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Sub-micron binderless tungsten carbide sintering behavior under high pressure and high temperature

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ABSTRACT

Pure tungsten carbide (WC) compacts of about 200 nm grain size were prepared by high pressure and high temperature (HPHT) method. The best property sample with high relative density (99.2%), high Vickers hardness (2925 $kg \cdot mm^{-2}$) and high fracture toughness (8.9 $MPa \cdot m^{1/2}$) was obtained in the condition of 1500 °C temperature and 5 GPa pressure. By means of scanning electron microscopy (SEM) and transmission electron microscope (TEM) observations, a large number of twins and stacking faults appeared in sintered samples, and the grain size of sintered samples maintained in the initial range. The XRD patterns of bulk samples reveal that there is a phase transition from WC to W_2C with the increasing of temperature. Moreover, the effect of HPHT condition for sintering kinetics, microstructure evolutions, and mechanical properties of the sintered samples were also discussed.

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1. Introduction

Tungsten carbide (WC) is primarily cemented carbide and is widely used in industrial processing (such as wear resistant components, cutting tools and drilling tools) owing to its high hardness, high thermal and electrical conductivity, high melting temperature and high chemical stability [1,2]. In order to produce a fully dense tungsten carbide body and improve its mechanical properties, a number of methods have been researched in recent years. The sintering methods of tungsten carbide mainly include liquid phase sintering method (LPS), spark plasma sintering method (SPS), hot isostatic pressing method (HIP), high frequency induction electric current sintering method (HFIES), etc. [3–7].

LPS method of WC originated in 1930s and is the main sintering method for WC industrial production now. In LPS method, WC powders are sintered with a binder (typically Co or Ni) at a temperature near the melting point of the binder metal. The formation of a liquid phase during sintering enhances the densification of the product and improves WC fracture toughness. Moreover, adding cobalt or nickel (low melting point materials) in WC also reduces the sintering temperature (1400–1500 °C in LPS method). Co is commonly used in WC hard alloy as a result of its good wetting behavior and excellent solubility among WC particles [2–3]. The fracture toughness of WC hard alloy greatly increased with increasing Co content, while the hardness decreased. The fracture toughness was 15.1 $MPa \cdot m^{1/2}$ and hardness was 1679 $kg \cdot mm^{-2}$ at WC–20 vol.%Co, but 6.2 $MPa \cdot m^{1/2}$ and 1928 $kg \cdot mm^{-2}$ at WC–5 vol.%Co in Kim HC et al. [2]. In addition, WC has great solubility in binder phase, with higher sintering temperature and longer holding time, the sintering WC grain size becomes much larger [5]. As the Hall–Petch effect between the grains and strength, WC's grain growth reduced the hardness, fracture toughness of sintering bulk samples [5–8]. It was reported that some additives add in WC–Co hard alloy inhibited WC grain growth and produced a fully dense WC–Co bulk material [9–10]. Grain growth inhibitors used in WC–Co alloy include chromium carbide, tantalum carbide, and vanadium carbide, however, the new phase of grain growth inhibitor also affects the fracture toughness and other mechanical properties of WC [9].

WC without binder phase has been successfully sintered and investigated by SPS method with the rapid development of spark plasma sintering technology [6,11–12]. Compared with the LPS method, the hardness of WC sintered by SPS significantly increased and the sintering time also was greatly shortened, but the toughness seriously decreased. Zhao et al. [12] reported that sintered WC with relative density of 99.5% and Vickers hardness of 2414 $kg \cdot mm^{-2}$ have been achieved when sintered at 1500 °C with no holding time, but the grain size increased from the nano-scale to micro-scale. In addition, sintered products showed the presence of brittle sub-carbide phase W_2C which decreases the fracture toughness and hardness of WC (as the W_2C phase had a Vickers hardness of 17.1 $kg \cdot mm^{-2}$, and a fracture toughness of 3.6 $MPa \cdot m^{1/2}$ [13]). Adding free carbon in initial material can reduce W_2C phase effect and get pure WC sintered sample [6,14]. But it had to be taken into account that carbon addition generates two effects

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that act in contrast to each other with respect to mechanical properties in Luca et al. [6]. Carbon addition reduces or eliminates the brittle phase W_2C and this allows an improvement in fracture toughness, but carbon promotes an abnormal grain growth and this second decrease fracture toughness of WC [6,13,15].

As mentioned above, it is clear that using conventional sintering methods to increase the hardness and meanwhile increase fracture toughness of WC is a challenging job. Using LPS sintering method with binder can increase relative density and fracture toughness while it easily leads to abnormal grain growth and decrease hardness of WC. Although no adding binder metal in SPS sintering method had achieved fully dense body and higher hardness, the W_2C phase and additives of free carbon affected the fracture toughness of sintered body and thus limited WC application. In this work, we present a novel method to sinter tungsten carbide without any additives at high pressure and high temperature (HPHT). HPHT sintering method is widely used in synthesis of materials. The major advantage is the effect of pressure on sintering materials, significantly improving the density, fracture toughness and hardness [16–18]. In our experiment, the sintered WC samples reach to near-full densification (relative density of 99.2%), have high hardness and high fracture toughness. Moreover, the abnormal grain growth of WC particles was effectively inhibited and grain sizes of sintering bulk samples still maintained in initial range. The effect of high pressure, high temperature and holding time for sintered WC mechanical properties were researched in this work, and the sintering kinetics and microstructure evolution were also studied.

