Rapid reactive synthesis of Ti₂AlC-TiB₂ composites by spark plasma sintering

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In this paper, dense Ti₂AlC/TiB₂ composites were successfully fabricated by a rapid reactive sintering process by a spark plasma sintering (SPS) technique using Ti, Al, TiC and B₄C 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 TiB₂ content. The maximum flexural strength (573 MPa) and fracture toughness (6.2 MPa·m²) were achieved through the addition of 10 vol% TiB₂. The incorporation of a TiB₂ phase makes a positive contribution to its electrical conductivity.

Key words: Spark plasma sintering, Ti₂AlC-TiB₂, Composite, Properties.

Introduction

The ternary compound Ti₂AlC is a representative of a family of new materials the so-called M₄AXₙ₊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 Ti₂AlC a highly promising candidate for diverse application. However, some weaknesses, such as low hardness and lower strength, limit the potential applications of Ti₂AlC 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 Ti₅SiC₂ [9-12] and Ti₅AlC₂ [13-15]. However, work on the strengthening of Ti₂AlC is very limited.

Owing to its high hardness, high modulus, excellent chemical stability, and appropriate thermal expansion coefficient, TiB₂ was chosen to produce Ti₂AlC/TiB₂ composites in order to increase the hardness and strength of Ti₂AlC. In this study, we synthesized fully-dense Ti₂AlC/TiB₂ composites from B₄C/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.

Materials and Experiment

High-purity powders of Ti (99.2%, 10.6 μm), B₄C (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 = Ti₂AlC and (2) 3Ti + B₄C = TiC + 2TiB₂, the volume fraction of TiB₂ 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, Iizumi Technology Co. Ltd). The samples were heated at a rate of 80 K·min⁻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 Ti₂AlC/TiB₂ composites with different contents of TiB₂ 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 performed to measure flexural strength and fracture toughness (KIC). The size of specimens for flexural strength testing was 3 × 4 × 36 mm³ and the crosshead...
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speed was 0.5 mm minute$^{-1}$. $K_{IC}$ was measured using a single-edge notch beam (SENB) method with specimen dimensions of $4 \times 8 \times 36$ 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, fracture 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$_2$AlC/TiB$_2$ composites

Fig. 1 shows the XRD diffraction patterns of Ti$_2$AlC/TiB$_2$ composites sintered at 1300 °C by SPS with (a) 5%TiB$_2$ (b) 10%TiB$_2$ (c) 20%TiB$_2$ (d) 30%TiB$_2$. It is worth noting that there was little TiC impurity in the Ti$_2$AlC/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$_2$AlC and TiB$_2$. Actually TiB$_2$ only dilutes the initial powders and delays the reaction process.

Mechanical properties of Ti$_2$AlC/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$_2$AlC/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$_2$AlC; the hardness increases from 4.8 GPa to a maximum of 10.8 GPa for the Ti$_2$AlC/30 vol% TiB$_2$ composite, which is much higher than that of the pure Ti$_2$AlC (2.8 GPa [8]).

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$_2$.

Fig. 2. The effect of TiB$_2$ on the relative density and Vickers hardness of Ti$_2$AlC/TiB$_2$ composites.

Fig. 3. The flexural strength and fracture toughness of Ti$_2$AlC/TiB$_2$ composites.

Room temperature electrical conductivity of Ti$_2$AlC/TiB$_2$ composites

The effect the TiB$_2$ content on the electrical conductivity of Ti$_2$AlC/TiB$_2$ composites is shown in Fig. 4. It can be
clearly seen that the electrical conductivity of the composites increases almost linearly with increasing TiB2 content in the range of 5-30 vol%. The electrical conductivity of monolithic Ti2AlC was 2.7 × 10^6 S·m⁻¹, which was reported by Barsoum et al. [3]. However, the electrical conductivity of the Ti2AlC/30 vol%TiB2 composite was 3.1 × 10^6 S·m⁻¹, which is slightly higher than that of monolithic Ti2AlC. The enhanced electrical conductivity can be mainly attributed to the lower resistance of TiB2 compared with the Ti2AlC matrix. Unlike other types of strengthening phases (such as SiC, Al2O3), incorporation of TiB2 makes a positive contribution to the electrical conductivity of Ti2AlC/TiB2 composites.

**Microstructure of Ti2AlC/TiB2 composites**

SEM micrographs of the fracture surfaces of the Ti2AlC/TiB2 composites are shown in Fig. 5. The laminated Ti2AlC grains can easily be identified in these micrographs. EDS analysis revealed that the fine particles in the composites were TiB2. The fracture was mainly an intergranular fracture, although some of the bigger platelet grains showed transgranular fractures. With an increase in the amount of TiB2 particles, the grain size and aspect ratio of the matrix decreased. With additions of TiB2 content higher than 10 vol%, agglomeration of TiB2 particles in the composites was obviously observed. This may explain how the mechanical properties of composites decreased when the TiB2 content exceeded 10 vol%.

**Conclusions**

Dense Ti2AlC/TiB2 composites were synthesized from B4C/TiC/Ti/Al by spark plasma sintering under a uniaxial pressure of 30 MPa in an Ar atmosphere at 1300 °C for 8 minutes. The introduction of TiB2, especially a 10 vol.% content, raises the hardness, flexural strength and toughness of the composite. But the fracture toughness of Ti2AlC/20 vol% TiB2 composite begins to decrease due to the agglomeration of the TiB2 particles.

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