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Short communication

Rapid synthesis of Ti_3AlC_2/TiB_2 composites by the spark plasma sintering (SPS) technique

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Abstract

Dense Ti_3AlC_2/TiB_2 composites were successfully fabricated from B_4C/TiC/Ti/Al powders by spark plasma sintering (SPS). The microstructure, flexural strength and fracture toughness of the composites were investigated. The experimental results indicate that the Vickers hardness increased with the increase in TiB_2 content. The maximum flexural strength (700 ± 10 MPa) and fracture toughness (7.0 ± 0.2 MPa $m^{1/2}$) were achieved through addition of 10 vol.% TiB_2, however, a slight decrease in the other mechanical properties was observed with TiB_2 addition higher than 10 vol.%, which is believed to be due to TiB_2 agglomeration.

Keywords: B. Composites; C. Mechanical properties; TiB_2; Ti_3AlC_2

1. Introduction

The ternary compound Ti_3AlC_2 is a representative of a family of new materials so-called M_nAX_{n+1} phase, where M is an early transition metal, A is an A-group element (mostly III A an IV A) and X is either C and/or N. It exhibits a surprising combination of properties of both ceramics and metals, including low density, high elastic modulus, good thermal and electrical conductivity, excellent thermal shock and high-temperature-oxidation resistance, damage tolerance and easy machinability [1–6]. The combination of these remarkable properties makes Ti_3AlC_2 a highly promising candidate for various applications. However, some weaknesses, such as low hardness and unsatisfied strength, limit the potential application of Ti_3AlC_2 as a high-temperature structural material. Incorporation of a second phase is an effective way to overcome these weaknesses. A number of works have been published on improving the mechanical properties of Ti_3SiC_2 [7–10]. However, work on the strengthening of Ti_3AlC_2 is very limited. More recently, Chen and Zhou studied the effect of Al_2O_3 on the properties of Ti_3AlC_2/Al_2O_3 composite directly from raw Ti/Al/C/Al_2O_3 powders prepared by spark plasma sintering (SPS) [11].

Owing to the high hardness, high modulus, excellent chemical stability, and close thermal expansion coefficient, TiB_2 herein is chosen to produce Ti_3AlC_2/TiB_2 composites in order to increase the hardness and strength of Ti_3AlC_2. Li et al. obtained fully dense hot pressed Ti_3AlC_2/TiB_2 composites starting power Ti, Al, graphite, and B_4C powders [12]. In this study, we synthesized fully dense Ti_3AlC_2/TiB_2 composites from B_4C/TiC/Ti/Al powders by the spark plasma sintering technique. The phase composition and microstructure of the composites were investigated as well as their room-temperature mechanical properties including hardness, flexural strength, and fracture toughness.

2. Experimental procedure

All of the work was conducted using power mixtures of (99.2%, 10.6 μm), B_4C (99.5%, 2.8 μm), TiC (99%, 2.6 μm), and Al (99.6%, 1.7 μm). (All from Institute of Non-Ferrous Metals, Beijing, China.) According to the nominal reaction: (1)

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$Ti + 2TiC + Al = Ti_3AlC_2$ and (2) $3Ti + B_4C = TiC + 2TiB_2$, the volume fraction of added TiB_2 in the composites was 5%, 10%, 20%, and 30%, respectively. After ball milling in ethanol for 24 h, the powders were dried, sieved, and compacted uniaxially under 20 MPa in a graphite mold pre-sprayed with a layer of BN. The admixture with a designed composition was firstly mixed in ethanol for 24 h, filled into graphite crucibles of 40 mm in diameter and finally spark plasma sintered in vacuum (Dr.1050, lzumi Technology Co. Ltd.). The temperature was measured by means of an optical pyrometer focused on to the sintered sample through a small hole in the die. The samples were heated at a rate of 80 °C/min, in vacuum of 0.5 Pa, and under a pressure of 30 MPa. The soaking time was 8 min.

