Characterization of Nanostructured WC-Co Deposited by Cold Spraying

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Nanostructured WC-Co coating was deposited by cold spraying using a nanostructured WC-12Co powder. The critical velocity for the particle to deposit was measured. The coating microstructure was characterized by X-ray diffraction analysis, scanning electron microscopy, and transmission electron microscopy. The coating hardness was tested using a Vickers hardness tester. The deposition behavior of single WC-Co particle was examined. WC particle size was measured for comparison of deposit properties to that of sintered bulk. The result shows that the nanostructured WC-Co coating can be successfully deposited by cold spraying using nanostructure powders. The coating exhibited a dense microstructure with full retention of the original nanostructure in the powder to the coating. The test of microhardness of the coating yielded a value of over 1820 Hv_{0.3}, which is comparable to that of sintered nanostructure dWC-Co. The deposition behavior of WC-Co powders as superhard cermet materials in cold spraying and powder structure effects is discussed.

Keywords	WC-Co,	nanocrystalline	material,	cold	spray,
-	annealing	g, critical velocity	, microhar	dness	

1. Introduction

WC-Co cermets are most important wear-resistant coating materials employed for thermal spraying. It is essential to reserve the designed phases of powders to the deposit to optimize wear resistance of deposit based on the theory of hardmetals. However, the requirement of heating of powder to certain degree during thermal spraying results in dissolution of carbide by the melted binder phase and thermal dissociation of WC, and also burning of carbon by oxidation (Ref 1, 2). These thermal effects lead to decarburization, which not only reduces wear-resistant hard phase, but also leads to the formation of brittle binder phase (Ref 3). Therefore, preventing carbide from decarburization is the essential concerns, during deposition of WC-based coatings. Numerous investigations were dedicated to study the phenomena associated with the decarburization of carbide during plasma spraying (Ref 4-8) and high velocity oxy-fuel spraying (Ref 1, 9-13) in last several decades as has been reviewed by Lovelock (Ref 2). The previous study (Ref 1) revealed that powder structure and heating degree during spraying process are basically two primary factors that influence decarburization and consequently microstructure of WC deposit. Owing to high velocity and low temperature of flame, using high velocity oxy-fuel process (HVOF) a stream of WC-Co particles with high velocity and limited heating are easily achieved than plasma spraying. Consequently, denser WC-Co coating with superior wear resistance can be deposited by HVOF, which has been very popular to deposit WC-Co coatings in last two decades. Although decarburization of WC and dissolution of WC into molten Co matrix take place, the use of proper powder and optimization of spray conditions can limit the above-mentioned deteriorative effects (Ref 1) and result in a WC-Co coating with an improved wear-resistance (Ref 14).

On the other hand, it is known that hardness of WC-Co cermet increases with the decrease of carbide particle size. WC-Co cermet manufactured from nanosized WC particles exhibits a high hardness (Ref 15, 16). Accordingly, a better wear resistance can be expected for nanostructured WC-Co coating, because the abrasive wear resistance of materials is generally increased with the increase of their hardness. Therefore, many attempts have been made to deposit nanostructured wear-resistant WC-Co coatings especially by HVOF (Ref 17-30). However, the decarburization and dissolution of WC during HVOF become severe as WC particle size decreases (Ref 1, 24). This fact derived many investigators to optimize the phase formation in the nanostructure deposit in a similar way to thermal spray of conventional microstructured WC-Co materials. Most investigations revealed that deposition of a dense WC-Co requires well heating of spray powders, while less decarburization needs to reduce heating degree

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of nanostructured powders but it leads to increase of porosity in the deposit (Ref 29). Accordingly, the optimization of HVOF deposition conditions should be performed by compromising between coating density and decarburization. The optimization of HVOF spraying conditions generally can lead to an increase of microhardness of nanostructured WC-Co deposits than conventional ones. The significant improvement of wear resistance was observed for vacuum plasma sprayed nanostructured WC-Co coating than conventional microstructured counterpart (Ref 31). Moreover, incorporating nanostructured WC into conventional powders, which constructed a multimodal powder in carbide size, led to a significant improvement of wear performance of the multimodal WC-Co cermet coating (Ref 32). However, many articles reported that wear resistance of HVOF sprayed nanostructured WC-Co coatings was not superior compared with conventional coatings (Ref 24, 29, 33). This fact was attributed to the sub-surface cracking along lamellar interface during wear test (Ref 33). The easy crack propagation along lamellar interfaces during wear test of HVOF cermet coating suggests that the bonding between lamellae in HVOF cermet coatings is limited, which is generally observed in plasma-sprayed ceramic coatings (Ref 34). Therefore, during HVOF spraying of nanostructured WC-Co, the severe dissolution of nanosized WC into melted Co matrix may occur and reduce wear-resistant phase (Ref 24) and weak interface bonding between lamellae inherent to thermal spray process (Ref 34) may be present in the coating. Those features make it difficult to effectively utilize the potential wear performance of nanoWC-Co by HVOF.

