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MECHANICAL PROPERTIES AND CONSOLIDATION OF NANOSTRUCTURED WC-CNT COMPOSITES BY HIGH FREQUENCY INDUCTION HEATED SINTERING

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Abstract. Highly dense WC and WC-CNT composites with a relative density of up to 99% were obtained by HFIHS under a pressure of 80 MPa within 3 minutes. The average grain size of WC was about 87 nm. The effect of CNT on sintering of WC, the hardnesses and fracture toughnesses of the dense WC-CNT composites produced by HFIHS were also investigated.

1. INTRODUCTION

The attractive properties of tungsten carbides are their high melting point, high hardness, high thermal and electrical conductivities, and relatively high chemical stability. Tungsten carbides are primarily used as cutting tools and abrasive materials in the form of composites with a binder metal, such as Co or Ni. However, these binder phases have inferior chemical characteristics and hardness compared to the carbide phase. Most notably, corrosion and oxidation occur preferentially in the binder phase. Hence, WC-TiC-TaC binderless cemented carbides have been developed for use in mechanical seals and sliding parts due to their enhanced corrosion resistance [1]. TiC has been used as a carbide-binder because it forms the WC-TiC solid solution [1]. In the case of WC-TiC-TaC binderless cemented carbide, however, it has been pointed out that carbon segregation occurs at the grain boundaries between the WC and TiC grains, resulting in a decrease in the wear resistance and toughness of the materials [2]. To improve on the mechanical properties of these materials, the fabrication of nanostructured material and the addition of CNT to form composites have been found to be effective. As nanomaterials possess high strength, high hardness, excellent ductility and toughness, undoubtedly, more attention has been paid for the application of nanomaterials [3]. CNT has a high harness, elastic modulus, strength, and good resistance to corrosion when compared to other structural materials [4].

Recently, nanocrystalline powders have been developed by co-precipitation, the thermochemical and thermomechanical method referred to as the spray conversion process (SCP), and high energy mechanical milling (HEMM). In the conventional sintering process, however, the grain size in the sintered materials becomes larger than that in the presintered powders due to the fast grain growth. Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the high frequency induction heating sintering method

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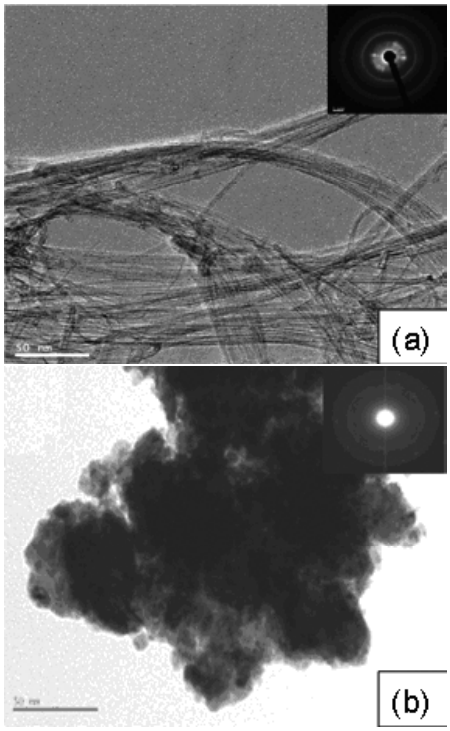

Fig. 1. TEM images of (a) CNT and (b) WC milled for 10 hr.

(HFIHS), which can make dense materials within 2 minutes, has been shown to be effective in achieving this goal [5].

In this study, we investigated the effect of CNT on sintering behavior and mechanical properties of WC**.**

2. EXPERIMENTAL PROCEDURE

The tungsten carbide powder with a grain size of 1.3 μm and CNT used in this research were supplied by TaeguTec Ltd. (Taegu, Korea) and Carbon nanotechnology Inc. respectively. The WC powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 h. Tungsten carbide balls (8.5 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30:1. WC-5vol.% CNT and WC-10vol.% CNT were milled by horizontal ball milling. The grain sizes of the WC was calculated from the full width at half-maximum (FWHM) of the diffraction peak by C. Suryanarayana and M. Grant Norton's formula [6].

After milling, the powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the HFIHS apparatus [5]. The HFIHS apparatus includes a 15 kW power supply which provides an induced current through the sample and applies a 50 kN uniaxial pressure. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. The induced current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. The shrinkage was determined by a linear gauge measuring the vertical displacement. The temperatures were measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the induced current was turned off and the sample cooled to room temperature. The process was carried out under a vacuum of 4 x10^{-2} Torr.

