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Sintering Behaviour of Binderless Tungsten Carbide

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Abstract
Binderless tungsten carbide, a very hard and abrasion resistant material, has many interesting applications and attracts scientists and toolmakers alike. Hitherto, binderless tungsten carbide has been used to make wear parts, water jet nozzles or pressing tools for forming glass lenses. The sintering behaviour and the necessary sintering temperature are controlled by the carbide grain size as well as the nature and the amount of grain-growth inhibitors. In this work, the sintering behaviour of binderless tungsten carbide materials with different grain growth inhibitors and grain sizes between 100 nm and 600 nm was studied using dilatometry and thermal gravimetric analysis at temperatures up to 1950 °C. The densification mechanisms (solid and contributions of liquid state sintering) are discussed. Furthermore, the microstructure of dense sintered specimens in addition to their mechanical properties were studied and, together with the thermal analysis results, compared to conventional WC-Co hard metals.

1. Introduction
Pure tungsten carbide or binderless tungsten carbide (bWC) is characterized by the absence of any metallic binder such as cobalt, iron or nickel. Due to the lack of a ductile metal binder binderless tungsten carbide has lower fracture toughness than cemented carbides but possesses a much higher hardness and high thermal and electrical conductivity. Compared to other ceramics hardness and fracture toughness are high. Furthermore, the absence of the metallic binder leads to a much higher resistance to oxidation and corrosion. The material has an extremely low creep rate and can withstand much higher temperatures than conventional cemented carbides. Therefore, the material is used to produce high corrosion resistance water jet nozzles, mechanical seals, sputter targets and pressing tools for forming glass lenses. Since no liquid phase sintering is possible and high temperatures are needed to get dense samples, only a few techniques and furnaces can be used. But it was shown that pure tungsten carbide can be completely densified by SinterHIP [1]. In addition to SinterHIP and the vacuum + HIP technique used in this work, the Spark-Plasma-Sintering (SPS) technique is also often used to produce samples at laboratory scale. Using the SPS-technique, temperatures as low as 1600°C were reported to produce dense samples [2],[3]. Studies using conventional vacuum and SinterHIP furnaces showed that without external pressure, temperatures as high as 2000°C [4],[5] and with external pressure or HIP temperatures around 1600-1900 °C [6],[7],[8] are necessary to produce dense samples. Since sintering temperature strongly depends on the grain size, a smaller starting powder size and a long milling can reduce the sintering temperature. Unfortunately, long milling and a very fine grain size tend to cause abnormal grain growth (AGG) with single WC-crystals having lateral dimensions of over 100 µm. To reduce grain growth and inhibit AGG, the same grain growth inhibitors (GGI), such as VC or Cr_3C_2 as in WC-based cemented carbides, can be used. Although both GGI prevent AGG and reduce grain growth their efficacy is quite opposite to WC-based cemented carbides. In bWC Cr_3C_2 shows to be a much more effective GGI than VC [9]. By carefully adjusting the milling condition, AGG free samples can also be made using pure WC without GGI [10].

To obtain detailed information about the sintering behaviour Dilatometry, especially together with Differential Scanning Calorimetry (DSC), is a very good instrument to use. Plenty of Dilatometry experiments were carried out for WC-Co samples (i.e. [11] and [12]) but only a few for bWC. So far studies only have used pure WC powders with different grain sizes and milling times and sintering temperatures in the range of 20 °C to 1600 °C and 1800 °C, respectively [13],[14]. Results show that with increasing milling time onset temperature and the full densification plateau are moved to lower temperatures.

In this work the sintering behaviour of bWC with different grain sizes of the starting powder, different milling conditions and different GGI contents are studied using Dilatometry, Differential Scanning Calorimetry and Themograviemtrie techniques.

2. Experimental

Experiments were carried out with two pure WC powders from H. C. Starck. The WC particle size of the finer powder, here named P115 was 115 nm (D_{BET}) and 400 nm (D_{FSSS}), respectively. For the slightly coarser powder, here named P200 it was 200 nm (D_{BET}) and 600 nm (D_{FSSS}), respectively. The added grain growth inhibitors Cr_3C_2 and VC had grain sizes of 470 nm (D_{BET})/1500 nm (D_{FSSS}) and 320 nm (D_{BET})/1200 nm (D_{FSSS}), respectively.

