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Ultrafine WC–Ni cemented carbides fabricated by spark plasma sintering

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ABSTRACT

With VC and TaC as WC grain growth inhibitors, ultrafine WC–Ni cemented carbides with different fractions (6–10 wt%) of binder metal nickel were fabricated by utilizing high energy milling together with spark plasma sintering. In the obtained samples, only WC and Ni phases were detected in X-ray diffraction limit. The microstructure of the specimens was examined on fractural, polished, and polished/etched surfaces by scanning electron microscopy, and the results revealed that the average WC grain size of the WC–Ni cemented carbides was about 330 nm, and there were lots of micro-pores in the samples. The relative density of the samples was all higher than 92%. But the measurement of hardness and flexural strength indicated that the existence of micro-pores had no significant influence on the performance of the obtained materials. On the basis of observation on the micro-fracture surface of the samples, it was found that fractures occurred along the binder metal, and the obtained ultrafine WC–Ni cemented carbides showed a very short binder mean free path (about 22 nm), thus resulting in excellent performance in mechanical strength.

1. Introduction

WC–Co cemented carbides have excellent properties, for instance, high hardness, high hot-hardness, high strength and toughness, and good wear resistance [1]; and thus they have been widely applied in many fields including cutting tools and geo-engineering equipment. However, because of the low corrosion and oxidation resistance of WC–Co cemented carbides [2], and high price of the binder metal cobalt [3], their applications have been limited. Additionally, in order to further improve the performance (hardness, friction coefficient and so on) of WC–Co cemented carbides, technological combination between WC–Co cemented carbides and diamond films has been applied. However, in case of chemical vapor deposition of diamond films onto WC–Co cemented carbides, the binder metal cobalt in cemented carbide surface layer is detrimental to the nucleation of diamond films from the gas phase and the formation of interfacial graphite, dramatically reducing the adhesion strength between diamond films and cemented carbide substrates [4,5]. Thus, engineers and scientists have endeavored for years to find new binder metals to replace cobalt in cemented carbides. To date, several metals have been proved to be possible substitutes for cobalt as binder metal phase in WC-based cemented carbides [6–8]. Among all those metals investigated, nickel is an exciting and promising candidate. It is not only because of its good wet ability to WC and relatively lower price than that of cobalt, but also due to the much better performance of WC–Ni cemented carbides in oxidation resistance and corrosion [2] than that of WC–Co cemented carbides. However, the mechanical properties (hardness and strength) of WC–Ni cemented carbides are relatively inferior to those of WC–Co cemented carbides [9].

The proposed ways to overcome the shortcomings of WC–Ni cemented carbides and to improve their performance in previous works [2–16] include two aspects. One, according to Hall–Petch formula, is to try to fabricate sub-micrometer or near-nanometer and even nanometer WC–Ni cemented carbides in the way of inhibiting the growth of WC grains in cemented carbides during sintering [2–14]. Another is to directly increase the strength and/or hardness of cemented carbides by adding some materials with high strength and/or high hardness into the matrix of WC–Ni cemented carbides [15,16].

In order to inhibit the growth of WC grains during sintering, two kinds of approaches have been proposed. One of them is to utilize some rapid sintering methods to shorten the duration of sintering so as to reduce the growth of WC grains [3,10,14]; and the results indicated that the hardness of the obtained WC–Ni cemented carbides was significantly higher than those of both WC–Co and WC–Ni cemented carbides sintered by conventional sintering methods, but the fracture toughness was a little bit reduced. Another is, as in the fabrication of WC–Co cemented

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Table 1
Basic physical and chemical parameters of the used WC powder.

Designation	Distribution by turbid meter (%)		Chemical (wt%)			
	0–1 μm	1–2 μm	Total carbon	Free carbon	Combined carbon	Oxygen
GWC002	97.5	2.5	6.11	0.04	6.07	0.31

carbides, to choose and apply WC grain growth inhibitors into the WC–Ni matrix [11–14]; and previous studies [12–14] proved that the most effective WC grain growth inhibitor in WC–Ni cemented carbides was VC, followed by TaC, Cr_3C_2, TiC and ZrC in sequence.

Using solid solution technology, Correa et al. [15] effectively improved the hardness and strength of WC–Ni cemented carbides by adding SiC powder into WC–Ni cemented carbides. The Vickers hardness of their WC–10 wt% (Ni–Si) cemented carbide was similar to that of conventional WC–Co cemented carbide with the same content of binder metal, and the flexural strength was even higher that that of the later.

Spark plasma sintering (SPS) is a kind of rapid sintering method; it enables the powder compact to be densified by Joule heating when the pulsed direct current goes through the powder sample. Because of the feature of rapid heating and cooling, short holding time and unique consolidation mechanism in SPS processes, the grain growth during sintering can be effectively inhibited [14,17].

