PREPARATION AND PROPERTIES OF NANOSTRUCTURED WC-Co COMPOSITE POWDERS AND COATINGS

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Abstract: In WC-Co composites, the hard carbide particles provide strength and the Co, toughness. WC-Co composites are used in the manufacture of cutting tools because of its high hardness, wear resistance and high temperature strength. Preparation of nanostructured (NS) composite powders is the first step in the synthesis of nanostructured composite coatings by thermal spraying. Nanostructured WC-17Co composite powders were prepared by high energy ball milling and the coatings using NS and as-received (AR) composite powders were prepared by HVOF thermal spraying on 3 mm thick AISI 310 sheet samples. This paper presents: (a) the effect of milling time on WC-17Co powder particle size and crystallite size; (b) the effect of heat treatment on phase changes; (c) mechanical properties of NS and AR WC-17Co coatings. Milling altered the powder morphology from rounded particles to facetted particles. The average particle size of the powder decreased with milling time to 8 hours and further increase in milling time resulted in particle agglomeration. The average crystallite size decreased to 32 nm after 24 hours of milling. In terms of thermal stability, no degradation was observed up to 350 °C. The hardness of the nanostructured coating was higher than that of the coating prepared with AR powders.

Keywords: *Tungsten carbide; powder properties; coatings; thermal stability*

1. Introduction

Increasing technological demands in areas such as electronics, catalysis, ceramics, magnetic data storage, structural components etc., have to some extent been met by reducing the grain size of materials to the nanometer scale. Nano-materials have exhibited interesting mechanical and physical properties like increased mechanical strength, enhanced diffusivity, higher specific heat and electrical resistivity compared to conventional coarse grained counterparts. Tungsten carbide has high hardness and good electrical as well as thermal conductivities. Brittleness limits its use as a load bearing structural material. Hence cobalt when added to WC to produce WC-Co provides toughness and the hard carbide particle provides strength. WC-Co is used in the manufacture of cutting tools because of its high hardness, wear resistance and high temperature strength [1].

Nanostructured coatings prepared by thermal spraying of nanocrystalline powders have exhibited higher hardness, strength and corrosion resistance. [2-4] Nanostructured WC-Co can be synthesized by many methods and include, the spray conversion process, co-precipitation, displacement reaction process, mechano-chemical synthesis and high energy ball milling [5-7]. Nanostructured powders are formed in high energy ball mills by repeated deformation, fracture and cold welding caused by continuous impact [1]. This technique also enables the production of large quantities of powders.

This paper presents: (a) the effect of milling time on WC-17Co powder particle size and crystallite size; (b) the effect of heat treatment on phase changes; (c) mechanical properties of NS and AR WC-17Co coatings.

2. Methods and materials

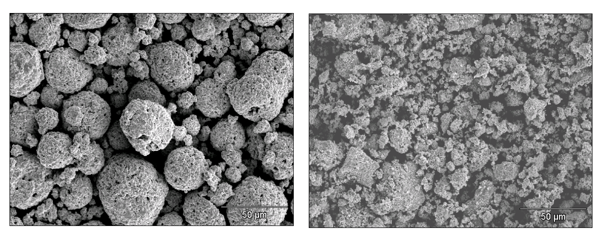
Commercially available WC-17Co powder with average particle size of 45 μm was used in this study. This powder was milled for 1, 2, 4, 8, 16 and 24 hours in a ZOZ high energy mill at 400 rpm and with a ball to powder ratio of 10:1. Milling was done in gaseous nitrogen. The particle size, morphology, grain size and phase constituents of the milled powders were determined as a function of the milling time. A CILAS particle size analyzer was used to determine the average particle size and a scanning electron microscope (SEM) coupled to an energy dispersive spectrometer (EDS) was used to examine particle morphology and determine the composition of phase constituents. X-ray diffraction (XRD) analysis was used to determine the crystallite size of the powders. The Scherrer equation was used to determine the crystallite size [8].