The powders were mixed with 2 wt.-% of paraffin, intensively milled for 24, 40 or 72 h in a ball mill, dried, granulated and compacted to bars at 300 MPa. After debindering, the specimens were sintered in a SinterHIP furnace between 1600 and 1900 °C and a pressure of 80 bar. Samples made of the coarser starting powders were also HIPed at 1400 °C and 90 bar.

The density was determined according to DIN ISO 3369. The sintered samples were cut and polished down to 1 µm using diamond slurries. The microstructure was observed using a field emission scanning electron microscope (FESEM) LEO 982 (Carl Zeiss SMT AG). Vickers hardness (HV10) of dense specimen was measured according to DIN ISO 3878 with a load of 98,1N. The fracture toughness (K_{1C}) was calculated from the Vickers indentation crack length using the Shetty equation [15]. The given relative density is based on the theoretical density of WC, VC and Cr_3C_2 which was calculated by means of the rule of mixture from the densities of WC, VC and Cr_3C_2. In order to obtain the Co content in the milled powders, the debindered bars were crushed and dissolved using HCl-acid and analysed using ICP-OES.

For studying the sintering behaviour, the pressed and debindered bars were cut to samples of 5*5*10 mm^3. The shrinkage behaviour was studied using the dilatometer NETSCH DIL 402 E7 in a temperature range from 600 °C to 1950 °C. For the simultaneous measurement of weight loss and thermal effects in a temperature range from 20 °C to 1570 °C, a Thermogravimetry-Differential Scanning Calorimetry – NETSCH STA 449 F1 - instrument was used.

3. Results and discussion

The influence of the GGI on the sintering behaviour of the short and heavy milled WC powders P115 can be seen in Figure 1. Samples with GGI showed to start sintering within the same temperature range of 800 to 1400 °C as the pure WC-sample but full densification is reached not until much higher temperatures. The highest shift of the shrinkage curve is seen with VC. Cr_3C_2 and the mixture of both GGI show a lower shrinkage shift, which shows that the shrinkage is shifted to higher temperatures in the following order:

Without GGI < Cr_3C_2 < Cr_3C_2+VC < VC

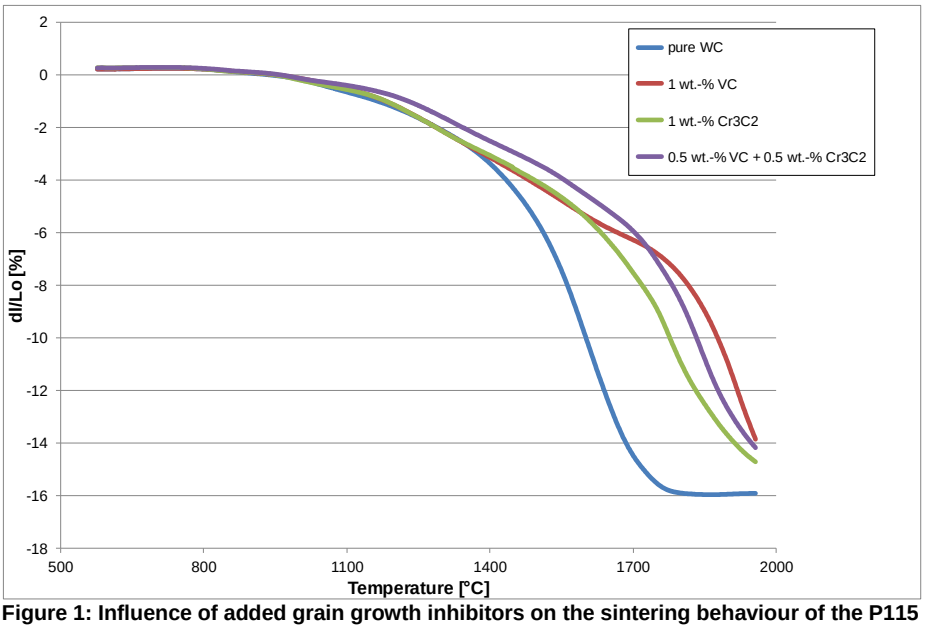

Figure 1: Influence of added grain growth inhibitors on the sintering behaviour of the P115 starting powder