Cold spraying process is recently emerging as a new coating process of thermal spray family. In this process, a coating is generally deposited through deformation of spray particles in completely solid state with high velocity on impact. The temperature of spray particles is much lower than the melting point of any phase in spray powder. This low temperature feature makes it possible to retain the thermally sensitive microstructure of a feedstock such as nano-structure to deposit. Then, this feature makes cold spraying suitable to form nanostructured deposits from nanostructured feedstocks. The depositions of different nanostructured metallic materials such as Fe/Si alloy (Ref 35), Fe/Al alloy (Ref 36, 37), MCrAIY (Ref 38), Al alloy (Ref 39) and so on have confirmed the feasibility of cold spray process to form nanostructured metal materials deposits.

With the recent development of cold spraying it was considered that cold spraying can be used as an alternative to HVOF to deposit nanostructured WC-Co. Therefore, deposition of nanostructured WC-Co coatings was attempted using cold spray process. The early work reported by Lima et al. (Ref 40) showed that only a nanoWC-Co with a limited thickness up to 10 μ m could be deposited. More recently, Kim et al. (Ref 41, 42) reported that a thick nanoWC-Co coating up to 1 mm was built up through cold spraying. It was demonstrated that the cold-sprayed WC-12Co coating presented a microhardness of about 2000Hv, which is comparable to sintered nanoWC-Co.

Generally, a dense cold spray coating is created through certain deformation of spray particles and the underlying substrate or previously deposited coating. In the case of ductile materials the plastic deformation benefits the dense compaction of deposition particles (Ref 43). The coating microstructure can be further modified by the tamping effect of impacting particle on the underlying deposited particles (Ref 43). With hard WC-Co alloy, shortage of ductility makes deposition of dense coating difficult. Although superhard nanostructured WC-Co coating has been successfully deposited, the physical phenomena involving particle deposition were still not understood.

In this article, a commercial nanostructured WC-Co powder made from agglomerating nanoWC with cobalt was employed to deposit coating. The critical velocity of the powder was experimentally measured. The microstructure of the nanostructured WC-Co deposit was characterized using scanning electron microscope (SEM), X-ray diffraction (XRD), transmission electron microscope (TEM). The influence of annealing treatment at a high temperature on the microstructure and microhardness of nanostructured coating was investigated. The deposition process of nanostructured WC-Co particles on impact was examined to understand the build-up process of hard WC-Co coatings.

2. Materials and Experimental Procedures

2.1 Materials and Coating Deposition

A commercial nanostructured WC-12Co powder (Inframat) was employed in this study. The powder was made from agglomeration of nanosized WC with cobalt followed by partially sintering. The powder particles had a size range from 5 to 44 μ m. The nominal WC grain size was 50-500 nm. A stainless steel plate was used as a substrate. Prior to deposition, the substrate was sandblasted with alumina grits.

Cold spray deposition was carried out using a homemade cold spraying system installed in our laboratory. The spray gun with a convergent-divergent nozzle was employed in the system. The nozzle of a downstream length of 100 mm has a throat diameter of 2 mm and exit diameter of 4 mm. The other details of the system installation were described elsewhere (Ref 43). Helium was used as both the accelerating and powder feeder gases. The gas pressure and temperature at the prechamber were 2 MPa and 600 °C, respectively. Spray distance was 20 mm.

2.2 The Critical Velocity of the Nanostructured WC-12Co

The critical velocity of the WC-12Co powder used in this study was estimated through employing the approach based on the measurement of the relative deposition efficiency at different spray angles with respect to normal impact (Ref 44). The detailed procedures of critical velocity measurement have been described in the previous report (Ref 44). Here, only the basic methodology is simply introduced. Based on the theory established in previous study (Ref 45), the relationship between deposition efficiency (E_d) and spray angle (θ) can be expressed using the particle size distribution parameters and the parameters representing the relation between particle size and velocity as follows:

$$E_{\rm d} = \left\{ 1 - \exp\left[-\left(\frac{\left(k\sin(\theta)/V_{\rm c}\right)^{1/n} - d_{\rm min}}{d_0}\right)^m \right] \right\} \\ \times \left\{ 1 - \exp\left[-\left(\frac{d_{\rm max} - d_{\rm min}}{d_0}\right)^m \right] \right\}^{-1} \times 100\% \quad ({\rm Eq}\ 1)$$

where, V_c is the critical velocity and all other parameters are the constants pertinent to particle size distribution and particle velocity distribution. Particle size distribution is expressed as follows through modifying Rosin-Rammler formula using cut-off sizes of particles (Ref 44):

$$f_{\rm m} = \left\{ 1 - \exp\left[-\left(\frac{d_{\rm p} - d_{\rm min}}{d_0}\right)^m \right] \right\} \\ \times \left\{ 1 - \exp\left[-\left(\frac{d_{\rm max} - d_{\rm min}}{d_0}\right)^m \right] \right\}^{-1} \times 100\% \quad ({\rm Eq}\ 2)$$

where, d_{\min} and d_{\max} are cut-off sizes of minimum and maximum particle sizes, respectively, d_0 and *m* are constants. These parameters can be determined by measuring quantitatively particle size distribution. In this study, particle size distribution was measured by a laser diffraction sizer (MASTERSIZER 2000, Malvern Instruments Ltd., UK).

