Microstructures of binderless tungsten carbides sintered by spark plasma sintering process

Seung I. Cha, Soon H. Hong *

Department of Material Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Taejon 305-701, South Korea

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Abstract

Pure WC was sintered by spark plasma sintering (SPS) process for a binderless cemented carbide application. The relative density of spark plasma sintered WC was over 98% when the SPS temperature was 1700 °C under 50 MPa pressure. Grain growth of WC could be suppressed with full densification by shortening sintering time. When the initial WC powder size was varied from 0.57 to 4.06 μm, the sintered density decreased with decreasing WC powder size. However, WC with an initial powder size of 0.57 μm could be sintered to densification by addition of free carbon. The higher amount of surface oxide in the finer WC powder is considered to have caused decarbonization during the sintering process. For WC powders of 4.06 μm, abnormal grain growth occurred when the sintering time was over 1 min if the sintering temperature was over 1700 °C. Also, with the sintering temperature and sintering time where no abnormal grain growth occurred, abnormal grain growth occurred by addition of carbon. This result shows that the abnormal grain growth in WC sintered by SPS process can be controlled by carbon addition. The abnormal grain growth in sintered WC somewhat increased fracture toughness by crack deflection.

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1. Introduction

WC is well known as a component of tool materials in the forms of cemented carbides mixed with metal binders such as Co, Fe and Ni. Cemented carbides have played a significant role as metal cutting tools since the 1930s. Many methods to improve mechanical performance of cemented carbides have been attempted since then, including modification of composition and refinement of carbide size. However, in some industrial fields, it is difficult to apply cemented carbides containing metal binders. In particular, in corrosive environments, cemented carbides are weak due to their metal binders.

In order to apply cemented carbides to corrosive environments, binderless cemented carbides (i.e. cemented carbides that do not contain any metal binders) were developed [1,2]. Owing to the absence of metal binder, binderless cemented carbides should have higher corrosion resistance and high hardness. Generally, it is very difficult to sinter pure WC by hot pressing or other conventional sintering processes without the addition of other carbides such as TiC and Mo₂C. TiC has been used as a carbide binder because it forms WC–TiC solid solution phase [1]. However, the fracture toughness of binderless cemented carbides is lower than that of cemented carbides, while the hardness is similar to that of cemented carbides. Therefore, due to the easy occurrence of surface fractures during friction or under abrasive conditions, the wear resistance is lower than that of cemented carbides [1,2]. These fractures have been known to be caused by C segregation near the WC/TiC interface [2].

For the purpose of hard and corrosion resistant tool materials, pure WC was also introduced [3]. In spite of difficulties in the sintering process, the C segregation near the interface can be prevented due to its single-phase microstructure. However, WC does not melt...
congruently. Also, even at the decomposition temperature, the non-stoichiometric range is narrow, i.e. it contains only a few vacancies. Therefore, the diffusion rate is too slow to obtain a dense sintered body. However, Omori et al. sintered pure WC carbides using a spark plasma sintering (SPS) process at 1900 °C [3]. The hardness and transverse rupture strength of the sintered pure WC were 24 and 1 GPa, respectively. However, the grain size of WC was over 1 mm due to the high sintering temperature. Therefore, if a fine WC

![Fig. 1. Schematics of SPS system used for consolidation of binderless WC.](image)

![Fig. 2. SEM micrographs of WC powders with various sizes. (a) 0.57 μm, (b) 1.33 μm and (c) 4.06 μm.](images)
could be obtained, higher hardness and strength is expected. In this study, a sintering process required to maintain the fine WC grain size and the mechanical properties is investigated.

2. Experimental procedure

Pure WC is sintered by a SPS system produced by Sumitomo Coal Mining Co., Ltd. A schematic of the SPS system is shown in Fig. 1. In the SPS process, the powders in the graphite mould were heated by an
applied pulsed electric current over 1000 A. The exact sintering mechanism during the SPS is not yet understood clearly. However, some mechanisms have been proposed. Tokita et al. suggest that the sparked plasma generated between the particles removes the oxide layer easily [4]. In addition, owing to the pulsed current, the high voltage and current are applied between particles by its large impedance.

The heating rate is maintained at 100 °C min−1 during the SPS process for WC. WC powders with various initial particle sizes were used to investigate the effect of initial powder size on sintering behavior. The morphologies of each powder were shown in Fig. 2 where the initial WC powder sizes were 0.57, 1.33 and 4.06 μm. The WC powders were sintered within a graphite mold and boron nitride was sprayed onto the mold surface to reduce reaction with the mold. A pressure of 50 MPa was maintained during the sintering process. The vacuum was maintained at 1 Pa during sintering. The dimensional change of the powder compact, temperature and pressure were monitored during the sintering process. The microstructures of sintered binderless WC were observed by SEM and an optical microscope after it was etched by Murakami solution. The density of sintered WC was measured according to ASTM B 311-93. The weight of each specimen was measured at least five times in air and water to calculate the density. The carbon content in sintered WC was measured by C-400 carbon determinator produced by Leco Corp.

