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Rapid reactive synthesis of Ti_2AlC-TiB_2 composites by spark plasma sintering

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In this paper, dense Ti_2AlC/TiB_2 composites were successfully fabricated by a rapid reactive sintering process by a spark plasma sintering (SPS) technique using Ti, Al, TiC and B_4C powders. The microstructure, flexural strength and fracture toughness of the composites were investigated. The experimental results indicate that the Vickers hardness increased with an increase in TiB_2 content. The maximum flexural strength (573 MPa) and fracture toughness (6.2 $MPa \cdot m^{1/2}$) were achieved through the addition of 10 vol%TiB_2. The incorporation of a TiB_2 phase makes a positive contribution to its electrical conductivity.

Key words: Spark plasma sintering, Ti_2AlC-TiB_2, Composite, Properties.

Introduction

The ternary compound Ti_2AlC is a representative of a family of new materials the so-called M_nAX_{n+1} phases, where M is an early transition metal, A is an A-group element (mostly IIIA or IVA) and X is either C and/or N. It exhibits a surprising combination of properties of both ceramics and metals, including low density, high modulus, good thermal and electrical conductivity, excellent thermal shock and high-temperature-oxidation resistance, damage tolerance and easy machinability [1-8]. The combination of these remarkable properties makes Ti_2AlC a highly promising candidate for diverse application. However, some weaknesses, such as low hardness and lower strength, limit the potential applications of Ti_2AlC as a high-temperature structural material. The 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 [9-12] and Ti_3AlC_2 [13-15]. However; work on the strengthening of Ti_2AlC is very limited.

Owing to its high hardness, high modulus, excellent chemical stability, and appropriate thermal expansion coefficient, TiB_2 was chosen to produce Ti_2AlC/TiB_2 composites in order to increase the hardness and strength of Ti_2AlC. In this study, we synthesized fully-dense Ti_2AlC/TiB_2 composites from B_4C/TiC/Ti/Al powders by a spark plasma sintering technique. The phase composition and microstructure of the composites were investigated. The room temperature mechanical properties including hardness, flexural strength, and fracture toughness of the composites were measured.

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Materials and Experiment

High-purity powders of Ti (99.2%, 10.6 μm), B_4C (99.5%, 2.8 μm), TiC (99.8%, 2.6 μm) and Al (99.6%, 1.7 μm) were selected as starting materials. According to the nominal reaction: (1) $Ti + TiC + Al = Ti_2AlC$ and (2) $3Ti + B_4C = TiC + 2TiB_2$, the volume fraction of TiB_2 in the composites was designed to be 5%, 10%, 20%, and 30%. After ball milling in ethanol for 24 h, the powders were dried, sieved, and compacted uniaxially at 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 and then was filled into graphite crucibles 40 mm in diameter and finally sintered in a vacuum in a spark plasma sintering system (Dr.1050, lzumi Technology Co. Ltd). The samples were heated at a rate of 80 $Kminute^{-1}$, in a vacuum of 0.5 Pa, and under a pressure of 30 MPa in the preparation process. The sintering temperature was 1300 °C and the soaking time was 8 minutes. The temperature was measured by means of an optical pyrometer focused on to the sintered sample through a small hole in the die.

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_2AlC/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 a dwell time of 30 s. Three-point bending tests were preformed to the measure flexural strength and fracture toughness (K_{IC}). The size of specimens for flexural strength testing was $3 \times 4 \times 36$ mm^3 and the crosshead

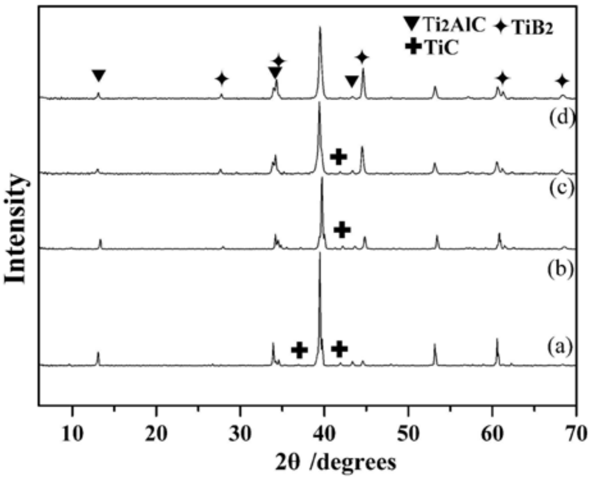

Fig. 1. X-ray diffraction patterns of composites sintered at 1300 °C by SPS with (a) 5%TiB_2 (b) 10%TiB_2 (c) 20%TiB_2 (d) 30%TiB_2.

speed was 0.5 mm minute^{-1}. K_{IC} was measured using a single-edge notch beam (SENB) method with specimen dimensions of 4 × 8 × 36 mm^3. A notch with a size of 4 mm in length and ~0.15 mm in width was made by an electrical discharge method. The notch root radius was about 0.15 mm. The crosshead speed for fracture toughness testing is 0.05 mm minute^{-1}. Powders drilled from the samples were used for X-ray diffraction (XRD) analysis. The microstructures, facture surfaces and crack propagation of the samples were investigated by scanning electron microscopy (SEM). The electrical conductivity of the samples was measured at room temperature using a four -point probe detector.