Before examination, the surfaces of the sintered samples were machined to remove the layer contaminated by the carbon sheet, using a fine grit; high speed diamond wheel. The density of Ti_3AlC_2/TiB_2 composites with different contents of TiB_2 was measured by the Archimedes method. The Vickers hardness was tested at a load of 9.8 N with dwell time of 30 s. Three-point bending tests were preformed to measure flexural strength of 3 mm × 4 mm × 36 mm specimens at a crosshead speed is 0.5 mm/min. Fracture toughness (K_{IC}) was measured using single-edge notch beam (SENB) method on 4 mm × 8 mm × 36 mm specimens with crosshead speed of 0.05 mm/min dimensions of the notch is 4 mm in length, 0.15 mm in width and 0.15 mm radius was made by the electrical discharge method. Powders drilled from the samples were used for X-ray diffraction (XRD) analysis. The microstructures and fracture surfaces of the samples were investigated by scanning electron microscopy (SEM). Transmission electron microscope (TEM) equipped EDS system was used for more detailed microstructural analysis.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of Ti_3AlC_2/TiB_2 composites. It is worth noting that there is no TiC_x impurity in Ti_3AlC_2/10–20 vol.% TiB_2 composites, when the TiB_2 content exceeds 20 vol.%, TiC appears, which indicate the reaction (2) cannot be fully finished because of incorporation with too much TiB_2 content. Meanwhile, there is no evidence that shows the reaction between Ti_3AlC_2 and TiB_2. Actually TiB_2 only dilutes the initial powders and delays the reaction process. The result was very similar to that of previous work [11].

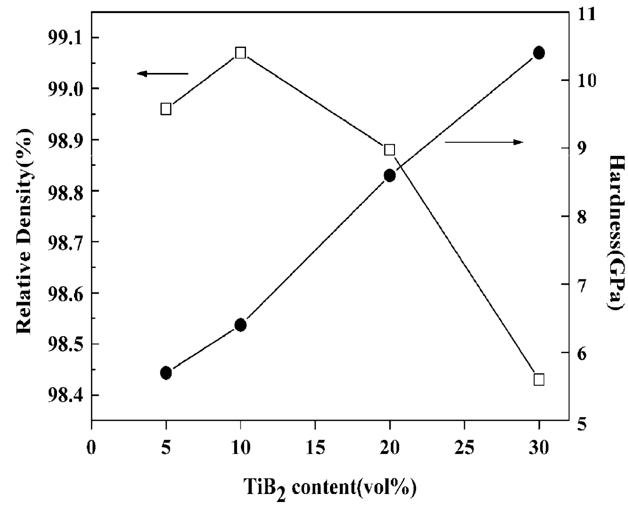

Fig. 2. The effect of TiB_2 on the relative density and Vickers hardness of Ti_3AlC_2/TiB_2 composite.

Fig. 2 shows the density of the sintered samples and Vickers hardness with different TiB_2 content. The measured density of all Ti_3AlC_2/TiB_2 composites is 98.4–99.2% of the theoretical density. A significant decrease in density is observed when the TiB_2 content exceeds 10%. The main reason is the agglomeration of the TiB_2 particles. The introduction of the TiB_2 phase enhances obviously the hardness of Ti_3AlC_2; the hardness increases from 5.1 GPa to maximal 10.4 GPa for the Ti_3AlC_2/30 vol.% TiB_2 composite, which is twice higher than that of the pure Ti_3AlC_2 (4 GPa).

Fig. 3 shows the effect of TiB_2 content on the flexural strength and fracture toughness of the composite. It can be seen that flexural strength increases from 621 to 700 MPa as the volume content of TiB_2 increased from 5 to 10% and decreases to 590 MPa at 30 vol.% TiB_2 content. While K_{IC} reaches a

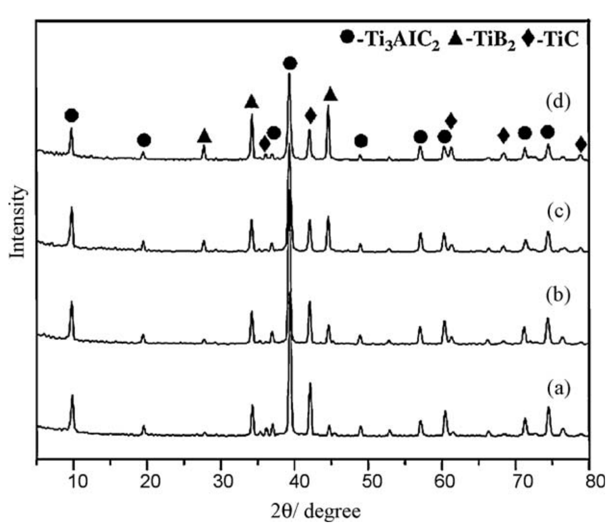

Fig. 1. X-ray diffraction patterns of content of TiB_2 sintered by SPS from (a) 5% TiB_2, (b) 10% TiB_2, (c) 20% TiB_2 and (d) 30% TiB_2, sintered at 1250 °C.