The thermal stability of milled powders in the range 300-400 °C was also determined using XRD, mainly to determine the acceptable maximum temperature for industrial applications without loss of either nanocrystallinity or phase change.

The 'High velocity oxygen fuel' (HVOF) thermal spray technique was used to deposit the as-received and milled WC-17Co powders on prepared AISI 310 stainless steel sheet specimens.

Fig. 1. HVOF deposition process and coated specimens

Figure 1 shows the deposition process and coated specimens. The average particle size of the powder used for deposition was 10 μm and the average coatings thickness was 50 μm. The Vickers hardness of the coatings was determined across the section using loads of 300g and 500g. The hardness of the two types of coatings was averaged from 5 or more measurements.



(a) (b)

Fig. 2. Morphology of: (a) as-received and (b) milled WC-17Co powder.

3. Results and discussion

The morphologies of the as-received and milled WC-17Co powder are shown in figure 2 and reveal marked differences. The as-received powder was rounded where as the milled powder was facetted.

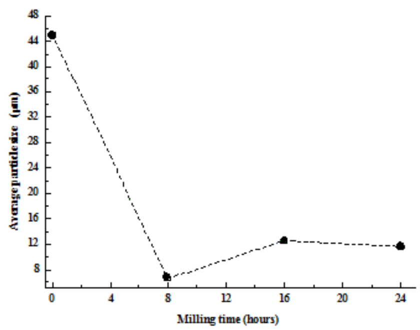


Fig. 3. Average particle size variation as a function of milling time.

The average particle size as a function of milling time is shown in figure 3 and it decreased to about 5 µm after 8 hours of milling. Milling for longer times resulted in particle size increase to around 12 µm, due mainly to particle agglomeration.

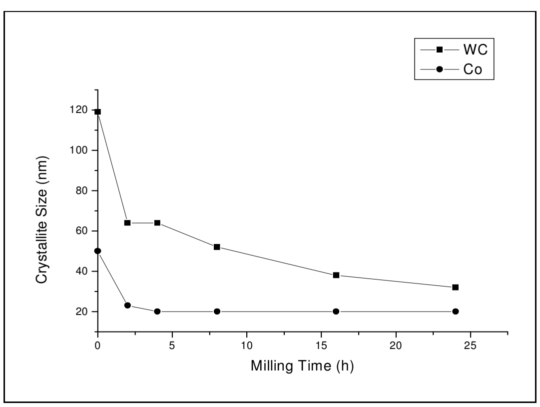


Fig. 4. Average crystallite size of WC-17Co powders as a function of milling time. The sizes were determined using the WC and Co peaks in the diffraction spectra.

The XRD spectra of the milled powders were used to determine the crystallite size. The diffraction peaks of the milled WC-Co powders were identified and the main WC and Co reflections were used to determine the crystallite size, utilizing Scherrer's equation. [8] Taking into consideration that microstrain and equipment conditions also influence diffraction peak broadening, Gaussian fitting, related to microstrain and Laurentian fitting, attributed to crystallite size, were done for the selected diffraction peak in the spectra. These fittings indicated that peak broadening was due mainly to crystallite size.

Figure 4 shows the average crystallite size determined from the main peaks of WC and Co in the XRD spectra of the milled powders. Marked reductions in crystallite size were observed upon using the WC peak. The main aspect of this data is the reduction in crystallite size determined from the main hard phase WC. Thus a reduction in crystallite sizes to 32 nm was obtained after 24 hours of milling.

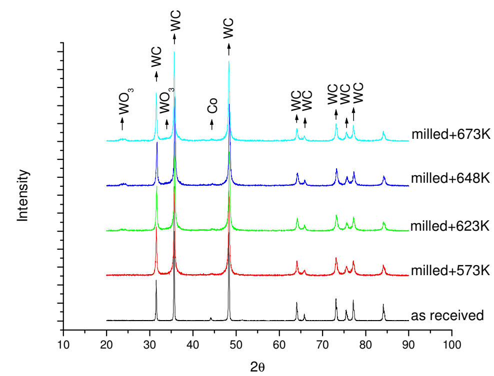


Fig. 5. XRD spectra of as-received WC-17Co and the same powder milled for 8 h and heat treated in air for an hour at 300 to 400 °C.

