Int. Journal of Refractory Metals & Hard Materials 28 (2010) 362–369

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Novel fine-grained hardmetals by use of multiphase powder precursors and reactive nitrogen sintering

D.S. Janisch [a], W. Lengauer [a,*], K. Rödiger [b], K. Dreyer [b], H. van den Berg [b]

[a] *Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-CT, 1060 Wien, Austria*
[b] *Kennametal Technologies GmbH, Münchener Straße 125-127, 45145 Essen, Germany*

ARTICLE INFO

Article history:
Received 23 September 2009
Accepted 29 November 2009

Keywords:
Hardmetal
Cemented carbide
Cermet
Sub-micron
Gradient
Nitrogen
Reactive sintering

ABSTRACT

Hardmetals typical of ISO class P which contain hexagonal WC together with fcc carbides and carbonitrides as hard phase constituents were prepared ranging from very low to very high carbonitride contents by a novel route. For this purpose specially designed multiphase hard phase powders containing both, WC and pre-alloyed fcc carbides were used. Green bodies were reactively sintered at various nitrogen pressures. During this step, not only carbonitride formation but also WC formation takes place. The sintered hardmetals were characterised by XRD, EBSD, SEM and LOM. They show sub-micron grain size of both, the WC and the fcc hard phase and thus substantially higher hardness (with only a small decrease in toughness) as compared to conventionally prepared bodies of the same overall composition. As a consequence, flank wear of cutting inserts is significantly reduced in milling of 4140 steel. Grain growth is retarded due to the pre-alloyed state of the powders and the interpenetration of hexagonal and fcc hard phases.

The applied method, both, in laboratory and industrial scale, allows not only adjustment of the bulk properties of the hardmetals during sintering but in addition, if desired, tailoring the near-surface microstructure with respect to the formation of various types of a functional gradient.

1. Introduction

In the search for ever higher performance and lifetime of hardmetal tools for metal cutting applications, the last years saw a strong decrease in grain size of the raw powders. Grain-growth inhibitors such as Cr and V allow the sintering of very fine-grained hardmetals of the WC–Co system [1]. A crucial point for the effectiveness of the inhibitors has always been their homogeneous distribution in the powder mix. In cermets, on the other hand, grain growth is very much dependent on the dissolution and re-precipitation processes of the carbides and nitrides forming the cubic phase (often a M(C,N) mixed crystal, M = Ti, W, Ta, Nb, Mo, V, ...) [2]. Alloying of the cubic phase during sintering can be limited if already pre-alloyed powder material is used. This lowers the concentration gradients between adjacent grains and diffusion is reduced. Less diffusion means less grain growth. Below, the term "pre-alloy" always refers to such solid solution carbonitrides, whereas "grade" refers to hardmetal compositions, that is, with binder.

Grain growth is also reduced when the average distance between grains of the same carbide is increased by the presence of another phase and immiscibility or only partial miscibility among the different carbides exists. This is the case in three-phase hardmetal grades WC–M(C,N)–Co(Ni). If the powder synthesis is done in a way that the WC and the M(C,N) phase are formed in the same process (e.g. by co-carburisation of the oxides), it is possible to obtain a powder with a very homogeneous phase mix, where the M(C,N) phase is already homogenised and also saturated with W. Grain-growth inhibitors can be introduced and homogenised in the powder mix in the same process. Thus, grain growth of both the hexagonal and the fcc hard phase is addressed simultaneously.

In this study, several hardmetal grades were prepared in this way. For the M(C,N) phase, a 1:1 ratio nitrogen:carbon was targeted. The pre-alloy was to be of sub-micron grain size. As complex carbonitrides of such a small grain size could not be obtained, but carbides were available, it was decided to add the nitrogen during the sintering process via the gas atmosphere. It is known that TiC can be gas-nitrided, giving Ti(C,N) and free carbon [3] (possible sub-stoichiometry of Ti(C,N) is neglected):

$$\mathrm{TiC} + \frac{1}{2}xN_2 \rightleftharpoons \mathrm{TiC}_{1-x}\mathrm{N}_x + x\mathrm{C} \quad 0 \leqslant x \leqslant 1 \tag{1}$$

Free carbon deteriorates the mechanical properties of the hardmetal, but it is common practice to correct a powder batch of too high carbon content by adding a small amount of W metal powder.