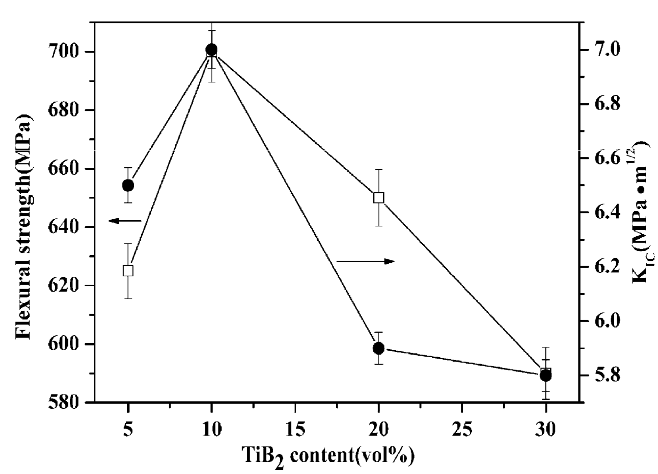

Fig. 3. The flexural strength and fracture toughness of samples.

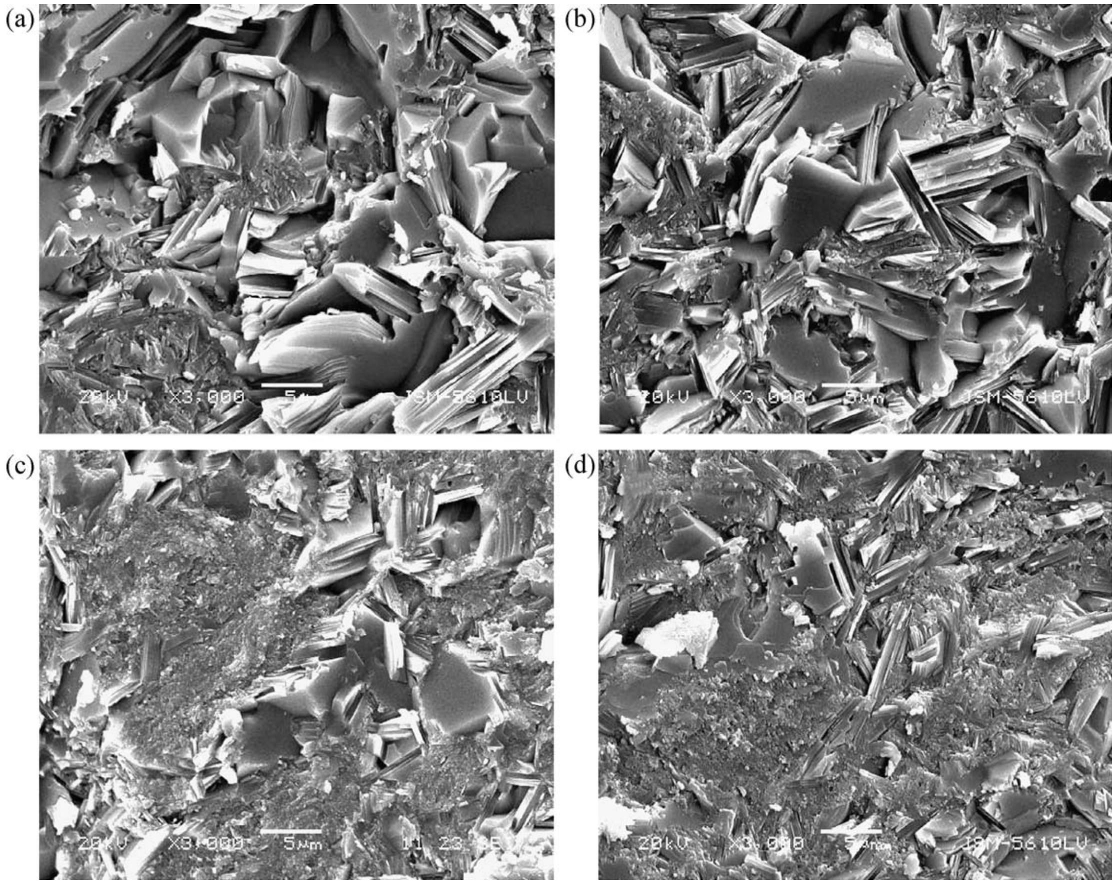

Fig. 4. SEM of the samples with different TiB_2 content sintered at 1250 °C: (a) 5% TiB_2, (b) TiB_2 10%, (c) 20% TiB_2 and (d) 30% TiB_2.

