



# Effects of synthesis temperature and Fe catalyst amount on the performance of in situ CNTs/TiB<sub>2</sub> composites

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## ABSTRACT

Carbon nanotubes (CNTs) were synthesized in situ over TiB<sub>2</sub> powders by using a Fe catalyst at temperatures ranging from 800 °C to 1000 °C. The CNT(Fe)–TiB<sub>2</sub> composites were then successfully consolidated by spark plasma sintering. Results indicated that CNT(Fe)–TiB<sub>2</sub> composites with 20 wt% Fe sintered at 1400 °C for 5 min provided the optimal combination of dense microstructures and excellent properties. These properties included the following: relative density, 97.3%; flexural strength, 985 ± 48 MPa; and fracture toughness, 11.8 ± 0.4 MPa m<sup>1/2</sup>. Retention of the perfect structure and homogenous dispersion at the molecular level of CNTs in TiB<sub>2</sub> matrix were identified as the main factors that contribute to the marked improvement of the mechanical properties of the composites.

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## 1. Introduction

Titanium diboride (TiB<sub>2</sub>) exhibits high refractoriness, good mechanical properties, chemical stability, superior thermal performance, and electrical characteristics [1,3]. These features are suitable for high-temperature structural applications, armors, refractory linings, cutting tools, electrodes, and microelectronics [4,5]. Owing to high melting point, strong covalent bonding, low self-diffusion, and presence of oxide on the surface of particles, densification of TiB<sub>2</sub> requires extremely high temperatures (>2000 °C) and external pressure; these requirements result in abnormal grain growth and microcracks, which harm the mechanical properties of the material [6,8]. Recent studies have demonstrated that high-density TiB<sub>2</sub>-based materials can be obtained at temperatures below 2000 °C by using various sintering additives. In the study by Namini et al. [9], a TiB<sub>2</sub>–(20 vol%)SiC ceramic with 98% of theoretical density was prepared by hot pressing at 1850 °C, with a holding time of about 2 h. Raju et al. [10] fabricated TiB<sub>2</sub>-based ceramics containing 2.5 wt% MoSi<sub>2</sub> by hot pressing at 1700 °C for 1 h; they reported that nearly full densification (>99%) could be achieved. Wu et al. [11] examined the densification, sintering reactions, and properties of TiB<sub>2</sub> with a high

volume fraction of Fe–Ni as an additive. They obtained a density of 98% with 35 vol% of Fe–Ni by vacuum pressureless sintering at 1700 °C for 1 h. However, intrinsic brittleness impedes the wide application of TiB<sub>2</sub>-based ceramics.

To overcome this limitation, a second phase with toughening capabilities (such as particles, whiskers, and fibers) has been introduced, with the aim of improving the mechanical properties of the materials [12,13]. However, the fracture toughness of TiB<sub>2</sub>-based ceramics is enhanced, but still does not exceed 6.0 MPa m<sup>1/2</sup>, which is not high to safely use in structural applications. Owing to their distinct properties, carbon nanotubes (CNTs) with an obvious aspect ratio have been proved to reinforce composites, particularly ceramic–matrix composites, such as ZrC [14], ZrO<sub>2</sub> [15], Si<sub>3</sub>N<sub>4</sub> [16], B<sub>4</sub>C [17], and Al<sub>2</sub>O<sub>3</sub> [18]. And CNTs have been successfully used to reinforce TiB<sub>2</sub> in our previous studies [19]. Results indicated that by spark plasma sintering, optimal properties of TiB<sub>2</sub>–15 vol% CNTs were achieved, as follows: flexural strength, 741 MPa; fracture toughness, 9.1 MPa m<sup>1/2</sup>; hardness, 23.4 GPa; and relative density, 98.9%. However, obtaining the uniform dispersion of CNTs in the TiB<sub>2</sub> matrix remains a challenge. CNTs lead to agglomeration at the TiB<sub>2</sub> grain junctions, hampering the improvement of the mechanical properties of TiB<sub>2</sub>–CNT composites. Consequently, clustering and agglomeration of CNTs should be avoided during the synthesis of TiB<sub>2</sub>–CNTs composites.

