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Solid state sintered nanoscaled hardmetals and their properties

J. Pötschke[a,*], T. Säuberlich[b], A. Vornberger[a], J.A. Meese-Marktscheffel[b]

[a] Fraunhofer IKTS, Fraunhofer Institute for Ceramic Technologies and Systems, 01277 Dresden, Germany
[b] H.C. Starck Tungsten GmbH, 38642 Goslar, Germany

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ABSTRACT

Hardmetals are conventionally manufactured by liquid phase sintering above 1350 °C. Due to their high surface activity, nanoscaled WC powders allow a complete densification already below 1200 °C. Extensive experiments carried out with different Co contents and grain growth inhibitors showed that a complete densification is possible between 1150 °C and 1230 °C. Here the microstructure shows a bimodal Cobalt distribution, with a thin Co layer between WC grains and a lot of small Co pools. These pools are homogenously distributed throughout the microstructure and inhibit the extension of cracks. By adjusting Co starting powders the size of these Co pools can be controlled to be around 1 µm and hardness as well as fracture toughness of these solid state sintered nanoscaled hardmetals can be enhanced. Their very fine predominant nanoscaled microstructures leads for a composition of WC-10 Co to hardness values way above 2000 HV10 units and the in a distance of 3 µm to 5 µm recurring and around 1 µm in diameter large Co pools lead to improved fracture toughness.

1. Introduction

Hardmetals or cemented carbides combine high hardness and acceptable fracture toughness, making them suitable for a wide range of applications, e.g. as tool material or wear parts. The most commonly used type of hardmetal is made up of the hard ceramic phase tungsten carbide WC and the metallic binder phase cobalt. The mechanical properties are commonly adjusted by varying the amount of metallic binder and the WC grain size. The main contribution to the hardmetal's hardness comes from the hard phase WC. Thus by lowering the amount of the binder phase Co the hardness increases [1]. It has also been shown that the Hall-Petch relation applies to common WC-Co alloys, which means that the hardness increases with decreasing WC grain size [2]. The fracture toughness on the other hand is mainly determined by the nature of the ductile binder phase Co. It is widely assumed that a large mean free path of the cobalt (which corresponds to high Co content as well as large WC grain size) leads to high fracture toughness [3]. The addition of grain growth inhibitors (GGIs) can affect binder distribution, microstructure and the WC-Co interface and thus has an influence on fracture toughness as well [4].

Altogether this leads to a general trend of decreasing toughness with increasing hardness. However, there are constant efforts to find new ways to improve the toughness/hardness ratio of hardmetals. One approach is the engineering of special microstructures such as double cemented carbide [5]. This type of carbide is a composite structure consisting of completely dense, large pre-sintered WC-Co granules embedded in a Co matrix phase. The large mean free path of Co results in a high fracture toughness, while the large, hard WC-Co particles yield superior wear resistance. The hardness, however, is much lower compared to conventional hardmetal [3]. A similar composite based on polycrystalline WC agglomerates instead of the WC-Co particles has been shown to achieve very high hardness in combination with good fracture toughness [6]. The disadvantages of these hardmetal types are the need for specific, elaborate manufacturing processes and special pre-products. This is avoided in the present approach by using a conventional hardmetal processing route to fabricate a bimodal distribution of Co, which enhances the fracture toughness considerably. Sintering at temperatures below the eutectic temperature of the WC-Co system is used and different carbides such as VC and Cr_3C_2 are added to study the effect of grain growth inhibitors [7]. The generated microstructure and the consequent mechanical properties are investigated.

2. Experimental

Nanoscaled to ultrafine grained hardmetals were produced by a conventional powder technological route. A nanoscaled WC powder (DN 4.0 from H.C. Starck Tungsten GmbH, Germany) was dry mixed with Co powder (Half-Micron from Umicore, Belgium). The particle sizes measured by BET method [8] were d_{BET} = 90 nm and 208 nm, respectively. For some experiments a coarser Co powder (S80 from Freeport Cobalt, d_{BET} = 520 nm) was used. Different amounts of grain growth inhibitors VC and Cr_3C_2 (H.C. Starck Tungsten GmbH,

* Corresponding author.
E-mail address: johannes.poetschke@ikts.fraunhofer.de (J. Pötschke).

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Germany, particle size d_{BET} 320 nm and 470 nm, respectively) were added to obtain a nanoscaled to ultrafine microstructure. Carbon black and 2 wt% paraffin were added to adjust carbon content and as a pressing aid. Powder mixtures were ball milled for 48 h in heptane, dried, sieve granulated and uniaxially pressed. Debindered samples were sintered in a sinterHIP furnace using temperatures between 1100 °C and 1250 °C and a gas pressure of 100 bar during holding time. The amounts of cobalt and GGIs are throughout this paper given in weight percent.

After sintering the magnetic saturation polarization of samples was measured as well as density according to ISO 3369. Magnetic saturation and density are given throughout this paper as relative values. The theoretical magnetic saturation was calculated based on the cobalt content of the hardmetal composition. Chromium carbide additions reduce the magnetic saturation value, making an adjustment necessary. The theoretical magnetic saturation value was thus corrected by reducing the original theoretical magnetic saturation polarization value of e.g. a WC-10 wt%Co composition by 8.7 % per wt% Cr_3C_2addition. The rule of mixtures was used to calculate the theoretical density. Only the main components WC, Co and the GGI were considered. Vickers hardness was measured according to DIN ISO 3878 with a load of 98.1 N. Indentation fracture toughness K_{1c} was determined using Shetty's formula [9]. Images of the microstructure of polished samples were made using a light microscope and a field emission scanning electron microscope (FESEM, LEO 982, Carl Zeiss SMT AG).

