Improved Mechanical Properties of Coatings and Bulk Components as a Function of Grain Size

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Thermal sprayed coatings produced from ultrafine- and nano- and near-nano grained powders of tungsten carbide-10 wt.% cobalt-4 wt.% chromium (WC-10Co-4Cr) are reported to provide improved properties as compared to conventional powders. These materials show great potential for applications in the aerospace, oil & gas, power, and many other industries. A study is proposed to investigate the influence of WC grain size on HVOF coating properties. Thermal spray coatings will be produced from powders consisting of grains of WC from micron- to near-nano in size in a Co-Cr matrix. The Hall-Petch relationship cites the strengthening of materials by reducing the average crystallite (grain) size. An examination of consolidated forms will be performed using the same powders used in thermal spray in the spark plasma sintering (SPS) consolidation. The mechanical properties of thermal spray coatings have been reported to relate to those of bulk materials. Improvements observed in the HVOF spray coatings will be compared to those of bulk samples.

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 properties. The Hall-Petch relationship cites the strengthening of materials by reducing the average crystallite (grain) size [2,10]. In terms of yield strength and hardness, the expressions are given as:

$$\sigma_y = \sigma_0 + kd^{-\frac{1}{2}} \qquad \text{(Eq 1)}$$

$$H = H_0 + k^{'}d^{-\frac{1}{2}} \qquad \text{(Eq 2)}$$

Where σ_y and H refer to the yield strength and hardness of the material, respectively, d is the grain diameter, and k and $k^{'}$ are constants unique to each material. Equations 1 and 2 show that when reducing grain sizes from the micron scale to the nanoscale, the mechanical strength of the materials increases significantly.

One of the most crucial parameters that affects the mechanical properties and wear performance in carbide-based cermet coatings (WC-10Co-4Cr) 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 a hydrogen-based HVOF system [12].

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

2 Experimental Approach

Materials

Powders consisting of tungsten carbide-10 wt.% cobalt- 4 wt.% chromium (WC-10Co-4Cr) were processed using two separate methods - thermal spray and 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 1.2 µm; (c) powder C, consisting of ultrafine WC grains (0.4 µm); and (d) powder D, consisting of nano- and near-nano WC grains in a Co-Cr matrix. The powder chemistry and average size of the WC grains are provided below in Table 1.

Table 1: Powder Chemistry and Grain Size

Item	Chemistry (wt.%)	Average Grain Size (µm)
A: Commercial	WC-10Co-4Cr	>1.2
B: CNO 104	WC-10Co-4Cr	<1.2
C: CNO 102	WC-10Co-4Cr	0.4
D: CNO 101	WC-10Co-4Cr	<0.1

Thermal Spray Processing

High velocity oxygen-fuel (HVOF) spraying was conducted with three powders consisting of CNO 104, CNO 102 (ultrafine WC), 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 the spray matrix 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

<u>Spark Plasma Sintering</u>

Spark plasma sintering (SPS) was conducted at California Nanotechnologies, Inc. (Cerritos, CA). The powders 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. A picture of the SPS in operation is provided in **Fig. 1**.

Fig. 1: *Spark Plasma Sintering*

Sintering parameters for SPS are provided in Table 3 for the sintering of 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 an infrared pyrometer
[2] Die temperature measured using a type K thermocouple

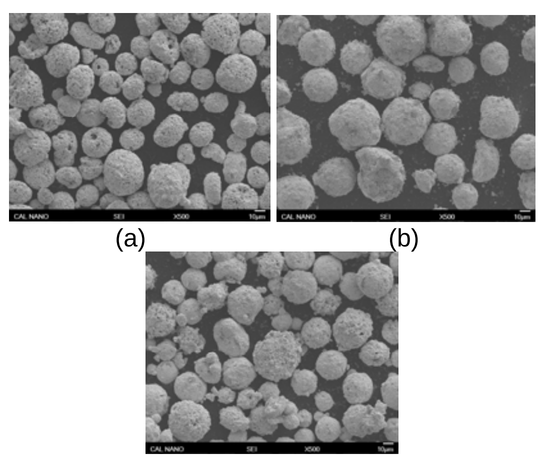
<u>Coating and Bulk Analyses</u>

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.

3 Results and Discussion

<u>Thermal Spray Powders</u>

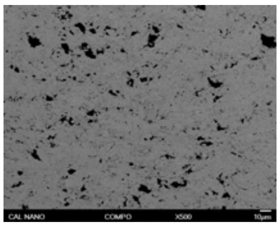
Scanning electron microscope (SEM) images of the powders used in thermal spraying are provided in **Figs**. **2a, b** and **c**.