The relative density of the sintered sample was measured by the Archimedes method. Microstructural information was obtained from product samples, which had been polished and etched using Murakami's reagent (10 g potassium ferricyanide, 10 g NaOH, and 100 mL water) for 1-2 min at room temperature. Compositional and microstructural analyses of the products were made by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

3. RESULTS AND DISCUSSION

Fig. 1 shows TEM images of CNT and WC milled for 10h. CNT has a very thin and a long aspect ratio. WC grain is very fine and agglomerate. Milling resulted in a significant reduction of the grain size. The average grain size of the WC milled for 10 h determined by Suryanarayana and Grant Norton's formula was about 40 nm.

The variations of the shrinkage displacement and temperature with the heating time for 80% of the total output power capacity (15 kw) during the sintering of the high energy ball milled WC, WC-5vol.%CNT and 10vol.%CNT under a pressure of 80 MPa are shown in Fig. 2. In all cases, the application of the induced current resulted in shrinkage due to consolidation. The shrinkage initiation temperature (↑) varied from 800 to 900 °C depending on CNT content. The temperature at which shrinkage started decreased with increasing CNT content. It is considered that CNT affected the rate of densification because grain growth of WC increases with addition of CNT [7]. The average grain sizes of the WC, WC-5vol.%CNT, and WC-10vol.%CNT calculated from the XRD data were about 90, 230, and 250 nm, respectively and their corresponding densities all were approximately 99%. Thus, the average grain size of the sintered WC is roughly the

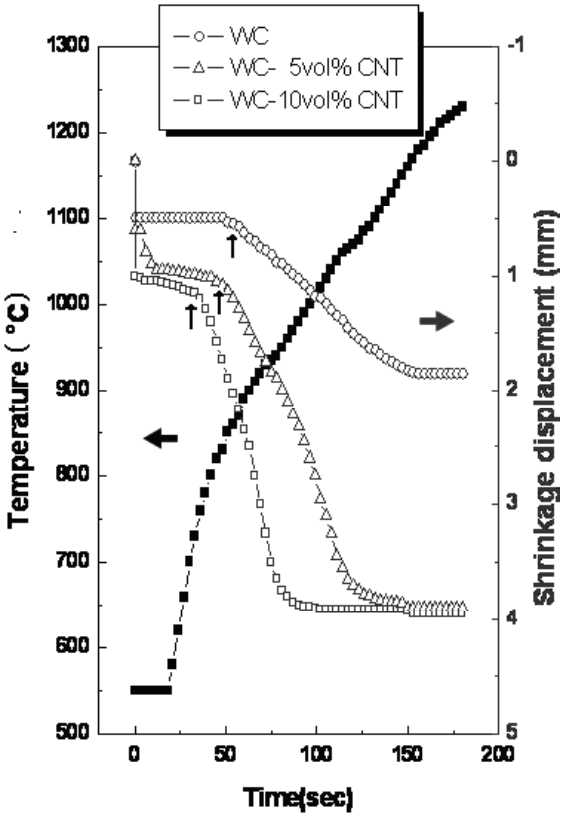

Fig. 2. Variations of temperature and shrinkage with heating time during the sintering of binderless WC, WC-5vol.%CNT, and WC-10vol.%CNT.

