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Fundamentals of sintering nanoscaled binderless hardmetals

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ABSTRACT

By reducing the metallic binder in cemented carbides, so-called binderless hardmetals or pure tungsten carbide ceramics can ultimately be achieved. Nanoscaled tungsten carbide has a very high hardness of above 3000 HV1 and still offers quite a good fracture toughness of up to 7.5 MPa∗m$^{1/2}$. Since only solid state sintering can be used, sintering temperatures as high as 2000 °C or higher are normally needed to completely densify these materials. At these temperatures abnormal grain growth which leads to a decrease in hardness is an often reported problem. However, using pressure assisted techniques such as SPS, ROC or HIP, WC ceramics can be produced at lower temperatures, although productivity and freedom in size and form are limited.

The aim of this work was to investigate the drivers for densification, grain growth as well as the microstructure and chemical phases occurring during solid state sintering in a conventional SinterHIP furnace. A WC starting powder with D_{BET} = 115 nm was milled to nanoscaled size (50 to 60 nm), sintered at different temperatures (interrupted sintering experiments) and then analysed by using FESEM, XRD, Rietveld analysis, dilatometry and other methods.

It could be shown that three main processes during sintering of slightly under-stoichiometric binderless WC hardmetals occur: first, the reduction of surface oxides at 800 °C after which densification starts due to cleaned surfaces and the existence of W in a nascent state; second, the secondary carburisation of WC and W at around 1400 °C; and, third, grain growth and pore annealing at around 1600 °C when a closed porosity exists. By adding Cr_3C_2 as grain growth inhibitor the secondary carburisation step was lowered to around 1000 °C and a solid solution of $(W,Cr)_2$ instead of pure W_2C was formed.

1. Introduction

Binderless hardmetals or pure tungsten carbide ceramics are, due to the absence of any metallic binder, very hard and offer high resistance to corrosion as well as high thermal and electrical conductivity [1,2]. Since no liquid phase sintering can be used to fully densify such WC ceramics, much higher temperatures and pressures are needed compared to conventional WC based hardmetals. Mainly hot-pressing, rapid omnidirectional compressing or nowadays also spark plasma sintering/field assisted sintering techniques can be used [3–6]. While first attempts of using conventional sintering techniques were made as early as 1957 [7], pure tungsten carbide completely densified by vacuum or pressurised gas sintering (SinterHIP) was made, due to the availability of very fine WC powders, only as recently as in the 1990s [8–12]. In contrast to conventional WC-based hardmetals, no liquid based sintering mechanisms such as the Kingery mechanism or basic dissolution–precipitation processes can be expected for densification [13,14]. Thus, sintering i.e. densification and grain growth as well as pore annealing has to happen essentially via diffusion of W or C atoms. Here diffusion is enhanced due to high amounts of dislocations [15,16] or to under- or over-stoichiometric C contents. The use of fine and sinter active powders further promotes pressureless sintering techniques due to the aspects of increased interface energy [17]. As in WC-based hardmetals sintering is expected to start as soon as surface oxides are reduced at round 750 to 800 °C. [18,19]. Here activated surfaces with W in a nascent state are believed to lead to the first high mass transfer needed for neck growth and initial densification. The influence of cobalt is believed to start at around 900 °C when Co wets WC and W [20,21]. However, in sintering tests done so far, complete dissolution and wetting of whole WC grains were only observed at around 1100 °C or higher [21,22]. Thus, until around 1000 °C both WC ceramics and WC based hardmetals should experience the same (solid state) sintering mechanism. Since sintering of pure WC ceramics is very unique due to the stoichiometric composition of WC with a C content of exactly 6.13 wt.% it is virtually impossible to keep the stoichiometric composition from the starting powder up to the dense sintered part. The main reason for that is that nearly all commercial WC powders are slightly under-stoichiometric (however, often some free C is added) and that nearly inevitably the surface of WC particles or grain will be oxidised during production, powder handling or forming. Thus, during sintering of WC ceramics an over- or under-stoichiometric C content will always

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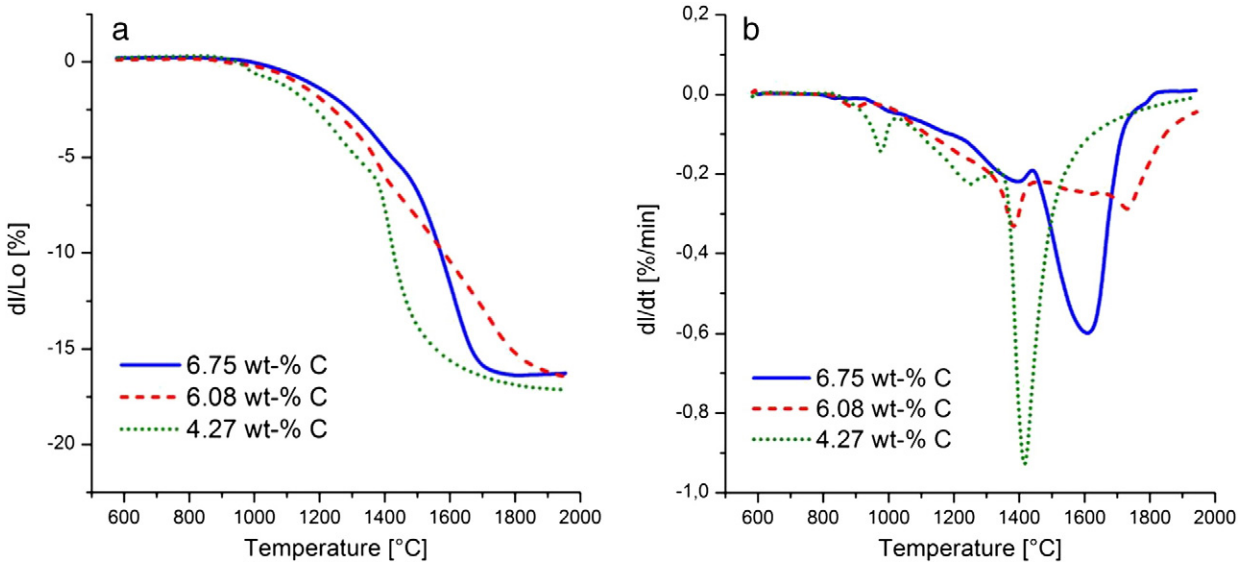