Moreover, it was found (Ref 46) that particle velocity can be expressed as the function of particle diameter (d) in the form of (k/d^n) as far as the velocity of the smallest particle is less than gas velocity. Here, k and n are constants. These two constants were obtained through simulation method based on the Computational Fluid Dynamics developed in the previous studies (Ref 46) for the tested spray conditions in this study. During simulation, a density of 10 g/cm³ was used.

Figure 1 shows the experimental result of the relative deposition efficiency of the WC-Co powder against spray angle. The regression of the theoretical relation (i.e., Eq 1) between the relative deposition efficiency and spray angle with the experimental data through the least-square fitting yields the critical velocity. The regression result was also shown in Fig. 1 for comparison. The present test yielded a critical velocity of 915 m/s for the present nanostructured WC-12Co. Therefore, deposition of the present nanostructured WC-12Co needs to employ a set of spray conditions to accelerate most particles to velocities higher than 915 m/s.

2.3 Coating Characterization

The microstructure of the coating and morphology of both spray powder and deposited particles were characterized by SEM. The microstructure of the coating was



Fig. 1 The relation between the relative deposition efficiency of nanostructured WC-Co and spray angle

also characterized by TEM. XRD was employed to characterize the phase structure of both the powder and coating. The microhardness of the coating was tested by a microhardness tester under a 300 g load for a loading time of 30 s. A coating was also subjected to a annealing treatment at a temperature of 1000 °C for 6 h to investigate the influence of the post-diffusion treatment on the microstructure and properties of the coating.

3. Results

3.1 Morphology of Nanostructured WC-12Co Feedstock Powder

Figure 2 shows the morphology of the powder at different magnifications. The powder exhibited a spherical morphology. Evidently, nanoWC particles were partially bonded together and voids appeared on the cross-section of powder. From XRD pattern of the powder shown in Fig. 3, it can be recognized that the powder consisted of WC and Co two phases.

3.2 Characterization of Nanostructured WC-12Co Coating

Figure 4 shows typical microstructure of cold-sprayed nanostructured WC-12Co coating. It was recognized that a dense coating can be built up to a thickness of 1 mm by cold spraying. The examination in details into microstructure revealed that WC particles were densely compacted in the coating although small voids were observed as shown in Fig. 4(b). WC particles in the coating had a broad size distribution. TEM examination (Fig. 5) exhibited that many WC particles having particle size of around 100 nm were present in the coating. From XRD pattern of the coating, shown in Fig. 2, it was recognized that only WC and Co phases were present in the coating. This fact means that no composition and phase structure changes



Fig. 2 Morphology of nanostructured WC-12Co feedstock (a) with detailed surface structure at a high magnification (b)



Fig. 3 XRD pattern of the cold-sprayed coating compared with that of the powder

occurred during deposition. However, it was noticed that the diffraction peaks of WC and Co were significantly broadened compared with those of WC-12Co feedstock.



Fig. 4 Typical microstructure of cold-sprayed nanostructured WC-12Co coating



Fig. 5 A TEM image of cold-sprayed nanostructured WC-12Co coating

One possible reason for peak broadening is the high atomic level strain in the coating induced by high velocity impact of high-density WC-Co particles. Another possible reason may be attributed to the reduction of WC particle size through fracturing of brittle WC particle under high



impact pressure of incident particle. This phenomenon will be discussed later in the discussion section.

3.3 Microhardness Test of the Nanostructure WC-Co Coating

The microhardness of the coating was tested from cross-section of the coating at a 300 g load. Nineteen tests were performed and an arithmetic average hardness of 1812 ± 121 Hv_{0.3} was obtained. A typical indent was shown in Fig. 6. It was observed that cracks occurred around some indents. Those cracks usually propagated along the direction of particle interface. This fact implies that the interfaces between deposited particles were not perfectly bonded. Moreover, the local collapse surrounding the periphery of the indent was also observed surrounding some indents, which may mean that carbide particles in the as-sprayed coating were not fully densely compacted. The hardness distribution was plotted using Weibull distribution as shown in Fig. 7. It is clear that the test data



Fig. 6 Typical indent on the coating after microhardness test



Fig. 7 The distribution of microhardness of cold-sprayed nanostructured WC-12Co coating

followed the Weibull distribution. A mean microhardness of 1869 $Hv_{0.3}$ was obtained following the Weibull distribution.

