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Grain growth during sintering of tungsten carbide ceramics ☆

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ABSTRACT

Grain growth and abnormal grain growth in tungsten carbide cobalt composites (cemented carbides, hardmetals) are usually discussed with respect to liquid phase sintering (Ostwald ripening). Densification and grain growth during solid state sintering are not as thoroughly studied but do play an important role in sintering hardmetals and, particularly tungsten carbide ceramics (binderless hardmetals). In this work the influences of sintering temperature, carbon content, additions of grain growth inhibitors, defects and dislocations (microstrain) introduced by milling on the densification and microstructure of WC ceramics were studied including density, micro structural, thermal and X-ray analysis. Microstrain promotes densification and results in lowering the sintering temperature, whereas free carbon seems to hinder densification at low temperatures and to promote it slightly at higher temperatures. Depending on sintering regime, free carbon and microstrain may drastically boost abnormal grain growth. By adding grain growth inhibitors, densification is shifted to higher temperatures. However, the addition prevents abnormal grain growth regardless of C-content and microstrain. Like in hardmetals grain growth inhibitors also inhibit normal grain growth. The findings are relevant for sintering of WC ceramics and hardmetals alike.

1. Introduction

Rapid grain growth and especially abnormal grain growth are interesting phenomena in research and production of ultrafine and nanoscaled materials. By using increasingly finer starting powders one is confronted with a grain size increase well above the original grain size. With nanoscaled powders one can occasionally produce materials with larger final grain sizes than one would get when using 10 times larger starting powders [1,2].

Within WC–Co hardmetals and cermets grain growth is often linked to liquid phase mechanisms. Here densification is explained to happen because of the diffusion of atoms from smaller grains to larger grains. Atoms dissolve within the liquid phase and are reprecipitated at existing solids [3]. This behaviour, called Ostwald ripening, shows that larger grains will grow at the expense of smaller grains which will dissolve. Thus, over time the smallest grains are vanishing and the overall grain size is increasing. First, numerical considerations done by Lifshitz, Slyozov and Wagner (L–S–W) led to the so called LSW-theory [4,5]. According to theory, the growth rate is supposed to be proportional to the driving force, which is the surface energy that is lowered by continuing grain growth.

However, since grain growth occurs already before the liquid phase exists, Ostwald ripening is only one of several grain growth mechanisms [6]. As studied before on WC–10 Co samples [7] grain growth and densification in hardmetals starts already at 1100 °C, well below the temperature at which any liquid phase exists.

Next to grain growth there also exists the so called abnormal grain growth (AGG). Abnormal grain growth is normally defined by the fact that some but not all grains have extraordinarily increased grain sizes. In hardmetals these grains can have a size of 10 to 1000 times of the overall undisturbed microstructure. Since abnormal grain growth is not explainable by Ostwald ripening many researchers have studied this phenomenon in hardmetals. Exner observes "discontinuous" grain growth at sintering times >10 h and summarizes earlier theories [8]. It is assumed that "discontinuous" grain growth is bound to the presence of cobalt and is correlated with the transformation of W_3Co_3C to WC and Co [9]. However, abnormal grain growth, i.e. the formation of crystals with dimension up to 1 mm was also observed in hot-pressed and SinterHIPed (HIP = Hot Isostatic Pressing) pure tungsten carbide samples [10,11]. An explanation is still missing.

But it is important to understand the sintering mechanisms of pure tungsten carbide (WC) since it is one component of the often studied system of WC–Co hardmetals. By studying the sinter behaviour of pure tungsten carbide the solid state sintering mechanism which becomes particularly important with finer grades can be studied separately from any influence of the liquid phase.

For the production of fully dense WC samples high temperatures are needed. Only a few techniques and high temperature furnaces can be used. At laboratory scale the Spark-Plasma-Sintering (SPS) technique is often used to produce small samples. However, the SinterHIP and the vacuum + HIP technique can be used to produce larger quantities of parts in one run [12]. Here studies showed that a temperature as high as 2000 °C is needed for full densification using conventional vacuum and SinterHIP furnaces [13,14]. With external pressure or HIP,

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temperatures between 1600 and 1900 °C are needed [15–17]. The occurrence of abnormal grain growth was often observed using the SPS technique [18,14,19]. Here abnormal grain growth was mostly explained to have happened because of carbon introduced through the graphite matrix normally used in SPS furnaces or due to free carbon present in the powder mixtures used [20,21]. However, in the case of SinterHIP sintering abnormal grain growth occurs as well, but can be retarded by adding the same grain growth inhibitors (like VC or Cr_3C_2) that were used in WC-based cemented carbides [22]. Nevertheless, in the case of the SinterHIP process it could also be shown that it is possible to produce samples free of abnormal grain growth without the presence of any grain growth inhibitors by carefully adjusting the milling conditions [23].

To study the influence of different milling intensities, different carbon contents and different grain growth inhibitor additions on grain growth and densification behaviour several mixtures were prepared and sintered. Sintering was done by using a dilatometry furnace to measure the shrinkage and densification behaviour during sintering and by sintering pressed cylinders in a SinterHIP furnace at 1900 °C. Additional to the densification behaviour the microstructure, carbon content, oxygen content, crystallite size and microstrain was studied using the SinterHIPed samples and Field Emission Scanning Electron Microscopy (FESEM), gas analysis (C and O-content) and XRD-analysis techniques.

