Investigation of Mechanical Properties of Coatings and Bulk Components of Various Grain Sized Tungsten-Carbide-Cobalt Based Materials

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Thermal sprayed coatings produced from ultrafine, near-nano and nano grained powders provide improved properties as compared to conventional (micron size) powders. These ultrafine, near-nano and nano grained materials show significant potential for applications in the aerospace, energy, oil & gas and a great many other industries. A study was conducted to investigate the influence of grain size on the microstructures formed and mechanical properties of conventional, ultrafine, near-nano and nano size WC materials. Powders and coatings as well as consolidated forms of tungsten-carbide-10% cobalt- 4% chromium (WC-10Co-4Cr) and tungsten-carbide-12% cobalt (WC-12Co) materials are examined. Thermal spray coatings are produced of carbides of several different grain sizes using high velocity oxygen-fuel (HVOF) thermal spray processing. Spark Plasma Sintering (SPS) is performed to provide consolidated forms of WC-10Co-4Cr materials. An examination of the thermal sprayed coatings is conducted using microstuctural analysis and mechanical property testing. A brief examination of the wear and bend performance of a near-nano, and nano-enhanced material will be compared to a conventional material (micron sized).

1 Introduction

Applications for nano- and near-nano materials in the thermal spray field are being developed and implemented in a variety of materials by numerous organizations around the world. This ranges from ceramics for biomedical uses [1,2] to superalloys intended for aerospace and industrial gas turbine applications [3-5], to carbide-based materials for wear and cutting tool applications [6-9]. Nanostructural materials offer the potential for significant improvements in material performance. The Hall-Petch relationship cites the strengthening of materials by reducing the average crystallite (grain) size [2,10].

One of the critical parameters that affects the mechanical properties and wear performance in carbide-based cermet coatings is the carbide grain size. Researchers have shown an increase in mechanical properties and in wear performance by reducing the carbide grain size [11]. Recent efforts have shown an improvement in wear performance of WC-10Co-4Cr spray coatings with reduced grain size in coatings sprayed with hydrogen-based and kerosene based HVOF systems [12, 13].

In this work, we studied the possible advantages in microstructural and mechanical properties (e.g., hardness) by reducing WC grain size in HVOF sprayed WC-10Co-4Cr and WC-12Co coatings deposited using a kerosene-based HVOF system.

2 Experimental Approach

Materials

Powders consisting of WC-10Co-4Cr and WC-12Co were thermal sprayed. WC-10Co-4Cr powders were consolidated using spark plasma sintering. These materials consisted of: (a) powder A, a commercially available powder used as a standard, consisting of WC grains larger than 1.2 µm; (b) powder B, consisting of WC grains with an average size of 0.2-0.4 µm; (c) powder C, consisting of ultrafine WC grains (0.2 µm); (d) powder D, consisting of nano- and near-nano WC grains; (e) powder E, consisting of WC grain additions with an average size of 0.2-0.4 µm; and (F) powder F, consisting of ultrafine WC grain additions of ~0.2 µm. The powder chemistry and average size of the WC grains in WC-10Co-4Cr powders A, B, and C are provided below in Table 1. The powder chemistry and WC grain size additions to WC-12Co powders E and F are shown in Table 1.

Table 1: Powder Chemistry and Grain Size

Item	Chemistry (wt.%)	WC Grain Size (µm)
A: Commercial	WC-10Co-4Cr	1.2<
B: CNO 104	WC-10Co-4Cr	0.2-0.4
C: CNO 102	WC-10Co-4Cr	0.2
D: CNO 101	WC-10Co-4Cr	<0.1
E: CNO 204	WC-12Co	0.2-0.4
F: CNO 202	WC-12Co	0.2

Thermal Spray Processing

High velocity oxygen-fuel (HVOF) spraying was conducted with five powders consisting of CNO 104, CNO 102, CNO 204, CNO 202, and powder A, the commercially available powder used as the standard given its wide use throughout the thermal spray industry. Powder A was sprayed as a test standard to confirm thermal spraying was performed to acceptable standards. The thermal spray activities were carried out at HFW Industries Inc. (Buffalo, NY). Thermal spraying was conducted using a Praxair JP-8000 High Velocity Oxygen Fuel (HVOF) system (Concord, NH).

The HVOF parameters were optimized for each powder using a design of experiments (DOE). The parameters varied were the oxygen and kerosene flow rates, and the HVOF gun barrel length for achieving optimized coatings. Coatings were produced using oxygen flow rates of 1800, 1900 and 2000 standard cubic feet per hour (scfh) and kerosene fuel flow rates of 6.0 and 6.5 gallons per hour (gph). HVOF gun barrel lengths of 4” and 6” were used. The spray distance, powder feed rate, carrier gas rate and other HVOF operating parameters were kept constant. The HVOF parameters are provided in Table 2.

