Effect of Grain Growth Inhibitors on Microstructure and Mechanical Properties of WC-2.5TiC-10Co Ultrafine-Grained Cemented Carbide Postprint

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Abstract

WC-2.5TiC-10Co ultrafine-grained cemented carbide was prepared by a combined method of high-energy ball milling and vacuum hot-press sintering, and the effects of Cr3C2, VC, TaC, and NbC additions on the microstructure and mechanical properties of the ultrafine-grained cemented carbide were investigated using characterization techniques such as X-ray diffractometer (XRD) and field emission scanning electron microscope (FESEM). The results show that: after planetary high-energy ball milling for 30 h at a ball-to-powder ratio of 10:1 and a rotation speed of 350 r/min, the particle size of WC powder decreased from 0.6 mm to less than 0.2 mm; after vacuum hot-press sintering at 1410℃ for 1 h, no new reaction products were detected by XRD. In the cemented carbides with additions of 0.45% Cr3C2, 0.3% VC, 0.5% TaC or NbC, there were a few abnormally grown WC grains, and the fracture surface was porous and flat. Analysis shows that larger WC grains underwent cleavage fracture under the action of stress concentration and became crack initiation sites for material failure. When the content of the inhibitors Cr3C2 and VC was further increased by 0.1%, WC grains could be controlled below 0.5 mm, the fracture surface became dense and exhibited a step-like morphology, and the transverse rupture strength could be increased by 20%; TaC and NbC did not exhibit significant effects on inhibiting WC grain growth, but the addition of NbC was most effective in improving the densification of the cemented carbide.

Full Text

Effects of Carbide Inhibitors on Microstructures and Mechanical Properties of Ultrafine-Grained WC-2.5TiC-10Co Cemented Carbide

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Abstract

Ultrafine-grained WC-2.5TiC-10Co cemented carbides were prepared by high-energy ball milling combined with vacuum hot-pressing sintering. The effects of Cr_3C_2, VC, TaC, and NbC additions on the microstructure and mechanical properties of the ultrafine-grained cemented carbides were investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and mechanical performance testing. The results indicate that after 30 hours of planetary high-energy ball milling at a rotation speed of 350 r/min with a ball-to-powder ratio of 10:1, the particle size of WC powder decreased from 0.6 m to less than 0.2 m. Following vacuum hot-pressing sintering at 1410°C for 1 hour, XRD analysis revealed no formation of new reaction products. In the cemented carbides with additions of 0.45% Cr_3C_2, 0.3% VC, 0.5% TaC, or NbC, a small number of abnormally grown WC grains were observed, and the fracture surfaces appeared loose and flat. Analysis showed that these larger WC grains underwent cleavage fracture under stress concentration, serving as crack initiation sites for material failure. When the contents of Cr_3C_2 and VC inhibitors were further increased by 0.1%, the WC grain size could be controlled below 0.5 m, the fracture surfaces became dense and exhibited step-like features, and the transverse rupture strength increased by 20%. TaC and NbC showed less pronounced effects on inhibiting WC grain growth, though NbC addition was most effective in improving the densification of the cemented carbide.

KEY WORDS metallic materials, powder metallurgy, ultrafine-grained cemented carbide, microstructure, mechanical properties, inhibitor

1. Introduction

Cemented carbides are cermet materials composed of hard refractory metal carbide particles (such as WC) and a ductile metallic binder phase (such as Co), fabricated through high-temperature sintering. These materials exhibit excellent properties including high hardness, high strength, corrosion resistance, wear resistance, and low thermal expansion coefficient, making them widely applicable in metal cutting, precision instruments, dental tools, and wear-resistant components [1-7]. With advances in science and technology, increasingly stringent demands are placed on cutting tools in mechanical machining, and conventional cemented carbides can no longer satisfy these performance requirements. Consequently, the development of novel ultrafine-grained cemented carbide materials has become a major research focus in materials science and engineering. Studies have shown that when the WC grain size in cemented carbides is reduced to the ultrafine range (<0.6 m), both strength and toughness increase simultaneously with decreasing grain size, while hardness is also significantly improved, making them ideal materials for precision cutting tools [1, 8-11].

