JTTEE5 14:183-186
DOI: 10.1361/105996304523791

Technical Note

Thin Film Coatings of WO_3 by Cold Gas Dynamic Spray: A Technical Note

Ha Yong Lee, Young Ho Yu, Young Cheol Lee, Young Pyo Hong, and Kyung Hyun Ko

(Submitted April 22, 2003; in revised form October 6, 2003)

Dense and adhesive WO_3 films were prepared on a silicon substrate by the cold gas dynamic spray process (or cold spray). In contrast to standard metallic coatings, there was no sizable crater formation and plastic deformation. However, the aggregation of raw powder particles of a relatively large size was found to be destroyed upon impact on the substrate, forming a highly irregular surface with very fine secondary particles and providing good interlocking powder and void reduction among the particles in the coating. High-resolution images of the substrate interface showed that particles at the interface were more densely packed and that good adhesion was obtained. Therefore, the particle bombardment onto the first layer of the coating could provide enhanced adhesion to the substrate mechanically and/or chemically.

Keywords cold spray, crater, gas dynamic spray, thin film, WO_3

1. Introduction

Coatings have been used in a variety of industrial applications such as insulation, corrosion, and wear resistance. The thermal spray process, in which powder is melted by a flame, plasma, or an electrical arc, has been used to apply these coatings (Ref 1-4). During the past several years, the cold gas dynamic spray (CGDS) process (or simply cold spray or kinetic spray) has been introduced and has been proved to have certain advantages over thermal spray. Because this technique employs high-velocity gas and not high temperatures to accelerate the powder particles to velocities on the order of 500 to 1000 m/s (Ref 5-12), the powders are neither melted nor are semimolten materials that impinge on the substrate. As the process names imply, the major source of energy is the kinetic energy of the particles that with high-velocity impact on the substrate form an integrated solid film at low temperature. When metallic powders are impinged onto the substrate, the conversion of the kinetic energy makes it possible to proceed with the mechanical deformation of the particles, resulting in relatively adherent coatings with low porosity. In addition, since the process does not involve melting or thermal softening, the original phase of the raw material can be maintained in the coatings. Therefore, metallic coatings of low oxide content and low thermal stress can be produced. According to Van Steenkiste et al. (Ref 9, 10), there are several stages of coating formation in the CGDS process with aluminum powder on metal substrate; stage 1 is "substrate cratering and first layer buildup of particles," stage 2 is "particle deformation and realignment," and finally stage 3 is "metallurgical bond formation and void reduction." However, the mechanism of the coating formation of oxide materials has not been well understood and reported because it would be difficult to form a solid film due to their lack of deformability. In this study, WO_3 films were coated on silicon substrates by CGDS. The interface between the film and the substrate, as well as the formation of cratering on the substrate (stage 1), was investigated. Also, interfaces and bonding characteristics between particles consisting of film were examined.

Ha Yong Lee, Young Ho Yu, Young Cheol Lee, Young Pyo Hong, and **Kyung Hyun Ko,** Department of Materials Science and Engineering, Ajou University, Suwon, 442-749, Korea. Contact e-mail: khko@madang.ajou.ac.kr.

2. Experimental Procedure

The particles were accelerated through a rectangular cross section using a homemade Laval nozzle, with an aperture of 4 by 6 mm and a throat diameter of 1 mm. Instead of the usual helium, compressed air was used as the propulsion gas. The powder feed rate was 0.1 g/s. The pressure prior to entering the gas heater was fixed at 0.7 MPa (100 psi), and the temperature of the gas through the nozzle was 300 °C. The standoff distance to the substrate was 5 mm, and silicon (100) of a single crystal, which was not sandblasted, was used as the substrate. The coating efficiency was less than 10%, because the ceramic feedstock does not deform plastically, and the coating thickness was about 2 μm. The as-purchased WO_3 particle size and shape (Kanto Chemical Co. Inc., Tokyo, Japan, 99.9% purity) analyzed using a scanning electron microscope (SEM) was approximately 30 to 50 μm. The structures of the WO_3 film and powder were analyzed by x-ray diffraction (XRD). The thickness and microstructure of the powder and film were determined by SEM and a field emission SEM (FESEM). The interface between the substrate and the film and among particles were evaluated by high-resolution transmission electron microscopy (HRTEM).