Thus, combining with the above methods, the present work tailors the synthesis of WC–Ni cemented carbides by using a rapid sintering method of SPS and applying VC and TaC as WC grain inhibitors to develop ultrafine WC–Ni cemented carbides, trying to obtain a good combination of flexural strength and hardness for WC–Ni cemented carbides.

2. Experimental procedures

2.1. Sample preparation

The raw powders used in this study include WC, hydroxyl-nickel (Ni), VC and TaC, which were all commercially bought industrial reagents. Table 1 lists the basic physical and chemical parameters of the applied WC powder (the main recipe). The fraction of Ni in the cemented carbides was 6–10 wt%; and the fractions of VC and TaC were constantly 0.7 wt% and 0.3 wt%, respectively. The particle sizes of the Ni, VC, and TaC powders were about 0.7, 2–4, and 1–1.5 μm, respectively. The balls for attrition milling were made from cemented carbide YG6 (ISO: K20) and their diameters were about 5 mm.

Owing to its face-centered cubic crystal structure of binder metal Ni, the Ni particle is susceptible to deformation and agglomeration during attrition milling. This would stimulate the formation of pores during sintering [13], which is detrimental for improving the relative density of the sintered samples. Therefore, in the present study, the raw powders were designedly mixed together at different milling stages and milled for disparate durations in absolute alcohol with a high energy attrition mill (Model: SY-1, China). The powder mixture of WC, VC and TaC was milled for 44 h in the first stage at a speed of 300 rpm; after that, the Ni powder was added into the slurry and milled for another 4 h at a speed of 80 rpm. For the milling, the mass ratio of ball to powder was 10:1 and that of powder to absolute alcohol was 3:1. After milling, the mixtures were dried in a vacuum oven with a pressure of 0.01 atm at 35 °C. The dried powder chunks were crashed into fine powder and sieved. After that, the resultant fine powder was loaded in a graphite die and sintered in a SPS oven (SPS-1050T, Japan). For sintering, the initial pressure applied on the graphite die was 30 MPa, the heating rate was 200 °C/min, the sintering temperature was 1350 °C, the duration of sintering was 6 min and the applied sintering pressure was 50 MPa, respectively. After sintering, the cooling rate was the same as that of heating. The sintered specimens were cylinders, and their dimensions were approximately ⌀20 mm (diameter) × 5 mm (height).

2.2. Materials characterization

X-ray diffraction (XRD, D/max2550HB+/PC, Cu Kα and $\lambda = 1.5418$ Å) was utilized to identify the phase composition of the as-prepared cemented carbides through continuous scanning mode with a speed of 5°/min. Three-point bending method was applied to measure the flexural strength of the samples on an AG-IC 20 kN Shimazu tester. The dimension of the testing bars was about 2 mm × 3 mm × 10 mm, and during the testing, the applied load rate was 0.5 mm/min. The microstructure of the specimens was examined on fractured (by LEO 1530 SEM), polished (by SSX-550 SEM), and polished/etched (by LEO 1530 SEM) surfaces, respectively. For the etching, the polished cemented carbide samples were soaked in a Murakami's reagent (1 g potassium ferricyanide, 2 g potassium hydroxide, and 30 g water) for about 2 min at room temperature. The apparent density of the samples was measured with Archimedes method according to international standard (ISO18754), and the relative density was the percentage of apparent density to theoretical density. The bulk Vickers hardness of the samples was evaluated by a LECO DM-400 hardness tester with a 1 kg load and 20 s dwell time. The WC grain size [18] and binder mean free path of the as-prepared samples were calculated by the linear intercept method from the SEM image with a Lince PC software, in which the binder mean free path was defined as the average thickness of the binder phase [19].

3. Results and discussion

3.1. Phase composition and microstructure

Fig. 1 presents the XRD patterns of the as-prepared WC–Ni cemented carbide samples. It reveals that the main phases of the

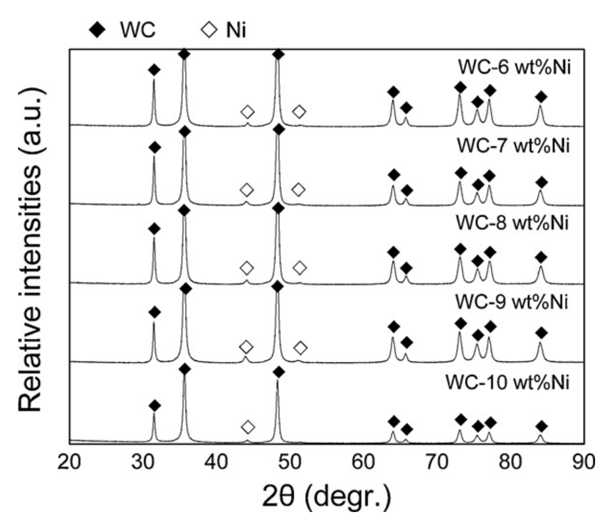

Fig. 1. XRD patterns of the as-prepared WC–Ni cemented carbides samples with different fractions of binder metal Ni.