4. Discussions

4.1 Deposition Behavior of WC-Co Particles in Cold Spraying

The present results clearly showed that a thick nanostructured WC-Co coating can be deposited by cold spraying. The results are consistent with those reported by Kim et al. (Ref 41, 42). It is known that a cold spray coating is built up via certain deformation of both spray particle and substrate on impact of spray particle on a substrate. When a hard particle impacts on a relative soft substrate, the intensive deformation of the substrate will cause the penetration of particle into the substrate. Figure 8 shows three typical particles having penetrated into the substrate surface to certain different depths. The size of individual particles can be also estimated from the morphology of penetrating particles showing in Fig. 8. Clearly, the relative penetration depth into the substrate depends on particle size. The smaller the particle size, the relatively deeper the particle penetrates into the substrate. Possibly, this is attributed to the difference in particle



Fig. 8 WC-Co particles penetrated into the stainless steel substrate. (a) Two particles of different diameters penetrating to different depths; large particle penetrated less depth than small particle; (b) a smaller particle of about 10 μ m diameter has almost embedded into the substrate completely

velocity because smaller particle is accelerated to a higher velocity. When the surface of a substrate is uniformly covered by implanted WC-Co particles completely, a thin layer of WC-Co coating of a maximum thickness about the mean particle size can be deposit. This fact corresponds to the result as reported by Lima et al. (Ref 40).

The successive building up of a WC-Co coating to a designed thickness via impact of solid particles under cold spray conditions requires the formation of a strong cohesion of impacting WC-Co particle with the underlying WC-Co coating. The creation of such cohesion requires certain deformation of both impacting particle and the underlying coating where the particle impacts on. On the other hand, the deformation is associated with particle velocity and powder structure. It can be considered that the minimum deformation corresponds to the critical velocity determined by powder structure. The successful deposition of nanostructured WC-Co coating was realized under the present spray conditions. This fact means that a fraction of particles reached the velocities larger than the critical velocity. In this case, a fraction of impacting particles fulfilled the necessary deformation requirements for coating deposition with the nanostructured WC-Co particles used in the present study. However, the deposition test using a conventional microsized-WC-Co powder with a densely sintered microstructure did not achieve coating building up instead of erosion of substrate under the same spray conditions. This fact indicated that the particle structure influences significantly the deposition behavior of hard materials by cold spraying.

From the morphology of the powder particle shown in Fig. 2, it can be found that although the WC particles in the powder used in this study were aggregated together, the voids were present within particle. Upon impact at high velocity, the compaction of particles near the impact area will occur through slipping of WC particle along cobalt binder, which is referred to as the pseudodeformation of the particle. As it has been revealed by previous studies, the significant deformation is limited to the region near particle impact area (Ref 43). Deformation degree changes from the contact surface of impacting particle to the top free surface. Such non-uniform deformation leads to also the partial compaction of porous microstructure inherent to original powder at the region near the interface between the particle and the underlying coating. On the other hand, the deformation near the free surface of the particle is much limited. From the morphology of particles penetrated into the substrate shown in Fig. 8, it can be observed that the fraction of the penetrated particles near the top surface was kept almost unaffected, which was present in the coating as a deformable porous surface layer. When a spray particle impacts on such layer, the deformation of both the top porous layer of previously deposited particles and bottom fraction of impacting particle near the interface region simultaneously occurs. This makes it possible to fulfill the requirements of the deformation of both substrate and impacting particle. Therefore, the particles having a velocity larger than the critical velocity can be adhered to the coating one by one through the above-mentioned

pseudo-deformation. A dense coating should be created by particle having a sufficient kinetic energy to cause the compaction of majority of porous particle materials on which it impacts. As WC particles in powder are bonded loosely by cobalt binder, it deforms easily upon impact. Consequently, it can be considered that a WC-Co powder with WC particles bonded to a certain porous state by cobalt is suitable for cold spraying. Moreover, the deformability of WC-Co powder can be improved by raising its temperature, which improves the deposition of WC-Co as reported by Kim et al. (Ref 41).

With densely sintered WC-Co particles with low cobalt content, the hardness of particles is high and deformability upon impact is much low. The deformation of impacting particle and the underlying cermet is also required to form the cohesion strong enough to promote successive deposition of WC-Co particle. The deformation behavior will be similar to all other dense materials rather than compaction of porous structure in the case of present nanostructured powder. When particle velocity is high enough to embed only mechanically on the coating surface through penetrating as shown in Fig. 8, the first cermet layer is deposited with the penetrated particles covering all soft steel substrate surface. Then, other spray particles will impact on the surface of the deposited hard cermet layer. However, low deformability of both deposited cermet layer and impacting particle would require much high velocity to achieve a sufficient deformation necessary for creation of sufficient cohesion. The present result suggests that with the conventional densely sintered WC-12Co cermet powder, under the present cold spray condition the deformation degree of WC-Co particles was not high enough to form a sufficient cohesion for successive coating deposition. On the other hand, the deposition of cermet particles may result in a rough surface due to limited deformation of particles. This surface condition in turn benefits the mechanical embedding of the incoming particles. As a result, a porous coating like that produced by mechanically pressing would be deposited as in the case of vacuum cold spraying with small solid ceramic particle (Ref 47). The microhardness of such coating is much low as reported (Ref 47) in comparison with bulk material.