Fig. 6. (a) Dimensional changes and (b) density of sintered WC at 1700 °C without holding time from various initial powder sizes.

Fig. 7. SEM micrographs of sintered WC from (a) 0.57 μm, (b) 1.33 μm and (c) 4.06 μm powders. Sintering temperature was 1700 °C and holding time was zero.
3. Results and discussion

3.1. Sintering behavior of binderless WC

In order to establish the sintering conditions for WC, WC of 4.06 μm particle size was spark plasma sintered at a temperature range from 1550 to 1800 °C without a holding time at sintering temperature under vacuum. Fig. 3 illustrates the dimensional changes of WC powder compact during the sintering at 1800 °C. The shrinkage of WC powder compact starts at 1200 °C, increases with increased temperature and ends at 1600 °C. The density of sintered WC with varied SPS temperatures without holding time is shown in Fig. 4. In this figure, if the sintering temperature is over 1700 °C, the full density of WC is obtained without holding time, i.e. heating at the sintering temperature followed by immediate cooling.

The microstructures of sintered WC are shown in Fig. 5. In this figure, the size and amount of pores within sintered WC decreases with increasing the sintering temperature from 1550 to 1700 °C. However, the size and amount of pores are not different between WC sintered at 1700 and at 1800 °C. Grain size of WC is almost 5 μm regardless of the sintering temperature. This result shows that short sintering time, such as heating to sintering temperature and immediately cooling, can produce fine WC sintered body when sintered at 1700 °C. This process is enhanced from Omori [3], where the WC grain size is over 1 mm.

3.2. Effect of initial WC particle size on microstructure of sintered WC

In order to control the grain size of spark plasma sintered WC, initial WC powder with size range from 0.57 to 4.06 μm was spark plasma sintered at 1700 °C without holding time. The dimensional change according to the SPS temperature in various initial powder sizes is shown in Fig. 6(a). In this figure, the shrinkage starts at a lower temperature when the initial WC powder size becomes finer, i.e. finer WC powders sintered at lower temperature. However, the density of

![Fig. 8](image1)

![Fig. 9](image2)

Fig. 8. (a) Carbon content of sintered WC from 0.57 and 4.06 μm powders and (b) variation of carbon content within sintered WC from 0.57 μm powder with increased carbon content.

Fig. 9. XRD analysis of sintered WC with (a) various initial WC powder size and (b) various carbon black content within 0.57 μm powders.
sintered WC at 1700 °C with no holding time, as shown in Fig. 6(b), decreases with decreased initial WC powder size. This is a quite unexpected result because generally fine initial powder size causes a denser sintered body.

In Fig. 7, the microstructures of sintered WC from 0.57, 1.33 and 4.06 μm size powders are shown. In this figure, there are a large amount of pores in the WC, and the WC is round shape near the pores sintered from 0.57 μm powder. As the initial WC powder size increases, the amount of pores decreases with the formation of the well-developed WC grain boundaries. Generally, the powders are expected to surround by an oxide layer under air condition. Also, the WC powder had been expected to contain surface oxides. When this powder was sintered under vacuum the surface oxide is reduced. However, in the case of carbides, an easier reduction process can occur. This is the reduction that occurs by carbon within the carbide powders. If the carbides have some range of non-stoichiometric compositions, this process does not severely cause porosities. However, in the case of WC, the stoichiometric range of carbon content is very narrow. Therefore, if carbon is consumed in the reduction of the surface oxide, there is a lack of carbon to maintain the WC. As shown in Fig. 8(a), the carbon content of WC sintered from 0.57 μm powder is much lower than that of 4.06 μm. This result shows that a large amount of carbon was consumed during the sintering process, i.e. it was decarbonized. The decarbonization of WC during sintering results in a formation of W₂C phase as shown in Fig. 9(a). In Fig. 9(a), the W₂C XRD peaks were shown in sintered WC from 0.57 and 1.33 μm powders while only WC peaks were shown in sintered WC from 4.06 μm powders.

