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Zirconia-toughened WC with/without VC and Cr_3C_2

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Abstract

The effects of Cr_3C_2 and VC on densification behavior, grain growth and mechanical properties of the WC-8 wt% ZrO_2 composites were investigated, and the relationship between the mechanical properties and microstructure was studied. The addition of VC and Cr_3C_2 not only retarded densification of the WC–ZrO_2 material, but also significantly suppressed the growth of WC-grains and ZrO_2-particles. For the WC–ZrO_2 composite without VC and Cr_3C_2, microstructure coarsening at elevated temperatures caused degradation in hardness, whereas the hardness maintained a high value of ~22 GPa for the composite with VC and Cr_3C_2 additives as the microstructure remained fine. The fracture toughness of the WC-based materials toughened by 8 wt% ZrO_2 seemed insensitive to the coarseness of microstructure, and achieved a value of ~11 MPa $m^{1/2}$ when VC and Cr_3C_2 were added.

Keywords: Tungsten carbide; Zirconia; Toughening; Microstructure; Grain-growth inhibitor

1. Introduction

WC-based cermets such as WC–Co are widely used in industry as cutting materials because of their excellent wear performance. The addition of Co metallic binder phase to WC considerably facilitates sintering and increases its toughness and strength. However, the hardness and wear resistance of the cemented carbides are inversely proportional to the metallic binder content. Moreover, the metallic binders are inferior to WC in terms of corrosion resistance [1]. In some researches, the Co binder has been replaced by ZrO_2, which also facilitates sintering and increases the toughness of the WC-based composite to a certain extent [2–9]. As a substitute for Co, ZrO_2 possesses some merits. For example, (i) it does not soften at elevated temperatures, (ii) it is resistant to electrochemical corrosion and (iii) it is expected to increase the fracture toughness due to transformation toughening [2,3]. Researches found that the mechanical properties of Y-TZP (Yttrium-cation-doped tetragonal zirconia polycrystals) ceramics can be tailored by modifying the microstructure. For example, the fracture toughness can be changed mainly through altering the grain sizes [10–12]. Similarly, to explore the potential toughening effect of ZrO_2 on WC materials, attention should be attracted to figuring out how the coarseness of microstructure relates to the fracture toughness. In common ways, the microstructure of WC-based materials can be tailored by altering sintering conditions (e.g. sintering temperature, dwelling time) and/or adding grain-growth inhibitors [13–17]. Considering that limited work has been done for this, in the present study we investigate the mechanical properties of WC–ZrO_2 composites with various grain sizes, and examine the effects of Cr_3C_2 and VC on densification behavior, grain growth and mechanical properties of WC–ZrO_2 composites sintered by spark plasma sintering (SPS).

2. Experimental procedure

2.1. Processing

The starting powders were WC (WC, ~0.8 μm, purity > 99.9%, Golden Egret Special Alloy Co. Ltd., China), WC (WCVCr, ~0.2 μm, containing 0.4% VC and 0.8% Cr_3C_2, Golden Egret Special Alloy Co. Ltd., China), VC (~0.8 μm, purity > 99.6%, Shandhai Chaowei Nami Keji Co. Ltd., China), Cr_3C_2 (~0.8 μm, purity > 99.9%, Shandhai Chaowei

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Nami Keji Co. Ltd., China) and ZrO_2 (~0.1 μm, 3 mol% Y_2O_3-stabilized tetragonal ZrO_2, Shanghai Chemson Chemicals Co. Ltd., China). The powder mixture with 98.8 wt% WC, 0.4 wt% VC and 0.8 wt% Cr_3C_2 was named as 08WCVCr, which was mainly used for studying the effects of Cr_3C_2 and VC on densification behavior of the WC-based composites sintered by SPS. WC–ZrO_2 powder mixtures with 92 wt% WC/WCVCr/08WCVCr and 8 wt% ZrO_2 were wet mixed on a planetary ball mill (QM-3SP2, Nanjing NanDa Instrument Plant, China) in ethanol for 30 h using cemented carbide milling balls (ball-to-powder weight ratio was 3:1) and cemented carbide vials (250 mL). To minimize the potential Co contamination from the milling balls or vials, milling was conducted in a low energy mode, in which the milling process paused every 30 min for staying 18 min, subsequently restarted reversely at a constant rotation speed of 180 r/min, and finally stopped after 60 cycles. Furthermore, the milled powders were dried and sieved in order to avoid agglomerates, which may lead to poor sinterability. The obtained WC–ZrO_2 powders were poured into a cylindrical graphite die with inner diameter of Ø20 mm and outer diameter of Ø50 mm. Then sintering was conducted on a Dr. Sinter Model SPS-825 Spark Plasma Sintering System (Sumitomo Coal Mining Co. Ltd., Japan) by spark plasma sintering (SPS) in vacuum ($\leq$ 6 Pa) at 1500–1700 °C for 5 min, with a heating rate of 100 °C/min and an applied pressure of 30 MPa. In the sintering, graphite paper was used to separate the powders from the graphite die or punch, and the die was surrounded by a 10 mm thick porous carbon felt insulation to minimize the radiation heat loss. An infrared pyrometer ($\geq$ 570 °C) was focused on the bottom of a central core hole in the die wall and about 7.5 mm away from the inner wall.