Long and soft milled samples made of the coarser P200 showed the same shrinkage behaviour regarding the influence of GGI (Figure 2). Pure WC can be densified at the lowest temperature while the addition of GGI shifts the shrinkage to higher temperatures. The sample containing VC requires the highest temperatures to densify. Specimens with additions of Cr_3C_2 or a mixture of VC and Cr_3C_2 shrink at lower temperatures. However, the most important difference between the dilatometry results for the two starting powders is the general shift of the shrinkage curve to lower temperatures in the

case of the P200 powder. In case of the P200 powder, shrinkage due to sintering is almost finished at approximately 1700 °C while in case of P115 powder for all samples the sintering rate except for the one of pure WC is still relatively high at 1950 °C.

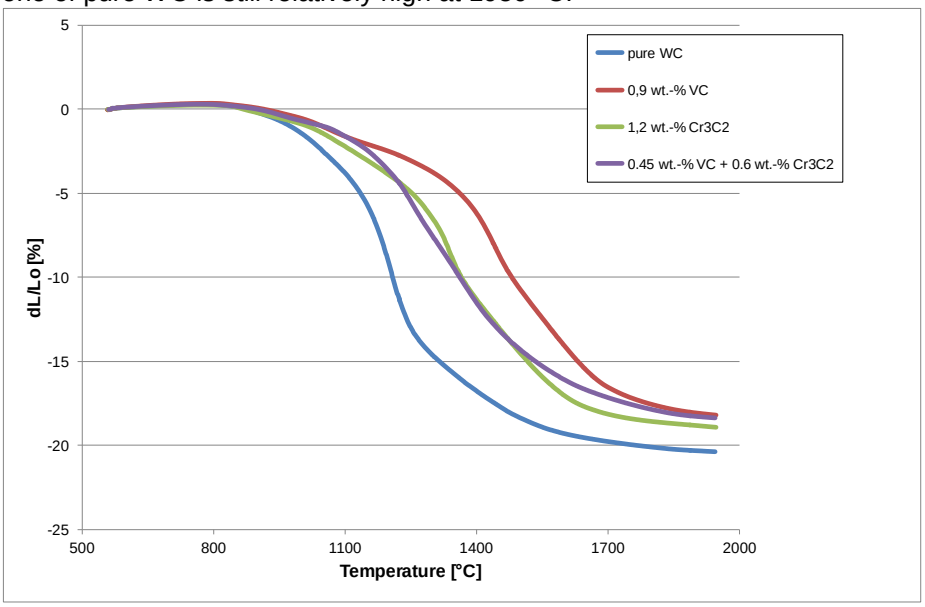

Figure 2: Influence of added grain growth inhibitors on the sintering behaviour of the P200 starting powder

The explanation for this surprising result is shown in Figure 3. Here dilatometry curves of the WC powder P115 show the influence of different milling conditions to the shrinkage behaviour. By increasing the energy input during milling, the plateau of full densification is shifted from a temperature above 1950 °C for a unmilled powder to around 1800 °C for the soft and even lower for a heavy milled powder. BET-measurements show that the surface of soft milled powder increased only slightly from 3.2 m²/g of the unmilled powder to 3.3 m²/g, while the heavy milled powder showed a relatively high surface of around 6.2 m²/g.

