

Research into preparation and properties of graded cemented carbides with face center cubic-rich surface layer

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ABSTRACT

This paper systematically investigated a set of functionally graded WC-TiC-Mo-Co cemented carbides with modified surface layer (called fcc-rich surface layer in this study), which is mainly composed of fcc phases (Ti(CN) and TiN) and WC. Nitridation at liquid phase sintering temperature is the key process making this fcc-rich surface layer. The functionally graded WC-TiC-Mo-Co cemented carbides synthesized in this study show 3 layer structure: the outer layer, i.e. the fcc-rich surface layer; the intermediate layer, which is characterized by abnormally large WC and high Co content; and the inner layer. It was found that TiC is the most critical component for the formation of fcc-rich surface layer. The higher content of TiC results in the thicker fcc-rich outer layer, higher (Ti(CN) and TiN) content in the outer layer, and higher hardness of the fcc-rich outer layer. The formation of this fcc-rich surface layer is mainly due to the nitridation process between Ti and N, which leads to the diffusion of Ti outwards (from the inside of the sample to the surface) and the subsequent migration of liquid cobalt inwards (from surface to the inside of the sample). The three-layer structure developed in this study provides the excellent combination of high wear resistance and high toughness, which is favorable for some applications.

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1. Introduction

Cemented carbides have been used widely in cutting, turning, and mining applications due to their high wear resistance and considerable toughness [1]. In recent years, functionally graded carbides (FGCs), especially the carbides with modified surface microstructures/properties have drawn more and more research interest [2–5]. One type of these FGCs with a special surface layer rich in face center cubic phases, such as titanium nitride (TiN) and titanium carbonitride Ti(CN), which is called carbide with fcc-rich surface in this paper, has demonstrated some promising potential for certain industrial applications [6]. The carbides with fcc-rich surface usually have the surface layer with higher contents of TiN and Ti(CN) and lower content of Co than the nominal levels, which contribute to the higher wear resistance of surface layer [6,7]. In addition, the carbides with fcc-rich surface, compared with conventional carbides, are more suitable for further PVD/CVD coatings due

to less thermal expansion mismatch and better chemical adhesion between coating and carbide substrate [7–10].

Quite a few investigations have been made to the carbides with fcc-rich surface currently [2,6–9]. The processing for these special carbides usually includes a WC-TiC-Co system and a nitrogen-containing atmosphere during sintering. The formation of fcc phase-rich surface layer (mainly Ti(CN) and TiN) at liquid phase sintering temperature is a process of thermodynamic coupling between Ti and N, where the diffusion of both nitrogen from sintering atmosphere and Ti from inside of the sample towards the carbide surface, followed by the reaction between Ti/TiC and N, is involved [7,8,11–14]. The transport media for diffusion is mainly the liquid cobalt binder phase due to the fact that the diffusivity of both nitrogen and Ti is higher in the liquid metal than in the solid carbides [10]. The formation of more and more TiN and Ti(CN) leads to the less cobalt binder in the surface layer. Because of the higher hardness of mixed carbides (WC + Ti(CN) + TiN, ~28 GPa) compared with WC (~22 GPa) as well as the less cobalt binder in the surface layer, the surface layer shows higher wear resistance compared with the inner portion [8,9].

Although it is quite clear that TiC is the key component for these carbides with fcc-rich surface, no systematic study has been made yet on the critical role of TiC. In this study, we selected a

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Table 1
Nominal compositions of Alloys 1–4 (wt.%).

Sample No.	WC	Co	TiC	Mo
Alloy 1	85.5	10	4	0.5
Alloy 2	81.5	10	8	0.5
Alloy 3	77.5	10	12	0.5
Alloy 4	73.5	10	16	0.5

special carbide system of WC–TiC (4–16 wt.%)–Mo (0.5 wt.%)–Co (10 wt.%). The effect of TiC on the formation of fcc-rich surface layer was investigated comprehensively. The study was focused on the microstructure and mechanical behavior of the fcc rich surface layer, as well as the formation mechanism of surface layer.

2. Experimental procedures

As shown in Table 1, 4 carbides (Alloys 1–4) with the same Co and Mo but different TiC contents (4–16 wt.%) were selected for this study. The samples were made with powder mixing, pressing, dewaxing, and followed by sintering at 1420 °C for 60 min as shown in Fig. 1. Ar was used as the main sintering atmosphere and N₂ of 5 bar was introduced into the sintering atmosphere at 1200 °C and stopped after soaking at 1420 °C for 60 min.

Microstructure analysis and chemical composition (EDS) were made to the polished cross section surface of the samples. XRD was made on the top surface of Alloys 1–4 and on the raw powder mixture of alloy 4 in order to investigate the effect of nitridation. The microhardness on the cross section of the sample was conducted using a microhardness tester (HXD-1000TM/LCD, China) with motorized turret under the load of 1.96 N (200 gf) for 20 s, and the measurement was spaced in 50 μm increment from the surface down to about 1000 μm from the sample surface. In addition, microhardness was made on the top surface of the sample with the same loading parameters in order to evaluate the actual hardness of the surface layer.