2.2. Density and mechanical property measurement

Based on the Archimedes principle, the sintered density was measured using water. The theoretical densities of the specimens were calculated according to the rule of mixture. The hardness (HV_{10}) was evaluated on a Vickers hardness tester (430SVA, Wilson Wolpert Co. Ltd., China) with a load of 98 N. The fracture toughness (K_{Ic}) was calculated based on the radial crack length produced by Vickers (HV_{10}) indentation, according to Niihara formula [18]. The reported value is the average of the data obtained from five indentation tests for each specimen. The elastic modulus (E) was calculated according to the Reuss rule of mixture [19], using a stiffness of 660 GPa and 200 GPa for pure WC and ZrO_2, respectively.

2.3. Microstructure observation and characterization

The microstructure of polished surface was examined by high-resolution scanning electron microscopy (SEM, Nova Nano 430, FEI, USA). The average grain size of WC matrix and the average ZrO_2-particle size were obtained by measuring over 300 grains/particles using Image-ProPlus software [20].

3. Results and discussion

3.1. Densification behavior

During SPS, the displacement of the lower punch which reflects the densification process of the sample is automatically stored by a record system. Fig. 1 shows the densification curves for the WC–8ZrO_2, 08WCVCr–8ZrO_2 and WCVCr–8ZrO_2 composites that were heated up to 1600 °C. For all of the tests, as the shrinkage rate turns positive, the powders start to densify, which lasts till the shrinkage rate is down to zero again. For the WC–8ZrO_2 composite, the densification process starts at ~780 °C and ends at ~1550 °C. In contrast, the densification processes of the 08WCVCr–8ZrO_2 and WCVCr–8ZrO_2 composite mainly occur from ~920 °C to ~1580 °C and from ~870 °C to ~1600 °C respectively. This indicates that the densification process of the composite is retarded by the VC and Cr_3C_2 additives. The phenomenon that grain-growth inhibitors retard the densification process was also observed in other researches [16,21]. Compared with the

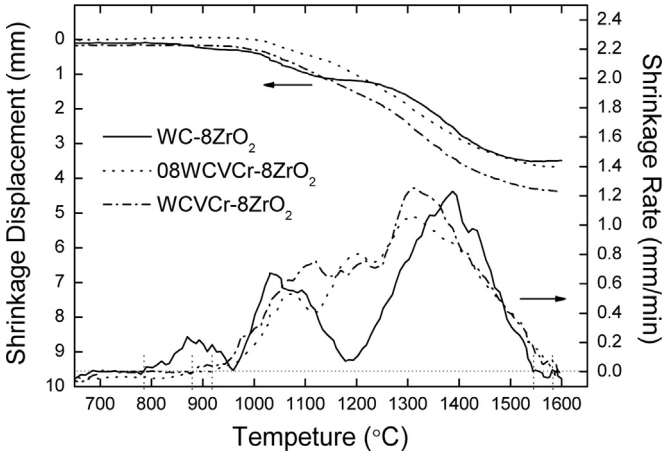

Fig. 1. Densification curves for the WC–8ZrO_2, 08WCVCr–8ZrO_2 and WCVCr–8ZrO_2 composites heated up to 1600 °C.

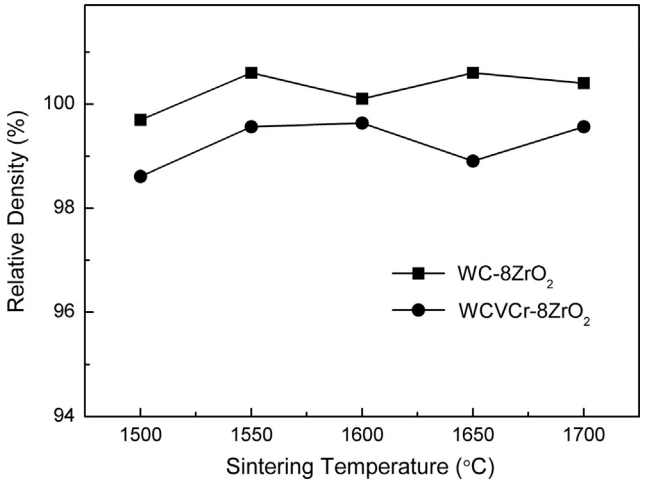

Fig. 2. Relative density of the sintered specimens with/without VC and Cr_3C_2 additives sintered at different temperatures.