This study is the first to present the in situ synthesis, rather than the conventional powder mixing, of CNTs in TiB<sub>2</sub> matrix by using Fe

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as the catalyst. Therefore, effective dispersion of CNTs within the TiB<sub>2</sub> matrix can be obtained. Meanwhile, Fe has been proved to be an effective sintering aid that can facilitate the formation of ceramics by decreasing the sintering temperature [11,20]. CNT(Fe)–TiB<sub>2</sub> composites with high mechanical properties are assumed to be related to the shape and dispersion of CNTs. This study evaluates the effects of synthesis temperature and Fe content on CNT growth by chemical vapor deposition. Dense CNT(Fe)–TiB<sub>2</sub> composites are produced by pressing and spark plasma sintering as-prepared powders.

## 2. Experimental procedures

Fe-catalyzed TiB<sub>2</sub> was prepared by directly mixing and dissolving Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98.5%, analytical reagent, Sigma–Aldrich) and TiB<sub>2</sub> powder (1–2 μm, purity > 99.9%, Shanghai ST-Nano Science & Technology Co. Ltd., China) in 1 L of distilled water to yield final Fe weight content in Fe/TiB<sub>2</sub> = *x* wt% (*x* = 5, 10, 15, 20, 25, and 30). NaOH (0.8 g, 0.02 mol, 99.9% purity) was dissolved in 500 mL of distilled water and then added to the mixture with constant stirring to obtain a binary colloid (Fe(OH)<sub>3</sub>–TiB<sub>2</sub>). The colloid was then filtered several times with distilled water until neutral pH was reached and dried in a vacuum furnace at 80 °C for 24 h. The colloid was subsequently calcined in N<sub>2</sub> at 400 °C for 2 h to obtain fine Fe<sub>2</sub>O<sub>3</sub>–TiB<sub>2</sub> composite powders and then sieved through a 100-mesh sieve. CNTs were produced using the CVD system (OTF-1200X-4-C4LVS, HF-Kejing Materials Technology Co. Ltd., China). To synthesize the CNTs, 40g Fe<sub>2</sub>O<sub>3</sub>–TiB<sub>2</sub> catalyst precursor distributed in a quartz boat was placed into a horizontal tube. The quartz tube, mounted in an electrical tube furnace, was heated to the prescribed reduction temperature in N<sub>2</sub> atmosphere (300 mL min<sup>-1</sup>, 99.99% purity). To convert the iron oxides to elementary Fe, the catalyst was reduced at 600 °C in hydrogen (100 mL min<sup>-1</sup>, 99.99% purity) for 2 h. Hydrogen flow was stopped, and the CVD was carried out at the synthesis temperature (800 °C, 850 °C, 900 °C, 950 °C, or 1000 °C) under N<sub>2</sub>. A mixture of CH<sub>4</sub>/N<sub>2</sub> (150/300 mL min<sup>-1</sup>, v/v, all with 99.99% purity) was introduced into the tube and then maintained for 2 h. After the growth, the furnace was cooled to room temperature under N<sub>2</sub> protection, and black powder was obtained. Carbon yield was calculated as follows:

$$\text{Carbon yield (\%)} = \frac{m_1 - m_2}{m_1} \times 100\% \quad (1)$$

where *m*<sub>1</sub> is the weight of the as-prepared product (g), and *m*<sub>2</sub> is the weight of the Fe–TiB<sub>2</sub> catalyst (g).

The as-prepared CNT(Fe)–TiB<sub>2</sub> powders were placed into a graphite die and subjected to spark plasma sintering at 1100 °C, 1200 °C, 1300 °C, 1400 °C, and 1500 °C for 5 min at an applied pressure of 30 MPa in vacuum. A heating rate of 100 °C·min<sup>-1</sup> was employed. To verify the reinforcing effect of the CNTs synthesized in situ for the bulk composites, we also prepared TiB<sub>2</sub>–5 wt% CNT composites using the traditional method. The process involved the preparation of TiB<sub>2</sub>–5 wt% CNT composite powders by ball-milling commercially available CNTs and TiB<sub>2</sub> powder and then subjecting the CNTs to spark plasma sintering at 1750 °C in vacuum, as described in our previous studies [19]. Monolithic TiB<sub>2</sub> ceramics were sintered under the same conditions.

