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One-step Sinter-HIP method for preparation of functionally graded cemented carbide with ultrafine grains

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Abstract

Ultrafine crystalline functionally graded cemented carbides (FGCCs) with a surface zone enriched in binder phase were prepared by a one-step Sinter-HIP method. The influence of sintering pressure and cubic carbide composition on the formation of gradient layer was examined. The results show that the ultrafine FGCC with surface zone enriched in binder phase can be formed by the one-step Sinter-HIP method. The process of the gradient layer formation is accelerated under higher sintering pressure; the gradient layer thickness increases with the sintering pressure increasing. The gradient layer thickness is controlled by diffusion distance of cubic carbide formers, such as Ti, Ta and Nb. The addition of (Ta, Nb)C leads to decrease the thickness of gradient layer.

Keywords: A. Sintering; B. Grain size; C. Diffusion; Functionally graded cemented carbide; Sintering pressure

1. Introduction

Coated cemented carbide tools are widely used for machining of metallic alloys. During the coating process, which requires high temperature chemical vapor deposition (CVD), cracks will unavoidably form in the coatings and might finally cause insert failure due to the different thermal expansion coefficient between coating and substrate. To prevent propagation of cracks into the bulk, functionally graded cemented carbide (FGCC) with tough surface zone, which are enriched in binder phase and depleted in cubic carbides, is used as a substrate for coated tools [1–3].

FGCC with the surface zone enriched in binder phase can be formed when nitrogen-containing alloys are sintered in vacuum or under denitriding conditions, which was shown firstly by Suzuki [4]. To prepare FGCC, Ti(C,N) is often added as gradient former [4–7]. The formation of gradient layer is controlled by decomposition of Ti(C,N) and inward Ti diffusion, outward N diffusion in the liquid binder during nitrogen free atmosphere sintering [8,9]. In order to get a dense body, FGCC with the surface zone enriched in cobalt is mainly prepared by a two-step sintering, in which the nitrogen-containing cemented carbide is first pre-sintered in vacuum furnace with negative pressure N_2 gas and then subjected to gradient sintering in a free nitrogen atmosphere [6,7]. Recently, a one-step vacuum sintering is proposed though adding ultrafine Ti(C,N), which has high sintering activity and decomposition ability for its high surface energy [10,11]. However, FGCC with the surface zone enriched in binder phase prepared by the above methods usually has medium-sized WC grain, so far.

Ultrafine cemented carbide is the major development trend in the future for its excellent mechanical properties [12–14]. Sinter Hot Isostatic Pressing (Sinter-HIP) is a sintering technology combined vacuum sintering and pressure sintering in one-step and the rising pressure can produce the effect of enhancing densification while suppressing grain growth

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[14–17]. Using the effect of Sinter-HIP, we have proposed a two-step process, where the cemented carbide is first Sinter-HIP pre-sintered and then subjected to a gradient sintering, to fabricate FGCC with ultrafine grains successfully [18]. Thus, if Sinter-HIP was used and the ultrafine Ti(C,N), which has high sintering activity and decomposition ability for its high surface energy, was added in ultrafine cemented carbides, the decomposition of Ti(C,N) and the diffusion of Ti and N could be achieved at lower temperature and short time, the process of the formation of gradient layer could be accelerated. Ultrafine FGCC with the surface zone enriched in binder phase would be fabricated through one-step Sinter-HIP and the production cycle and costs could be reduced.

Therefore, in this work, ultrafine WC and Ti(C,N) powders were chosen. Ultrafine FGCC with the surface zone enriched in binder phase was fabricated by the Sinter-HIP in a one-step sintering process. Ultrafine (Ta,Nb)C powders, which has the same cubic (NaCl) structure as Ti(C,N) and the inward diffusion of Ta and Nb also occur during the formation of gradient layer [19], were used to clarify the effect of ultrafine Ti(C,N) on the formation of gradient layer. The effect of the sintering pressure on grain size and gradient formation were also studied.