---

* Corresponding author. Tel.: +43 1 58801 16127; fax: +43 1 58801 16490.
E-mail address: Walter.Lengauer@tuwien.ac.at (W. Lengauer).

0263-4368/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijrmhm.2009.11.012

It was to be proved whether this worked also if a large part of the WC originated from the in situ reaction of nitrogen gas, cubic carbide, and tungsten:

$$\mathrm{TiC} + x\mathrm{W} + \frac{1}{2} \times \mathrm{N}_2 \rightleftharpoons \mathrm{TiW}_y\mathrm{C}_{1-x}\mathrm{N}_x + (x-y)\mathrm{WC}$$
$$0 \leqslant x \leqslant 1 \quad 0 \leqslant y \leqslant x \tag{2}$$

An important point was that it should be possible to realise this reaction sintering process in common vacuum sintering furnaces, with only small modifications of state-of-the-art sintering cycles. Furthermore, the application of a reactive atmosphere provides not only a tool to influence the bulk properties of the hardmetal but also to tailor the near-surface region for increased hardness or toughness as well as coating adhesion properties by exploitation of diffusion processes and phase stabilities [4,5].

2. Experimental

Four grades were made by using a two-phase carbide/carbonitride pre-alloy powder. The pre-alloy was to contain all the cubic carbide, some Cr dopant (dissolved in the cubic carbide), and part of the WC of the final hardmetal composition. W powder was added to form WC together with carbon that was produced by the reaction of the cubic carbide with nitrogen (Eq. (2)). The remaining WC was added as WC powder. Addition of Co or Co–Ni and small corrections with single carbides completed the composition (Table 1). The carbon balance was adjusted with small additions of C or W. The four experimental grades A–D were designed to cover a wide range of composition, from 8 to 80 wt.% of cubic carbonitride in the hard phase. Grade A corresponds to commercial hardmetal grades of ISO class P on the market, used for metal machining applications. The composition of grade B (50 vol.% carbonitride) is quite rare on the market, while grades like C (50 % carbonitride by mass) are not available nowadays. In grade D the carbonitride content was so high (80 wt.% of hard phase) that all W was to be dissolved in the cubic carbonitride after sintering, so that this produced in fact a two-phase grade of binder and cubic carbonitride, i.e. a cermet. In C and D the nitrogen was introduced via $\mathrm{TiC}_{0.3}\mathrm{N}_{0.7}$, while A and B were started with a composition free from N, which was introduced via the sintering atmosphere. As Eq. (2) shows, the nitrogen must be balanced with W. The hardmetal's designed composition limits the amount of W addition, thus this concept is not feasible in grades of high carbonitride content like C and D.

The composition of the carbide pre-alloys for the hardmetal grades is listed in Table 2. The pre-alloys, products of a co-carburisation process, were mainly composed of a cubic carbide (MC) and WC. Most W and all of the Cr were dissolved in the cubic carbide, which in this case could be described as (Ti,Ta,Nb,W,Cr)C solid solution. The amount of free WC was measured with quantitative XRD.

With increasing carbonitride content a higher binder volume fraction was necessary in order to still achieve full densification, as wetting of the binder is not as good on carbonitrides as on WC. The mass fraction of the binder increases even more, simply because the grades get lighter from A to D. For grade D, half of the Co was substituted with Ni, because of the better wetting of Co/Ni on carbonitrides.

