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Grain growth inhibition of hardmetals during initial heat-up

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ABSTRACT

Ultrafine and nanoscaled hardmetals show a significant grain growth already before reaching liquid phase sintering temperature. To limit grain growth during this stage of sintering the known grain growth inhibitors, mostly metal carbides like Cr_3C_2 or VC can be used. To investigate grain growth inhibition and dissolution of these carbides both the solid state sintering without Co (binderless tungsten carbide) and with 10 wt-% Co were investigated in the temperature range between 600 °C and 2000 °C and 1500 °C, respectively. It could be shown that e.g. the Cr_3C_2 starts to decompose already below 800 °C into a Cr-rich and C-rich phase. In both types of material with and without Co this leads to earlier reduction of W-oxides and the formation of Cr-based oxides which alter the chemical processes during sintering and change the grain growth behaviour. By using thermo-analytical methods as well as interrupted sintering experiments and their characterisation by FE-SEM and XRD, the direct influence of Co and grain growth inhibitors regarding the change in the chemical processes happening during sintering was studied.

1. Introduction

Densification of hardmetals can be separated into two steps: densification during solid state sintering and densification during liquid phase sintering above the eutectic temperature of the W-C-Co system. With decreasing WC grain size the percentage of densification taking place during solid state sintering increases [1,2]. For submicron and ultrafine hardmetals solid state sintering can contribute up to 90 % of total densification [3–5]. In case of nanoscaled hardmetals even near to 100 % can be achieved without external pressure [6,7], with pressure (SinterHIP) totally dense samples can be achieved even at the low temperature of 1150 °C [8]. For these fine starting powders densification starts as early as 800 °C, after W-oxides are reduced and Co starts to wet WC surfaces [9,10]. Furthermore, a significant amount of grain growth can already be observed between 1000 °C and 1250 °C [7,11,12]. In the same temperature range the first effects of grain growth inhibitors could also be seen in nanoscaled samples with and without Co [13,14]. It is also known that grain growth inhibitors retard grain growth in binderless WC as well [15,16] and that they seem to decompose already at quite low temperatures of < 1100 °C [17,18]. Thus, it is clear that for finer WC powders grain growth and also grain growth inhibition already takes place during solid state sintering and long before the liquid phase occurs. So far, however, it is not clear how grain growth inhibitors retard grain growth during solid state sintering. To study which processes take place during solid state sintering binderless WC samples as well as WC samples containing 10 wt% Co binder made from nanoscaled starting powders, with and without the addition of grain growth inhibitors, are studied in this work.

2. Experimental

For all experiments a nanoscaled WC powder from H.C. Starck Tungsten GmbH with the designation DN3.0 was used. For mixtures with Co an ultrafine Co powder from Unicore with the designation Co Half Micron was added. In order to study the most common grain growth inhibitors Cr_3C_2 and VC, the corresponding standard grades from H.C. Starck Tungsten GmbH with the designation 160 were used. Details on grain size and chemical composition are given in Table 1.

The powders were dry mixed, ball milled under N_2 and heptane for 48 h, dried, granulated and uniaxially pressed to bending bars ($6 \times 6 \times 45\ mm^3$) with 300 MPa pressure. Prior to milling 2 wt-% of paraffin from Terhell was added as pressing aid to the mixtures with Co.

WC-Co samples were debindered under a gas mixture of 95 % argon and 5 % hydrogen and afterwards sintered using a SinterHIP furnace. Dense samples were prepared at 1200 °C and 100 bar gas pressure while samples for the interrupted sintering experiments were sintered in vacuum (10 mbar Ar) at 600 °C, 800 °C, 1000 °C, 1100 °C, 1200 °C and 1300 °C without holding time. Binderless mixtures of WC and WC with grain growth inhibitors were sintered using a SinterHIP furnace and gas pressure of 100 bar. For interrupted sintering experiments pressed binderless WC samples were sintered within the temperature range of 800 °C to 2000 °C with 5 K/min under vacuum (10 mbar Ar) and held for 30 min before cooling.

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Table 1
Used starting powders.

Powder designation	d_{FSSS} [nm]	d_{BET} [nm]	C content [wt-%]	O content [wt-%]
WC DN3.0	400	120	6.06	0.27
Co half micron	770	200	0.19	0.76
VC 160	1200	320	17.71	0.90
Cr_3C_2 160	1500	470	13.03	0.68

Density of sintered and partially sintered samples was measured according to ISO 3369. Relative densities were calculated by using the rule of mixture and the densities of WC, Co, VC and Cr_3C_2. Magnetic properties, magnetic saturation polarisation and coercivity were determined according to ISO 3326. For microstructural analysis of dense samples, samples were embedded in resin and polished down to 1 μm using diamond slurries. Samples from 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 SEM (FE-SEM) Ultra 55 (Carl Zeiss SMT AG). Grain sizes were estimated on the basis of FE-SEM images.

Densification, shrinkage and mass change was studied using a dilatometer NETZSCH DIL 402 E7, 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. A heating rate of 10 K/min was used and the temperature range of 650 °C to 2000 °C for dilatometry and 650 °C to 1450 °C for DSC/DTA analysis studied.

