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Impact of crystal defects on the grain growth of cemented carbides☆

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ABSTRACT

Two different WC-Co powder mixtures were produced through a 200 h milling process. One of these mixtures were heat treated with the aim to remove the crystal defects from the WC grains. Image analysis showed that the two powders had the same average WC grain size and grain size distributions. X-ray diffraction showed much more narrow peaks for the material produced from the heat treated powder thus interpreted to have much less crystal defects.

The powder mixtures were used to produce cemented carbides. Image analyses showed a clear difference for the WC grain sizes where the material produced from the heat treated powder had a significantly smaller mean WC grain size. It is therefore concluded that the crystal defects are of importance and facilitate WC grain growth during sintering.

1. Introduction

During sintering of a cemented carbide material, the average WC grain size increases. Smaller WC grains are dissolved in the binder due to their higher solubility. Through diffusion, W and C atoms are transferred to larger undissolved WC grains where growth takes place, a process called Ostwald ripening. The process is limited by the diffusion and interfacial reactions as explained by the LSW theory [1–2]. However, the LSW theory cannot predict or explain abnormal grain growth (AGG). That is when few grains grow very fast compared to the growth of the surrounding grains during the sintering process. Several studies on AGG have been performed showing the importance of WC grain shape and initial WC grain size distribution [3–5]. Another parameter of importance is the milling process [5–6]. Milling is expected to introduce defects in the WC crystals but simultaneous also to reduce the carbon content, possibly due to creation of more surfaces able to react with oxygen [6]. These types of decarburization processes during vacuum annealing of various nanocrystalline WC powders have been examined in rather detail by using XRD and particle size analysis [7]. A changed carbon potential during sintering will additionally have an effect on the WC grain shape where carbon rich alloys cause more faceted WC grains and tungsten rich alloys will cause WC grains with slightly rounded corners [8]. It is now the aim of this study to separate and study possible effect of defects in the WC crystals on the WC grain growth during sintering. Introduction of defects and changes of microstructure during the milling process can result in significant line broadening of the X-ray diffraction peaks. Line profile analysis has earlier been applied to nanocrystalline WC to determine strain and size and effects of line broadening has been observed when cemented carbides are ball-milled under prolonged times [9].

2. Experimental

A powder mixture was produced through a mixing of 90 wt% WC powder and 10 wt% Co. The metal powder and additional 2 wt% polyethylene glycol (PEG) were milled in ethanol with 8 kg cylindrical milling bodies for 200 h in a 2.4 dm^3 rotating mill with the inner diameter 142.8 mm at 63 rpm. This is to introduce at least as much defects in the WC crystals as what would have been the case in a commercial production route. In order to be able to analyze the WC grains, the Co and the PEG were removed trough mixing the powder mixture in diluted hydrochloric acid with a final rinsing in water followed by drying in hot air. The resulting product was deagglomerated for 1 h through an ASTM standardized procedure. From the deagglomerated powder, two 23 g samples were taken to produce the powder batches B-heat and B-ref. Batch B-heat was mixed with 12 g carbon and put in a graphite crucible which was heated to 1500 °C in a furnace for 1 h in Ar atmosphere. The resulting soot was separated using a 150 μm sieve. Also batch B-ref was sieved in order to ensure the same treatment.

In order to prepare the powders for scanning electron microscopy

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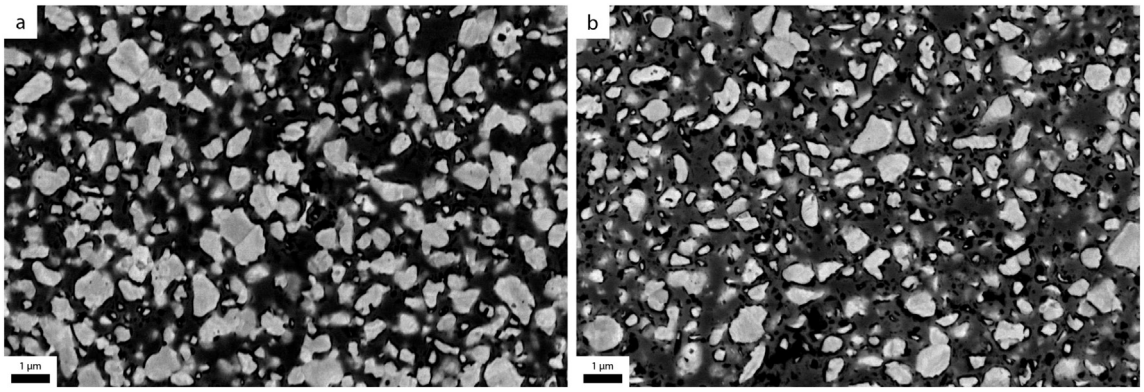

Fig. 1. SEM micrographs of powder (a) B-heat (b) B-ref.