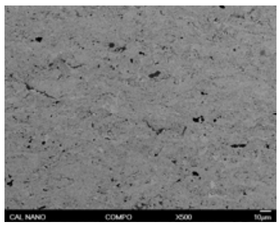


(a) (b) (c)

Figure 2a, b, *and* ***c***: *SEM images (500x) of (a) Powder A, widely used commercial powder; (b) Powder B (CNO 104); and (c) Powder C (CNO 102)*

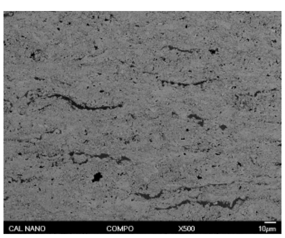
Thermal Spray Coatings
The thermal spray powders were sprayed to the parameters shown in Table 2 to produce coatings. The HVOF spraying using the parameters in Table 2 with a 6" gun barrel produced superior coatings to those produced with a 4" gun barrel. SEM images of thermal sprayed coatings produced using powder A and 4" and 6" HVOF gun barrels are shown in **Figs. 3a** and **b**.

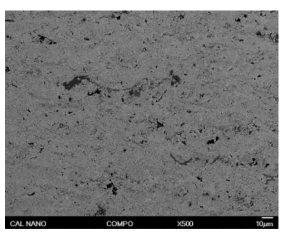

(a)


(b)

Figures 3a *and* ***b****: SEM images (500x) of cross-sectioned coating samples (a) Coating C (CNO 102), using a 4" HVOF gun barrel; (b) Coating C, using a 6" HVOF gun barrel*

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. 4a, b** and **c**.


(a)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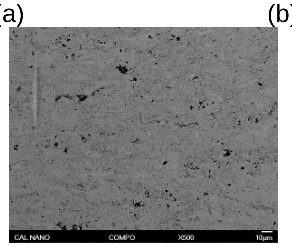
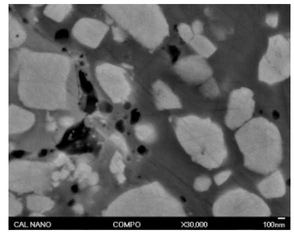
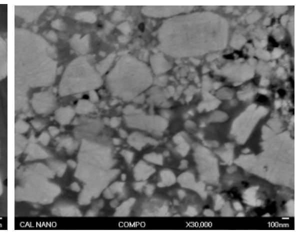

(c)

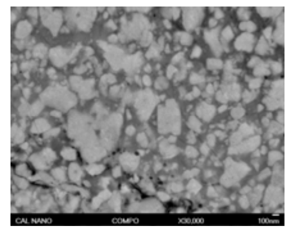
Figures 4a, b*, and* ***c****: SEM images(500x) of cross-sectioned coating samples (a) Coating A; (b) Coating B; and (c) Coating C*

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. 5a, b** and **c**.

The size of the WC grains in coating B are much smaller than the size of the WC grains in coating A. The size of the WC grains in coating C are smaller than the WC grains in coating B.


(a)


(b)


(c)

Figures 5a, b *and* ***c****: High resolution (30,000x) SEM images of cross-sectioned thermal spray coatings showing the WC grains: (a) Coating A (commercial powder); (b) Coating B; and (c) Coating C (ultrafine WC grains)*

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 $\pm$ 125.1	1266.9 $\pm$ 118.4
Coating B	1085.2 $\pm$ 88.8	1211.0 $\pm$ 107.7
Coating C	1173.4 $\pm$ 159.8	1258.1 $\pm$ 130.8

Spark Plasma Sintering
Spark plasma sintering operations were performed on powders B, C, and D. Consolidated forms produced from these powders are, similarly, identified as bulk forms B, C, and D, respectively. A cross-sectioned sample of SPS processed form D showed excellent bonding of adjacent grains 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 1.2 µm (powder B) to 0.4 µm (powder C), and to nano- and near-nano sized WC grains (powder D). The nano- and near-nano grains of WC are observed in the consolidated form of the CNO 101 material in **Fig. 6**.

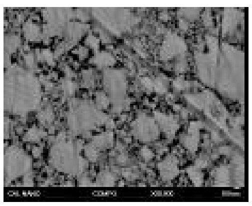


***Fig. 6**: SEM image(30,000x) of nano- and near-nano WC grains in consolidated bulk form (CNO 101)*

4 Conclusion

Thermal spraying of WC-10Co-4Cr 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 WC grains (0.4 µm), 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 quality of the HVOF coating improved. The coating microstructure improved when going from a 4" to a 6" HVOF gun barrel (e.g., Fig. 3).

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.

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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