Journal of Korean Powder Metallurgy Institute
Vol. 10, No. 3, 2003

Spark Plasma Sintering Behavior of Binderless WC Powders

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(Received 16 May 2003 ; Accepted form 9 June 2003)

Abstract Pure WC powders which does not include a binder phase were consolidated by spark plasma sintering (SPS) process at 1600~1850°C for 0~30 min under 50 MPa. Microstructure and mechanical properties of binderless WC prepared by SPS were investigated. With increasing sintering temperature, sintered density and Vickers hardness of binderless WC increased. The fracture toughness of binderless WC was 7~15 MPa $m^{1/2}$ depending on the sintered density and decreased with increasing the Vickers hardness. It is found that the binderless WC prepared by SPS at 1750°C for 10 min under 50 MPa showed nearly full densification with fine-grained structure and revealed excellent mechanical properties of high hardness (~ HV 2400) and considerably high fracture toughness (~7 MPa $m^{1/2}$).

Keywords : Spark plasma sintering (SPS), Binderless WC, Vickers hardness, Fracture toughness

1. Introduction

Tungsten carbide (WC) has long been known for its high hardness, excellent wear resistance, a high modulus of elasticity and retention of its room temperature hardness at elevated temperatures. These properties encourage its widespread use for cutting tools and wear-resistant parts. Considering the high melting point of WC, it is obviously difficult to sinter WC without Co or other low melting point binders using a conventional process in which the liquid phase is partly necessary during the sintering process. For WC-Co cemented carbides, the binder phase has several fundamental functions; it promotes the sintering to a fully dense body, controls the bonding among WC grains and increases the toughness of cemented carbides. A major disadvantage with WC-Co cemented carbides is the low corrosion/oxidation resistance of the Co binder phase[1]. This problem can be avoided by replacing the Co with other binder phase such as Ni or by reducing the amount of Co phase as much as possible. Research on WC-TiC-TaC binderless cemented carbide was reported which have been applied in mechanical seals and sliding parts due to their enhanced corrosion resistance and hardness[2]. In the case of WC-TiC-TaC binderless cemented carbide, however, it is pointed out that carbon precipitation at the grain boundaries between WC and TiC grains takes place and thus results in decrease of the wear resistance and toughness of materials[3].

In this study, we tried to prepare the pure WC body by means of spark plasma sintering (SPS) process. The SPS technique enables rapid heating and facilitating rapid sintering at relatively low temperature compare with conventional sintering process by direct resistance heating generated by high pulsed electric current[4]. The SPS process is similar to conventional hot pressing, in that the powders are loaded in a graphite die and a uniaxial pressure is applied during the sintering. However, instead of using an external heating source, a pulsed direct current is applied to pass through the graphite die and powder sample. This means that the die also acts as a heating source and that the powder sample is heated from both outside and inside. When an instantaneous high electric pulsed current is applied, the electric discharge generated among powder particles results in concentrated heat effects and in-situ cleaning of the surface oxides of powder particles. The subsequent resistance heating may lead to concentrated heat effects, and the applied external pressure may assist enhanced consolidation but limit grain growth. Since SPS process does not require long holding times at the sintering temperature to obtain a fully dense body, it is expected to minimize undesirable grain growth. Recently, there is an attempt to reduce the Co content of WC-Co cemented carbides in order to use the original high hardness of WC. According to SPS process, therefore, it was considered that production of dense WC body without binder phase was possible[5-7]. As that result, test on the WC body without Co phase for use as a tool was enabled[5]. Nevertheless there is still a lack of knowledge on binderless WC body. In this study, the SPS process to consolidate pure WC without any binder phase was investigated. The sintering behavior and mechanical properties of binderless WC were studied.

2. Experimentals

Raw powder used in this study is pure WC powder with an average particle size of 1.8 μm. The pure WC powder without binder phases was poured in a graphite die, and then the die was set up inside of the SPS apparatus, SPS-515S (Sumitomo Coal Mining Co., Japan) with a pulse duration of 2.8 ms. Pulse sequence consisting of 12 pulses followed by 2 periods (5.6 ms) of zero current is used during sintering. The schematic diagram of SPS system is shown in Fig. 1. Samples of 15 mm in diameter and 5 mm in thickness were prepared in vacuum, under uniaxial pressure of 50 MPa. This pressure was applied at room temperature and held constant until the end of the sintering period.