From XRD pattern of the present cold spray nanostructured coating, the significant broadening of XRD diffraction peaks was clearly recognized. One possible reason is attributed to atomic level strain resulting from high velocity impact effect. This effect may change the hardness of the coating. On the other hand, the atomic strain can be released by post-annealing treatment. It was found that the annealing treatment of the present coating at 1000 °C for 6 h did not change microhardness numbers of the coating. Therefore, the effect of the atomic strain on the broadening of XRD diffraction peaks may be limited. Another possible reason is the refinement of grain size. The examination at the selected region using TEM suggests that the refinement of WC particles occurred during deposition. Figure 9 shows a typical large WC block in the coating. It can be observed that the cracks exist in the particle and two small chips in about 100 nm thick tended to separate from the block bulk. It was estimated that the



Fig. 9 TEM microstructure of WC particles in cold-sprayed coating representing the refining of particle size through cracking of large WC particle

critical velocity of present powders was over 900 m/s. The high velocity impact induced high intensity of stress. Moreover, the impact also induces a shock wave in the coating. The intensity of stress wave may be strong enough to cause the fracture of brittle WC particles, which leads to the refinement of grain size of WC particles. As a result, the broadening of diffraction peaks of WC occurred.

4.2 Hardness of Cold-Sprayed Nanostructured WC-Co Coating

The hardness test yielded a mean microhardness of 1869 $Hv_{0.3}$ following Weibull distribution plotting. This hardness value is much higher than those reported for thermally sprayed nanostructured WC-Co coating (Ref 24, 33, 48, 49). It can be found that the microhardness of sintered nanostructure bulk WC-12Co materials ranges from 1800 to 2400 $Hv_{0.3}$, depending on WC particle size (Ref 15). Figure 10 shows a typical backscattering electron image (BEI) of the cold-sprayed nanostructured WC-Co coating taken using the field emission SEM at a high magnification. WC particles can be clearly recognized from each other.

Thereafter, the cross-sectional area of individual WC particles was measured through image analyzing technique and WC particle size in an equivalent diameter was estimated by assuming that WC particles are present in a spherical shape. Figure 11 shows the statistical result of WC particle size. It can be found that the size of most WC particles ranged from about 50 to 300 nm. With WC-12Co sintered bulk made from superfine WC particles in the size from 100 to 300 nm, microhardness of 1800-1900 Hv_{0.3} can be found from literature (Ref 15). Compared with WC particle size and microhardness obtained in this study, it is clear that the as-sprayed nanostructured WC-12Co coating achieved a microhardness value comparable to that of the sintered bulk of comparable composition and WC particle size. Therefore, it can be considered that it is possible to deposit both the nanostructured WC-Co



Fig. 10 BEI image of cold-sprayed nanostructured WC-Co coating



Fig. 11 WC particle size distribution in as-sprayed coating

coating and bulk through design of powder structure and control of spray conditions.

4.3 Strengthening of Cold-Sprayed Nanostructured WC-Co Coating through Annealing Treatment

Due to low temperature feature of cold spray process, the compositions of the as-sprayed WC-Co coating by cold spraying are the same as that of powders. The coating consisted of the same WC and cobalt two phases as the starting powder. Because the deformation of particle is more concentrated at the region near the interfaces during deposition of a spray particle in cold spraying, the deformation degree along the interface would not be uniform. Accordingly, the bonding at the interfaces between apparent WC-Co particles may be different from one place to another. The weakly bonded interface, or even nonbonded interface are as observed commonly in a thermal spray coating, may possibly present in the coating.

With HVOF-sprayed nanostructured WC-Co, the limited lamellar bonding inherent to thermal spray coating



Fig. 12 Microstructure of the cold-sprayed nanostructured WC-12Co after annealing at a temperature of 1000 $^{\circ}$ C



Fig. 13 Indent on the annealed coating cross-section made by microhardness test

(Ref 34) leads to crack propagation along the interface under wear loading, which is responsible for a lower wear resistance than conventional WC-Co counterpart (Ref 33). The attempt to improve wear resistance of HVOF WC-Co through curing the interface bonding at a high temperature was also made (Ref 50). However, the brittle matrix phase composed of the precipitated M12C carbide, which is evolved during annealing treatment through Co-rich Co-W-C ternary matrix formed through dissolution WC into melted Co, causes the cracking and limits the improvement of wear performance.

On the other hand, due to high purity of the binder cobalt phase in cold-sprayed WC-Co coating, it can be considered that annealing at an adequate temperature promotes the diffusion of the binder and subsequently improve the bonding between the particles in the coating. The examination of cross-sectional microstructure of the WC-Co annealed at a temperature of 1000 °C for 6 h evidently showed that WC particle was uniformly distributed in the coating and particle size did not changed (Fig. 12). Moreover, small voids observed in the as-deposited state as shown in Fig. 8 also significantly decreased. This fact indicates that post-spray annealing treatment would lead to a densifying effect of coating. Microhardness test yielded an average of 1822 ± 127 Hv_{0.3}, which is almost the same as that of the as-sprayed coating. Therefore, annealing treatment influenced little the coating hardness. Moreover, as shown in Fig. 13, the measurement of microhardness yielded a regular indent without any collapse surrounding the indent. The lateral cracking was also not observed. Those facts suggest that the particle interface bonding and the further compaction of the cold-sprayed WC-Co can be improved by annealing treatment.