3. Results and Discussion

The SEM images of WO_3 powders are shown Fig. 1. To confirm the particle size and shape change before and after spraying, the impacted and bounced WO_3 powders from the substrate were gathered and analyzed by SEM. Compared with the relatively larger size (30-50 μm) of the particles in the original feedstock (Fig. 1a), the WO_3 particles after collision were fractured into smaller fragments (Fig. 1b). It appears that shape change

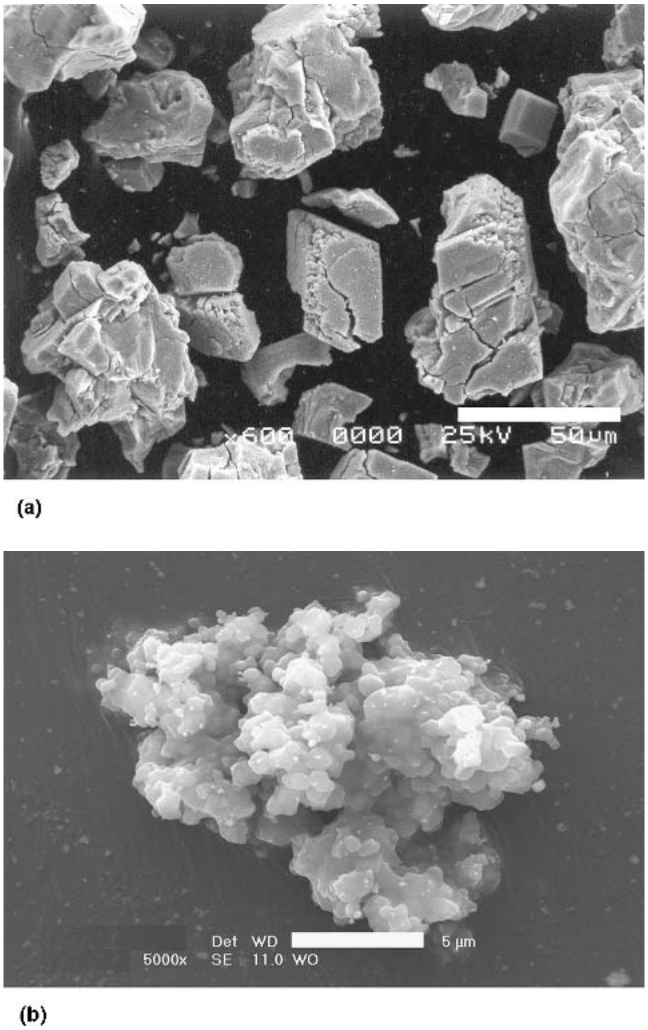

Fig. 1 The SEM images of the WO_3 powders. (a) Before coating (600×). (b) After impact (magnification 5000×)

