ARTICLE IN PRESS

Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Fabrication of dense nano-laminated tungsten carbide materials doped with Cr_3C_2/VC through two-step sintering

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ARTICLE INFO

Keywords:
TSS
FGM
Cr_3C_2/VC
Mechanical properties

ABSTRACT

This work investigates the critical roles of two-step sintering (TSS) and laminated structure on the sintering behavior and mechanical properties of functionally graded WC-TiC-Al_2O_3 nanostructured composite materials doped with Cr_3C_2/VC. Results show that excellent mechanical properties are achieved for tailored TSS conditions with a hardness of 27.91 ± 2.3 GPa and a flexural strength of 1423.3 ± 23.5 MPa. The desirable mechanical properties are attributed to the suppressed grain growth without densification deterioration. TSS is more effective in facilitating the favorable dispersion of secondary phase toughening nano-particulates in a WC matrix than conventional sintering (CS). Cr_3C_2/VC dopant plays an important role in maximizing and shifting the temperature range of the kinetic window for WC-Al_2O_3 composites. Al_2O_3 crack deflection, transgranular Al_2O_3, microcracking, WC crack bridging and plate-like WC crack deflection are the major toughening mechanisms. Residual surface compressive stress induced by the graded structure is also an appreciated contribution to the improvement of mechanical properties.

1. Introduction

WC-Co cemented carbides, dubbed “teeth of industry”, is the most important industrial tool material widely used in metal machining, rock drilling, construction, and a wide range of engineered applications requiring both extreme wear and impact resistance [1–3]. Though facilitating the sintering compact to realize a fully dense bulk and rendering the alloys excellent strength and toughness, the addition of metal binder phase as Co, Ni or Fe yields the deterioration in hardness, oxidation/corrosion resistance along with elevated temperature performance [4,5]. Furthermore, it is easy to generate thermal stress due to the thermal expansion misfit. When machining metal with high plasticity as such pure iron using conventional WC-Co cemented carbide, chip tends to adhere on the rake face of cutting tool, resulting in serious adhesive wear due to the existence of cobalt with low melting point. It is suggested that the acute pulmonary toxicity including macrophage toxicity of WC and Co mixture is higher than that of single WC and Co, so human health may suffer hazard in the process of fabricating conventional cemented carbides [6]. This issue is exacerbated when cobalt resources may face depletion and economic crises for cobalt occurred because of the excessive development for growing application of cobalt for rechargeable accumulators (batteries) and in super-alloys for high-performance jet turbines. Therefore, because of its industrial essentiality, such as high-end optical components [7] sliding mechanical cushions [5], massive efforts have been performed to consolidate tungsten carbide comprising low content or no metal binder phase, but possessing exceptional combination of desired hardness, toughness, oxidation and corrosion resistance in recent years [8,9].

However, monolithic tungsten carbide is not suitable to be applied as high-speed cutting tools due to its poor shock resistance, ductility and fracture toughness. Al_2O_3 and TiC may be ideal substitutes for metal binder phase to facilitate the WC compact sintering and avoid the drawbacks for metal binder phase addition, so as to enhance the performance of hardmetals with better reliability advancing them to further wide applications, and prepare the hardmetals in a way that is environment friendly, harmless to human health and low in production cost. As a carbide binder, TiC improved the hardness of WC-based composites by the formation of WC-TiC cubic solid solution phase [10,11]. On the other hand, TiC can result in the formation of plate-like WC grains to a certain extent for the reason that the anisotropic and precipitation of W atoms in the carbide binder phase can substantially weaken the function of the grain growth inhibition [12]. Furthermore, oxidation resistance of WC-based composites can be significantly enhanced by the addition of TiC [13]. As an oxide binder, adding Al_2O_3 to

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https://doi.org/10.1016/j.jeurceramsoc.2018.02.037
Received 21 September 2017; Received in revised form 5 February 2018; Accepted 28 February 2018
0955-2219/

WC ceramics gives rise to an improvement in the fracture toughness because that Al_2O_3 additives facilitate sintering and suppress the formation of W_2C [14]. Besides this, it is proffered by Shon et al. [15] that Al_2O_3 played a beneficial role in inhibiting the grain growth of WC.

Recent advances associated with grain size refinement especially nanocrystalline grain structure can assist in significant property improvements [16,17,18]. Many studies have brought forth that Hall-Petch-like relationship is applied to polycrystalline WC and the effective inhibition of grain growth is crucial for the hardness enhancement of WC polycrystalline ceramics [19]. However, rapid growth is always inevitable for nanosized powders during conventional sintering. The addition of grain growth inhibitors, such as vanadium carbide (VC) and chromium carbide (Cr_3C_2), are considered as the most feasible approach to inhibit WC grain growth.