Cemented carbide tools still occupy an important position in metal cutting applications, but issues such as built-up edge and crater wear frequently occur during cutting processes [10-13]. Recent research has demonstrated that introducing carbides such as TiC, ZrC, TaC, and NbC into conventional WC-Co systems [2, 14-20] (hereinafter denoted as MC for carbides other than WC) can effectively improve the oxidation resistance of cutting tools while enhancing resistance to crater wear and built-up edge formation. This represents an important approach for modifying cemented carbide properties, particularly for high-speed steel machining. However, cost is also a critical factor affecting the industrial application of tool materials. Therefore, TiC is commonly used as an additive in cemented carbides due to its relatively low price. Xiong et al. [2] investigated the wear performance of WC-5TiC-10Co cemented carbide during dry cutting of AISI H13 steel, attributing its excellent machining performance to ultrafine grain structure, high hardness, and low high-temperature softening tendency. Lee et al. [20] prepared WC-TiC-10Co cemented carbides with varying TiC contents and explored the relationship between microstructure and mechanical properties by examining the WC/TiC grain size ratio. Additionally, Weidow et al. [16] added TiC, ZrC, NbC, and TaC separately to WC-Co cemented carbides and fabricated WC-MC-Co ternary system alloys via powder metallurgy, investigating phase boundary segregation in these systems. It is well known that different carbides play distinct roles in cemented carbides. The cutting industry urgently requires new cemented carbide materials with high strength, good hot hardness, and wear resistance. However, introducing only one type of carbide into WC-Co cemented carbides is insufficient to meet multiple performance requirements, particularly regarding the inhibition of grain growth after adding second hard phases such as TiC [20-22]. Therefore, in-depth research on this topic is necessary.

In this study, WC-2.5TiC-10Co cemented carbides were prepared using high-

energy ball milling and vacuum hot-pressing sintering. The effects of high-energy ball milling on the particle size of WC-2.5TiC-10Co composite powders were investigated. By adjusting the contents of Cr_3C_2, VC, TaC, and NbC, the influence of these carbides on the microstructure, mechanical properties, and fracture mechanisms of the cemented carbides was studied, and the inhibitory effects of carbides on abnormal WC grain growth were discussed.

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2. Experimental Methods

The raw materials used in this study were primarily WC, TiC, and Co powders with average particle sizes of approximately 0.6 m, 0.5 m, and 0.3 m, respectively. The grain growth inhibitors Cr_3C_2, VC, TaC, and NbC were nano-sized powders. First, WC and other powders were weighed according to the compositions listed in and placed in cemented carbide milling jars. Anhydrous alcohol and liquid paraffin were added as dispersing media at 40 wt% and 2 wt% of the total carbide powder weight, respectively. The ball-to-powder ratio was set at 10:1. Milling was performed using a planetary ball mill at a rotation speed of 350 r/min for 30 hours. Due to the significant heat generated during high-energy ball milling, the ambient temperature was maintained at -10°C to avoid excessive temperature rise.

After drying, the milled composite powders were placed in graphite dies with an inner diameter of 50 mm, cold-pressed, and then loaded into a vacuum hot-pressing furnace. The furnace was evacuated to 1.0$×10^{-2}$ Pa before heating at a rate of 10°C/min. Hot-pressing was conducted at 1410°C under a pressure of 20 MPa for 1 hour, followed by furnace cooling.

Hardness testing was performed using a KB3000BVRZ-SA universal hardness tester. Transverse rupture strength specimens with dimensions of 4.5 mm × 4.5 mm × 40 mm were tested at a span of 30 mm and loading rate of 1 mm/min using an Instron 1343 hydraulic servo universal testing machine. Phase identification was conducted using an XD-5A X-ray diffractometer (Cu Kα radiation). Microstructural characterization was performed using a Supra 35 field emission scanning electron microscope (FESEM).

2.1 Effect of Ball Milling Parameters on Composite Powder Morphology

[Figure 1: see original paper] shows the morphology of the initial composite powders, where a small number of WC particles larger than 0.6 m can be observed. Since the fabrication temperature for cemented carbides is relatively high, grain growth during processing is inevitable. To obtain cemented carbides with grain sizes below 0.6 m, reducing the raw powder particle size is an effective approach. High-energy ball milling was applied to the WC-2.5TiC-10Co mixture.

After 15 hours of milling, a few particles approximately 1 m in size remained, as shown in [Figure 1: see original paper]b. When the milling time was extended to 30 hours, the composite powder particle size was reduced to below 0.5 m with relatively uniform distribution, as shown in [Figure 1: see original paper]c.