08WCVCr–8ZrO_2 composite, the WCVCr–8ZrO_2 composite involves finer starting WC-powders, which can facilitate densification due to higher surface energy [1]. Resultingly, the WCVCr–8ZrO_2 composite shows a little lower starting-temperature of densification.

Dwelling for 5 min, all of the specimens sintered at 1500–1700 °C obtain relative density > 98% based on the calculated theoretical density (shown in Fig. 2). However, the relative density of some specimens exceeds 100%, which indicates that the theoretical density of the composites is underestimated due to the formation of solid solutions in the actual materials [22]. Considering this factor, the relative density for the specimens reported here should be overestimated. Sintering at the same condition respectively, the specimens with VC and Cr_3C_2 additives show a lower relative density than those without VC and Cr_3C_2, which confirms the retarding effect exerted by the grain-growth inhibitors on densification of the WC-based material.

3.2. Microstructure and mechanical properties

Fig. 3 illustrates the microstructure of the WC–8ZrO_2 composite and WCVCr–8ZrO_2 composite sintered at 1500–1700 °C for dwelling 5 min, which mainly consists of bright WC-grains, gray ZrO_2-particles and/or dark pores. Judging from these micrographs, it is intuitive that the microstructure (coarse/fine) of the composite can be tailored by altering sintering temperature and/or adding the grain-growth inhibitors (VC and Cr_3C_2). For the WC–8ZrO_2 composite, the microstructure turns coarser and coarser when the sintering temperature increases from 1500 to 1700 °C, as shown in Fig. 3a–d. When VC and Cr_3C_2 are added, the microstructure