X-ray analysis was done on the starting powders as well as on ion polished samples using a Bruker D8 diffractometer. Measurements were done using Bragg-Brentano geometry and CuKα (λ = 0.15418 nm) radiation, the chosen 2θ range was 20 ° - 130 °. Thermodynamic calculations were done using the program FactSage (Version 6.3).

3. Results and discussion

3.1. Binderless tungsten carbide

Significant grain growth of WC grains does not only happen in WC-Co based hardmetals but also in so called binderless hardmetals, meaning hardmetals without any metallic binder such as Co. This can be avoided by using optimized milling and sintering parameters. Otherwise grain growth is promoted when inhomogeneities within the starting powder are present, milling is too extensive or sintering temperature and time are not chosen correctly. As shown in Fig. 1, grain growth in materials without grain growth inhibitors is mostly visible by the presence of abnormal grains but also through the increased average grain size as compared to samples sintered with grain growth inhibitors or samples which were produced by controlled production processes.

With both kind of grain growth inhibitors the average WC grain size (abnormal grains not included) is nearly half the size of the samples without added grain growth inhibitors.

Thermal analytic measurements as well as interrupted sintering experiments between 800 °C and 1900 °C were carried out to study the densification and grain growth of mixtures of WC with and without Cr_3C_2 or VC. The grain growth inhibitor amount used was 1 wt-% and all mixtures were slightly substoichiometric. Here no Co was added.

As shown in Fig. 2, the densification behaviour of binderless WC is significantly influenced by the presence of grain growth inhibitors. With grain growth inhibitors, densification starts later and is in case of VC for the whole temperature range shifted to higher temperatures. For pure WC the densification rate shows three main minima. The first occurs at around 800 °C, the second at 1350 °C and a broader one at around 1700 °C. As shown in Fig. 3, these minima of the densification rate partially correlate with the weight change and the DTA curve during sintering.

For pure WC the two densification rate minima correspond to the DTA signals at 850 °C and 1350 °C. Thus, here two exothermal reactions are expected. As known from literature [19] both the reduction of W-oxides and the formation of W_2C happen at these temperatures. With both grain growth inhibitors added this behaviour changes. First, the temperatures at which the DTA peaks occur change (decrease) for the two lower temperatures (compare pure WC with WC + Cr_3C_2) and second, the DTA peaks at higher temperatures correlate for the grain growth inhibitor containing grades to the weight change behaviour (in contrast to the pure WC). Thus, the W-oxide reduction step as well as the W_2C formation seems to have changed with the presence of small additions of grain growth inhibitors. To investigate what happens during sintering interrupted sintering experiments were carried out and the samples were analysed by XRD and FE-SEM images of ion polished samples.

3.1.1. Pure WC mixtures

X-ray analysis of pure WC interrupted sintering samples are shown in Fig. 4. During sintering three different phases occur: W (bcc), WC and W_2C. At low temperatures as well as in the as-milled powder (not shown) just WC is present. At 900 °C W peaks can be detected which increase in intensity up to 1300 °C before they disappear completely at 1400 °C. W_2C can be detected from 1300 °C onwards until the highest sintering temperature is reached.

The evolution of these phases can be connected to reduction and carburisation processes during sintering. At lower temperatures the thin oxide layer on WC particles is reduced, which leads to the formation of nascent W. At higher temperatures of approximately 1400 °C W and WC react to W_2C.

To get more visual information on the correlation between chemical processes and shrinkage, selected samples were ion polished and analysed by FE-SEM (Fig. 5).

After sintering at 800 °C samples with a low C content show a lamellar phase between most WC grains. EDS point measurements of these samples showed that these structures (dotted circle in Fig. 5, 800 °C) consist of W and O and are thus complex W-oxides which cannot be identified by XRD. After these oxides are gone the microstructure shows more and more connected WC grains as shown in Fig. 5, 1300 °C. Above 1400 °C more and more areas show a closed porosity and at 1700 °C larger pore free areas with WC and W_2C grains can be observed.

Thus, during sintering shrinkage is connected to chemical processes taking place in the temperature range of 800 °C to 1400 °C. At lower temperatures W-oxides are present which hinder densification. As soon as these oxides are reduced at around 800 °C to 900 °C, nascent W is present and densification is enhanced, probably by better wetting behaviour of W with WC. When at ca. 1400 °C W and WC react to W_2C, the sample has already reached a density of around 75 % TD, meaning that half of the densification has happened during the presence of nascent W.

3.1.2. WC mixtures with grain growth inhibitors

The x-ray analysis shown in Fig. 6 revealed that with Cr_3C_2 addition no W phase is present during sintering. However peaks for W_2C can be detected already at 300 K lower temperatures as compared to Cr_3C_2 free samples. Furthermore, the peak position is shifted to lower 2θ angles. This is due to the solid solution of W_2C with Cr-carbide and the formation of the solid solution $(W,Cr)_2C$ phase. However, the most important result of the XRD measurement is that no nascent W was detected.

The main difference in the microstructure to the one of the pure WC samples presented in Fig. 5 is the presence of homogeneously distributed Cr_3C_2 grain growth inhibitor particles. However, even at