On the other hand, the grain growth may well be impeded to some degree by employing suitable sintering methods at relatively lower temperature and/or higher sintering rate [20], such as in two-step hot-pressing employing external pressure [21], spark plasma sintering [22] or plasma pressure compaction [23]. However, it is not affordable to most researchers and the associated equipment is not sufficiently demonstrated at the industrial level. Two-step sintering (TSS) methodology, put forward by Chen and Wang [24] as a promising approach to obtain high-density final sintered compact with nano-sized grains, has been widely applied to plenty of materials such as Al_2O_3-based nanoceramics [25], Y_2O_3 [26], SiC nanostructured ceramics [27], $BaTiO_3$ nanometric composition [28] and so on. It is proposed that temperature interval exists between when grain boundaries migration start and densification occurs [29]. According to the TSS methodology, the green body would be heated to a high temperature and then immediately cooled to a lower temperature with a long soaking time.

Functionally graded materials (FGMs) can be another feasible method to the balance between the wear resistance and the fracture toughness [30,31]. In the present research, by employing two-step hot-press sintering, functionally graded WC-TiC-Al_2O_3 nanosized composite materials were fabricated with the auxiliary of combined grain growth inhibitors (Cr_3C_2 and VC) and dispersant (PVP and PEG). The effects of two-step sintering on the microstructure and mechanical properties of the developed WC-based composites were investigated.

2. Experimental procedure

2.1. Preparation

The starting materials utilized in the present study were all commercially available, including tungsten carbide (WC), titanium carbide (TiC), vanadium carbide (VC), chromic carbide (Cr_3C_2), Aluminum Oxide (Al_2O_3), PVPK-12 and PEG powders. Their corresponding specifications are listed in Table 1. The compositions of powder mixtures for designed WC-based ceramics are given in Table 2. In this paper, the starting materials were first ultrasonically dispersed by PVPK-12 and PEG in absolute alcohol for 3 h maintaining a temperature of 80 °C. After dispersing, the mixed slurries were milled for 56 h in a high energy attrition mill with cemented carbide milling ball and absolute ethanol medium. The processing parameters of ball milling are demonstrated in Table 3.

Table 2
Compositions of powder mixtures for designed samples (wt.%).

Composites	WC	Al_2O_3	TiC	Cr_3C_2	VC
Surface layer	94	3	2	0.6	0.4
Interlayer	89	6	4	0.6	0.4
Core layer	84	9	6	0.6	0.4

Table 3
The processing parameters of ball milling.

Milling drum diameter/m	Rotational speed/ r/min	Ball-to-powder mass ratio	Liquid-to-solid mass/ml:kg
0.15	70	15:1	200

2.2. Sintering and characterization

The powder mixtures were loaded into a circular die (42 mm in diameter) in the following order: surface layer mixtures, interlayer mixtures, core layer mixtures, interlayer mixtures and then surface layer mixtures. Finally, the composite powders were sintered by two-step hot-pressing in an inductive hot-pressing vacuum furnace (Model: ZRC85-25T, China). Fig. 1 illustrates one example of the two-step sintering trajectories.

The flexural strength of the specimens was performed on a WDW-50E tester by employing a three-point bending method with a 0.5 mm/min loading rate and a 14.5 mm span. The hardness (HV_{10}) was measured employing a Vickers indenter (Model: MHVD-30AP, China) with a load of 98N [32–34] and a duration time of 15 s using a diamond frustum of rectangular pyramid indenter with an opposite angle of 136°.

The microstructures of the samples were observed by a scanning electron microscope (SEM, QUANTAFEG 250, FEI Inc., USA) and the element distribution was investigated by energy dispersive spectroscopy (EDS, X-MAX30, Oxford Instruments Inc., UK). X-ray diffraction (XRD, D8ADVANCE, Bruker AXS Inc., Germany) were determined to characterize the phase identification of the specimens. The surface residual stress was measured by X-stress (XSTRESS 3000 ×, G2R system, Stresstech Oy Inc., Finland). The principle of X-ray measurement is based on Bragg's law, the sine-square-psi (sin2Ψ) method. CrKα radiation and 138.5° diffraction angle were chosen. The residual stress was measured at five different locations in two perpendicular directions.

3. Results and discussion

3.1. Determination of two-step sintering process

It is claimed by Chen et al. [24] that the choices of first-stage temperature T_1 and second-stage temperature T_2 are essential to the success of TSS. The effects of sintering temperature on the relative density and WC average grain size of so-designed composites consolidated by different conventional sintering process are demonstrated in Fig. 2. Though combination of Cr_3C_2 and VC was added, WC average grain size increased gradually with the densification process in case of CS conditions. The relative density enhanced from 82.3% to 92% and WC average grain size increased from 275 nm to 310 nm as the sintering temperature increased from 1600 °C to 1700 °C, indicating that the

Table 1
Specifications of starting materials used for the preparation of WC-based ceramics.

	WC	Al_2O_3	TiC	VC	Cr_3C_2	PVPK-12	PEG
Purity (wt.%)	> 99.9%	> 99.9%	> 99.8%	> 99.9%	> 99.9%	> 99.9%	> 99.9%
Particle size	300 nm	100 nm	40 nm	80 nm	100 nm	–	–