



Pressureless sintering of titanium carbide doped with boron or boron carbide



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ABSTRACT

Titanium carbide ceramics with different contents of boron or B₄C were pressureless sintered at temperatures from 2100 °C to 2300 °C. Due to the removal of oxide impurities, the onset temperature for TiC grain growth was lowered to 2100 °C and near fully dense (>98%) TiC ceramics were obtained at 2200 °C. TiB₂ platelets and graphite flakes were formed during sintering process. They retard TiC grains from fast growth and reduced the entrapped pores in TiC grains. Therefore, TiC doped with boron or B₄C could achieve higher relative density (>99.5%) than pure TiC (96.67%) at 2300 °C. Mechanical properties including Vickers' hardness, fracture toughness and flexural strength were investigated. Highest fracture toughness (4.79 ± 0.50 MPa m^{1/2}) and flexural strength (552.6 ± 23.1 MPa) have been obtained when TiC mixed with B₄C by the mass ratio of 100:5.11. The main toughening mechanisms include crack deflection and pull-out of TiB₂ platelets.

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1. Introduction

Titanium carbide (TiC) is an important ceramic material for applications in various extreme environments due to its high melting point, excellent chemical resistance, high hardness, good thermal conductivity and good corrosion resistance [1,2]. It shows potential applications in many fields, including cutting tools, aerospace engineering, nuclear reactors and so on [3–7].

However, the densification of TiC is difficult, which greatly limits its applications. Its poor sinterability is mainly attributed to three reasons: its low self-diffusion coefficient is unfavorable to mass transfer; the rapid grain growth at high temperatures leads to entrapped pores in grains; the oxide impurity in powder inhibits the densification [8]. In previous studies, hot pressing (HP) or spark plasma sintering (SPS) technique were used for compacting monolithic TiC ceramics. Ono et al. obtained TiC ceramics with relative density of 98% by hot pressing (2000 °C, 40 MPa) [9]. Cheng et al. got near fully dense monolithic TiC ceramic by SPS at 1600 °C with 50 MPa applied pressure [10]. The relative density of TiC ceramic

prepared by diffusion reaction of carbon into titanium with SPS was only 85% and a tiny content (2–3 vol%) of residual carbon existed [11]. Besides monolithic TiC ceramic, TiC based ceramics toughened and strengthened with particles or fibers (such as ZrC [3], graphite [9], fiber [12], SiC [13–15]) were also usually obtained by SPS or HP. All these results indicated that high pressure and temperature could provide enough driving force for densification of TiC based ceramics. But HP and SPS methods, cannot fabricate components to near-net shape and cost more than pressureless sintering (PLS). The applying of PLS in TiC based ceramics can make them became more economical and widely used.

Unfortunately, pressureless sintering of TiC based ceramics has been few investigated. The reasons of its poor sinterability are similar to that of other carbide ceramics. Referring to pressureless sintering of other carbide ceramics, such as ZrC, HfC, TaC and SiC, using ultrafine starting powders and introduction of sintering aids were effective. Liu et al. achieved densification of HfC (relative density 96.7%) [16] and TaC (relative density 97.5%) [17] at 2300 °C without applied pressure by using ultrafine starting powders. Zhao et al. [8] obtained near fully dense ZrC based ceramics via high-energy ball milling as well as introduction of graphite and SiC as sintering additives. Sciti et al. [18] showed that 5–20vol% MoSi₂ could be effective to densify HfC at relatively low temperature due to the formation of liquid phase. But the mechanical properties decreased with more MoSi₂. Pressureless sintering of SiC could be

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achieved with liquid-phase forming additives, like Al_2O_3 [19]. Some reactive additives (such as boron, carbon or boron carbide) also promoted densification by removing oxides (especially the oxide scale on the surface) in raw SiC powders [20,21].

Based on the above discussion, liquid-phase forming additives or reactive additives may be useful to achieve pressureless sintering of TiC ceramics. The objective of this work is to find proper sintering aid to achieve the densification of TiC based ceramics at relatively low temperature without applied pressure. In this paper, boron carbide and boron were used as the sintering aids for pressureless sintering of TiC ceramics. The influence of sintering temperatures and aids' amounts on densification behavior, microstructure evolution and mechanical properties were investigated.

2. Experimental procedures

The raw materials were titanium carbide (SICCAS, purity >99%, mean diameter $\sim 0.56 \mu\text{m}$), boron carbide (Jingangzuan Boron Carbide Co. Ltd. Mudanjiang, China, purity >96%; mean diameter $\sim 1\text{--}2 \mu\text{m}$), boron (Japan Pure Chemical Co. Ltd, Japan, purity >99%; mean diameter $\sim 1\text{--}2 \mu\text{m}$). Fig. 1 shows the SEM images of raw materials.

In this study, 0.5, 1, 2 and 4 g boron were added into 100 g TiC, named as TB0.5, TB1, TB2 and TB4 (TBx), respectively. Similarly, 0.64, 1.28, 2.55 and 5.11 g boron carbide were mixed with 100 g TiC, the corresponding samples were designed as TBC0.5, TBC1, TBC2, TBC4 (TBCx). These two groups have same amount of boron element. The raw mixtures were ball-milled in ethanol at a speed of 300 rpm for 5 h, using ZrO_2 balls as the mixing media. The slurry was dried at 60°C in a rotary evaporator and sieved through a 200 mesh screen. Then, powder mixtures of about 15 g were pressed at 20 MPa and then cold isostatic pressed at 200 MPa. The samples were heated (in vacuum, $\sim 10 \text{ Pa}$) and sintered at $2100^\circ\text{C}\text{--}2300^\circ\text{C}$ for 1 h (under flowing argon) in a graphite furnace (MRF3338, Materials Research Furnaces Inc., Suncook, USA).