The XRD spectra of the WC-Co powders in the as-received condition and after milling for 8 h followed by heating in air for 1 hour at various temperatures in the range 300-400 °C (573-673 K) is shown in figure 5. Comparison of the XRD spectra of the as-received and the heat treated powders reveals that the reflections of the WC phase in the milled powders are broadened and the Co peaks disappear. No new phases were observed in the milled powder despite the fact that nitrogen and oxygen contents were significantly higher. Also no evidence indicating that significant oxidation of the milled powders occurred in air below 648 K This is an advantage with regards to storage, transportation and agglomeration of milled powders as the powders may be exposed to air during spray drying which is normally conducted at temperatures between 373 and 473 K [9]. At 623 K oxidation occurred in the milled powder exposed to air. The WO_3 oxide phase was detected by XRD.

Table 1. Vickers microhardness of WC-17Co coatings prepared with as-received and nanostructured powder (load 300g)

Coating	Vickers microhardness VPN 300
As-received	1110
Nanostructured	1334

The Vickers microhardness of the two types of coatings are shown in table 1. The nanostructured coating had a higher hardness compared to the coating prepared with as-received powder. SEM examination of the coating sections with the hardness test indents revealed cracks that emanated at various regions like the indent diagonal, WC-Co phase boundaries and the WC-CO composite phase, as shown in figure 6. This characteristic although typical of a material that hardens forming mixed phases such as WC_2-Co due to heating during the spraying process, precluded determination of the fracture toughness of the coating.

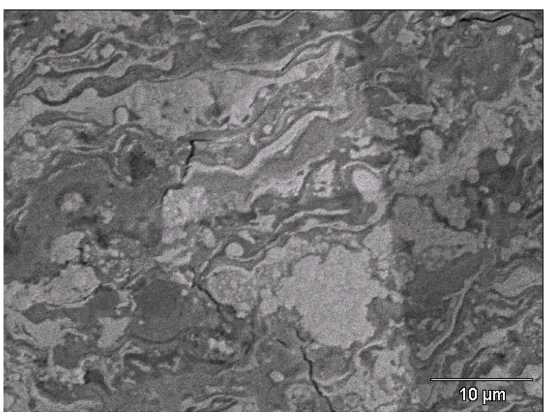


Fig.6. Cracks at the hardness test indents.

4. General discussion

The hardness of thermally sprayed coatings is influenced by the characteristics of the powders and the spraying technique. In HVOF spraying the particle velocity is high and the thermal energy low. This contributes to the higher hardness of sprayed coatings. Besides, nanostructured materials in general exhibit higher hardness than corresponding conventional coarse grained materials, but significantly less than that stipulated by the classical Hall-Petsch equation. This aspect was verified in this study and the nanostructured WC-Co coating was harder than the coating prepared with as-received powders of the same material. This is due to decomposition of the WC phase with subsequent dissolution of W and C in the Co matrix to produce complex phases Co_xW_yC, W_2C and W_3C. [10,11] This phase also has the propensity to increase cracking in HVOF sprayed coatings [10] and was observed in this study at the hardness test indents.

5. Conclusions

1. Milling altered the WC-17Co powder morphology from rounded particles to facetted particles.
2. The average particle size of WC-17Co powder decreased with increase in milling time to 8 hours and further increase in milling time resulted in particle agglomeration.
3. The average crystallite size of WC-17Co powder decreased significantly with increase in milling time and reached 32 nm after 24 hours of milling.
4. The thermal stability tests revealed no degradation with oxide formation up to 350 °C.
5. The hardness of the nanostructured coating was higher than that prepared with as-received powders of WC-17Co.
6. Phase changes during thermal spraying also contributed to increase in hardness of the coating.

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