The as-grown powders were sonicated in ethanol for 10 min and then transferred to the copper grids for microscopic examination by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Tecnai G<sup>2</sup>F30 TEM, 300 kV). Scanning electron microscopy (SEM) (ZEISS EVO18, Germany) equipped with energy dispersive spectroscopy (EDS) (Oxford Instruments X-Max<sup>N</sup>, UK) was employed to analyze the microstructure of grown CNTs and the

fracture surface of CNT(Fe)–TiB<sub>2</sub> composites. The average grain size was determined using the linear intercept method. The component of the as-prepared samples was characterized by X-ray diffraction (XRD; PANalytical X'Pert PRO, Holland, CuKα = 1.5418 Å). Raman spectroscopy was conducted using the 532 nm line of Ar<sup>+</sup> laser as the excitation source to verify the presence of CNTs in the composite powders.

The density of the resulting samples was measured using the Archimedes method, with deionized water as the immersion medium. Relative density was calculated by dividing the bulk density by the theoretical density. The flexural strength (*σ*) of the CNT(Fe)–TiB<sub>2</sub> composite was evaluated via the 3-point bending method on 3 mm × 4 mm × 36 mm (width × height × length) bars with a 30 mm length and a loading speed of 0.5 mm min<sup>-1</sup>, according to the Chinese Standard GB/T6569-2006 [21]. The flexural strength could be evaluated as follows:

$$\sigma = \frac{3PL}{2h^2w} \quad (2)$$

where *P* denotes the load at fracture, *h* and *w* denote the thickness and width of the specimen, respectively, and *L* represents the span of the specimen between the supporting positions. Linear elastic plane-strain fracture toughness (*K*<sub>IC</sub>) was obtained according to the Chinese Standard GB/T23806-2009 [22], which was measured using the single-edge notched beam test with a 16 mm span and a crosshead speed of 0.05 mm min<sup>-1</sup>. The test bars, 2 mm × 4 mm × 22 mm (width × height × length), were notched with a 0.1 mm thick diamond saw; the notch length was about half the height of the bar.

$$K_{IC} = Y \cdot \frac{3PL}{2wh^2} \sqrt{a} \quad (3)$$

where *a* denotes the length of the crack, and *Y* is the numerical factor. *Y* can be calculated using the following formula [23]:

$$Y = 1.93 - 3.07\left(\frac{a}{h}\right) + 14.53\left(\frac{a}{h}\right)^2 - 25.11\left(\frac{a}{h}\right)^3 + 25.80\left(\frac{a}{h}\right)^4 \quad (4)$$

All test bars were cut with the tensile surface perpendicular to the direction of the pressure. The surfaces of each specimen were carefully polished to a 1 μm finish, and the edges of all specimens were chamfered to minimize the effect of stress concentration caused by machining flaws. At least 6 samples were tested under each experimental condition.

## 3. Results and discussion

To evaluate the effect of synthesis temperature on CNT growth, the morphology and structure of CNT(Fe)–TiB<sub>2</sub> powders synthesized at 800 °C–1000 °C are presented in Fig. 1; the same catalyst with 10 wt% Fe was used. Compared with the pure TiB<sub>2</sub> (Fig. 1a), only some carbon spheres are formed and no CNTs can be observed when the synthesis temperature is lower than 900 °C (Fig. 1b, c, and 1d). A lower temperature impedes CNT growth because of the lower catalytic activity of Fe and the chemical reaction of carbon atoms at lower temperatures. Thus, a low carbon yield can be obtained. Fig. 1e reveals the presence of CNTs synthesized at 950 °C. The as-grown CNTs have a clean surface and an average length of about 2 μm. As the synthesis temperature is increased to 1000 °C (Fig. 1f), the Fe ions maintain high liquidity and cover the TiB<sub>2</sub> particles. The catalytic activity sites for CNTs decrease. Consequently, a smaller quantity of CNTs is obtained, but a mass of carbon sphere can be observed.

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