5. Conclusions

Nanostructured WC-12Co coatings were deposited by cold spraying using a nanostructured feedstock. Critical velocities of about 915 m/s were measured for the present feedstock powder. The microhardness value of the assprayed coating was about 1800 $Hv_{0.3}$, which is comparable to that of sintered bulk of a similar composition and microstructure. It was considered that certain degree of deformation of both impacting particle and deposited layer is required to build up a thick coating. With nanostructured WC-Co, a porous structure originated from agglomeration permits the pseudo-deformation through compaction of particles. The deposition of a dense WC-Co coating requires pseudo-deformation of WC-Co particles on impact on the previously deposited coating layer. Therefore, it can be considered that a WC-Co powder with WC loosely bonded by the binder is suitable for cold spraying. The high velocity impact of WC-Co particles evidently caused the refinement of WC particles possibly through fracture of large WC particles. The annealing treatment at a temperature of 1000 °C had little influenced on the microhardness of the coating. On the other hand, it seemed that the bonding between deposited WC-Co particles and the toughness of the cold-sprayed WC-Co coatings can be improved by post-annealing treatment.

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References

- C.-J. Li, A. Ohmori, and Y. Harada, Effect of Powder Structure on the Structure of Thermally Sprayed WC-Co Coatings, *J. Mater. Sci.*, 1996, **31**, p 785-794
- H. Lovelock, Powder/Processing/Structure Relationships in WC-Co Thermal Spray Coatings: A Review of the Published Literature, J. Thermal Spray Technol., 1998, 7, p 357-373
- D.A. Stewart, P.H. Shipway, and D.G. McCartney, Abrasive Wear Behavior of Conventional and Nanocomposite HVOF-Sprayed WC-Co Coatings, *Wear*, 1999, 229, p 789-798
- M. E. Vinayo, F. Kassabji, J. Guyonnet, and P. Fauchais, Plasam Sprayed WC-Co Coatings: Influence of Spray Conditions (Atmospheric and Low Pressure Plasma Spraying) on the Crystal