Table 2: HVOF Spray Parameters

Element	Parametric Value
Oxygen (scfh)	1800, 1900, 2000
Kerosene (gph)	6.0, 6.5
Gun barrel length (inch)	4, 6
Carrier gas, nitrogen (scfh)	15
Spray distance (inch)	13
Spray rate (lbs./hr.)	10

Spark Plasma Sintering

Spark plasma sintering (SPS) was conducted at California Nanotechnologies, Inc. (Cerritos, CA). The WC-10Co-4Cr materials in Table 1 were SPS sintered to consolidate the powders into bulk forms for analyses. Spark plasma sintering was conducted using a Syntex Inc., Dr. Sinter Lab™, model SPS-515S (Syntex Inc., Kanagawa, Japan). In SPS, powder is placed in a graphite die and pressed uniaxially while a pulsed electric current is applied through graphite punches. The graphite die produced WC-10Co-4Cr disks ranging from 20 to 25.4 mm in diameter, and up to 8 mm in height. A type-K thermocouple and infrared pyrometer were used to monitor and control die temperature. The pyrometer was a Chino Works America Inc., model IR-AHS2. The SPS in operation is shown in **Fig. 1**.

***Fig. 1**: Spark Plasma Sintering*

Sintering parameters for SPS are provided in Table 3 for sintering the WC-10Co-4Cr powders.

Table 3: Spark Plasma Sintering

Element	CNO 104	CNO 102	CNO 101
Temp. (°C)	1100[1]	1100[1]	1025[2]
Press. (MPa)	60	60	50
Time (min.)	10	10	10

[1] Die temperature measured using infrared pyrometer
[2] Die temperature measured using type K thermocouple

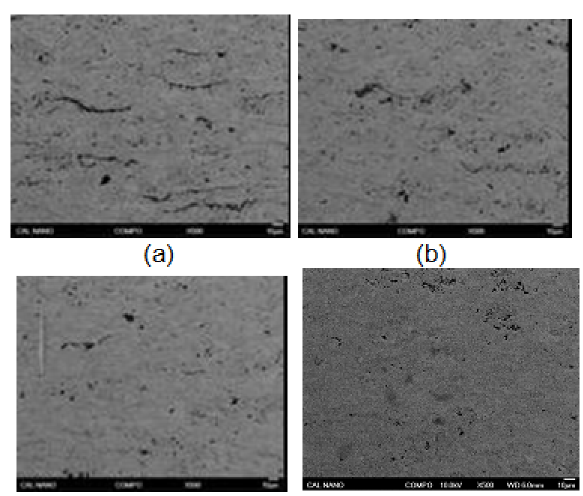
Coating and Bulk Analyses

Microstructural analyses of the thermal spray coupons and bulk consolidated forms were performed using a JEOL, JSM- 7000F Field Emission Scanning Electron Microscope (Tokyo, Japan). All cross-section micrographs were imaged using back-scattered electrons. Microhardness was measured using a Struers hardness tester, model S140 (Copenhagen, Denmark). A 500 gram load was used for WC-10Co-4Cr materials. Hardness measurements were carried out taking a minimum of ten Knoop indentations on each specimen. Measurements were carried out on cross-sectioned HVOF coating samples. SPS samples were prepared for hardness measurements by surface grinding and polishing the top surface of the consolidated samples. Wear testing was conducted in a modified ASTM G105-02 test with Coatings A, B and C. The abrasive media consisted on 0.30 micron tungsten-carbide. Bend testing was conducted with the WC-10Co-4Cr materials with Coatings A, B and C. HVOF (JP-5000) was used to spray the coatings on mild carbon steel coupons of dimensions 0.75" wide x 4" long x 0.059" thick.

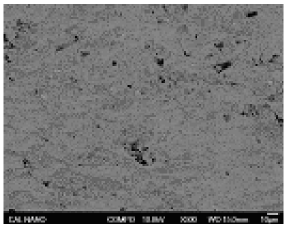
3 Results and Discussion

Thermal Spray Coatings

The thermal spray powders were sprayed to the parameters shown in Table 2 to produce coatings. The HVOF parameters producing the best thermal spray coatings were found at 2000 scfh of oxygen flow, 6.5 gph of kerosene using a 6” HVOF gun barrel. Scanning electron microscopy (SEM) images of the thermal sprayed coatings are shown in **Figs. 2a, b, c, d** and **e**.