(SEM) analysis, B-heat and B-ref were mixed with Cu powder, pressed into tablets and heated in a furnace at 1100 °C for 10 min. This is advantageous due to the non-reactive properties between Cu and W and C and also due to the high conductivity of Cu, needed for good SEM analyses. The specimens were molded in bakelite and polished with diamond slurry with the final step being performed with 1 μm diamond particles. For SEM imaging, the specimens were etched for 40 s with a 20% Murakami solution. SEM imaging was carried out using a Hitachi S-4300 FEG instrument run at 10 kV acceleration voltage. 10 images were taken at higher magnifications for both specimens. Due to lack of contrast between different grains, each boundary was filled in by hand. The scanned images were analyzed with the image analysis program Leica QWin Pro 2.8. The measured grain areas were assumed to be circular and from these, equivalent diameters were calculated.

XRD measurements of both powders were performed on a PANalytical X'Pert Pro MPD in Bragg-Brentano geometry (CuKα radiation, $\lambda = 1.5418$ Å, 45 kV, 40 mA). Diffraction data were collected in the $20^\circ < 2\theta < 140^\circ$ angular range with a step size of 0.008°. The XRD patterns were analyzed with the HighScore Plus (PANalytical) software.

The carbon contents in B-heat and B-ref were measured using a LECO carbon apparatus and C was added to B-ref ensuring the same composition. Also, Co was added to both powder mixtures. The powder mixtures were shaken by hand for 5 min in order to reduce the risk of introducing new defects. No PEG was added due to the small sample size. The powder mixtures were pressed into 1 g cylinders and sintered at 1430 °C for 1 h, producing material C-heat-1 and C-ref-1, and for 32 h, producing C-heat-32 and C-ref-32.

Magnetic properties were measured for the as-sintered materials using a Koerzimat CS 1.096 instrument. The materials were imaged and analyzed with SEM using the same preparation and analysis route as for the Cu powder tablets.

3. Results

Fig. 1 shows SEM micrographs of the powders B-heat and B-ref. As seen, the two powders showed similar appearance.

Table 1 and Fig. 2 show the results from the image data analyses of powders B-heat and B-ref. As seen, the two powders have the same WC mean grain size and grain size distribution.

Fig. 3 shows the results from the XRD analyses. It is clear that the peaks from the reference powder are significantly broader, that is they have a larger full width half maximum (FWHM).

Table 1
Data from image analyses of the WC powders.

Powder	Grains investigated (#)	WC mean radius (μm)	Standard deviation (μm)
B-heat	1746	0.17 ± 0.004	0.09
B-ref	1470	0.17 ± 0.004	0.09

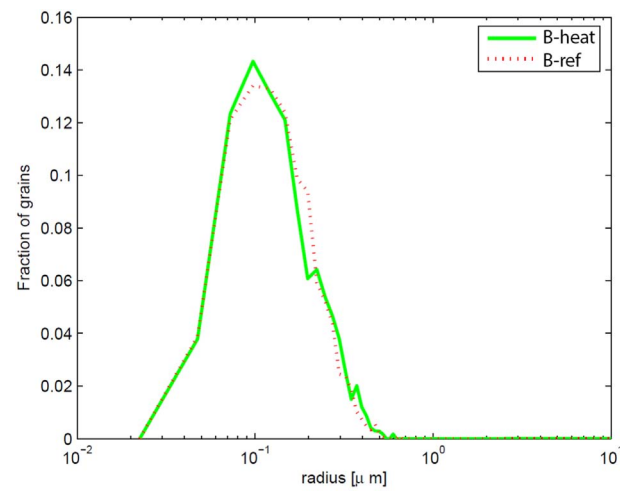

Fig. 2. Image analyses of the WC grain sizes for the powders.

Fig. 4 shows SEM micrographs of the cemented carbide materials C-heat-1 and C-ref-1 and Fig. 5 shows the corresponding micrographs of the cemented carbide materials C-heat-32 and C-ref-32. No dramatic differences could be observed comparing C-heat-1 to C-ref-1 and the same is also true for comparing C-heat-32 to C-ref-32. However, the materials sintered for 32 h have significantly larger WC grains than the materials sintered for 1 h.

Table 2 shows values from the magnetic measurements as well as WC mean grain sizes from the SEM image analyses of the cemented carbide materials. It is noted that that the cemented carbide materials produced from the heat treated materials have a slightly lower magnetic saturation relative to Co. It is observed that for a specific sintering time, the materials produced from heat treated WC powder has a higher coercivity and a smaller WC grain size compared with the materials produced from the reference powder.

Fig. 6 shows the WC grain size distributions for the sintered materials. In particular, the materials produced from the heat treated powder have a larger fraction of relatively small WC grains compared to the materials produced from the reference powder.

4. Discussion

The reason for adding Co to the initial powder mixture was to create an environment as similar as possible to real production. Co is not expected to add to the introduction of dislocations in the WC grains, rather the opposite due to the softer nature of Co.

Powders B-heat and B-ref were similar with respect both to mean