Considering that the crushing efficiency of ball milling might differ for TiC and WC particles, FESEM was used to further analyze the effect of milling on TiC and WC particle sizes, as shown in [Figure 2: see original paper]. The results indicate that most powder particles were approximately 0.2 m in size, and their energy-dispersive spectroscopy (EDS) analysis showed almost no Ti characteristic peaks [Figure 2: see original paper]b, suggesting the main components were WC and Co. However, a small number of particles measuring 0.3–0.4 m were also observed, whose EDS spectra exhibited distinct Ti characteristic peaks [Figure 2: see original paper]c. This demonstrates that after 30 hours of milling, the TiC powder particle size (0.3–0.4 m) was slightly larger than that of WC powder (0.2 m), likely due to differences in wear resistance and impact toughness between TiC and WC powders.

2.2 Properties and Microstructure of Cemented Carbides

Under identical vacuum hot-pressing conditions, the density and mechanical properties of WC-2.5TiC-10Co alloys showed significant variations. presents the measured densities and relative densities (ratio of measured to theoretical density) of the ultrafine-grained WC-2.5TiC-10Co cemented carbides. With the addition of trace amounts of Cr_3C_2 and VC, the density and relative density of Samples 2 and 4 increased noticeably compared to Samples 1 and 3, indicating that Cr_3C_2 and VC as grain growth inhibitors are beneficial for improving the density and densification of cemented carbides. Comparing Samples 1 and 3, as well as Samples 2 and 4, under otherwise identical compositions, the densities and relative densities of alloys containing NbC were higher than those containing TaC. It is known that the formation of a small amount of liquid phase during powder metallurgy can facilitate hot-pressing and densification, as the liquid phase can improve powder plastic deformation and fill pores. The sintering temperature of 1410°C is slightly below the melting point of Co (1495°C), and the Co binder at this temperature can be considered an ideal solution. The addition of carbides such as Cr_3C_2 and VC lowers the liquidus temperature of the Co solution [23]. During the initial stage of high-temperature sintering, the concentration distribution of these carbides in the Co solution is not uniform, and local regions with higher solute concentrations may develop small solid-liquid equilibrium zones. Therefore, the addition of trace Cr_3C_2 and VC enhanced the density and densification of the cemented carbides. When the Co solution contained equal concentrations of TaC and NbC, further increasing the NbC content would increase the liquid phase fraction in the Co solution according to the aforementioned mechanism, thereby generating more solid-liquid equilibrium zones. Consequently, the cemented carbide with NbC addition exhibited

higher density and densification.

[Figure 3: see original paper] shows the HRA hardness and transverse rupture strength of the WC-2.5TiC-10Co ultrafine-grained cemented carbides. Comparing with the compositions in , when the Cr_3C_2 content increased from 0.45% to 0.55% and the VC content from 0.3% to 0.4%, the hardness increase was not significant, but the transverse rupture strength improved substantially. Furthermore, comparing Samples 1 and 3, as well as Samples 2 and 4, the mechanical properties of alloys with TaC addition were slightly higher than those with NbC addition under otherwise identical compositions.

[Figure 4: see original paper] presents the X-ray diffraction patterns of Samples 1–4, showing only diffraction peaks of WC, TiC, and Co. Although Lee et al. [20] observed minor (W, Ti)C formation in WC-20TiC-10Co systems, no reaction products such as (W, Ti)C were detected in this study, likely due to the lower TiC content.

[Figure 5: see original paper] shows FESEM images of the WC-2.5TiC-10Co ultrafine-grained cemented carbides. Due to the lower atomic number of Ti, TiC particles appear darker in backscattered electron images. As shown in [Figure 5: see original paper], black TiC particles are dispersed between WC grains with grain sizes below 0.5 m. When the Cr_3C_2 (0.45%) and VC (0.3%) contents were low, a few abnormally grown WC grains (>0.6 m) were observed, as shown in [Figure 5: see original paper]a and c. Previous studies [24-27] have reported the inhibition effectiveness ranking for WC grain growth as VC > Cr_3C_2 > NbC > TaC > TiC > ZrC. Although the alloy contained 2.5% TiC and 0.5% TaC or NbC, TiC, TaC, and NbC exhibit relatively weak inhibition effects on WC grain growth. The low additions of Cr_3C_2 and VC were insufficient to completely suppress abnormal WC grain growth during hot-pressing sintering. Additionally, comparing the milled powder morphology ([Figure 2: see original paper]) with the sintered microstructure ([Figure 5: see original paper]), TiC did not react significantly.