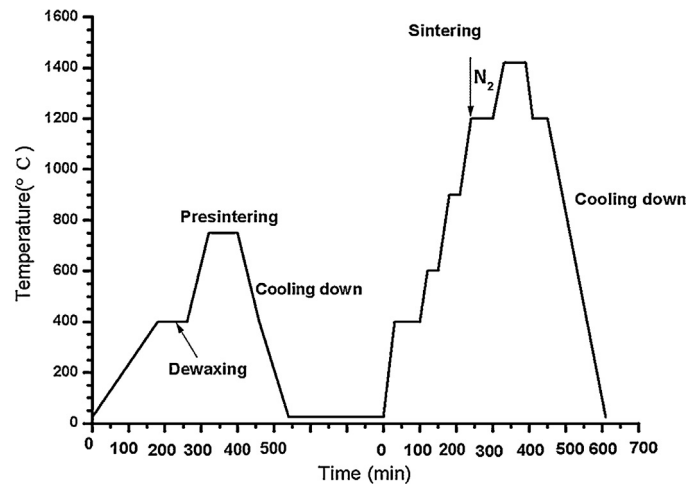


Fig. 1. Dewaxing and sintering/nitridation processes for this study. Ar is the main sintering atmosphere. 5 bars of N₂ was introduced at 1200 °C and stopped when soaking at 1420 °C for 60 min was finished.

3. Results and discussion

Fig. 2 shows the cross-section microstructure of carbides with different TiC contents varying from 4 wt.% (Alloy 1) to 16 wt.% (Alloy 4). For all the carbides, the surface region can be divided into three portions, i.e. the outer layer, the intermediate layer, and the inner layer. It can be seen that the initial TiC content has significant effect on the thickness of outer layer. The thickness of outer layer is about 3 μm for the carbide with 4 wt.% TiC (Alloy 1), 7 μm for 8 wt.% TiC (Alloy 2), 10 μm for 12 wt.% TiC (Alloy 3) and 20 μm for 16 wt.% TiC (Alloy 4). The intermediate layer in Fig. 2 is characterized by abnormally large WC grains and the inner layer has finer WC compared with that in the intermediate layer, which is similar to the inner portion of the sample. The detailed microstructures for outer layer,

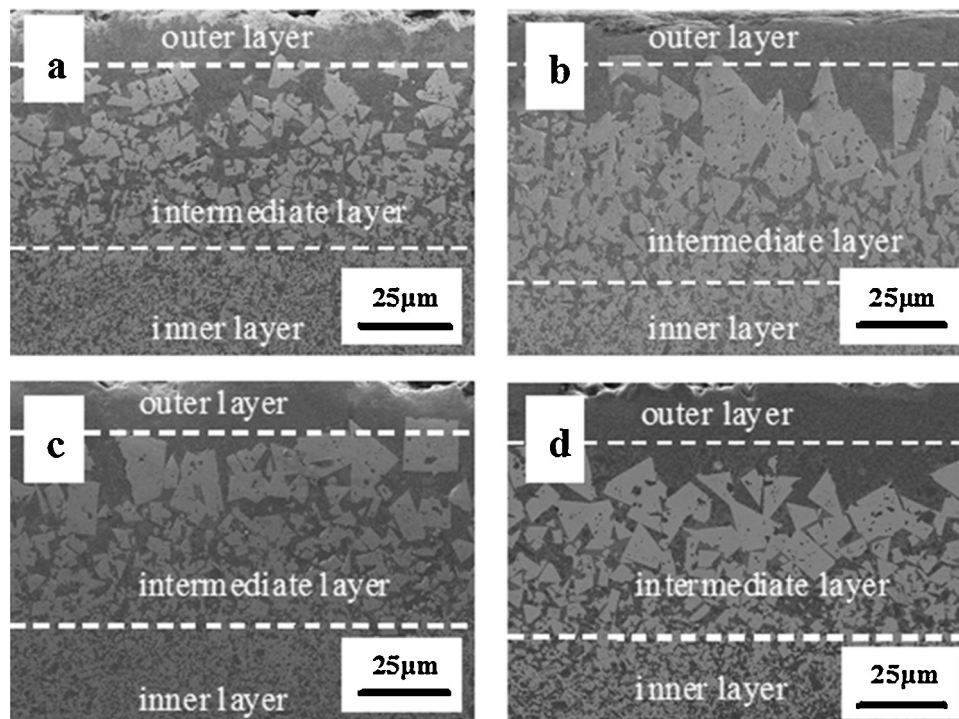


Fig. 2. Microstructure of fcc-rich surface layers for carbides sintered at 1420 °C for 60 min. (a) Alloy 1–4 wt.%TiC, (b) Alloy 2–8 wt.% TiC, (c) Alloy 3–12 wt.% TiC, and (d) Alloy 4–16 wt.% TiC.

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