Structure, Porosity, and Hardness, J. Vac. Sci. Technol. A, 1985, 3, p 2483-2489

- J. Subrahmanyam, M.P. Srivastava, and R. Sivakumar, Characterization of Plasma-Sprayed WC-Co Coatings, *Mater. Sci. Eng.*, 1986, 84, p 209-214
- S. Rangaswamy and H. Herman, Metallurgical Characterization of Plasma Sprayed WC-Co Coatings, Advances in Thermal Spraying (Proceedings of 11th International Thermal Spray Conference), September 8-12, 1986 (Montreal, Canada), Welding Institute of Canada, Pergamon Press Canada Ltd., 1986, p 101-110
- A. Tronche and P. Fauchais, Hard Coatings (Cr₂O₃, WC-Co) Properties on Aluminium or Steel Substrates, *Mater. Sci. Eng.*, 1987, 92, p 133-144
- V. Ramnnath and N. Jayaraman, Characterization and Wear Performance of Plasma Sprayed WC-Co Coatings, *Mater. Sci. Technol.*, 1989, 5, p 382-388
- 9. G. Barbezat, E. Muller, and B. Walser, Applying Tungsten Carbide Cobalt Coatings by High Velocity Combustion Spraying, *Sulzer Tech. Rev.*, 1988, **4**, p 27-33
- H. Kreye, D. Fandrich, H.-H. Muller, and G. Reiners, Microstructure and Bond Strength of WC-Co Coatings Deposited by Hypersonic Flame Spraying (Jet-Kote Process), Advances in Thermal Spraying (Proceedings of 11th International Thermal Spray Conference), September 8-12, 1986 (Montreal, Canada), Welding Institute of Canada, Pergamon Press Canada Ltd., 1986, p 121-128
- H. Nakahira, Y. Harada, and K. Tani, Properties of Tungsten Cermet Coatings by High Energy Flame Spraying, *Proceedings of International Symposium on Advanced Thermal Spray Technology and Allied Coatings*, A. Ohmori, Ed., May 13-15, 1988 (Osaka, Japan), Japan High Temperature Society, 1988, p 79-88
- C.-J. Li, A. Ohmori, and Y. Harada, Formation of an Amorphous Phase in Thermally Sprayed WC-Co, J. Thermal Spray Technol., 1996, 5(1), p 69-73
- Y. Ishikawa, J. Kawakita, S. Osawa, T. Itsukaichi, Y. Sakamoto, M. Takaya, and S. Kuroda, Evaluation of Corrosion and Wear Resistance of Hard Cermet Coatings Sprayed by Using an Improved HVOF Process, *J. Thermal Spray Technol.*, 2005, 14(3), p 384-395
- C.-J. Li, Y.-Y. Wang, G.-J. Yang, A. Ohmori, and K. A. Khor, Effect of Solid Carbide Particle Size on Deposition Behavior, Microstructure and Wear Performance of HVOF Cermet Coatings, *Mater. Sci. Technol.*, 2004, **20**, p 1087-1096
- V. Richter and M.V. Ruthendorf, On Hardness and Toughness of Ultrafine and Nanocrystalline Hard Materials, *Int. J. Refractory Met. Hard Mater.*, 1999, **17**, p 141-152
- K. Jia and T.E. Fischer, Abrasion Resistance of Nanostructured and Conventional Cemented Carbides, *Wear*, 1996, 200, p 206-214
- J.H. He, M. Ice, S. Dallek, and E.J. Lavernia, Synthesis of Nanostructured WC-12 pct Co Coating Using Mechanical Milling and High-Velocity Oxygen Fuel Thermal Spraying, *Metall. Mater. Trans. A*, 2000, **31**, p 541-553
- D.A. Steward, P.H. Shipway, and D.G. McCartney, Microstructural Evolution in Thermally Sprayed WC-Co Coatings: Comparison Between Nanocomposite and Conventional Starting Powders, ACTA Mater., 2000, 48, p 1593-1604
- 19. Y.F. Qiao, Y.R. Liu, and T.E. Fischer (USA), Sliding and Abrasive Wear Resistance of Thermal-Sprayed WC-CO Coatings, J. Thermal Spray Technol., 2001, 10, p 118-125
- J.H. He, L. Ajdelsztajn, and E.J. Lavernia, Thermal Stability of Nanocrystalline WC-Co Powder Synthesized by Using Mechanical Milling at Low Temperature, J. Mater. Res., 2001, 16, p 478-488
- J.H. He, Y.R. Liu, Y.F. Qiao, T.E. Fischer, and E.J. Lavernia, Near-Nanostructured WC-18 pct Co Coatings with Low Amounts of Non-WC Carbide Phase. Part I. Synthesis and Characterization, *Metall. Mater. Trans. A*, 2002, 33, p 145-157
- Z.G. Ban and L.L. Shaw, Synthesis and Processing of Nanostructured WC-Co Materials, J. Mater. Sci., 2002, 37, p 3397-3403
- Z.G. Ban and L.L. Shaw, Characterization of Thermal Sprayed Nanostructured WC-Co Coatings Derived from Nanocrystalline WC-18 wt.%Co Powders, *J. Thermal Spray Technol.*, 2003, **12**, p 112-119

