the change of the deformability of the deposit may be important for continuous deposition of WC-Co cermet coating by cold spraying using a relatively dense powder.

4. Discussion

The three porous WC-12Co powders in the present study showed different microhardness and different porosity values. The hardness of the powder decreases with the increase of porosity, which increases deformability of the powder. The HP powder had the highest porosity and the greatest deformability among the three powders. From the results of the single-particle deposition test, it was clearly observed that the HP powder deformed more intensively and flattened on the substrate surface. The MP powder deformed greatly but not as intensively as the HP powder. On the other hand, the LP powder had the highest microhardness and could embed into the substrate easily, but it presented much less deformation. Such fact suggests that the LP powder may not be

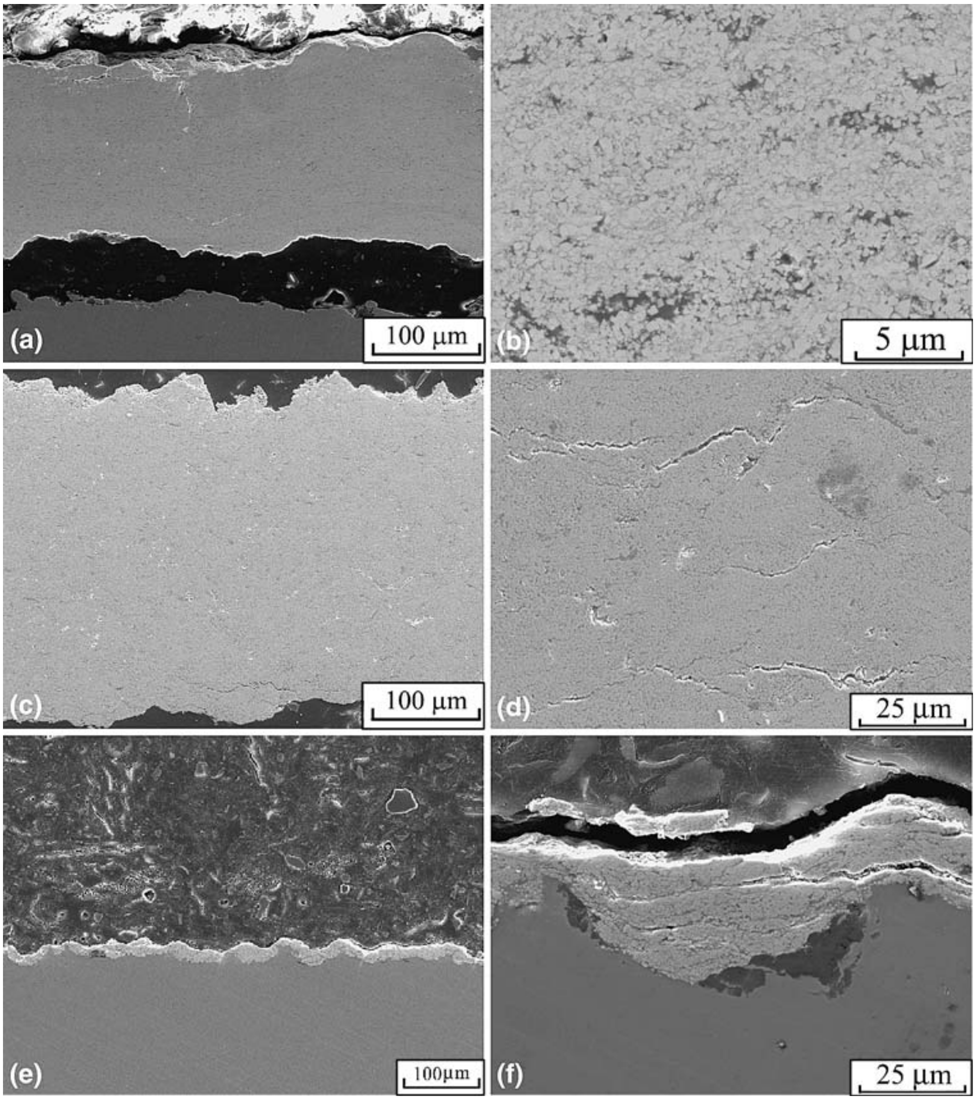

Fig. 3 Typical microstructure of WC-Co coatings by three powders: (a, b) HP, (c, d) MP, and (e, f) LP

favorable to continuous build up of WC-Co coating. This was consistent with the coating deposition test result as shown in Fig. 3. Kim et al. (Ref 17, 18) reported that the nanostructured WC-Co of high hardness comparable to bulk materials was deposited through preheating of spray powder. The preheating of spray powder caused softening effect and consequently enhanced the deformability of the particle on impact. It can be considered that realizing the continuous coating built-up using the porous WC-Co powder in the present study resulted from the similar enhanced deformability effect to that reported by Kim et al.