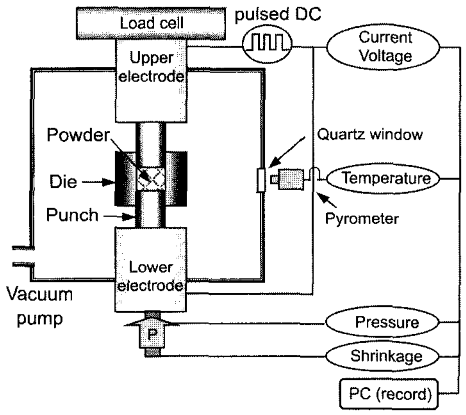

Fig. 1. Schematic diagram of SPS system.

Samples were heated to different sintering temperatures in the range of 1600~1850°C and held at each for 0~30 min. A heating rate was 100°C/min from 600°C to the 1400°C and then down to 50°C/min from this temperature to the final sintering temperature. The temperature was measured with an optical pyrometer focused on the surface of the graphite die. The initial heating stage from room temperature to 600°C over a period of 3 min was controlled by a preset heating program. After sintering was completed, the pulsed direct current was shut down, the pressure was reduced to zero, and the sample was allowed to cool naturally in vacuum. The cooling rate is about 300°C/min in the temperature range 1850~800°C. The SPS system is provided with a dilatometer for recording the shrinkage and shrinkage rate of samples, and the data were stored on a computer.

The density of sintered compacts was evaluated by a method based on Archimedes' principle. Samples were etched using Murakami's reagent for approximately 3 min to expose grain boundaries. The microstructure of the cross section of the samples was observed by scanning electron microscopy (SEM).

For the hardness and fracture toughness measurements, the samples were carefully polished, by standard diamond polishing techniques, down to an diamond particle size of 1 μm. The hardness (HV) at room temperature was measured by Vickers Hardness tester at a load of 20 kg. The fracture toughness (K_{IC}) was evaluated by the Vickers indentation technique at a load of 20 kg and calculated by using the following equation[8],

$$K_{IC} = 0.026\, E^{1/2} \cdot P^{1/2} \cdot a \cdot c^{-3/2}$$

where E is Young's modulus, P is indentation load, a is half an mean diagonal of indent and c is mean crack length.

3. Results and Discussion

The shrinkage behavior of binderless WC sintered compact during heating up to 1800°C under 50 MPa shown in Fig. 2. The shrinkage starts at ~1100°C and is finished at ~1800°C. During this interval, a maximum in the shrinkage rate curve is observed at about 1650°C and then the sample is rapidly densified due to remarkable increase of shrinkage amount. Fig. 3 shows the variation in sintered density of samples with

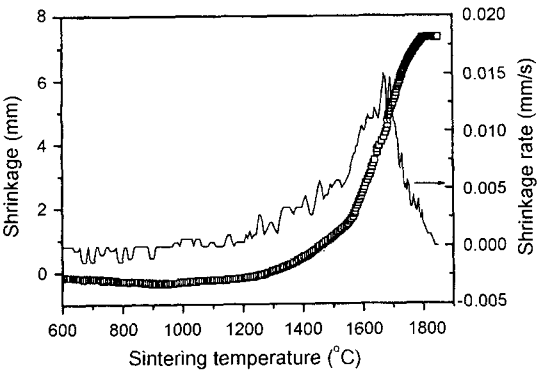

Fig. 2. The variation of shrinkage and shrinkage rate during SPS of binderless WC powder.

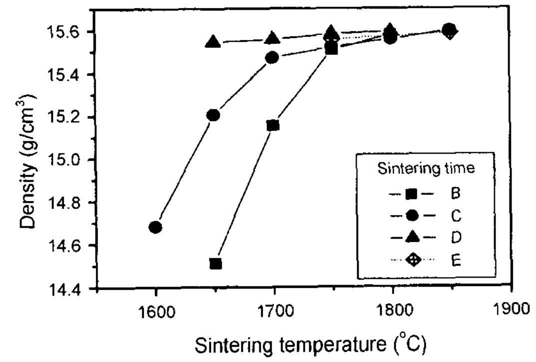

Fig. 3. The variation of sintered density of binderless WC with varying sintering temperature.

increasing sintering temperature for each holding times ranging from 0 to 30 min. The density of the binderless WC increased rapidly with increasing the sintering temperature. When the holding time at each sintering temperature increased, higher density was obtained at lower sintering temperature. When the sintering was performed for 10 and 30 min, respectively, high densities of more than 98% theoretical density were obtained in all samples. The binderless WC sintered at 1750°C for 10 min showed nearly full densification as a density of 15.58 g/cm^3.

