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Grain growth inhibition in ultrafine hardmetals

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ABSTRACT

Ultrafine and nanoscaled hardmetals show mechanical properties like hardness and bending strength which lie way above conventional fine or submicron grained hardmetals. To achieve such fine microstructures very fine WC starting powders as well as grain growth inhibitors such as Cr_3C_2 or VC are needed. To study the grain growth inhibition in ultrafine hardmetals investigations on samples made from nearly nanoscaled WC and Co starting powders with and without the addition of Cr_3C_2 were done. For studying the dissolution behaviour of Cr_3C_2 and the evolution of density, magnetic properties and lattice parameters of WC during sintering, interrupted sintering experiments were carried out. Thermal analysis techniques including TG-MS and DSC were used, to link the observed changes to expected reactions. The results show that grain growth inhibitors greatly influence the sintering behaviour already way below the eutectic melting of WC-Co. Especially dissolution of Cr_3C_2 and homogenous distribution of Cr within the samples already starts below 800 °C with the reduction of W surface oxides and the creation and spreading of Cr oxides. The findings are relevant for optimising sintering regime, composition (amount of grain growth inhibitors) as well as the microstructure and mechanical properties.

1. Introduction

Hardmetals are tungsten carbide (WC) based composites, which consist of WC as a hard phase and metals like Co, Fe or Ni as ductile binder matrices. Hardmetal properties can be mainly tailored through the amount of metallic binder and grain size of the sintered material. For the production of sub-micron to nanoscaled hardmetal grades grain growth inhibition during sintering is the most important step. Already shortly after hardmetals were developed by Skaupy, Schröter and Fehse [1], patented by Schröter [2] in 1923 and brought to market by Krupp as WIDIA N (wie Diamant - like diamond) in 1926 [3,4], the first fine grained grade (grade H1) was produced from fine starting powders. Even finer grades were enabled by using so called grain growth inhibitors (GGI) VC and TaC in 1939 [5]. These grades showed a significant increase of hardness, while keeping the same composition regarding the Co content. During the next decades many scientific studies were carried out to investigate the influence of initial grain size and grain growth inhibitors on the grain size and the properties of sintered hardmetals [6–12]. They revealed a strong influence of grain size and grain size distribution of sintered hardmetals on hardness, fracture toughness and bending strength. However, until this point most researchers still used WC powder with a particle size above 1 μm. Furthermore, the sintered hardmetal showed grain sizes above 1 μm as well. The first sub-micron hardmetal grades were introduced in the 1970's by Wimet, Sumitomo, Krupp Widia and others [13]. The grain size of these hardmetal grades was in the area of 0.5 μm to 0.9 μm including some small numbers of larger grains above 1 μm. The reduction in grain size resulted in a significant increase of hardness. For hardmetals with the composition WC-10 Co it rose from ~1450 HV10 for a fine grained hartmetal (~1 μm) to 1650 HV10 for a sub-micron grained hardmetal (~0.7 μm) [14]. At the same time nanoscaled WC powders ($d_{50} < 50$ nm) were developed at H. C. Starck GmbH and at ZFW Dresden [15]. These powders were used to produce ultrafine hardmetal grades (>0.5 μm). For a composition of WC-10 Co (without any GGI), for instance, a hardness of ~1750 HV10 was achieved [12]. In the late 1980s ultrafine carbides became very popular, due to the need for micro-drills to machine printed circuit parts, drilling glass-fibre and other reinforced synthetic materials [16–18].

For classification of the wide range of WC based hardmetals a definition of size and designation was developed during this time by the German Arbeitskreis Hartmetall. It is now part of DIN IS0 4499-2. Here nanoscaled hardmetals were classified as hardmetals with a sintered grain size below 200 nm and ultrafine hardmetals with a grain size below 500 nm.

Nanoscaled WC powders surfaced again with the introduction of powders from A.L.M.T. Corp. and H. C. Starck GmbH in the late 1990s [19,20]. These powders had a specific BET-surface in range of 2.2 m^2/g to 3.5 m^2/g, which corresponds to BET grain size d_{BET} of 170 nm and 110 nm, respectively. With a composition of WC-10 Co a hardness

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within the range of 2000 HV10 was achieved. Pure or binderless WC composites could be made of these materials using conventional SinterHIP or SPS technique. They showed excellent hardness values of around 2700 HV10 to 2900 HV10 while keeping some good fracture toughness values of around 6 MPa $*$ $m^{1/2}$ to 7 MPa $*$ $m^{1/2}$ [21–26]. Nowadays even finer nanoscaled WC powders, such as the WC DN4.0 grade from H. C. Starck Tungsten GmbH with a d_{BET} of 90 nm are available and allow to produce even finer hardmetal grades. Yet, when using even smaller starting powders, grain growth inhibition is getting more and more important. Traditionally small amounts of VC, Cr_3C_2 and/or TaC are added. The exact way they work is until now not fully understood and in some parts controversially discussed. The most agreed upon opinion is that grain growth inhibition is based on a) dissolution of Cr/V/Ta within the Co binder and the therefore limited ability for W to dissolve within Co, leading to a decreased solution and precipitation of W during liquid phase sintering and b) poisoning the growth sites on the tungsten carbide crystal hindering tungsten atoms to be integrated in the lattice. Nevertheless, since for ultrafine and nanoscaled hardmetals ~90% of densification happens during solid state sintering [27], grain growth also already happens at this stage, way below the eutectic temperature for Co-W-C-(Cr/V/Ta) [28,29].