From the coatings prepared with HP and MP powders at the same deposition parameters, it could be found that the deposited coatings exhibited different deposition efficiency and microhardness. Moreover, it seemed that a higher deposition efficiency was associated with a lower microhardness of the coating. It can be considered that the difference in the deposition efficiency with two powders is mainly associated with the integrity of the particles on impact. The fracture or collapse of the HP powder on impact possibly is one reason that led to the low deposition efficiency. On the other hand, the low deposition efficiency may contribute more accumulative densification effect by multi-tamping. As a result, the low deposition efficiency was possibly associated with an increased coating hardness.

With the MP powder, it was found that the spray pass influenced significantly the deposition efficiency and coating hardness. During cold spraying, the substrate was changed with the deposition of WC-Co particles. Once a WC-Co layer is deposited on the initial substrate, spray particles will impact on the surface of the deposited layer; therefore, the previously deposited WC-12Co layer acts as a new substrate. Moreover, the densification through successive impacts of spray particles would harden the deposited WC-Co. As a result, the hardness of the deposited WC-Co would be increased intensively. The

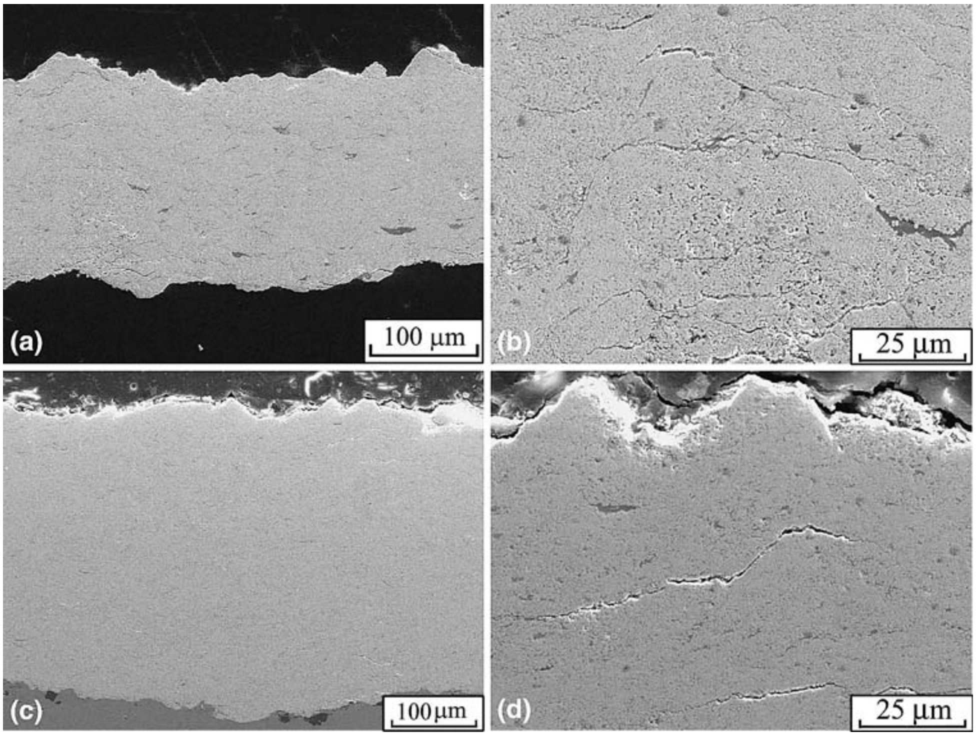

Fig. 4 Microstructure of WC-Co coatings deposited with MP powder by different passes: (a, b) 1 pass and (c, d) 10 passes

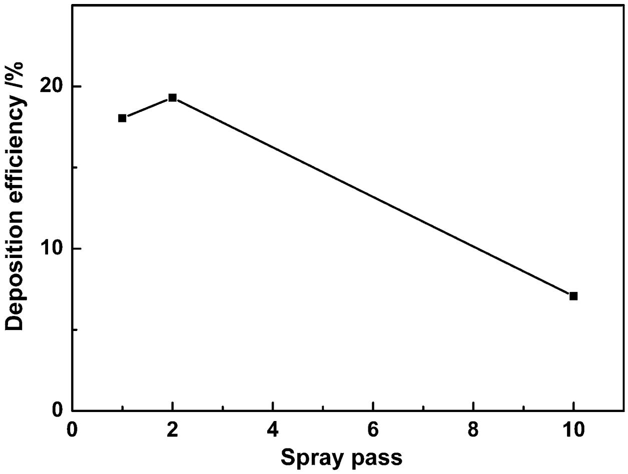

Fig. 5 Deposition efficiencies of MP powder at different spray passes

Table 2 Effect of spray pass on the coating thickness and coating hardness using MP powder