2. Experimental

All experiments were carried out with a pure WC powder from H.C. Starck. The WC particle size of the nanoscaled powder was 115 nm (D_{BET}) and 400 nm (D_{FSSS}), respectively. For experiments with grain growth inhibitors Cr_3C_2 and VC from H. C. Starck were used. The measured particle sizes were 470 nm (D_{BET})/1500 nm (D_{FSSS}) and 320 nm (D_{BET})/1200 nm (D_{FSSS}), respectively. In order to diversify the C-content carbon black was added.

For the experiments with varying C-contents and the addition of grain growth inhibitors the powders were mixed with carbon black and intensively milled under N_2 for 72 h in heptane using a ball mill, dried, granulated and cold isostatically pressed (CIPed) to cylinders (10 mm Ø, 20 mm long) at 3000 bar. After the CIPing, the specimens were sintered in a SinterHIP furnace at 1900 °C and a pressure of 100 bar. For the experiments with varying milling conditions the powders were milled with different milling energies and pressed as well as sintered like the other samples. Here the gas adsorption on the surface according to the Brunauer–Emmett–Teller (BET) theory: [24], the BET surface area per gram was measured using a ASAP 2010 device from Micromeritics and a five point analysis.

Density was measured according to DIN ISO 3369. To study the microstructure sintered samples were cut and polished down to 1 μm using diamond slurries. Images were taken using a field emission scanning electron microscope (FESEM) LEO 982 (Carl Zeiss SMT AG). Grain size measurements were done using FESEM images and counting at least 500 grains using the chord length method.

Vickers hardness (HV10) of dense specimen was measured according to DIN ISO 3878 with a load of 98.1 N. The fracture toughness (K_{1C}) was calculated from the Vickers indentation crack length using the Shetty equation [25]. The relative density was calculated by means of the rule of mixture from the densities of WC, VC and Cr_3C_2.

In order to determine the Co content in the milled powders, small parts of powders were dissolved using HCl-acid and analysed using ICP-OES (Inductive Coupled Plasma Optical Emission Spectroscopy). To measure the C content of the starting powder, the milled powders and the sintered samples were oxidized and the evolved CO_2 was measured in a gas analyzer WC600 from LECO Inc. Oxygen content of the milled powders was measured using the gas analyser LECO TCH 600.

The densification, shrinkage and sintering behaviour within a temperature range from 600 °C to 1950 °C and a heating rate of 10 K/min was furthermore studied using a dilatometer NETZSCH DIL 402 E7.

The phase composition of the sintered samples was determined by X-ray analysis. Polished samples were analysed using a Bruker D8 diffractometer. The Bragg–Brentano geometry and CuKα ($\lambda = 0.15418$ nm) radiation was used and the samples were X-rayed in the 2θ range of 20–130°.To obtain detailed information about crystallite size, microstrain (internal stress) and phase composition (content of W_2C) a Rietveld refinement was done using the computer programme TOPAS (DIFFRAC.SUITE TOPAS, from Bruker).

3. Results and discussion

3.1. Influence of milling condition

After ball milling pure WC powder with different milling intensities a decrease of the particle size d_{BET}, the C content, and the crystallite size d_{XRD} and an increase of the microstrain ε_{XRD} was observed with increasing milling energy (Table 1).

As is well known, a significant decrease of the particle size can be achieved by milling with high milling intensities. Here the size of the already very fine particles was reduced by 50% in case of the heavily milled powders compared to the unmilled or softly milled powder. The decrease in C content can be explained by carbon loss due to oxidation. The fact that even when the particle size of the softly milled compared to the unmilled powders stays unchanged and the crystallite size decreases just by 30 % the microstrain increased drastically from 0.03 to 0.14% (an increase of 450%) is very interesting. On the assumption that the increase of strain is caused by dislocations and surface defects [26] the increase of strain shows that even softly milling leads to an activation of the powders without any significant reduction in particle size d_{BET}. By measuring the Co-content using ICP-OES technique an increase of the Co content from <0.01 wt.% for the unmilled powder to over 0.04 wt.% for the softly milled up to 0.11 wt.% for heavily milled WC powder was observed. The increase of the Co content due to the abrasion of the ball milling equipment consisting of WC–Co cemented carbide components is still quite low but could be the reason for already enhanced sinterability.

To study the influence of the different milling energies samples made from unmilled, softly milled and heavily milled powders were sintered at 1900 °C and analysed. Density and porosity of the specimens, remarks on their microstructure, carbon content, crystallite size and microstrain are given in Table 2.

The sample made from the unmilled powder shows a porous microstructure with a density of 89.3 % TD (Theoretical Density) Fig. 1a. Both, softly heavily milled samples show low levels or no porosity but quite different microstructures (Fig. 1b and c).

While with the softly milled powder a fine homogenously grained microstructure can be produced, with the heavily milled powders abnormal grain growth occurs with some abnormal grains having a lateral dimension of up to 100 μm or even more (Fig. 2). Here abnormal grain growth is defined whenever grains with a lateral dimension of above 100-times the size of the normal grain size in comparable samples of the same starting powder are present. Abnormal grains are defined as grains which grow beyond 100-times the grain size of the starting powder.

Since the abnormal grains are thin tungsten carbide triangles, which mostly grow in the direction of the hexagonal basis face ({1110}

Table 1
Measured properties of pure WC powders after milling with different milling energies.

Milling condition	Particle size d_{BET} [nm]	C content [wt.%]	O content [wt.%]	Crystalite size d_{XRD} [nm]	Microstrain ε_{XRD} [%]
Unmilled	119	6.14	0.40	52	0.03
Softly milled	117	6.13	1.02	36	0.14
Heavily milled	61	6.07	1.30	19	0.17