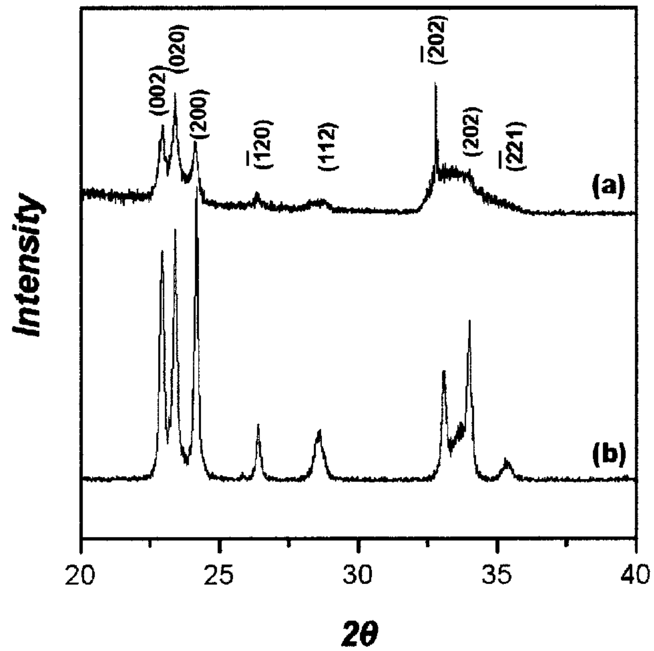

Fig. 2 XRD patterns of the WO_3 powder and the film coated by the CGDS process. (a) Film. (b) Powder

occurred by fracture and not by deformation. In Fig. 1(a), the original powder seems to be an aggregation of smaller particles, which are defined by several cracks; fragmentation could happen easily during impact.

Figure 2 shows the XRD patterns of WO_3 powder and film coated by CGDS. The main XRD peaks of the film were the same as those of the WO_3 powder. Furthermore, no significant changes in lattice dimension and chemical composition were observed. Therefore, it seems that the CGDS coating of the WO_3 powder on the silicon substrate was carried out without significant crystallographic and chemical alteration. The FESEM images of the WO_3 film coated by CGDS process on the silicon substrate are shown in Fig. 3. Remarkably, it was found that, although the coating seems to be dense, not only the shape but also the size of particles in the coating were greatly changed from those of the original WO_3 powders.

According to Van Steenkiste et al. (Ref 9, 10), the original aluminum powders with spherical shape were deformed by high impaction energy, and densification had occurred between those particles (stage 2). From these results, it was assumed that, unlike the "splat" coating that accompanied severe plastic deformation and was frequently found in aluminum and copper metal coatings (Ref 8), the less deformable WO_3 powders were fractured into smaller particles in a brittle manner by high-velocity impact and were shattered around the silicon substrate.

As reported by different researchers (Ref 9-11), when the metal powders are accelerated by the CGDS process and impact the metal substrates, craters are usually observed as a result of the high kinetic energy of the incident particles. However, in the authors' work, craters on the substrate caused by the incident high-velocity WO_3 particles were not observed at the interface between the WO_3 film and the silicon substrate (Fig. 3c). It was assumed that the primary WO_3 particles impinging on the substrate could not create craters because much of the energy was absorbed by fragmentation. To clarify the crater formation at the interface between the WO_3 film and the silicon substrate, cold-sprayed WO_3 films were completely removed from the silicon substrate by chemical etching. As shown in Fig. 3(d), it was confirmed that the craters were not observed on the surface.

To investigate the interface between the WO_3 film and the substrate and the interface of the WO_3 particles in the film, a cross section of the WO_3 film was analyzed by HRTEM (Fig. 4). It was found that the interface was not mechanically damaged by the high-energy impact of WO_3 powders (Fig. 4a). From the higher-resolution image (Fig. 4b), it was also confirmed that the interface showed clear lattice fringes and the thin native oxide (SiO_2) layer had not been removed despite the impact of the WO_3 particles. Noticeably, the particles closest to the substrate were smaller and more densely packed than those above them. Furthermore, as the thickness increased, the particles of WO_3 were loosely packed (Fig. 4a). Judging from Fig. 3 and 4, dissimilar to the microstructures observed for metallic coatings, it was assumed that the void reduction of interparticles was en-