Pass number	Thickness, μm	Hardness, $HV_{0.3}$
1	200	400 ± 11
2	330	670 ± 38
10	350	1340 ± 78

deformability of the deposited WC-Co would become gradually poorer. Therefore, with increasing overlying spray passes, the deposition efficiency was evidently decreased and the hardness of the coating was increased. The previous study on the Ti coating deposition clearly revealed that the top porous layer can be gradually densified by tamping effect of the later coming particles (Ref 21). With porous WC-Co powders, the limited deformation of the particle on impact leads to the deposition of partial porous layer. The accumulative impacts by particles jet seem effective to densify the coating. As a result, the coating hardness can be significantly increased. However, as the cracks were observed especially near the surface region, it can be considered that the adequate particle impact pressure is required to eliminate the cracks

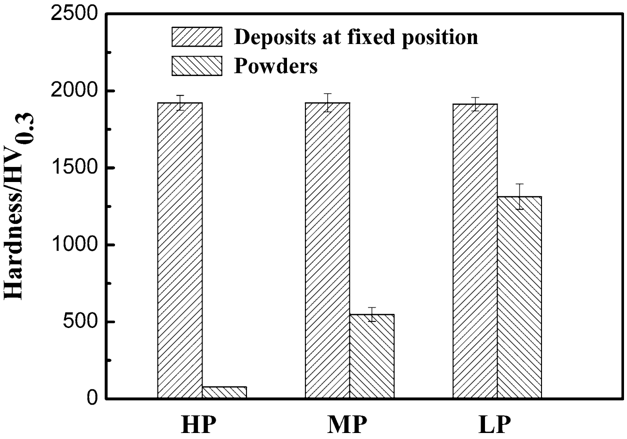

Fig. 6 Microhardness of the nanostructured powders and cold-sprayed deposits at fixed position

through densification. The excessively high impact pressure may cause the propagation of the preexisted cracks and subsequently spalling of the deposited layer as clearly observed during deposition using LP powder. To avoid the spalling on impacts of spray particles, the sufficient cohesion within the deposited layer is necessary. Therefore, using an adequately designed porous spray powder, controlling of dynamic impact pressure, and particle cohesion through spray conditions would be essential for continuous build-up of a cermet coating with high hardness.

Moreover, besides the deformability of spray powder, low density of the powder with high porosity may also be beneficial to WC-Co particle deposition. High powder porosity in the same powder size would correspond to light weight under the same spray conditions, and the lighter particles would be accelerated to a higher velocity. Correspondingly, powders with higher porosity would be accelerated to a higher velocity which would be more easily deposited onto the substrate than the powders with lower porosity.

It was found that the traverse speed of spray gun influences significantly the deposition behavior of WC-Co. When the traverse speed was reduced to zero, that is, performing deposition at a fixed position, dense WC-Co deposits, with the hardness values comparable to those of bulk materials, were continuously built up. This is possibly due to the improved deformability of deposited WC-Co top layer resulting from the intensive heating of gas stream. Recently, it has been reported (Ref 22) that under the stationary nozzle operation a significant heat transfer from the supersonic gas jet to the substrate occurs and the heat transfer could bring out a significant temperature increasing of the substrate, especially near the deposited top layer surface. Such temperature increasing of the deposited WC-Co layer would decrease the surface hardness of WC-Co (Ref 23, 24). As a result, the deformability of the WC-Co substrate on which WC-Co impacts will be enhanced. Therefore, the transient softening of the top surface of WC-Co layer on which spraying particles impacts during spraying also influences significantly the built-up of the hard WC-Co coating. At a very low traverse speed, even to zero (i.e., at a fixed position), the deposited particles were kept at a high temperature so that the deformability of the previous deposited particles was kept at a higher level. The high deformability of the surface deposit layer leads to the continuous deposition of dense WC-12Co of high hardness.

The hardness test of the WC-Co deposits sprayed at the fixed position yielded a comparable mean hardness of about 1900 Hv despite powder microstructure. Those hardness numbers are comparable to those of bulk materials, which is consistent with that reported by Kim et al. (Ref 17, 18) However, it is clear that the hardness of the coatings built up with continuous traversing was significantly influenced by the powder structure and gun traverse speed. It is clear that with the decrease of traverse speed gun and increase of powder porosity the hardness of cold-sprayed WC-Co coating was increased. Those facts clearly indicated that the deformation of both the deposited layer and impacting particle are responsible for the deposition of hard coating.

5. Conclusions

WC-Co coating can be successfully built-up using the porous powders with WC particles bonded more loosely. The build-up of the coating was mainly contributed by the deformation of porous powders on impact. It was found that the deposition efficiency was significantly influenced by the porosity levels of the powders. Moreover, the deposition efficiency tended to decrease with the increase of coating thickness. The densification effect resulting from the successive tamping of the later impacting particles increased the coating hardness and, on the other hand, decreased the deposition efficiency. The high intensive impact with harder particles can cause spalling rather than densification of the deposited layer. Therefore, designing a porous WC-Co powder with adequate hardness is one important approach to deposit hard WC-Co cermet coating by cold spraying through controlling the deformability of spray powder. The deposition test at a fixed position suggested that the enhancement of the deformation of the deposited top layer at the impact of spray particle benefits the deposition of dense and hard WC-Co coating.

Acknowledgments

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