maximum value of 7.0 MPa $m^{1/2}$ at 10 vol.% TiB_2 content, and then decreases dramatically to 5.8 MPa $m^{1/2}$. The decrease in the number of columnar of plate-like grains and TiB_2 agglomeration are the main reasons for the decrease in flexural strength and fracture toughness. The result is also proved by other researchers [12].

Fig. 4 shows SEM micrographs of the fracture surfaces of the Ti_3AlC_2/TiB_2 composites. The laminated Ti_3AlC_2 grains can easily be identified in these micrographs. EDS analysis revealed that fine particles in the composites were TiB_2. The fracture was mainly intergranular, although some of the bigger platelet grains showed transgranular fractures. The relatively flat fracture surface conformed to the low toughness of the TiB_2. The protruded TiB_2 platelet grains and the deep elongated holes were the evidence of the pullout of the TiB_2 grains, which attribute to the high fracture toughness of the composite. With the increased amount of TiB_2 particles, the grain size and aspect ratio of the matrix decreased.

Further microstructural analysis was carried out by TEM for the Ti_3AlC_2/10% TiB_2 composites. Fig. 5(a) shows the

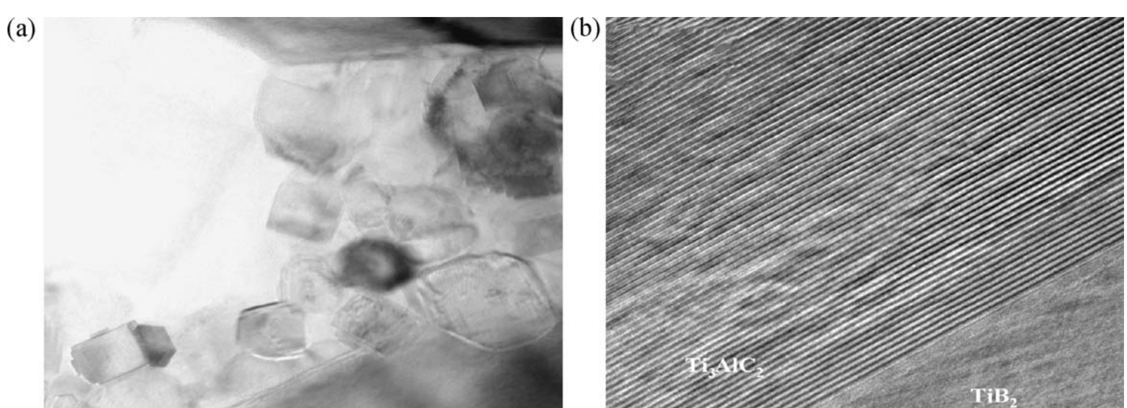

Fig. 5. Transmission electron microscopic images of a Ti_3AlC_2/10% TiB_2 composite showing (a) the existence of TiB_2 as fine grains and (b) HRTEM image.

TEM images of the microstructure of the Ti_3AlC_2/10% TiB_2 composites. Most of the TiB_2 grains possess regular platelet morphologies with straight edges and are very fine with an average diameter of 100 nm. Additionally, there is no reaction between Ti_3AlC_2 and TiB_2. As shown in Fig. 5(b), no obvious reaction products in Ti_3AlC_2–TiB_2 interface. The high relative density and the homogeneous dispersed submicrometer-size TiB_2 particles contributes to the excellent mechanical properties of Ti_3AlC_2/10% TiB_2 composites.

4. Conclusions

Dense Ti_3AlC_2/TiB_2 composites were synthesized from B_4C/TiC/Ti/Al by spark plasma sintering under a uniaxial pressure of 30 MPa in an Ar atmosphere at 1250 °C for 8 min. The introduction of TiB_2, especially 10 vol.% content, raises the hardness, flexural strength and toughness of the composite. However, the fracture toughness of Ti_3AlC_2/20 vol.% TiB_2 composite begins to decrease caused by TiB_2 agglomeration.

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