Effect of high energy milling on WC-Co powder features, composition and thermal stability

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Keywords: Nanostructure, tungsten carbide –cobalt, milling, powder features, thermal stability

Abstract

The effects of high energy milling WC-17Co powder on its particle size, crystallite size and phase composition were studied. The oxidation behavior in air at 500-700 °C and thermal stability of milled powders in the range 300-400 °C were determined. The WC-Co powders were milled in gaseous nitrogen. The particle and crystallite sizes decreased markedly with milling time to 8 μm and 32 nm respectively. Oxidation rate of the powder increased with temperature and became linear above 600 °C with formation of WO_3. The x-ray diffraction spectra of milled WC-17Co powders that was heat treated revealed disappearance of the Co peak with increase in temperature and formation of WO_3 above 350 °C.

Intoduction

Nanomaterials are experiencing rapid development in recent years due to their existing and/or potential applications in a variety of technological areas such as electronics, catalysis, ceramics, magnetic data storage, structural components etc. To meet the technological demands in these areas, the size of the materials is reduced to the nanometer scale. As the size reduces into the nanometer range, the materials exhibit interesting mechanical and physical properties like increased mechanical strength, enhanced diffusivity, higher specific heat and electrical resistivity compared to conventional coarse grained counterparts. The main characteristics of WC are high hardness and good electrical as well as thermal conductivities. Brittleness limits its use as a load bearing structural material. This resulted in the development of cermets. Cobalt was added to WC to produce the cemented carbide WC-Co in which Co acts as the cement around the carbide particles. The hard carbide particle provides strength and the Co provides toughness. WC-Co cermets are used as cutting tools because of its high hardness, wear resistance and high temperature strength [1].

During the last 15 years coatings prepared by thermal spraying of nanostructured powders have exhibited higher hardness, strength and corrosion resistance. [2-4] Preparation of nanostructured powders is the first step in the synthesis of nanostructured coatings by thermal spraying. Nanostructured WC-Co can be synthesized by many methods and include, the spray conversion process, co-precipitation, displacement reaction process, mechanochemical synthesis and high energy ball milling [5-8]. 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 high energy ball milling duration on WC-17Co powder particle size and crystallite size; (b) the high temperature oxidation behavior of WC-Co powders; (c) the effect of heat treatment on phase changes.

Materials and methods

Conventional WC-17Co powder with average particle size of 45 µm was used in this study. These powders were 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 (1) was used to determine the crystallite size [9]. This relates crystallite size (D) and the full-width at half-maximum (FWHM), referred to as Δ (2θ) of XRD reflections.

$$D = 0.9\lambda / \Delta (2\theta) \cos\theta \qquad (1)$$

Where λ is the wavelength (in the case of a Cu target, λ = 0.15406) and θ is the diffraction angle. The use of this equation is based on the physical origin of broadening of the XRD reflections being associated with the small grain size only. The true peak broadening Δ (2θ) can be obtained using the equation (2):

$$\Delta (2\theta) = [(\Delta(2\theta)_h)^2 - (\Delta(2\theta)_g)^2]^{1/2} \qquad (2)$$

where $\Delta(2\theta)_h$ is the FWHM of the measured profile and $\Delta(2\theta)_g$ is the FWHM of the profile from the standard sample for the same reflection. The grain size thus obtained is volume averaged in a direction perpendicular to the diffraction plane.

The composition of WC-Co powders milled for different periods was determined using x-ray fluorescence analysis. 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.

Results and discussion

The morphologies of the as-received and milled WC-17Co powder are shown in figure 1 and reveal marked diferences. The as-received powder was rounded where as the milled powder was facetted.