2. Experimental

Ultrafine WC and Co powders with average particle size of 0.4 μm (D_{FSSS}) and 1 μm (D_{FSSS}) provided by Xiamen Golden Egret Special Alloy Co. Ltd. of China were used in the experiment. Ti(C,N) with a nominal C/N ratio of 50/50 was added as gradient former. A small amount of VC and Cr_3C_2 with average particle size of 1 μm (D_{FSSS}) was added as grain inhibitors [20]. The powders of Ti(C,N), (Ta,Nb)C, VC and Cr_3C_2 were provided by Zhuzhou Cemented Carbide Group Co. Ltd. of China. The ultrafine powders of Ti(C,N) and (Ta,Nb)C with average particle size of 0.2 μm (D_{FSSS}) were obtained by high energy ball milling. The composition of the investigated alloys is shown in Table 1. About 2% polyethylene glycol 4000 (PEG 4000) was added as a pressing agent which was removed during the sintering. The raw powders were milled for 64 h by using pure ethanol as liquid medium, with a ball-to-powder weight ratio of 14.5:1 and a rotation speed of 64 rpm. The powder mixtures were dried on tray at 85 °C for 1 h, and then pressed to inserts with the sizes of 6.5 mm × 5.25 mm × 21 mm for sintering.

Pressed pieces were sintered in a Sinter-HIP furnace. The sintering process contained several stages, including dewaxing under H_2 flow, densification and gradient formation. Ar gas of 9.0 MPa or 5.8 MPa was introduced when the temperature reached 1410 °C and this was held for 30 min before cooling to room temperature. The sintered specimens were cut perpendicularly to the original surface so as to make a cross-section visible, embedded in resin and polished according to standard metallographic sample preparation method. A field-emission scanning electron microscopy (FESEM) was used to observe the morphology of the prepared cemented carbide. The thickness of the gradient layer was measured according to the line intercept method from the FESEM images of the surface zone, and about 5 observed fields were randomly selected for each specimen to perform the measurements. To determine the gradient, the content of Co, Ti, Ta and Nb elemental concentration profiles perpendicular to the surface was measured using an electron probe microanalysis (EPMA). The electron beam was moved 3 μm perpendicular to the surface, to perform a new point. The measurement of WC grain size was carried out by using of the Win ROOF software. The grain sizes of the WC with different shapes and areas were measured according to the equivalent diameter method from the FESEM images. We randomly selected about 600 grains for each specimen to perform the measurements.

Table 1
The composition of the investigated alloys in wt%.

Specimen	Compounds					
	WC	Co	Ti(C,N)	(Ta,Nb)C	VC	Cr_3C_2
Ti(C,N)	bal.	12	4	–	0.35	0.65
(Ta,Nb)C	bal.	12	4	6	0.35	0.65

3. Results and discussion

The surface microstructure of Ti(C,N)-alloy and (Ta,Nb)C-alloy prepared with different sintering pressure is shown in Figs. 1 and 2, respectively. In the micrograph, bright contrast is WC phase, gray is cubic phase, and dark is binder phase. The microstructure has great difference between the surface

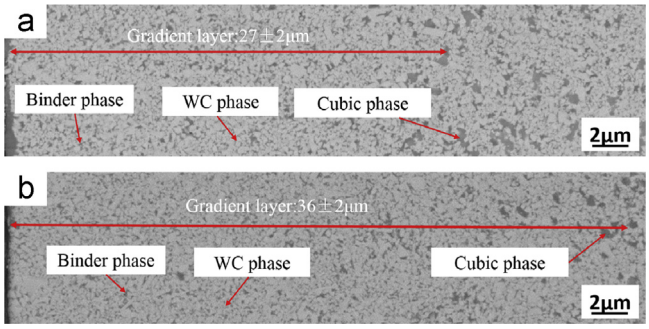

Fig. 1. The microstructure in the surface zone of the Ti(C,N)-alloy with the sintering pressure (a) 5.8 MPa and (b) 9.0 MPa.

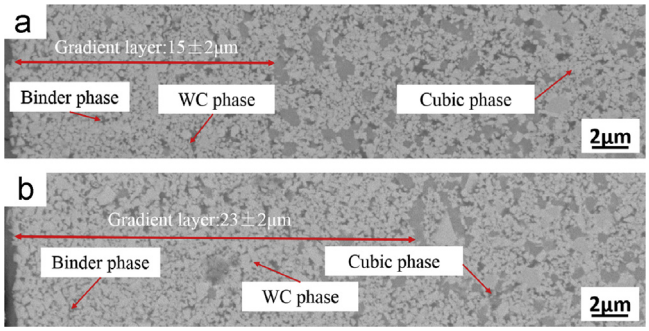

Fig. 2. The microstructure in the surface zone of the (Ta,Nb)C-alloy with the sintering pressure (a) 5.8 MPa and (b) 9.0 MPa.