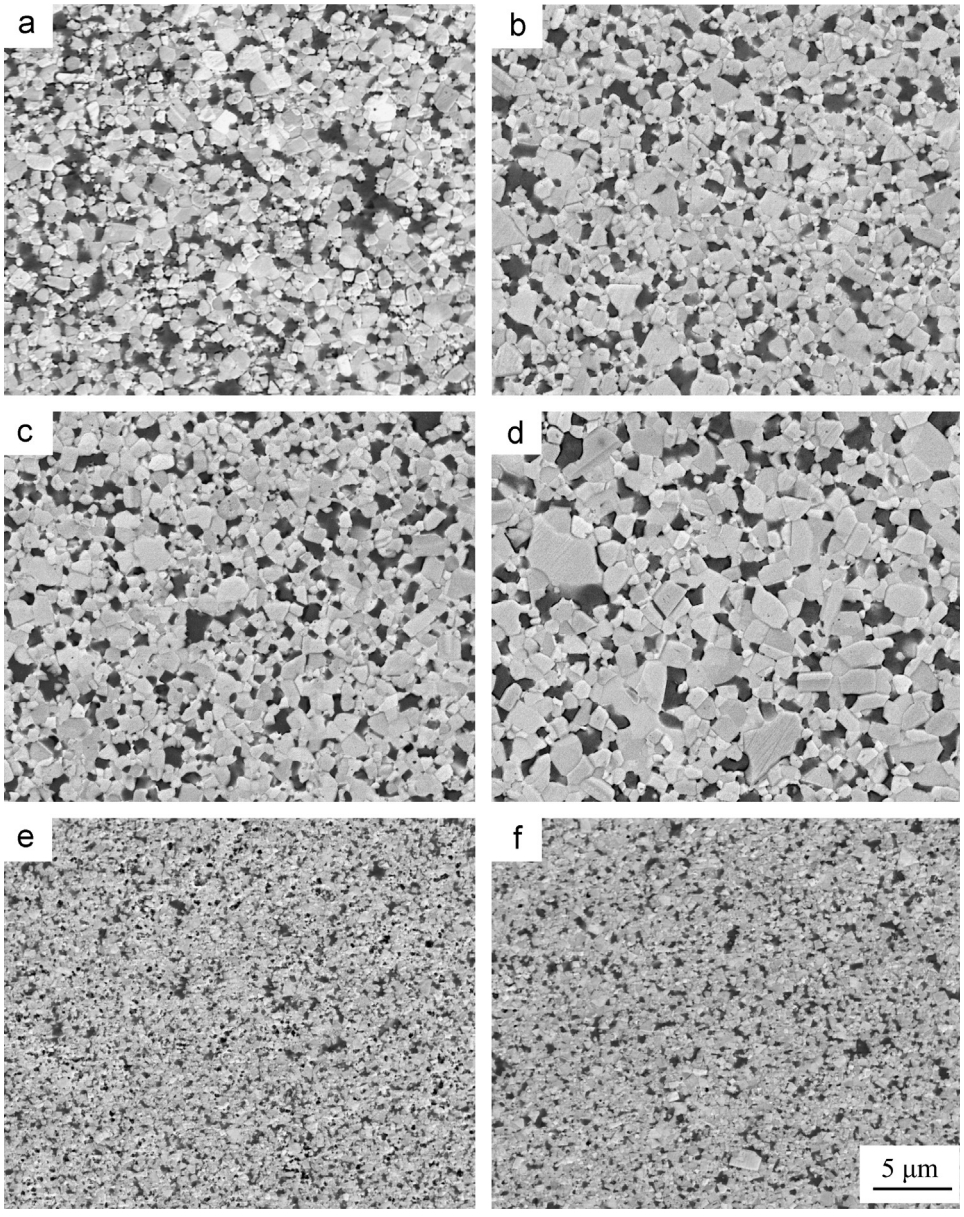

Fig. 3. SEM micrographs of (a) the WC–8ZrO_2 specimen sintered at 1500 °C, (b) 1600 °C, (c) 1650°C and (d) 1700 °C for dwelling 5 min, and (e) the WCVCr–8ZrO_2 specimen sintered at 1500 °C and (f) 1700 °C for dwelling 5 min.

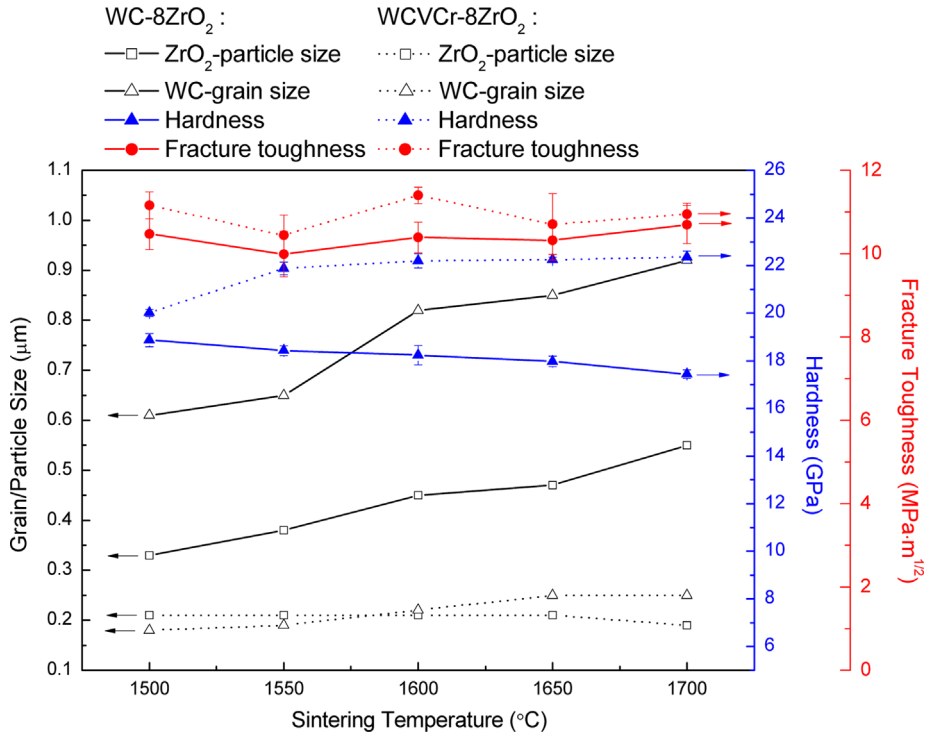

Fig. 4. WC-grain size, ZrO_2-particle size, hardness and fracture toughness versus sintering temperature for the WC/WCVCr–8ZrO_2 composites sintered at 1500–1700 °C for dwelling 5 min.