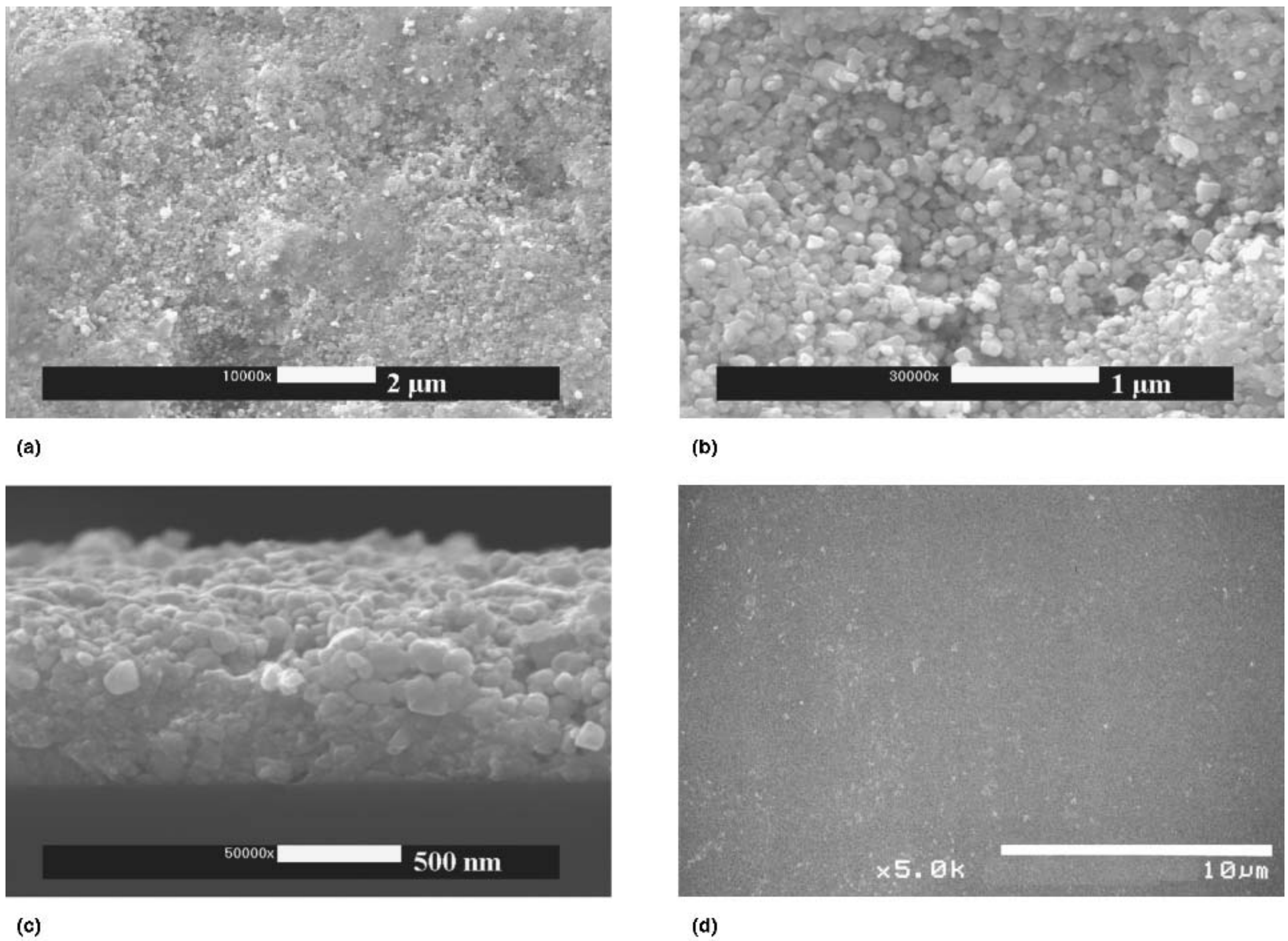

Fig. 3 The FESEM images of the WO_3 film coated by the CGDS process on the silicon substrate. (a) Surface (magnification 10,000×). (b) Surface (magnification 5,000×). (c) Cross section (magnification 50,000×). (d) The surface of silicon substrate after etching WO_3 film (magnification 20,000×)