The scanning electron microscopic images of binderless WC sintered at 1650°C for 0 min, 3 min and 1750°C for 10 min, respectively, are shown in Fig. 4. These microstructures indicate that the WC grains are directly bonded with each other, without the use of a binder phase. It was found that the WC grains were round shape, like initial WC shape of the raw powder, and many pores were present in irregular form when sintered at 1650°C for 0 min. When the holding time was prolonged to 3 min, however, round WC grains were almost changed to the faceted shape and large pores were also decreased. The sample sintered at 1750°C for 10 min showed a dense and fine-grained structure without considerable grain coarsening. However there are very small pores less than 300 nm in the triple points and these pores did not disappeared in spite of sintering at higher temperatures for a long holding time of 30 min.

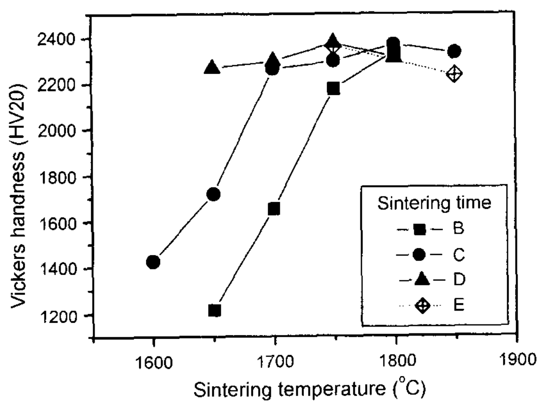

Fig. 5. The variation of Vickers hardness of binderless WC with varying sintering temperature.

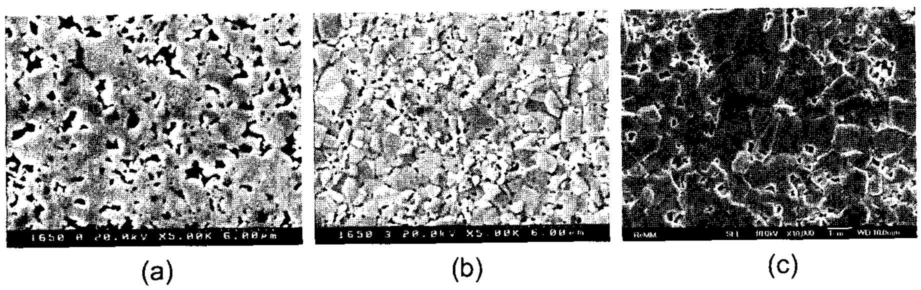

Fig. 4. Scanning electron micrographs of binderless WC sintered at (a) 1650°C for 0 min, (b) 1650°C for 3 min and (c) 1750°C for 10 min.

The variation of Vickers hardness of binderless WC measured under a load of 196N showed in Fig. 5. The Vickers hardness of samples sintered with the holding time of 0 and 3 min, respectively, drastically increased from ~HV 1200 to ~HV 2400 with increasing the sintering temperature. But, all samples sintered at each temperature for more than 10min were showed high Vickers hardness over ~HV 2250 in spite of sintering temperature. This tendency of Vickers hardness variation with increasing sintering temperatures was similar with that of the density variation with increasing sintering temperatures as shown in Fig. 3. Therefore it is considered that the increase of Vickers hardness results from the increase of sintered density. On the other hand, once a maximum hardness was obtained, the Vickers hardness decreased slightly with increasing the sintering temperature due to a grain growth. The measured Vickers hardness values are plotted versus the sintered density in Fig. 6. As shown, the hardness increases as the sintered density increases, yielding values of ~HV 2400 for samples showing full densification over 15.5 g/cm^3 in measured density. Therefore, the high Vickers hardness of binderless WC is considered a consequence of the higher density, and also it is regarded that the WC/WC interface solid-state bonded without binder phase is sufficiently strong to endure the stress necessary to deform the material.