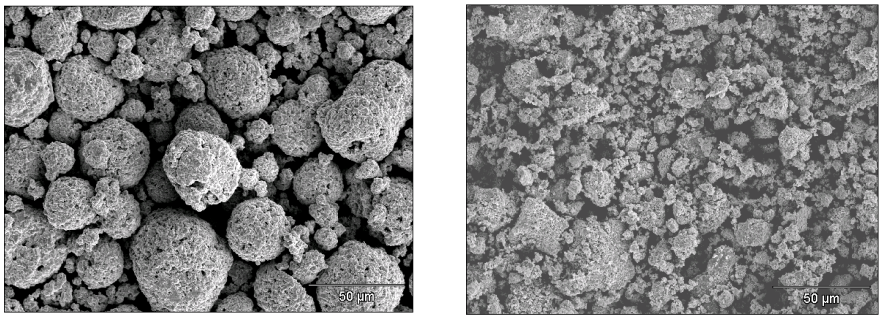

Figura 1. Morphology of as-received and milled WC-17Co powder.

The average particle size, determined in a CILAS particle size analyzer, as a function of milling time is shown in figure 2. The average particle size 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.

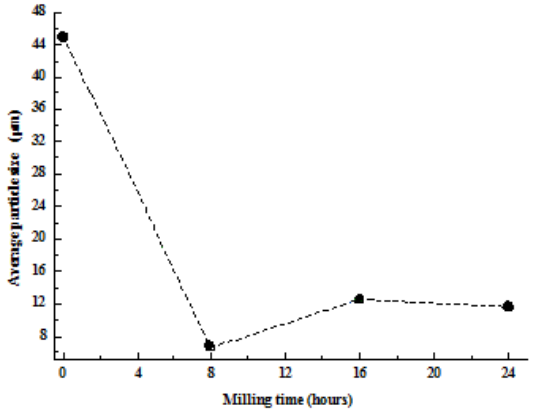

Figure 2. Average particle size variation as a function of milling time.

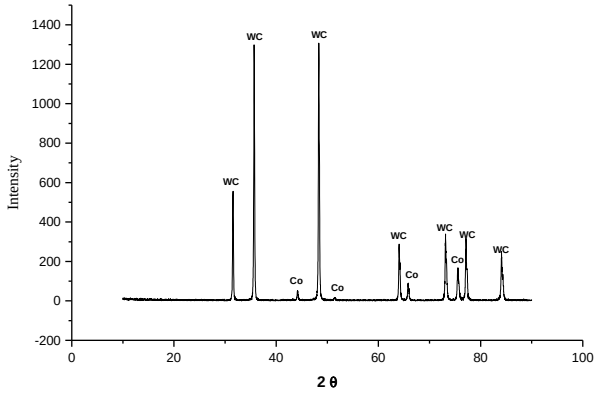

Figure 3. XRD spectra of WC-17Co powder milled for 8 hours.

Figure 3 shows a typical XRD spectrum of WC-17Co powder milled for 8 hours. Marked peak broadening was observed in the powders milled for 24 hours indicating significant crystallite size reduction. 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. 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 diffration 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. In subsequent studies powders prepared by milling for 8 and 24 hours were used.

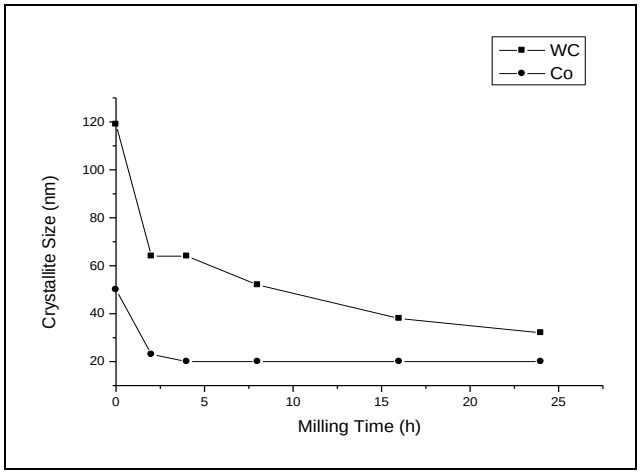

Figure 4. Average crystallite size of WC-17Co powders as a function of milling time. The sizes were determined using the WC and Co peaks in the diffraction spectra.

The chemical composition of WC-17Co powder milled for 8 and 24 hours is shown in table 1. Increase in Fe and Cr content with increase in milling time is evident. This could be attributed to the erosive effect of the WC-17Co powder on the stainless steel balls and mill wall.

Table 1. Chemical composition (wt%) of milled WC-17Co powders.