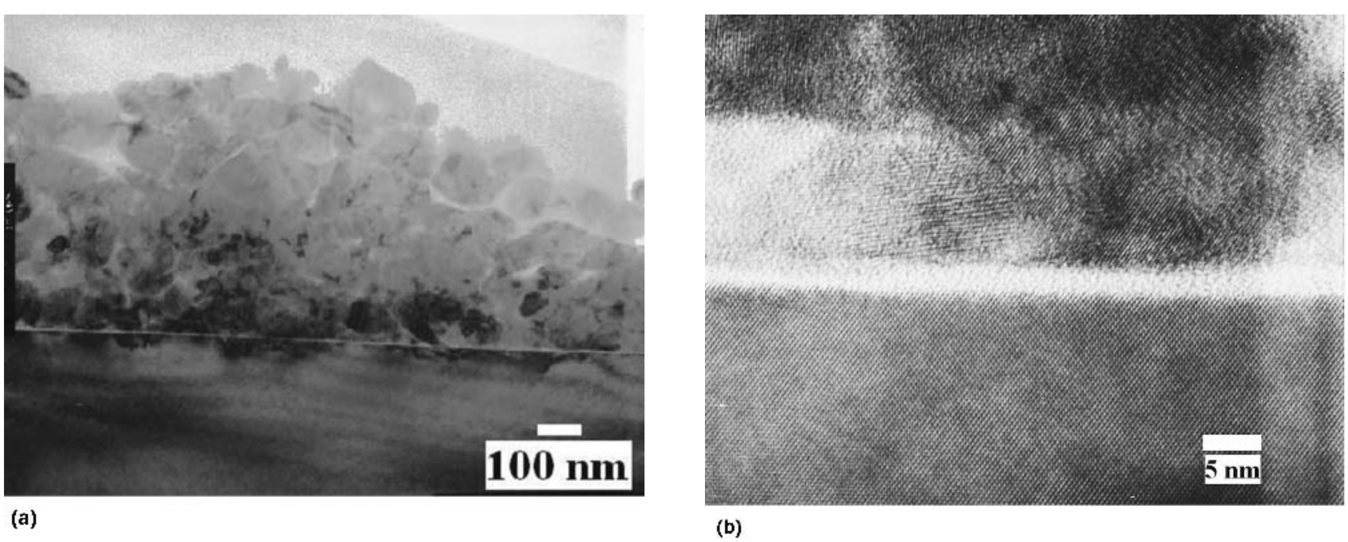

Fig. 4 The HRTEM images of cross-sectional WO_3 film. (a) Low magnification (magnfication 50,000×). (b) High resolution (magnification 2M×)

hanced mainly by the mechanical interlocking among fine fragmented particles with highly irregular shapes, rather than by substantial particle flow, the so-called peening effect on the surface (stage 2) (Ref 10). Figure 5 shows the HRTEM images of the interface between particles in the film. It was found that the particles were well packed and interlocked with each other.

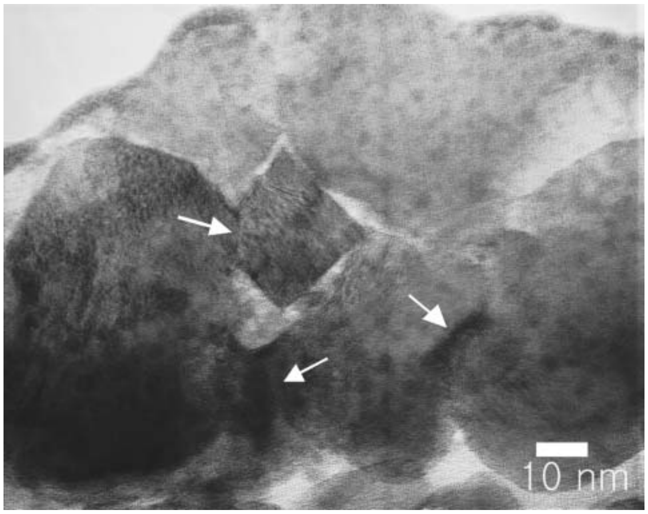

Fig. 5 The HRTEM image of the interface of the interparticles with WO_3 in the film (magnfication 500,000×). The arrows indicate the interlocking of the WO_3 powders.