Table 2
Composition of the two-phase carbide pre-alloys for the grades in Table 1 (wt.%) and lattice parameter of the cubic phase, *a*. $\mathrm{WC}_{\mathrm{free}}$ determined with XRD.

Pre-alloy	TiC	TaC	NbC	$\mathrm{Cr}_3\mathrm{C}_2$	$\mathrm{WC}_{\mathrm{tot}}$	$\mathrm{WC}_{\mathrm{free}}$	a/Å
A	17.16	52.70	17.59	0.95	11.60	1	4.4214
B	46.49	16.14	5.54	0.99	30.85	5	4.3366
C	39.56	24.61	8.33	0.98	26.53	5	4.3538
D	45.34	17.64	5.97	0.99	30.06	4	4.3382

The powders were ball-milled, die-compacted to 16 × 16 × 6 mm SNUN geometry, and dewaxed, following common industrial procedures. The green bodies were sintered in a graphite crucible in a laboratory scale vacuum induction furnace with nitrogen supply. The design of the furnace, with a very small heated load, allowed high cooling rates up to 500 °C/min. This made it possible to interrupt the sintering cycle at certain stages and draw samples to analyse the early stages of microstructure evolution.

During the sintering cycle the samples were heated to 1450 °C with 4 °C/min (Fig. 1). The heating ramp was interrupted by a 15-min dwell at 1100 °C, where the nitrogen atmosphere was introduced, and another 15-min dwell at 1300 °C (A and B) or 1330 °C (C and D), to allow for heat equilibration just before the onset of binder melting. Sintering time at 1450 °C was 30 min, followed by a cooling ramp of 8 °C/min. For bulk nitridation (grades A and B) N_2 was filled in at 1100 °C without further pressure control. For grades C and D the goal was to keep the N content constant. Therefore only a low N_2 pressure was allowed at 1100 °C and was increased at 1330 °C. In Fig. 1 the points where the sintering was interrupted and samples were drawn are marked with arrows.

Cross sections of the obtained samples were polished with diamond slurries down to 1 µm, followed by a 1 min polishing treatment with colloidal silica. Light-optical microscopic (LOM) images were taken on a reflected light optical microscope in oil immersion (at 1000×). Scanning electron micrographs (SEM) were taken at

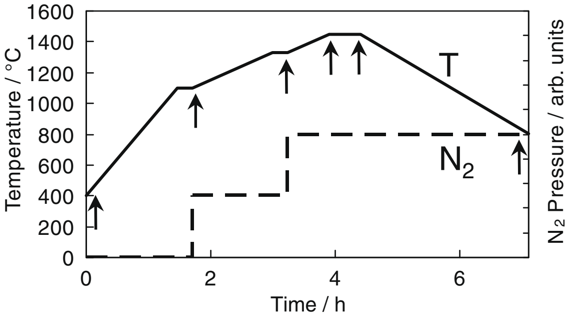

Fig. 1. Sintering cycle for interrupted sintering, with interruption points marked with arrows. The displayed cycle, with the second dwell and an increase of the nitrogen pressure at 1330 °C was used for grades C and D. For grades A and B, the second dwell was at 1300 °C, with a constant nitrogen pressure from 1100 °C.

Table 1
Powder formulation for interrupted sintering experiments of the various grades (wt.%). "Pre-alloy" refers to the carbide/carbonitride solid solution, "grade" refers to the hardmetals made from these.

Grade	Co	Ni	$\mathrm{TiC}_{0.3}\mathrm{N}_{0.7}$	TaC	$\mathrm{Cr}_3\mathrm{C}_2$	WC	W	$\mathrm{W}_{0.5}\mathrm{Ti}_{0.5}\mathrm{C}$	Pre-alloy
A	6.01			0.02	0.23	80.44	3.54	1.92	7.84
B	10.18			0.41	0.15	24.34	26.99		37.86
C	13.00		25.58	0.10	0.40	34.63			25.75
D	8.00	8.00	42.93	0.09	0.45	4.78			35.76