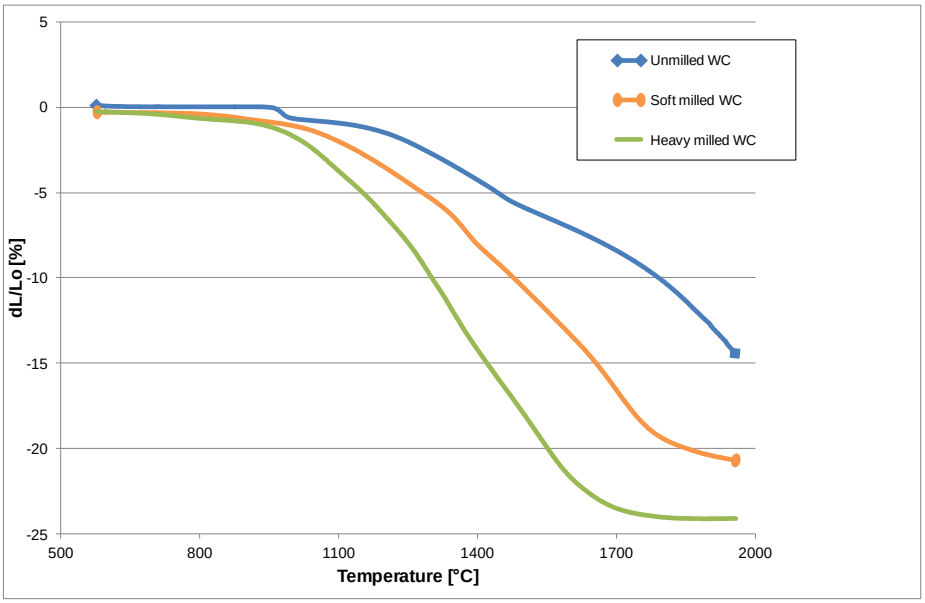

Figure 3: Influence of milling conditions on the sintering behaviour of the P115 starting powder

By DTA/DSC as well as TG measurements of WC P115 powders it was shown that the reduction of oxides depends on the added GGI type (Figure 4). With specimen without any GGI the DTA-peak and the drop in the TG curve occur at 850 °C. At this temperature oxides are reduced and shrinking starts. With VC and Cr_3C_2 additions two further endothermic DTA-peaks appear. With VC a second peak at 940 °C and with Cr_3C_2 a second peak at 990 °C hint on the reduction of GGI oxides at higher temperatures. Between 1400 °C and 1570 °C no further peaks could be found. Therefore, the shift of

the sintering rate of the samples containing GGI cannot be explained by any exothermic or endothermic phase transition.