3. Results

As known from previous work hardmetals made from ultrafine and nanoscaled powders seem to show a complete densification even before eutectic melting of the Co binder at 1330 °C to 1370 °C [7,10]. To investigate in detail at which temperatures dense samples can be achieved different compositions and sintering temperatures were evaluated.

3.1. Variation of sintering temperature and grain growth inhibitor content

Experiments were started with WC-10 % Co hardmetals with different contents of grain growth inhibitors (GGIs) which were sintered at temperatures between 1150 °C and 1300 °C. The relative densities of these samples are shown in Fig. 1. Sintering at 1200 °C and above leads to relative densities of over 98 %. Without the addition of grain growth inhibitors (GGIs) a density of over 98 % is already achieved at 1150 °C. These samples show some open porosity in the surface area, but are in the bulk completely dense as can be seen in Fig. 2. Micrographs of WC-10 % Co samples with different GGI content and sintered at 1200 °C and 1300 °C are shown in Figs. 3, 4, 5 and 6. Micrographs of samples sintered at 1250 °C are not shown because the microstructure of samples sintered at 1250 °C and 1300 °C is very similar.

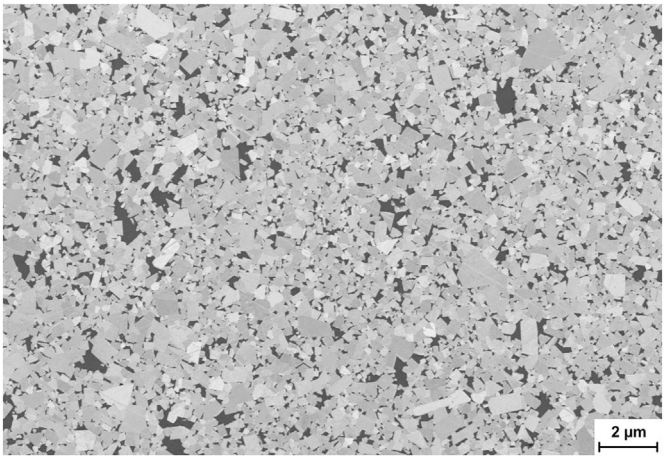

Fig. 2. FESEM micrograph of WC-10 % Co without grain growth inhibitors, sintered at 1150 °C.

As expected the sample without GGI addition shows pronounced grain growth with increasing sintering temperature. It is remarkable that the effect of GGI addition is here already visible at very low temperatures such as 1200 °C. This contrasts to previous reports, where grain growth inhibition by VC or Cr_3C_2 was mostly connected to liquid phase sintering [11,12]. The finest grain size was achieved with the addition of 0.9 % VC. The microstructure of samples sintered at 1250 °C or 1300 °C is homogeneous whereas samples sintered at 1200 °C show an inhomogeneous bimodal cobalt distribution, namely the occurrence of so called cobalt pools or lakes. The size of these pools is around 1 µm, i.e. in the medium range of Co phase in submicron hardmetals.

The differences in microstructure are reflected in the measured mechanical properties, which are shown in Fig. 7. Typically hardness decreases with increasing grain size. Thus the hardness decreases with increasing sintering temperature due to grain growth. Consequently the fine grained microstructure obtained by the addition of GGIs and sintering at the lowest possible temperature of 1200 °C leads to higher hardness values than the coarse grained microstructure of the sample without GGIs. The measured hardness values are approx. 2075 HV10 (compositions with 0.9 % VC as well as with 0.6 % VC and 0.3 % Cr_3C_2, mean WC chord length ≈ 0.1 µm) and 1650 HV10 (no GGIs, mean WC chord length ≈ 0.25 µm), respectively.

With increasing grain size the fracture toughness usually increases due to the increased mean free path of the Co phase. This is also true for most compositions shown above, but some compositions show a deviating behavior. The fracture toughness of the sample with VC addition is lowered from 8.3 ± 0.2 MPa·$m^{1/2}$ to 7.9 ± 0.2 MPa·$m^{1/2}$ when the sintering temperature is increased from 1200 °C to 1300 °C. The hardness, however, is decreasing with increasing sintering temperature as

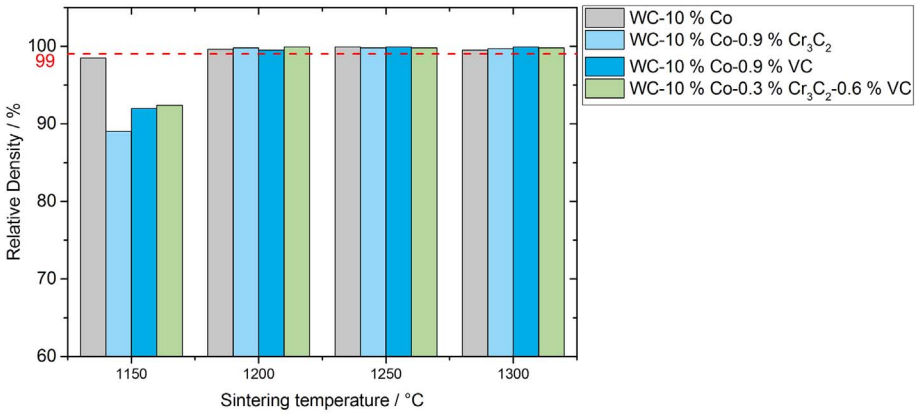

Fig. 1. Relative density of WC-10 % Co hardmetals as a function of sintering temperature.