Milling time (h)	W	Co	Fe	Cr	P	S
8	75,12	20,79	0,62	0,51	0,43	0,11
24	74,54	20,99	0,78	0,64	0,59	0,11

Figure 5 shows the isothermal oxidation behavior of as-received WC-17Co powders in the range 500 °C – 700 °C. The isothermal oxidation behavior of the as-received and milled powders were identical. With increase in temperature from 500 to 700 °C the oxidation rate became linear with formation of large quantities of WO_3, as determined by XRD.

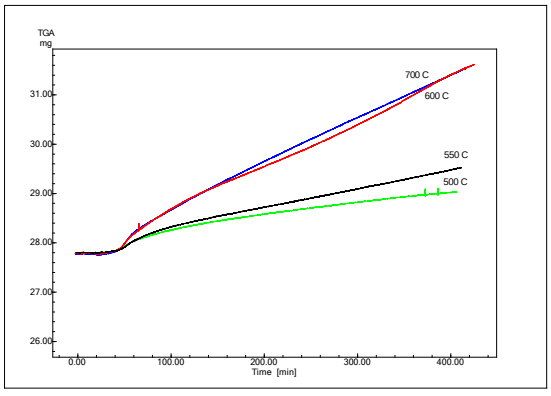

Figure 5. Isothermal oxidation curves of WC-17Co powders in the range 500-700 °C

In general the oxidation of WC at 500 °C is quite intense and follows a parabolic law in the initial stages, after which it proceeds to a linear law up to 700 °C [10, 11]. In the temperature range 500-600 °C a thin dark grey oxide film forms on the surface of WC-17Co and consists mainly of $CoWO_4$, a complex oxide and small amounts of $WO_{2.9}$, with a tetragonal lattice and of WO_3 with a triclinic lattice [12]. This oxide also contains pores, voids and defects due to burn out of carbon. The formation of $CoWO_4$ gives a certain amount of resistance compared to that at the higher temperatures. The WO_3 scale formed at the higher temperature has no protective properties. The cobalt oxidizes to its oxide and forms a complex oxide $CoWO_4$

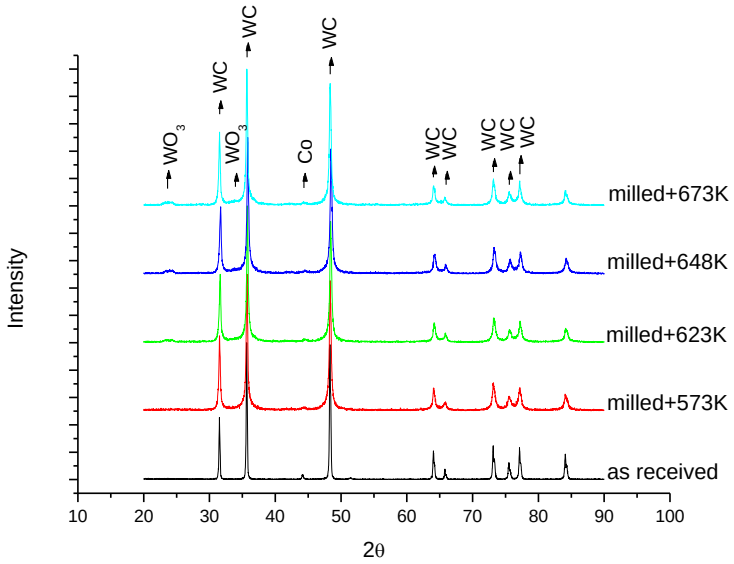

Figure 6. XRD spectra of as-received WC-17Co and the same powder milled for 8 h and heat treated in air for an hour in the temperature range 300 to 400 °C.

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 6. 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 accurred 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 [13]. At 623 K oxidation occurred in the milled powder exposed to air. The WO_3 oxide phase was detected by XRD. Phases that form as a result of decarburization of WC, such as W_2C and metallic W phases were not detected.

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 oxidation rate of WC-17Co powder increased with temperature and attained a linear rate at > 600 °C.

5. The thermal stability tests revealed no degradation with oxide formation up to 350 °C.

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