Therefore, the mechanical and/or some chemical bond formation among the particles also could be enhanced by consecutive bombardment onto previously interlocked particles.

4. Conclusions

In conclusion, a WO_3 film was prepared successfully by the CGDS process on the silicon substrate. It was found that the less deformable oxide layer formed in a different way from that of classic metallic coatings. On the arrival of an accelerated particle, fracturing and shattering around aggregated raw materials occurs first. During this process, secondary particles of irregular shapes, possibly having highly jagged surfaces, form so that mechanical interlocking, rather than peening and void reduction, can be achieved. As for crater formation, there were no sizable craters at the interface between the coating and the substrate. However, because particles at the interface seem to be more densely packed and well interlocked, additional energy for enhancing microinterlocking and/or some chemical bonding between the coating and the substrate could be supplied by consecutive bombardment.

Acknowledgments

This research was supported by a grant from Center for Advanced Materials Processing of the 21st Century, and by the Frontier R&D Program funded by the Ministry of Science and Technology, Republic of Korea.

Reference

1. L. Gil and M.H. Staia, Influence of HVOF Parameters on the Corrosion Resistance of NiWCrBSi Coatings, *Thin Solid Films,* Vol 420, 2002, p 446-454
2. B. Hwang, J. Ahn, and S. Lee, Correlation of Microstructure and Wear Resistance of Ferrous Coatings Fabricated by Atmospheric Plasma Spraying, *Metall. Mater. Trans., A,* Vol 33, 2002, p 2933-2946
3. H. Kim, S. Odoul, C. Lee, and Y. Kweon, The Electrical Insulation Behavior and Sealing Effects of Plasma-Sprayed Alumina-Titania Coatings, *Surf. Coat. Technol.,* Vol 140, 2001, p 293-301
4. J. Matejicek and S. Sampath, Intrinsic Residual Stresses in Single Splats Produced by Thermal Spray Process, *Acta Mater.,* Vol 49, 2001, p 1993-1999
5. R. McCune, W. Donion, O. Popoola, and E. Cartwright, Characteristics of Copper Layers Produced by Cold Gas-Dynamic Spraying, *J. Thermal Spray Technol.,* Vol 9 (No. 1), 2000, p 73-82
6. K. Sakaki and Y. Shimizu, Effect of the Increase in the Entrance Convergent Section Length of the Gun Nozzle on the High-Velocity Oxygen Fuel and Cold Spray Process, *J. Thermal Spray Technol.,* Vol 10 (No. 3), 2001, p 487-496
7. R. Dykhuizen, and M. Smith, Gas Dynamic Principles of Cold Spray, *J. Thermal Spray Technol.,* Vol 7 (No. 2), 1998, p 205-212
8. R. Dykhuizen, M. Smith, D. Gilmore, R. Neiser, X. Jiang, and S. Sampath, Impact of High Velocity Cold Spray Particles, *J. Thermal Spray Technol.,* Vol 8 (No. 4), 1999, p 559-564
9. T. Van Steenkiste, Kinetic Spray Coatings: A New Coating Process, *Key Eng. Mater.,* Vol 197, 2001, p 59-86
10. T. Van Steenkiste, J. Smith, and R. Teets, Aluminum Coatings via Kinetic Spray with Relatively Large Powder Particles, *Surf. Coat. Technol.,* Vol 154, 2002, p 237-252
11. D. Gilmore, R. Dykhuizen, R. Neiser, T. Roemer, and M. Smith, Particle Velocity and Deposition Efficiency in the Cold Spray Process, *J. Thermal Spray Technol.,* Vol 8 (No. 4), 1999, p 576-582
12. R.S. Lima, J. Karthikeyan, C.M. Kay, J. Lindermann, and C.C. Berndt, Microstructural Characteristics of Cold-Sprayed Nanostructured WC-Co Coatings, *Thin Solid Films,* Vol 416, 2002, p 129-135