2. Experiment

Tungsten carbide powder (99.9% purity, ChaoWei Nanometer Materials Co., Ltd., China) with particle sizes in the range of 150–250 nm was used as the starting material. Scanning electron microscopy (SEM) image and X-ray diffraction (XRD) pattern of the starting material are shown in Fig. 1.

High pressure sintering experiments were performed on a DS6 × 14 MN cubic press apparatus. Before sintering, the starting powder was packed into a molybdenum (Mo) capsule and pre-compressed at about 400 MPa into thick discs (about 11.0 mm in diameter and about 4.5 mm in height) with a relative density of about 75%. The sample is surrounded by a NaCl tube which could provide a quasi-hydrostatic pressure environment for sample at HPHT sintering process. The sample cell assembly used in this work and calibration of pressure and temperature have been described elsewhere [19,20]. The sintering procedure as follows: Sample was firstly compressed to a predetermined pressure (5 GPa) at room temperature and then by heating rate 100 °C·m min^{-1} to the predetermined temperature (1100–1600 °C), and then holding 20–30 min at HPHT. The temperature was reduced to ambient temperature with a cooling rate of 100 °C·min^{-1} after holding 20–30 min and then the pressure was released. The sintered samples are thick discs with a diameter of about 10.3 mm and thickness of about 4.2 mm. The package of the samples was removed by polishing machine.

The phase composition of the sintered sample was analyzed by XRD experiments and the densities were measured by the Archimedes method. The fracture section of samples and average grain size were obtained by the Field Emission Scanning Electron Microscope (SEM, S-4800 II, Hitachi, Japan). The particle shape and internal structure were attained by Field Emission Transmission Electron Microscope (TEM, Tecnai G2 F20 S-TWIN). The sintered WC samples were all cylinder-shaped and well-polished before hardness tests. Vickers hardness of polished samples were tested by a Vickers hardness tester (FV-700 B, Future-Tech, Japan) with 98 N applied load for 15 s dwelling time. Each hardness data was averaged by 5 to 6 indentations for obtaining an accurate value. Vickers indentation crack length was used for calculating the fracture toughness.

3. Results and discussion

3.1. XRD analysis

WC powder about 200 nm particle size has been sintered at 1100–1600 °C for 20 min or 30 min isothermal holding time under 5 GPa pressure. Fig. 2 shows the XRD patterns of samples sintered at different temperatures for 20 min at 5 GPa. As initial material, the WC phase was pure and had no other phase affection in Fig. 1. XRD investigations of sintered samples showed only WC phase and no presence of W_2C below 1500 °C temperature. W_2C phase appeared in sintered samples at 1500 °C and 1600 °C. With higher temperature, more and more content of W_2C phase appeared. The W_2C phase formation is attributed to the reduction of surface oxides on sintering due to the carbon–oxide reaction. The reason and detailed explanation of W_2C phase occurrence can be seen in reference [11].

3.2. Microstructure

The fractured microstructures of samples sintered at different temperatures for 20 min have been observed by SEM and are shown in Fig. 3. The morphology of initial WC powder is shown in Fig. 1. In Fig. 3(a) and (b), we can find that sintered WC bulk sample particles maintain in the starting WC powder size, and the grains are well-distributed and have no grain growth. In addition, we also find the obvious pores between grains and the combination between grains majority are mechanical connections. In Fig. 3(c), (d) and (e), with temperature increasing from 1200 °C to 1600 °C, the shape of WC grains becomes regular. The regular shape of WC grains is caused by grain growth [4]. Grain to grain boundary becomes stronger and there are less pores

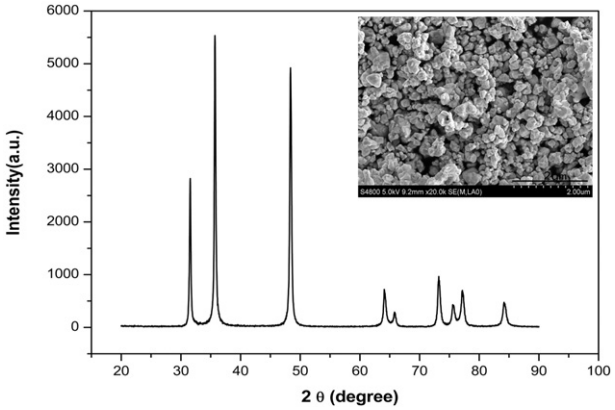

Fig. 1. SEM image and XRD pattern of the initial WC powder.

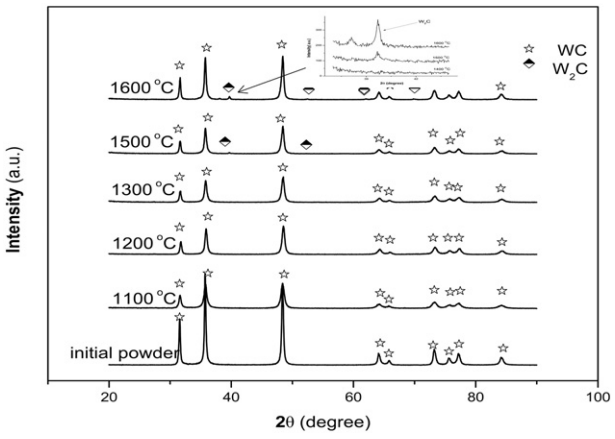

Fig. 2. XRD patterns of WC samples sintered at different temperatures for 20 min isothermal holding time.

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