Fig. 1. Densification behaviour a) as shrinkage over temperature and b) as densification rate over temperature for WC mixtures with different carbon contents.

be present. Due to this fact the formation of W_2C is anticipated in case of an under-stoichiometric C content [23,24]. For sintering of mixtures of W and C the formation of W_2C has been observed at temperatures between 1100 and 1300 °C [25–27], while for mixtures of WC and W the carburisation of W has been observed at temperatures of around 1400 °C [28,29]. Next to reduction and recarburisation processes no further reactions are expected. At higher temperatures, however, grain growth occurs. In case of high dissolocation densities and under-stoichiometric mixtures or for all GGI free over-stoichiometric mixtures abnormal grain growth can be found, with some WC grains having lateral dimensions of several hundred micrometres [30–32,16]. To inhibit grain growth and especially abnormal grain growth the same grain growth inhibiters (GGI) as used in WC-based hardmetals, such as VC and Cr_3C_2 can be used [33–37]. Since in case of the pure WC ceramics the inhibition effect cannot be connected to the dissolution and reprecipitation of W from and to WC like in WC–Co hardmetals [38] where GGI can dissolve in the binder phase, the question arises how the inhibition effect works and where the GGI go to. To study the way GGI and other MeC influence grain growth and where they go to during sintering, different possibilities were investigated so far. The study of diffusion couples of WC and MeC found that most MeC do not show a diffusion of MeC into WC [39]. Only with Cr_3C_2 a Cr-containing WC interlayer with up to 1.5 at.% Cr could be detected using a WDS-EPMA. For the production of Cr doped WC powders [40] from W, Cr_3C_2 and C it could be shown that by a two phase reaction up to around 7 wt.% Cr can fit into a hexagonal WC. However, direct carburisation tests with WC, Cr_3C_2 and C showed no solid solution of (W,Cr)C. Investigations in how far and under which conditions MeC can dissolve within WC during sintering of WC–Co based hardmetals were done using atom probe tomography [41]. The results and calculations show that Ta, Nb, Cr and V have a solubility in the range of 0.1 to 1 at.% and that only the Me-atoms which substitute W should contribute to the Me solubility in WC. Even though WC–Co mixtures were used, it could be shown that some amount of MeC can solute into WC during solid state sintering. Another, nowadays widely accepted concept for the inhibition of WC-based hardmetals is that GGI like VC and Cr_3C_2 dissolve within Co and segregate at WC-Co interfaces where they inhibit further dissolution by creating a very thin cubic carbide film [42–44]. Since especially in nanoscaled WC hardmetals grain growth is already happening before the liquidus temperature of Co, the dissolution of GGI is expected to happen independent of Co and at lower temperatures [45,46].

In order to study the reactions and processes which occur during sintering, different mixtures of WC and C as well as WC and W were prepared and interrupted sintering experiments (ISE) were carried out. Pressed samples were sintered in vacuum at temperatures of 800 to 2000 °C with 100 K steps and a holding time of 30 min. Samples were analysed using density measurement, X-ray analysis and further studied by FESEM. For studying the influence of GGI, mixtures with Cr_3C_2 and different C contents were prepared and analysed similar to the pure WC mixtures. In addition to the ISE, thermal analytical analysis of the mixtures using dilatometry and thermal gravimetry techniques were carried out. Furthermore, fully dense samples were prepared of all mixtures using a SinterHIP furnace at 1900 °C and an Ar pressure of 100 bar.

Table 1
Maxima in densification rate for WC mixtures with different carbon contents.

Carbon content [wt.%]	1. Maxima [°C]	2. Maxima [°C]	3. Maxima [°C]	Comment
6.75	780	1400	1600	1 maximum very small
6.08	890	1370	1700	–
4.27	980	1420	none	No 3rd maximum detected

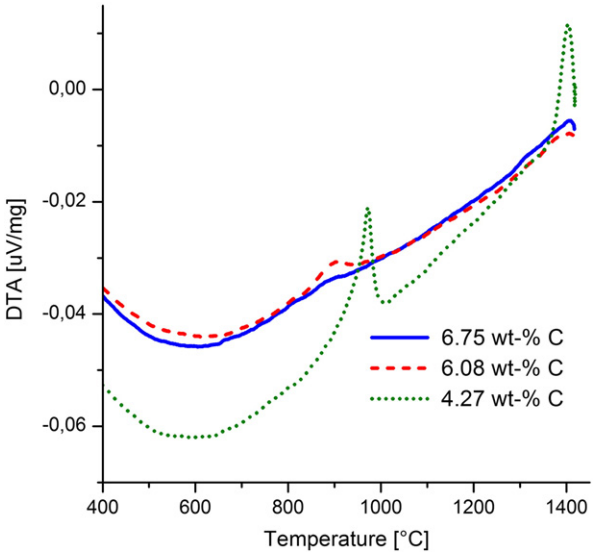

Fig. 2. Differential thermal analysis results of the thermogravimetry measurement for WC mixtures with different carbon contents.