Results and Discussion

Synthesis of Ti_2AlC/TiB_2 composites

Fig. 1 shows the XRD diffraction patterns of Ti_2AlC/ TiB_2 composites sintered at 1300 °C. It is worth noting that there was little TiC impurity in the Ti_2AlC/TiB_2 composites, even when the TiB_2 content reaches 30 vol%, which indicates the in-situ reaction may be complete. Meanwhile, there is no evidence that shows a reaction between Ti_2AlC and TiB_2. Actually TiB_2 only dilutes the initial powders and delays the reaction process.

Mechanical properties of Ti_2AlC/TiB_2 composites

Fig. 2 shows the density of the sintered samples and Vickers hardness with different TiB_2 contents. The measured density of all the Ti_2AlC/TiB_2 composites is 98.3-99.6% 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 obviously enhances the hardness of Ti_2AlC; the hardness increases from 4.8 GPa to a maximum of 10.8 GPa for the Ti_2AlC/30 vol% TiB_2 composite, which is much higher than that of the pure Ti_2AlC (2.8 GPa [8]).

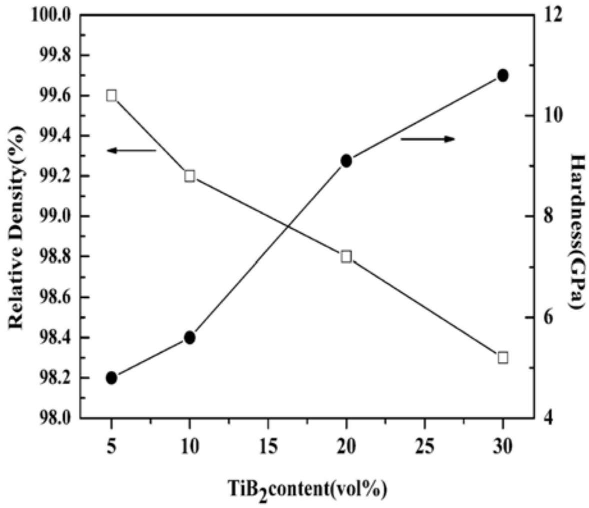

Fig. 2. The effect of TiB_2 on the relative density and Vickers hardness of Ti_2AlC/TiB_2 composites.

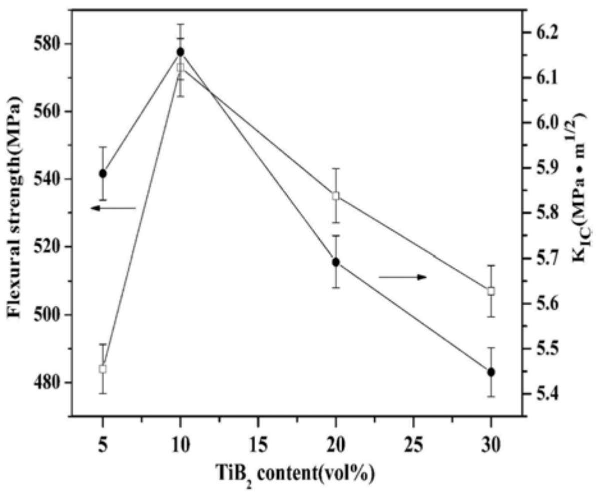

Fig. 3. The flexural strength and fracture toughness of Ti_2AlC/TiB_2 composites.

Fig. 3 shows the effect of the TiB_2 content on the flexural strength and fracture toughness of the composites. It can be seen that flexural strength increases from 484 to 573 MPa as the volume content of TiB_2 increased from 5 to 10% and decreases to 507 MPa at a 30 vol.% TiB_2 content . K_{IC} reaches a maximum value of 6.2 MPa·m$^{1/2}$ at 10 vol.% TiB_2 content, and then decreases dramatically to 5.4 MPa·m$^{1/2}$. The flexural strength and fracture toughness of monolithic Ti_2AlC reported by Wang and Zhou [8] were 275 MPa and 6.5 MPa·m1/2, respectively. Compared with monolithic Ti_2AlC, the strengthening effect is rather significant for the flexural strength, while there is little effect on fracture toughness value.