To investigate the grain growth inhibition process in hardmetals made from nanoscaled WC starting powders two different mixtures with and without addition of Cr_3C_2 as grain growth inhibitor were prepared and the sintering behaviour was studied. Densification, shrinkage and mass change including analysis of occurring gases was done using different thermal analysis techniques. Furthermore, interrupted sintering experiments of the two mixtures were carried out between 600 °C and 1300 °C and the samples were studied by means of density, magnetic properties, microstructure, element distribution, crystallite size and lattice parameter measurement by X-ray techniques as well as high resolution element mapping.

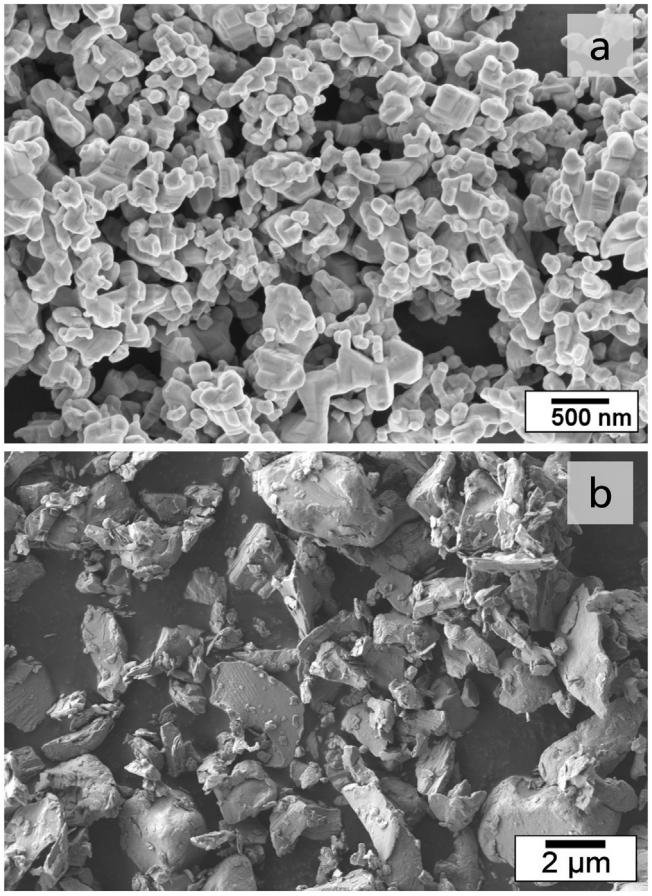

Fig. 1. FESEM images of the used WC powder DN3–0 (a) and Cr_3C_2 powder 160 (b).

2. Experimental

The experiments were carried out with a nanoscaled WC powder with the designation DN3.0 from H. C. Starck Tungsten GmbH as shown in Fig. 1. The WC particle size was 115 nm (d_{BET})/400 nm (d_{FSSS}). An ultrafine Co powder with a particle size of 180 nm (d_{BET})/770 nm (d_{FSSS}) from Umicore was used as metallic binder. As grain growth inhibitor Cr_3C_2 with the designation 160 from H. C. Starck Tungsten GmbH was used. The measured particle size was 470 nm (D_{BET})/1500 nm (D_{FSSS}). 2 wt% of paraffin from Terhell was added as pressing aid.

The powders were dry mixed, intensively ball milled under N_2 and heptane for 48 h, dried, granulated and uniaxial pressed to bending bars ($6 \times 6 \times 45$ mm^3) at 300 MPa.

After debindering in a two-component gas mixture containing 95% argon and 5% hydrogen, the samples were sintered using a SinterHIP furnace. Dense samples were prepared by sintering at 1300 °C and 50 bar while samples for the interrupted sintering experiments were sintered in vacuum at 600 °C, 800 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C without holding time and rapid cooling.

Density of sintered and partially sintered samples was measured according to DIN ISO 3369. The theoretical density was calculated by means of the rule of mixture from the densities of WC, Co and Cr_3C_2. Magnetic properties, magnetic saturation polarisation and coercivity were determined according to DIN ISO 3326. For microstructural analysis dense samples were polished down to 1 µm using diamond slurries and samples from the interrupted sintering experiments were polished using the broad ion beam (BIB) technique to produce polished sections without any mechanical pressure. Images of the microstructure were taken using a field emission scanning electron microscope (FESEM) Ultra 55 (Carl Zeiss AG). The grain size distribution was measured using FESEM images and the chord length method, with at least 500 WC grains having been counted. Vickers hardness (HV10) of dense samples was measured according to DIN ISO 3878 with a load of 98.1 N. Fracture toughness (K_{1C}) was calculated from the Vickers indentation crack length using the Shetty eq. [30].

The densification, shrinkage and mass change within a temperature range of room temperature to ~1450 °C and a heating rate of 10 K/min was studied using a dilatometer NETZSCH DIL 402 E7, the differential scanning calorimetry (DSC) system NETZSCH DSC 404 and a simultaneous thermal analysis system NETZSCH STA 429 with a coupled mass spectrometer QMS 421 from Balzers.

X-ray analysis was done on the starting powders as well as on polished samples 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 lattice parameter a Rietveld refinement was done using the computer program TOPAS (DIFFRAC·SUITE TOPAS, from Bruker).

Thermodynamic calculations were done using the program Factsage (Version 6.3) and a special in-house made dataset for carbides.

3. Results and discussion

3.1. Conventional sintered samples

As expected, the sinterHIPed samples made of mixtures with and without 0.9 wt% Cr_3C_2 and 10 wt% Co showed significant differences in coercivity and mechanical properties as shown in Table 1.

With Cr_3C_2 addition an ultrafine hardmetal with a median cord length of ~250 nm was achieved, without the addition of the grain growth inhibitor a submicron hardmetal with a median cord length