The fracture toughness values of samples prepared under various sintering conditions, calculated from the crack length induced by the Vickers indentation test under a load of 196N, are plotted versus the Vickers hardness in Fig. 7. The fracture toughness of binderless WC was 7~15 MPam$^{1/2}$ according to sintered density and revealed the tendency to decrease with increasing the Vickers hardness of samples, yielding values of about 7 MPam$^{1/2}$. The relationship between fracture toughness and Vickers hardness of binderless WC is similar with that of conventional cemented carbides, i.e. fracture toughness decreases with increasing hardness[9]. But, in samples showing high hardness around HV 2300°C, the fracture toughness values were found to wide range between 7 and 11 MPam$^{1/2}$. Fracture toughness describes the ability of a material to withstand crack propagation. For WC-Co cemented carbides fracture toughness depends on Co content and WC grain size. In this case, the Co binder phase plays an important role to prevent the crack propagation by shielding a stress field in front of crack tip[10]. Considering the microstructure of binderless WC that does not contain the ductile Co phase, however, the fracture toughness values obtained are considerably high compared with that of conventional WC-Co cemented carbides. In binderless WC the crack induced by Vickers indentation propagated along the WC/WC interface and, in some cases, penetrated a large WC grains existed against crack propagation path. Therefore it is considered that the large WC grains as well as very small pores remained act to impede crack growth and absorb more fracture energy, thus the binderless WC exhibits considerably high fracture toughness.

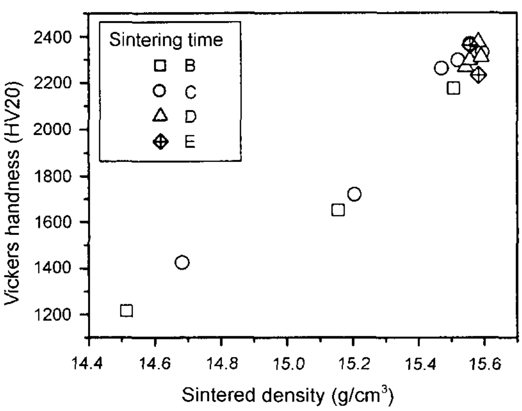

Fig. 6. Plot of Vickers hardness versus sintered density.

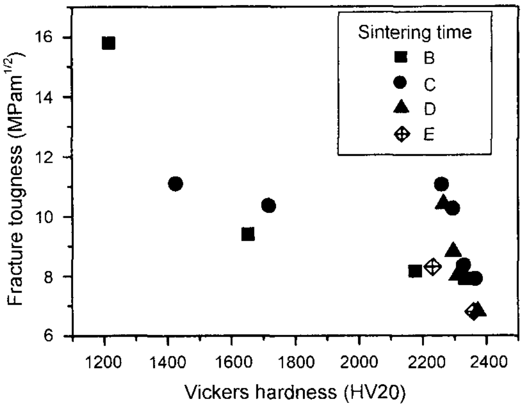

Fig. 7. Plot of fracture toughness versus Vickers hardness.

4. Conclusions

A pure WC powder that does not contained binder phases could be fully densified with fine-grained structure by SPS process. Shrinkage of binderless WC powder compact started at about 1100°C, and then a maximum shrinkage rate was observed at about 1650°C. As increasing the sintering temperature, the morphology of WC grains changed to faceted shape and also many pores decreased remarkably. Sintered density increased rapidly with increasing sintering temperature and the sample sintered at 1750°C for 10 min under 50 MPa showed 99.9% theoretical density (15.5 g/cm^3). Vickers hardness increased with increasing the sintering temperature, yielding values of ~HV 2400 for samples showing over 95% theoretical density. The fracture toughness of binderless WC was 7~15 MPam$^{1/2}$ according to sintered density and revealed the tendency to decrease with increasing the Vickers hardness of samples.

Acknowledgement

This work has been supported by the Korea Science and Engineering Foundation (KOSEF) through the ReMM at University of Ulsan, and the Korea Ministry of Commerce, Industry and Energy through the New Technology Utilizable Technology Development Program (SPIN-OFF Field) of 2002

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