The fracture surfaces exhibited distinctly different morphologies, as shown in [Figure 6: see original paper]. [Figure 6: see original paper]a and c show low-magnification SEM images of the fracture surfaces of Samples 1 and 3, which appear flat, loose, and rough, with numerous microcracks oriented at various angles to the fracture plane. This indicates that the fracture surfaces formed by the interconnection of numerous microcracks. [Figure 6: see original paper]b and d show low-magnification SEM images of the fracture surfaces of Samples 2 and 4, which exhibit step-like features with clean, dense surfaces and no microcrack formation. Evidently, the step-like fracture surfaces can absorb more energy than flat ones, resulting in higher strength for Samples 2 and 4.

High-magnification FESEM observations of the fracture surfaces are shown in [Figure 7: see original paper]. Unlike the easily observable black TiC particles in [Figure 5: see original paper], few exposed TiC particles are visible on the fracture surfaces because fracture occurred primarily in the Co binder phase,

which enveloped the TiC particles. On the fracture surfaces of Samples 1 and 3, WC grains larger than 0.6 m were observed, which underwent cleavage fracture [Figure 7: see original paper]a and c.

As shown in [Figure 3: see original paper]b, when the Cr_3C_2 and VC additions were increased to 0.55% and 0.4%, respectively, the transverse rupture strength of the WC-2.5TiC-10Co cemented carbide increased by approximately 20%. This strength improvement correlates with the fracture surface characteristics. Previous studies [28] have shown that due to non-uniform size distribution of reinforcement particles in composites, significant stress concentration occurs at larger reinforcement particles under loading, leading to failure of the larger particles or interfacial debonding. In Samples 1 and 3, numerous WC particles larger than 0.6 m were present. Although these coarse WC grains were few in number, they were randomly distributed throughout the alloy. During bending tests, the large WC grains fractured first, forming crack initiation sites. The microcracks generated were randomly distributed within the cemented carbide, and the fracture surface formed by the interconnection of these microcracks, leaving numerous residual microcracks within the material. Consequently, the fracture surfaces of Samples 1 and 3 appeared rough with many microcracks at various angles. Moreover, as WC is a brittle material, the fracture of coarse WC grains exhibited cleavage characteristics, as shown in [Figure 7: see original paper]a and c.

In Samples 2 and 4, the hard phase particles were more uniformly distributed with smaller sizes [Figure 7: see original paper]b and d. No cleavage fracture of hard phase particles was observed, and failure occurred primarily in the Co binder phase, as evidenced by the serpentine slip patterns characteristic of plastic deformation in the binder phase remaining on the hard phase surfaces. The fracture mechanism differed fundamentally from that of Samples 1 and 3. Microcracks likely initiated near the tensile surface of the specimens and propagated inward, ultimately leading to failure, resulting in denser fracture surfaces. It should be noted that the interfacial bonding between the hard phase and Co binder in the WC-2.5TiC-10Co cemented carbide was strong, with virtually no interfacial debonding observed.

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3. Conclusions

1. After planetary high-energy ball milling for 30 hours at a ball-to-powder ratio of 10:1 and rotation speed of 350 r/min, the WC powder particle size could be reduced from 0.6 m to below 0.2 m.

2. Following vacuum hot-pressing sintering at 1410°C under 20 MPa for 1 hour, the relative density of WC-2.5TiC-10Co cemented carbide could reach above 98.9%. Slight increases in Cr_3C_2 and VC contents improved the densification of the cemented carbide.

3. TaC and NbC showed limited effectiveness in inhibiting WC grain growth, but NbC addition was most effective in improving cemented carbide densification. The WC-2.5TiC-10Co ultrafine-grained cemented carbide with 0.5% NbC, 0.55% Cr_3C_2, and 0.4% VC achieved a relative density of 99.91%.

4. In cemented carbides containing 0.5% TaC or NbC, the addition of 0.45% Cr_3C_2 and 0.3% VC grain inhibitors was insufficient to completely control abnormal WC grain growth, resulting in loose and flat fracture surfaces. Analysis revealed that the larger WC grains underwent cleavage fracture under stress concentration, serving as crack initiation sites. When the inhibitor contents of Cr_3C_2 and VC were increased to 0.55% and 0.4%, respectively, the WC grain size could be controlled below 0.5 m, the fracture surfaces became dense and step-like, cracks propagated along the Co binder phase with some plastic deformation characteristics, and the transverse rupture strength increased by 20%.

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Note: Figure translations are in progress. See original paper for figures.