(a) (b) (c) (d)

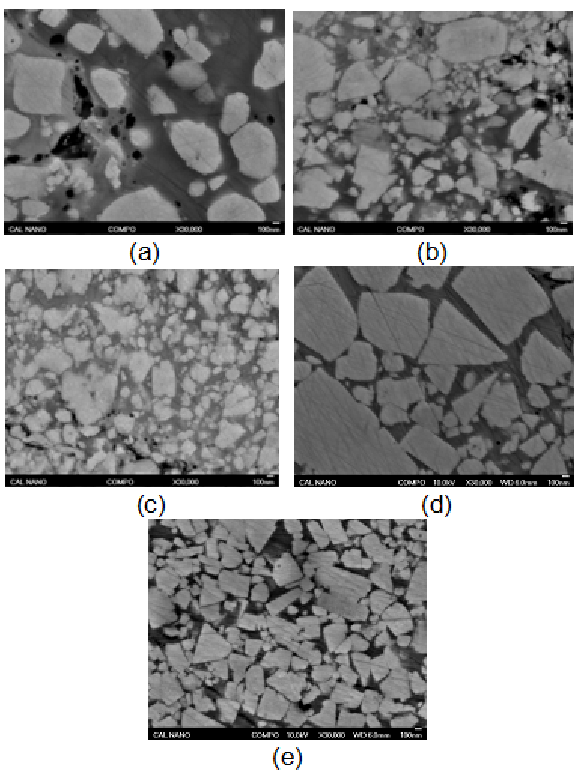


(e)

***Figure 2a, b, c, d** and **e**: SEM images (500x) of cross-sectioned coating samples (a) Coating A, widely used commercial powder; (b) Coating B (CNO 104); (c) Coating C (CNO 102);(d) Coating E (CNO 204); and (e) Coating F (CNO 202)*

SEM cross-section images of these thermal spray coatings at high resolution show the WC grains and size distribution in each coating as shown in **Figs. 3a, b, c, d** and **e**.

In the WC-10Co-4Cr materials, the size of the near-nano and nano WC grains in coating B are much smaller than the size of the average WC grains in the commercial coating A. The size of the WC grains in coating C are smaller than the grains in coating B.



***Figures 3a, b, c, d** and **e**: High resolution (30,000x) SEM images of cross-sectioned thermal spray coatings showing the WC grains: (a) Coating A (commercial powder); (b) Coating B; (c) Coating C; (d) Coating E; and (e) Coating F*

In WC-12Co materials, the near-nano and nano WC grains are distributed throughout the matrices, and are smaller than the WC carbide sizing typically found in commercial WC-12Co powders.

Thermal Spray Coating Hardness

Hardness measurements were performed on HVOF sprayed coatings produced using 4" and 6" gun barrels. These coatings were sprayed to the parameters of Table 2. The hardness values of HVOF coatings produced with the various powders are provided in Table 4.

Table 4: Hardness Values of HVOF Sprayed Coatings

Element	**Knoop Hardness (HK_{500g})**	**Knoop Hardness (HK_{500g})**
	4" barrel	6" barrel
Coating A	931.3 ± 125.1	1266.9 ± 118.4
Coating B	1085.2 ± 88.8	1211.0 ± 107.7
Coating C	1173.4 ± 159.8	1258.1 ± 130.8

Spark Plasma Sintering

Spark plasma sintering operations were performed on WC-10Co-4Cr powders B, C, and D. Consolidated forms produced from these powders are, similarly, identified as bulk forms B, C, and D, respectively. Cross-sectioned samples of SPS processed materials show excellent consolidation of the powders as a result of the SPS process. The hardness values of the SPS consolidated forms are provided in Table 5.

Table 5: Hardness Values of SPS Consolidated Forms

Element	**Knoop Hardness (HK_{500g})**
Bulk form B	1938.0 ± 109.7
Bulk form C (ultrafine)	2074.4 ± 30.3
Bulk form D (near-nano)	2144.7 ± 29.7

The hardness of the samples increased in value as the size of WC grains in the consolidate forms decreased.   The hardness increased as the average size of the WC grains decreased from 0.4 µm (powder B) to 0.2 µm (powder C), and to nano- and near-nano sized WC grains (powder D).

Wear Testing

Wear testing was conducted on WC-10Co-4Cr coatings comparing the near-nano and nano-enhanced WC-10Co-4Cr, CNO 104 material to the commercial material and D-2 steel. The CNO-104 showed improved performance as compared to a leading commercial WC-10Co-4Cr powder.