Room temperature electrical conductivity of Ti_2AlC/TiB_2 composites

The effect the TiB_2 content on the electrical conductivity of Ti_2AlC/TiB_2 composites is shown in Fig. 4 It can be

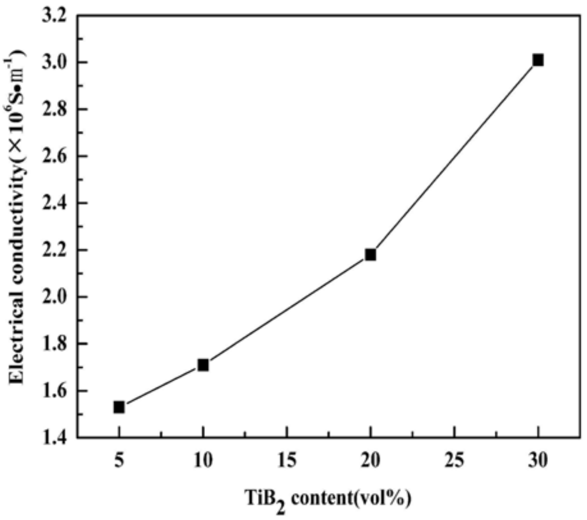

Fig. 4. The effect of TiB_2 on the electrical conductivity of Ti_2AlC/TiB_2 composites.

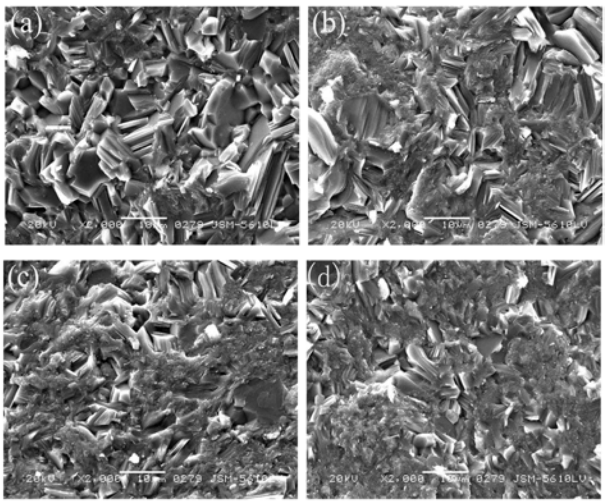

Fig. 5. SEM of the samples with different TiB_2 contents sintered at 1300 °C (a) 5% TiB_2 (b) 10% TiB_2 (c) 20% TiB_2 (d) 30% TiB_2.

clearly seen that the electrical conductivity of the composites increases almost linearly with increasing TiB_2 content in the range of 5-30 vol%. The electrical conductivity of monolithic Ti_2AlC was $2.7 \times 10^6 S \cdot m^{-1}$, which was reported by Barsoum *et al*. [3]. However, the electrical conductivity of the Ti_2AlC/30 vol%TiB_2 composite was $3.1 \times 10^6 S \cdot m^{-1}$, which is slightly higher than that of monolithic Ti_2AlC. The enhanced electrical conductivity can be mainly attributed to the lower resistance of TiB_2 compared with the Ti_2AlC matrix. Unlike other types of strengthening phases (such as SiC, Al_2O_3), incorporation of TiB_2 makes a positive contribution to the electrical conductivity of Ti_2AlC/TiB_2 composites.

Microstructure of Ti_2AlC/TiB_2 composites

SEM micrographs of the fracture surfaces of the Ti_2AlC/TiB_2 composites are shown in Fig. 5. The laminated Ti_2AlC grains can easily be identified in these micrographs. EDS analysis revealed that the fine particles in the composites were TiB_2. The fracture was mainly an intergranular fracture, although some of the bigger platelet grains showed transgranular fractures. With an increase in the amount of TiB_2 particles, the grain size and aspect ratio of the matrix decreased. With additions of TiB_2 content higher than 10 vol%, agglomeration of TiB_2 particles in the composites was obviously observed. This may explain how the mechanical properties of composites decreased when the TiB_2 content exceeded 10 vol%.

Conclusions

Dense Ti_2AlC/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 1300 °C for 8minutes.The introduction of TiB_2, especially a 10 vol.% content, raises the hardness, flexural strength and toughness of the composite. But the fracture toughness of Ti_2AlC/20 vol% TiB_2 composite begins to decrease due to the agglomeration of the TiB_2 particles.

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