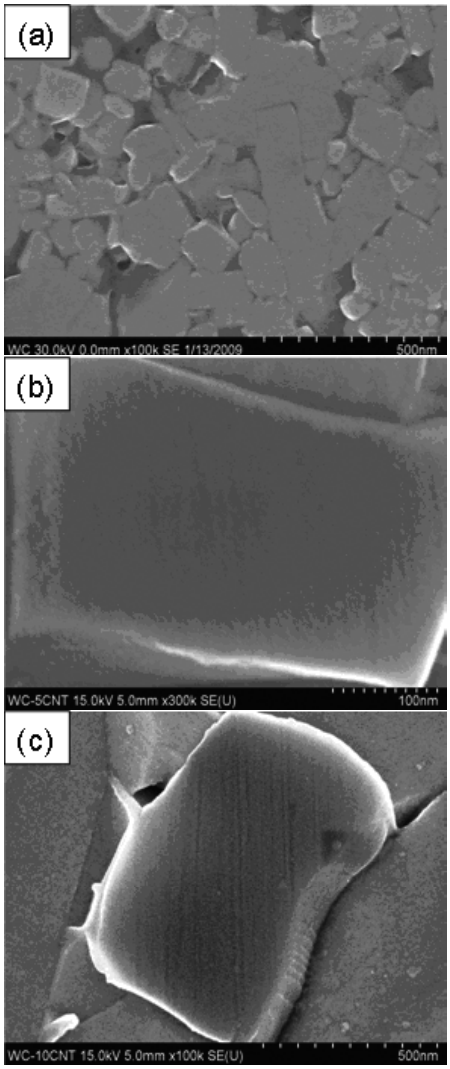

Fig. 3. FE-SEM micrographs of sintered WC with different CNT contents: (a) 0 vol%, (b) 5 vol.%, (c) 10 vol.%.

same as that of the initial powder, indicating the absence of grain growth during sintering. This retention of the grain size is attributed to the high heating rate, the relatively short term exposure of the powders to the high temperature and the intrinsic contribution of the current to the mass transport [8]. FE-SEM image of WC sintered after milling for 10 h is shown in Fig. 3. It is confirmed that the sintered sample consists of nanophase of WC. The use of spark plasma sintering (SPS) to successfully consolidate WC powders (without a binder) has been demonstrated in several investigations. An example of this is a recent work in which unmilled 40-70 nm WC powders were consolidated at 1500 °C to a relative density of up to 95.5% under a pressure of 126 Mpa and a current of 3000 A [9]. Comparing the above study with ours, the sintering temperature of the high energy mechanical milled WC is lower then that of the unmilled powder, due to the increase in the reactivity of the powder, the internal and surface energy as well as the surface area, which all contribute to its so-called mechanical activation [10].

Vickers hardness measurements were performed on polished sections of the WC samples using a 10 kgf load and 15 s dwell time. Indentations with large enough loads produced radial cracks emanating from the corners of the indent. The length of these cracks permits the fracture toughness of the material to be estimated using Anstis' expression [11]. The Vickers hardnesses of the WC, WC-5vol.%CNT and WC-10vol.%CNT were 3020, 2440, and 2140 $kg \cdot mm^{-2}$ and their fracture toughnesses were 7, 10.5, and 11 $MPa \cdot m^{1/2}$, respectively. Fig. 4. shows FE-SEM image of crack propagation of WC-CNT composites. Crack propagated deflectively (↑). It is reported that CNT in composite blocked crack propagation and improved fracture toughness [5]. In this study, hardness of WC-CNT composite was

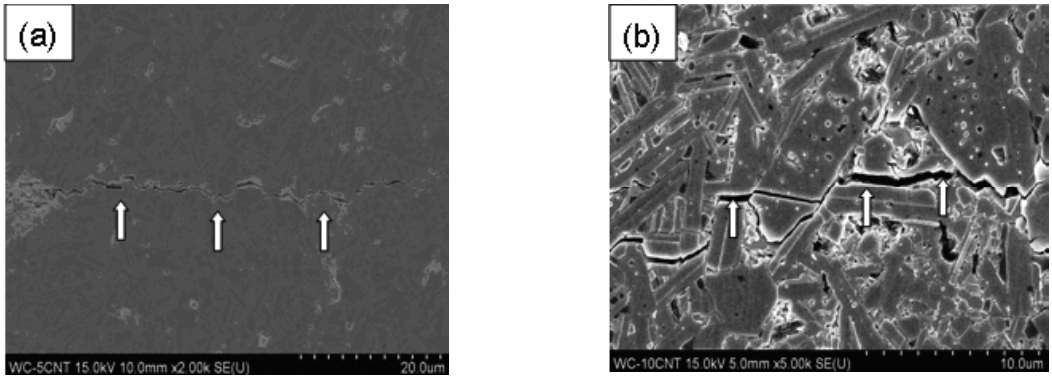

Fig. 4. FE-SEM mictographs of crack propagation in (a) WC-5vol.%CNT and (b) WC-10vol.%CNT.

lower than that of WC due to larger grain size but fracture toughness of WC-CNT composite was higher than that of WC due to addition of CNT.

4. SUMMARY

Nanostructured WC was sintered from mechanically activated WC powder by high frequency induction heated sintering within 3 minutes. The temperature at which shrinkage started decreased with increasing CNT content. And CNT affected the rate of densification because grain growth of WC increases with addition of CNT. The Vickers hardness of WC-CNT composite was lower than that of WC due to larger grain size but fracture toughness of WC-CNT composite was higher than that of WC due to addition of CNT.

ACKNOWLEDGEMENTS

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