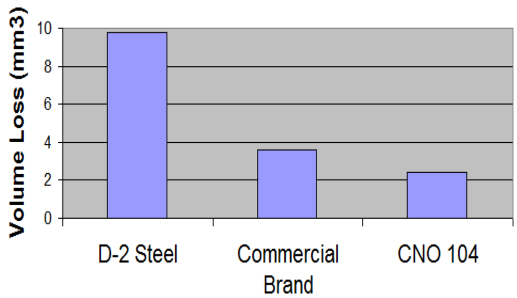
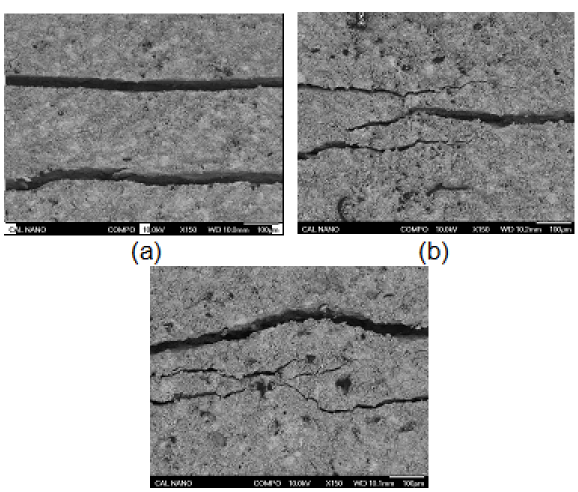


Fig. 4: *Wet Abrasion Wear Testing, G105-02*

<u>Bend Testing</u>

Bend testing was conducted on the WC-10Co-4Cr materials with Coatings A, B and C. HVOF (JP-8000) was used to spray the coatings on mild carbon steel coupons of dimensions 0.75" wide x 4" long x 0.059" thick. Crack deflection appeared to be occurring in Coatings B (CNO 104) and C (CNO 102) from the ultrafine, near-nano and nano WC grains in the matrix, whereas, the cracking appeared to run straight across the sample without much deflection in Coating A (commercial brand), having micron size WC grains. SEM images of the coatings from the bend testing are shown in **Figs. 5a, b** and **c**.



(a) (b) (c)

***Figures 5a, b** and **c**: SEM images (150x) of bend test samples showing coating cracks: (a) Coating A (commercial powder); (b) Coating B; (c) Coating C*

4 Conclusion

Thermal spraying of WC-10Co-4Cr and WC-12Co powders consisting of WC grains of different sizes show an influence on the mechanical properties of the resultant coatings. As the size of the WC grains present in the powders sprayed was decreased, the resultant coating showed less sensitivity to the spray conditions used to produce the coating. In WC-10Co-4Cr powders consisting of ultrafine and near-nano WC grains, the change in hardness of the coating was much less than the change in hardness in powders consisting of larger WC grains. In the ultrafine powder, the Knoop hardness increased from 1173.4 to 1258.1 HK, as the quality of the HVOF coating improved (e.g., less porosity). In comparison, powders consisting of larger WC grains (1.2 µm <) had a greater change in hardness (931.1 to 1266.9 HK) as the HVOF coatings were optimized. The coating microstructure improved when going from a 4" to a 6" HVOF gun barrel. The ultrafine, near-nano and nano-grained coatings were more consistent in hardness with a change in HVOF parameters.

Bulk powder consolidation (e.g., SPS) provides a technique to understand the influence of grain size on the properties of the consolidated materials, including HVOF thermal spray deposits. When the same powders used for the HVOF spraying were used in spark plasma sintering, an increase in hardness occurred with the decrease in the size of the WC grains. The material property improvements in the SPS processed WC-10Co-4Cr materials follows the concept established by the Hall-Petch relationship.

Wear testing was conducted on WC-10Co-4Cr coatings comparing the near-nano and nano-enhanced WC-10Co-4Cr, CNO 104 material to the commercial material and D-2 steel. The CNO-104 showed improved wear performance as compared to a leading commercial WC-10Co-4Cr powder.

Crack deflection appeared to be occurring in Coatings B (CNO 104) and C (CNO 102) from the ultrafine, near-nano and nano WC grains in the matrix, whereas, the cracking appeared to run straight across the sample without much deflection in Coating A (commercial brand), having micron size WC grains.

The mechanical properties of thermal spray coatings have been reported to relate to those of bulk materials. Thus, the improvements observed in the HVOF spray coatings produced in this experiment may, similarly, be related to the improved mechanical properties observed in SPS from the use of ultrafine and nano- and near-nano size WC grains.

5 Literature

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