of the WCVCr–8ZrO_2 composite always remains fine even if it is sintered at 1700 °C for dwelling 5 min. The microstructure of the composites is also numerically denoted by evaluating the average sizes of WC-grains and ZrO_2-particles, as shown in Fig. 4. When the sintering temperature is raised, the sizes of both WC-grains and ZrO_2-particles increase significantly for the WC–8ZrO_2 composite, while the growth of WC-grains and ZrO_2-particles is completely suppressed for the WCVCr–8ZrO_2 composite. For the conventional WC-Co cemented carbides, an often mentioned theory of the way how inhibitors affect the WC-grain growth during sintering is that the inhibitors dissolve in the binder and then segregate at WC grain boundaries, which hinders the dissolution-reprecipitation process of WC grains [13,23,24]. However, in the case of binderless WC-based materials, grain-growth inhibitors cannot dissolve into the metal binder phase or influence the reprecipitation of dissolved WC. In some early researches, grain-growth inhibitors were found to be enriched at WC-grain boundaries and assumed to alter the surface and interface energy of WC grains by segregating at WC–WC grain boundaries [15,16,25], which resulted in a decreased rate of grain growth during the sintering of binderless WC-based materials.

With different sintering conditions and/or grain-growth inhibitors addition, the WC–ZrO_2 composites obtain varied hardness and fracture toughness, which are shown in Fig. 4. As expected, the hardness of the WC–8ZrO_2 composites decreases gradually with increasing sintering temperature because the microstructure turns coarser. For the WCVCr–8ZrO_2 composites, the hardness is almost independent of the sintering temperature unless when it reaches 1500 °C. As shown in Fig. 3e, a few pores are still observed in the specimen sintered at 1500 °C, which results in lower hardness. Even after sintered at 1700 °C for dwelling 5 min, the hardness of WCVCr–8ZrO_2 specimen still maintains ~22 GPa, which is much higher than ~17.5 GPa for the WC–8ZrO_2 composite. The higher hardness is undoubtedly attributed to the suppression of microstructure coarsening, which results from the use of starting powders containing Cr_3C_2 and VC.

In comparison with the fracture toughness of 4–6 MPa $m^{1/2}$ for pure WC [26–29], that of WC–ZrO_2 composites was reported to significantly increase to ~10 MPa $m^{1/2}$ due to a dominant toughening mechanism of transformation [8,9]. In this study, the highest fracture toughness obtained for the WC–ZrO_2 composites is 11.4 ± 0.2 MPa $m^{1/2}$. However, it is somewhat unexpected that the fracture toughness of the composites is nearly unchanged with varied coarseness of microstructure, while the fracture toughness increases with increasing grain size in Y-TZP ceramics [10–12]. About the toughening contribution by transformation of t→m-ZrO_2, it is directly proportional to the volume fraction of the transformed tetragonal phase, the critical transformation stress and the transformation zone size [11]. Generally, the volume fraction of the transformed tetragonal-phase increases with the increase of the transformation zone size which is determined by the critical transformation stress. For a given composition and testing temperature (where $T > M_s$), an often mentioned opinion is that larger tetragonal zirconia grains have a greater propensity to undergo the stress-induced t→m transformation due to a higher martensite start temperature M_s for the transformation, resulting in a lower critical transformation stress [11,30,31]. However, at a certain temperature (e.g. room temperature),

there exists a critical inclusion/grain size, below which t-ZrO_2 can be retained and above which it cannot [30]. That is to say, as the ZrO_2-particlse size increases, the volume fraction of retained t-ZrO_2 in material may decrease. To explain the experiment result that the fracture toughness of the WC–8ZrO_2 composites is nearly constant with coarsening in microstructure, we surmise that the decreasing volume fraction of retained t-ZrO_2 compensates for the increasing transformation zone size that resulted from a lower critical transformation stress. The fracture toughness of the WCVCr–8ZrO_2 composites is a little higher than that of the WC–8ZrO_2 composites, which is supposed to due to the much finer grain size of the matrix [32,33].

4. Conclusions

WC–ZrO_2 composites with various coarseness of microstructure treated at different sintering temperatures and/or incorporating VC and Cr_3C_2 additives were prepared by spark plasma sintering. The addition of VC and Cr_3C_2 not only retarded densification of the WC–ZrO_2 material, but also significantly suppressed the growth of WC-grains and ZrO_2-particles. For the WC–8ZrO_2 composite without VC and Cr_3C_2, microstructure coarsening at elevated temperatures caused degradation in hardness, whereas the hardness maintained a high value of $\sim$22 GPa for the WCVCr–8ZrO_2 composite as the microstructure remained fine. The fracture toughness of the WC-based materials toughened by 8 wt% ZrO_2 in this study seemed insensitive to the coarseness of microstructure, and achieved a value of $\sim$11 MPa $m^{1/2}$ while VC and Cr_3C_2 were incorporated.

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