The bulk densities were measured by the Archimedes' method. The phase composition was examined by X-ray diffraction (XRD; D/max 2550 V, Rigaku Corporation, Tokyo, Japan). Microstructural observations were performed using scanning electron microscopy (SEM; TM3000, Hitachi, Japan) and transmission electron microscopy (TEM; Tecnai-F20, FEI Co., USA). Flexural strength via four-point bending was tested on $2 \text{ mm} \times 2.5 \text{ mm} \times 25 \text{ mm}$ bars with a speed of 0.5 mm/min. Vickers' hardness and fracture toughness were performed using the Vickers indentation method at a load of 9.8 N and a dwell time of 10 s. The fracture toughness could be calculated by Eq. (1):

$$K_{\text{IC}} = P \left(\pi \left(\frac{C_1 + C_2}{4} \right) \right)^{-\frac{3}{2}} \tan(\beta)^{-1} \quad (1)$$

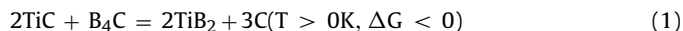
Where P is the indentation load (N), C_1 and C_2 are the measured diagonal crack lengths (m), and β is an angle constant (68°).

3. Results and discussion

3.1. Reaction processes and phase compositions

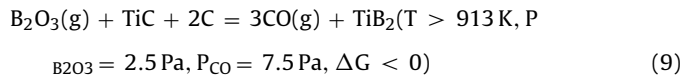
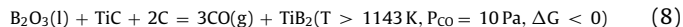
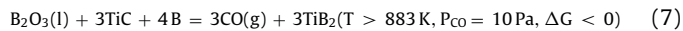
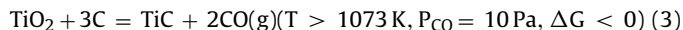
Fig. 2 shows the X-ray diffraction analysis of different samples after being heated to $800\text{--}1900^\circ\text{C}$ without holding time. The diffraction peaks of TiB_2 began to appear at 1300°C in TiC/ B_4C system and at 1000°C in TiC/B system. With the increase of temperatures, the diffraction peaks of TiB_2 became stronger. TiB_2 was mainly resulted from reactions (1) and (2), which were consistent with thermodynamic data compiled by HSC6.0 (a commercial software program, HSC Chemistry, Fairfield, CA, USA). Same reactions

also happened in hot-pressed $\text{B}_4\text{C}/(\text{W,Ti})\text{C}$ composites at 1850°C [22] and in TiC/B composite powders at 1000°C [23].



There was no trace of graphite. One possible reason is that the amount of graphite was too little to be detected. Another reason should be the formed carbon was in amorphous state before sintering temperatures. To identify the existing state of carbon, the powders before and after heat treatment at 1900°C were observed by HRTEM and are shown in Fig. 3. There was amorphous layer (AL) on raw TiC particles (Fig. 3a). EDS result indicated that this amorphous zone contained titanium, carbon and much oxygen. This is a common feature of non-oxide ceramic powders. Though heated to 1900°C , it was still existed (Fig. 3b).

With moderate amount of B_4C or B, the amorphous scale (assumed as TiO_2) could be removed thoroughly (Fig. 3c) via two reaction process models (shown in Fig. 4). Based on XRD results, the reaction was mainly happening at $1000^\circ\text{C}\text{--}1500^\circ\text{C}$ in vacuum environment. Since the diffusion of carbon is faster than boron [24,25], carbon diffused rapidly from boron carbide into oxide scale and removed oxide impurity during the initial stage via reaction (3). Then the boron atoms diffused into TiC and reaction (1) occurred. As a result, there was few B_2O_3 formed during sintering process. When the additive was boron, it diffused into amorphous layer and TiO_2 was initially reduced according to reactions (4)–(6), which had previously been confirmed by Guo et al. [26]. Wang et al. [23] also reported TiBO_3 was formed by B and oxide impurities in TiC/B system and was consumed by further reacting with boron. After the oxide scale being exhausted, reaction (2) occurred. On the other hand, newly formed B_2O_3 existed as liquid phase and began to evaporate at high temperature ($>1300^\circ\text{C}$) [26,27]. It was consumed by reacting with TiC, residual boron and C (originated from reaction (2)), as shown in reactions (7)–(9).



However, with more additions, more carbon was produced and tended to be existed as graphite layer on the surface of TiC particles in both two systems (Fig. 3d and f). Consequently, carbon formed in TiC– B_4C and TiC–B systems during temperature rising process could be confirmed to be graphite, which was agreed with the result reported by Sigl [28].

Moreover, Ti–B–C phase diagram [29] shows that TiB_2 and C are stable with TiC at sintering temperatures. It is easily found dispersed graphite flakes on the typical fracture surfaces of TB4 and TBC4 sintered at 2300°C (Fig. 5c–d). Therefore, the samples doped with boron or boron carbide actually consisted of TiC– TiB_2 –C. Assuming all additives were consumed by reactions (1) and (2), the theoretical phase compositions of all specimens are listed in Table 1. Apparently, these two groups had same amount of TiC and TiB_2 , while TBCx had more graphite than TBx.

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