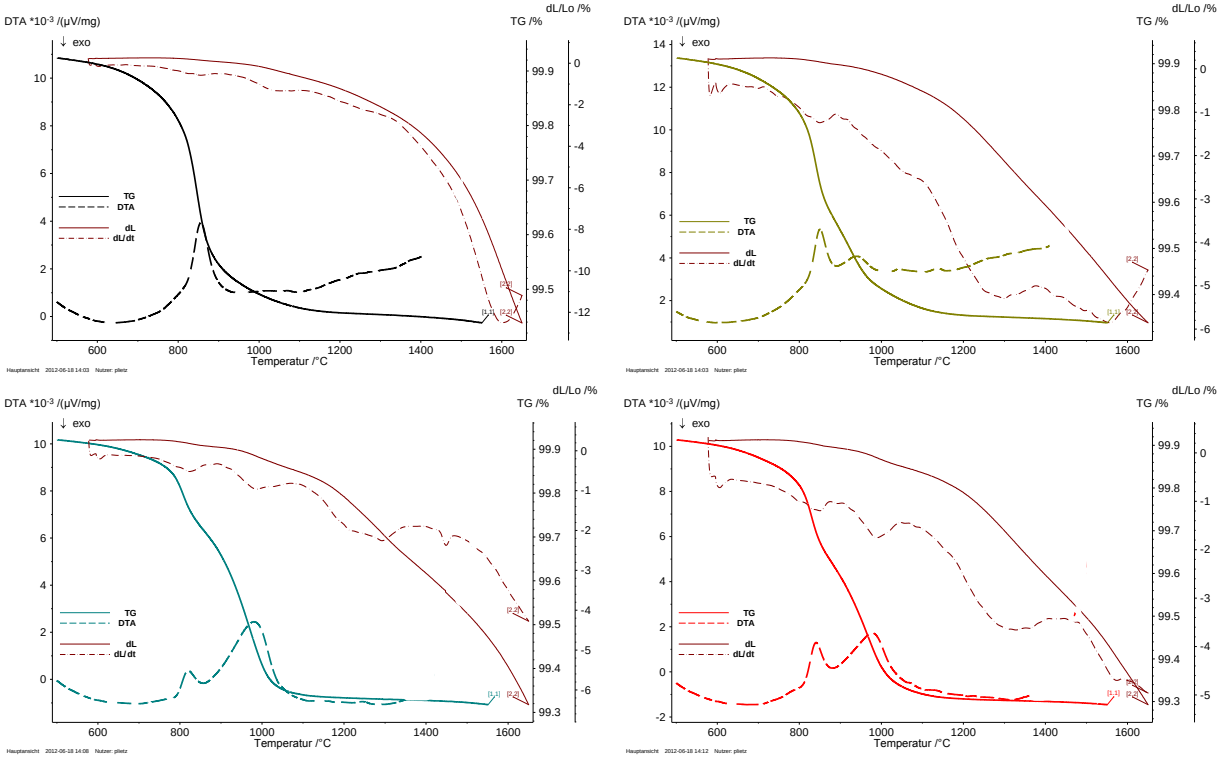

Figure 4: Influence of grain growth inhibitors on DSC, TG and dilatometry curves of the P115 starting powder (top left without any GGI, top right with VC, bottom left with Cr_3C_2 and bottom right with VC and Cr_3C_2)

The mechanical properties of powders sintered in a SinterHIP furnace are given in Table 1. The *soft + long* milled samples of both WC powders show excellent mechanical properties with hardness up to around 2600 HV10 and fracture toughness up to 6,5 MPa√m. Finer powders designated as P100 had even hardness and fracture toughness of about 2700 HV10 and 7,2 MPa√m, respectively. The short or long but heavy milled powders showed AGG with all mixtures without GGI. Even with GGI the hardness and fracture toughness is not as high as compared to soft milled samples. The samples with AGG had a hardness between 1350 and 1600 HV10 and fracture toughness around 5 to 6 MPa√m. With GGI these values increased up to around 2450 HV and 6,8 MPa√m.

Table 1: Mechanical properties of sintered binderless WC with and without GGI

WC-Powder	Milling condition	Grain refiner	Content wt-%	Density %	Hardness HV10	Fracture Toughness MPa√m
P200	soft+long	none	0.0	98.7	2520	6.5
P200	soft+long	VC	0.9	99.9	2410	6.2
P200	soft+long	Cr_3C_2	1.2	98.2	2580	5.8
P200	soft+long	VC+Cr_3C_2	1.0	98.7	2580	6.5
P115	heavy+short	none	0.0	99.8	1370	5.6
P115	heavy+short	VC	1.0	99.9	2340	6.8
P115	heavy+short	Cr_3C_2	1.0	99.9	2410	6.7
P115	heavy+short	VC+Cr_3C_2	1.0	99.8	2450	6.7
P115	soft+long	none	0.0	99.9	2540	6.6
P115	heavy+long	none	0.0	99.0	1600	5.0
P100	soft+long	Cr_3C_2	1.0	99.3	2710	7.2

To answer the question whether only small amounts of cobalt introduced by milling enables one to produce dense bWC samples, the Co content after milling of the P115 samples was measured using ICP-OES. As given in Table 2, the Co content increased only slightly from 20 to around 30 ppm. Virtually no extra Co was introduced to the composition by milling in cemented carbide milling vials.

Table 2: Co content before and after milling, measured using ICP-OES

WC-Powder	Milling condition	Grain refiner	Co content [ppm]
P115	unmilled	none	21
P115	heavy+short	none	29
P115	heavy+short	VC	30
P115	heavy+short	Cr_3C_2	33
P115	heavy+short	VC+Cr_3C_2	26

An overview of microstructure development as a function of milling condition is given in Figure 5.