If carbon is applied, a sound microstructure can be obtained from fine WC. In order to add excess carbon, 0.57 μm WC powders were ball milled with carbon black for 24 h using alumina balls and then sintered at 1700 °C without holding time. The carbon content within the sintered WC increases with increased addition of carbon black, as seen in Fig. 8(b). In XRD results in Fig. 9(b), the W₂C peaks were disappeared by the addition of carbon black during sintering. The addition of carbon

Fig. 10. SEM micrographs of sintered WC from 0.57 μm powders with addition of (a) 0 wt.%, (b) 0.1 wt.%, (c) 0.2 wt.% and (d) 0.5 wt.% carbon black.
enhanced the microstructure of WC sintered from 0.57 μm powders as shown in Fig. 10, which also shows that pores were reduced by the addition of carbons.

3.3. Abnormal grain growth during sintering

The WC spark plasma sintered from 4.06 μm powders shows abnormal grain growth if the holding time is over 1 min at SPS temperatures of 1700 and 1800 °C, as shown in Fig. 11. Although not yet clearly understood, the origin of abnormal grain growth in solid polycrystalline material is considered to be the grain growth restriction due to its singular grain boundary. A singular grain boundary requires special growth mechanisms for grain growth such as 2-D nucleation and screw dislocations [5,6]. If the driving force for grain growth is sufficiently large, the 2-D nucleation process cannot restrict its growth. However, if the driving force is small, then the grain growth will be affected by the rate of 2-D nucleation on the singular surface. In this case, even a small amount of singular boundary among the total grain boundaries could inhibit the total grain growth by pinning the grain boundary movement at the triple point [5,6].

In the case of WC, the grain boundary is regarded as singular. Therefore, according to the above theory, there exists sufficient possibility to result in abnormal grain growth. This may be the main reason for the large grain size of WC in former studies [3]. Therefore, in order to

Fig. 11. Optical micrographs of WC sintered from 4.06 μm powders at (a) 1800 °C and (b) 1700 °C for 1 min.

Fig. 12. Optical micrographs of WC sintered (a) without and (b) with inserted carbon layer at 1700 °C for 0 min.

Fig. 13. Schematic of abnormal grain growth due to addition of C.
avoid abnormal grain growth hence fabricate fine WC, the holding time at SPS should be reduced as much possible.

Besides the effect of holding time, the addition of C also causes abnormal grain growth. In Fig. 12, if a carbon layer is inserted within the WC powder compact, abnormal grain growth occurs near the carbon layer, while without the carbon layer, there is no abnormal grain growth under the same SPS process conditions. The reason for this abnormal grain growth occurring by carbon addition is not clearly understood. One possible explanation is that the added carbon increases the driving force of grain growth, i.e. it reduces the energy barrier for 2-D nucleation for the growth of WC grain boundary to grow. This occurs because the sintered WC contains a small amount of C compared with the stoichiometric composition. Some amount of C seems to be needed at the grain boundaries for grain growth. Therefore, the addition of C can decrease the 2-D nucleation barrier. In this case, some grain could grow with the same rate as rough grain boundaries. This situation is shown in Fig. 13. This assumption is supported by the observation that during the sintering the grain growth in the matrix grain is small. However, further research is required for a more accurate analysis.

The results above indicate that the densification and grain growth behavior of binderless WC are sensitively dependent on the C content within WC. In particular, the addition of carbon enhances densification, grain growth and abnormal grain growth. Therefore, for the given sintering conditions such as sintering temperature, holding time and pressure, the microstructure of WC is controlled by the addition or removal of carbon.

The WC grain size distribution caused from abnormal grain growth appears to affect the fracture toughness. In the case of WC, as shown in Fig. 14, the crack length near the indentation is reduced by half after a Vicker's indentation with 9.8 N, i.e. toughness increases by two times, if abnormal grain growth of WC occurs. Similar toughening effect was shown in Si₃N₄ ceramics [7,8]. During the liquid phase sintering of α-Si₃N₄, some α-Si₃N₄ reprecipitates into β-Si₃N₄ with high aspect ratio.
and fibre-like shaped. This α/β-Si₃N₄ ceramic composite shows high strength and fracture toughness than monolithic one. Therefore, if we are able to control abnormal grain growth of a fine WC sintered body, further improvement can be possible.

4. Summary

(1) Binderless WC is successfully sintered by SPS process at 1700 °C without holding time.

(2) The density of sintered WC decreases as the initial particle size decreases. This is caused by decarbonization due to reduction of surface oxide. The addition of carbon enhances the density while causing precipitation of free carbon.

(3) The WC shows abnormal grain growth at 1700 and 1800 °C with a holding time of 1 min. Moreover, without holding time, the addition of C promotes abnormal grain growth.

(4) The abnormal grain growth of WC in binderless WC enhances the fracture toughness.

References