- 24. Y-.Y. Wang, C.-J. Li, J. Ma, and G.-J. Yang, Effect of Flame Conditions on the Abrasive Wear Performance of HVOF Sprayed Nanostructured WC-12Co Coatings, *Trans. Nonferrous Met. Soc. China*, 2004, **14**(special 2), p 72-76
- 25. J.H. He and J.M. Schoenung, Nanostructured Coatings, *Mater. Sci. Eng. A*, 2004, **336**, p 274-319
- P.H. Shipway, D.G. McCartney, and T. Sudaprasert, Sliding Wear Behaviour of Conventional and Nanostructured HVOF Sprayed WC-Co Coatings, *Wear*, 2005, 259, p 820-827
- J.M Guilemany, S. Dosta, J. Nin, and J.R. Miguel, Study of the Properties of WC-Co Nanostructured Coatings Sprayed by High-Velocity Oxyfuel, *J Thermal Spray Technol.*, 2005, 14(3), p 405-413
- C. Bartuli, T. Valente, F. Cipri, E. Bemporad, and M. Tului, Parametric Study of an HVOF Process for the Deposition of Nanostructured WC-Co Coatings, *J. Thermal Spray Technol.*, 2005, 14(2), p 187-195
- B.R. Marple and R. S. Lima, Process Temperature/Velocity-Hardness-Wear Relationship for High-Velocity Oxyfuel Sprayed Nanostructured and Conventional Cermet Coatings, *J. Thermal* Spray Technol., 2005, 14(1), p 67-76
- J. O. Berghaus, B. Marple, and C. Moreau, Suspension Plasma Spraying of Nanostructured WC-12Co Coatings, J. Thermal Spray Technol., 2006, 15(4), p 676-681
- Y.-C. Zhu, K. Yukimura, C.-X. Ding, and P.-Y. Zhang, Tribological Properties of Nanostructured and Conventional WC-Co Coatings Deposited by Plasma Spraying, *Thin Solid Films*, 2001, 388, p 277-282
- G. Skandan, R. Yao, R. Sadangi, B.H. Kear, Y. Qiao, L. Liu, and T.E. Fischer, Multimodal Coatings: A New Concept in Thermal Spraying, J. Thermal Spray Technol., 2000, 9(3), p 329-331
- D.A. Ateward, H.P. Shipway, and D.C. McCartney, Abrasive Wear Behaviour of Conventional And Nanocomposite HVOF-Sprayed WC-Co Coatings, *Wear*, 1999, 225-229, p 789-798
- 34. C.-J. Li and A. Ohmori, Relationship Between the Structure and Properties of Thermally Sprayed Deposits, *J. Thermal Spray Technol.*, 2002, **11**, p 365-374
- C.-J. Li, W.-Y. Li, W.-H. Ma, and H. Fukanuma, Characterization of Microstructure of Nanostructured Fe–Si Coating Deposited by Cold Spraying, *Thermal Spray 2004: Advances in Technology* and Application, May 10-12, 2004 (Osaka, Japan), DVS, 2004, p 371–377
- 36. H.-T. Wang, C.-J. Li, G.-J. Yang, and C.-X. Li, Formation of Fe–Al Intermetallic Compound Coating Through Cold Spraying, Building on 100 Years of Success: Proceedings of the 2006 International Thermal Spray Conference, B.R. Marple, M.M. Hyland, Y.C. Lau, R.S. Lima, and J. Voyer, Eds., May 15-18, 2006 (Seattle, WA, USA), ASM International, 2006
- H.-T. Wang, C.-J. Li, G.-J. Yang, C.-X. Li, and Q. Zhang, Microstructural Characterization of Cold-sprayed FeAl Intermetallic Compound Coatings, *J. Thermal Spray Technol.*, 2007, in this issue
- Q. Zhang, C.-J. Li, C.-X. Li, G.-J. Yang, and X.-R. Wang, Preliminary Study of Oxidation Behavior of Cold Sprayed Nanostructure NiCrAIY Bond Coatings, *Global Coating Solutions: Proceedings of the 2007 International Thermal Spray Conference*, B.R. Marple, M.M. Hyland, Y.-C. Lau, C.-J. Li, R.S. Lima, and G. Montavon, Eds., May 14-16, 2007 (Beijing, China), ASM International, 2007
- L. Ajdelsztajn, A.Zuniga, B. Jodoin, and E.J. Lavernia, Cold-Spray Processing of a Nanocrystalline Al-Cu-Mg-Fe-Ni Alloy with Sc, J. Thermal Spray Technol., 2006, 15, p 184-190
- R.S. Lima, J. Karthikeyan, C.M. Kay, J. Lindemann, and C.C. Berndt, Microstructural Characteristics of Cold-sprayed Nanostructured WC-Co Coating, *Thin Solid Films*, 2002, **416**, p 129-135
- H.-J. Kim, C.-H. Lee, and S.-Y. Hwang, Superhard Nano WC-12%Co Coating by Cold Spray Deposition, *Mater. Sci. Eng. A*, 2005, **391**, p 243-248
- H.-J. Kim, C.-H. Lee, and S.-Y. Hwang, Fabrication of WC-Co Coatings by Cold Spray Deposition, *Surf. Coat. Technol.*, 2005, 191, p 335-340
- C.-J. Li and W.-Y. Li, Deposition Characteristics of Titanium Coating in Cold Spraying, *Surf. Coat. Technol.*, 2003, 167, p 278-283

- 44. C.-J. Li, W.-Y. Li, and H.-L. Liao, Examination of the Critical Velocity for Deposition of Particles in Cold Spraying, J. Thermal Spray Technol., 2006, 15, p 212-222
- C.-J. Li, W.-Y. Li, Y.-Y. Wang, G.-J. Yang, and H. Fukanuma, A Theoretical Model for Prediction of Deposition Efficiency in Cold Spraying, *Thin Solid Films*, 2005, 489, p 79-85
- 46. C.-J. Li and W.-Y. Li, Optimization of Spray Conditions in Cold Spraying based on the Numerical Analysis of Particle Velocity, *Trans. Nonferrous Met. Soc. China*, 2004, **14**(special 2), p 43-48
- S.-Q. Fan, G.-J. Yang, G.-J. Liu, C.-X. Li, C.-J. Li, and L.-Z. Zhang, Characterization of Microstructure of TiO₂ Coating

Deposited by Vacuum Cold Spraying, J. Thermal Spray Technol., 2006, 15(4), p 613-517

- J. He and J. M. Schoenung, A Review on Nanostructured WC-Co Coatings, Surf. Coat. Technol., 2002, 157, p 72-79
- 49. Y. Qiao, T. E. Fischer, and A. Dent, The effects of Fuel Chemistry and Feedstock Powder Structure on the Mechanical and Tribological Properties of HVOF Thermal-Sprayed WC-Co Coatings with Very Fine Structure, *Surf. Coat. Technol.*, 2003, 172, p 24-41
- D.A. Atewart, P.H. Shipway, and D.G. McCartney, Influence of Heat Treatment on the Abrasive Wear Behavior of HVOF Sprayed WC-Co Coatings, *Surf. Coat. Technol.*, 1998, 105, p 13-24