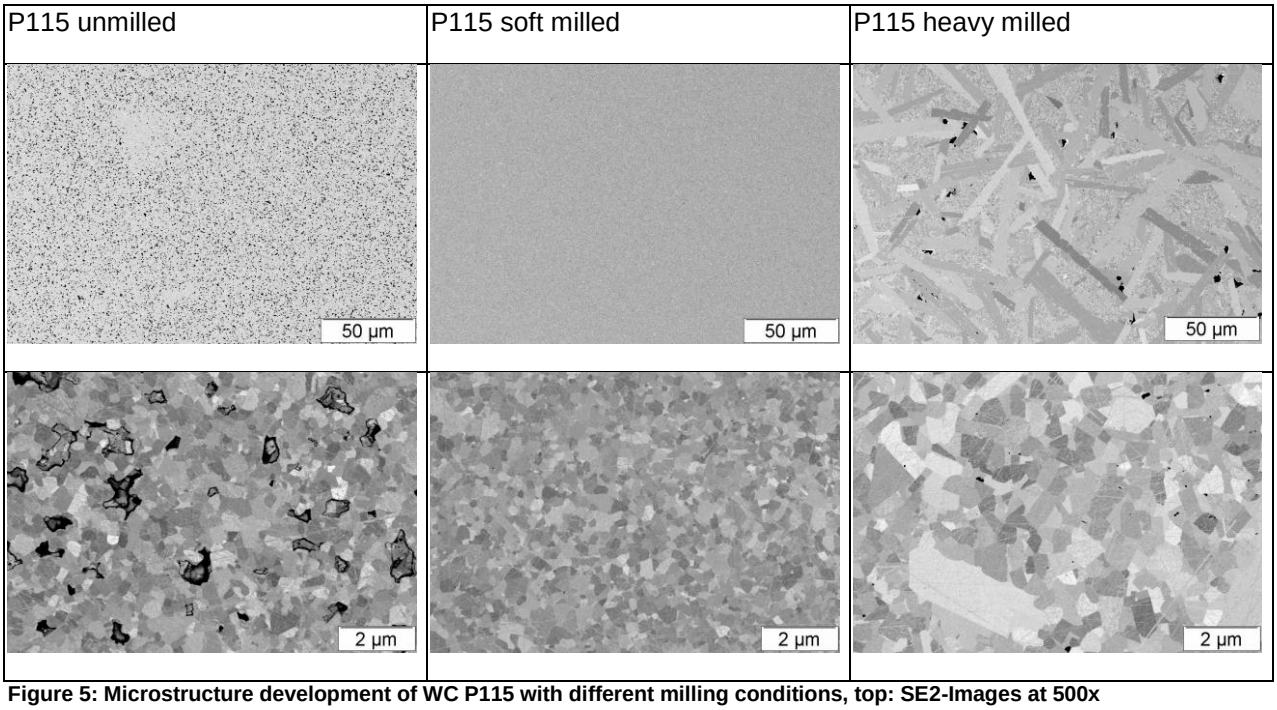

Figure 5: Microstructure development of WC P115 with different milling conditions, top: SE2-Images at 500x magnification - below: AsB-Images at 10000x magnification

As can be clearly seen in Figure 5, the sample prepared using the unmilled powder possesses a porous but fine microstructure. The soft milled powders enable a dense and pore free microstructure with grain sizes smaller than the unmilled powders. The heavy milled powders show AGG with some abnormal crystals having a lateral dimension greater than 100 µm. Between the abnormal grains a dense and fine microstructure can be seen.

4. Discussion and Summary

Dilatometry measurements showed that GGI strongly influence the shrinking behaviour of binderless WC. With two WC powders of different grain size, the temperature at which full densification is achieved is shifted to higher temperatures by GGIs with the shift growing in the following order: Cr_3C_2 < Cr_3C_2+VC < VC.

The milling condition has a much more important influence. Two different milling conditions characterized by differences in milling time and speed were studied: soft milling and heavy milling. While heavy milling leads to a reduction of grain size soft milling does not. Still, soft milling activates the surface and introduces lattice defects. This results in a higher sinterability with lower temperatures needed to sinter to full density. Appropriate milling conditions enhance the sinterability and simultaneously prevent AGG even without GGI. When using GGI, a higher sintering temperature is

needed for full densification but AGG can certainly be inhibited. Since adding of Cr_3C_2 showed to produce better mechanical properties and microstructures than the adding of VC, the grain retarding effect seems not to be connected to the shift of the shrinkage curve to higher temperatures but to a better distribution of the GGI within the sample.
Comparing the sintering curves of binderless WC to WC-Co the sintering is shifted to higher temperatures by grain growth inhibitors in the same order as described for WC (during solid state sintering of WC-Co) [12].

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