

In situ reaction synthesis and characterization of $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2/\text{SiC}$ composites

D.T. Wan^{a,b}, Y.C. Zhou^{a,*}, Y.W. Bao^a, C.K. Yan^a

^a Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, PR China

^b Graduate School of Chinese Academy of Sciences, Beijing 100039, PR China

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Abstract

The reaction route, microstructure, and properties of $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2/\text{SiC}$ composites with 5–30 vol.% SiC content prepared by in situ hot pressing/solid–liquid reaction synthesis process are investigated. In contrast to monolithic $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$, the SiC particle-reinforced composites exhibit higher elastic modulus, Vickers hardness, fracture toughness, improved wear, and oxidation resistance, but have a slight loss in flexural strength. The improvement in the properties is mainly ascribed to the contribution of SiC particles, and the strength degradation is due to the residual tensile stresses in the matrix.

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1. Introduction

Ti_3SiC_2 is a layered ternary carbide that possesses unique properties combining excellent characteristics of metals and ceramics such as low density, high strength and modulus, damage tolerance at room temperature, good machinability, and good resistance to thermal shock and oxidation below 1100 °C [1–6]. However, the low hardness (Vickers hardness of 4 GPa) and unsatisfied oxidation resistance above 1100 °C limit the application of Ti_3SiC_2 as high-temperature structural components. Previous study investigating on the electronic structure disclosed that low hardness originated from weak bonding between the Ti–C–Ti–C–Ti covalent bond chain and the Si atomic layer [7], which resulted in low shear modulus C_{44} [8]. Poor oxidation resistance above 1100 °C was caused by lack of continuous SiO_2 layer on the subsurface of the oxidized sample [9–11]. We have shown that the oxidation resistance can be improved by increasing the silicon content in the material [12] whereas hardness

enhancement can be realized by particulate strengthening [13–15]. To achieve these goals, SiC particles were incorporated into a Ti_3SiC_2 matrix to fabricate $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites. SiC was selected because it is hard, resistant to high temperature oxidation and creep, and thermodynamically stable with Ti_3SiC_2 [16]. In addition, the increased silicon content brought by the incorporated SiC particles was beneficial to the oxidation resistance of Ti_3SiC_2 . It is thus expected that $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites will exhibit improved hardness, wear, and oxidation resistance.

Due to these expected salient properties, a number of studies dealing with $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites have been carried out. Tong et al. [2] fabricated a $\text{Ti}_3\text{SiC}_2/20$ vol.% SiC composite and studied its high-temperature mechanical properties. Li et al. [17] and Radhakrishnan et al. [18] synthesized a $\text{Ti}_3\text{SiC}_2/14.2$ vol.% SiC composite using displacement reactions to improve the mechanical properties of Ti_3SiC_2 . Ho-Duc et al. [19] fabricated a $\text{Ti}_3\text{SiC}_2/30$ vol.% SiC composite by hot isostatic pressing (HIP) method. They found that hardness increased but strength was reduced compared to monolithic Ti_3SiC_2 . It is worth noting that the $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites fabricated by these methods always

* Corresponding author. Tel.: +86 24 23971765; fax: +86 24 23891320.
E-mail address: yczhou@imr.ac.cn (Y.C. Zhou).

contain TiC and/or TiSi₂ impurities. We know that TiC is advantageous for enhancement of hardness and strength but deleterious to high-temperature oxidation resistance of Ti₃SiC₂-based materials [9,10]. The ill effects of TiC on oxidation resistance can be eliminated by substitution of Si with Al to form Ti₃(Si_{1-x}Al_x)C₂ solid solutions because Al is favorable in the formation of Ti₃Si(Al)C₂ and is effective in removing the TiC impurity from Ti₃SiC₂ [20,21]. To understand the effects of SiC on the mechanical properties and oxidation behavior of Ti₃SiC₂ better, we use TiC free Ti₃Si(Al)C₂ as the matrix for Ti₃Si(Al)C₂/SiC composites in this study. In the present paper, we describe the synthesis, microstructure, mechanical properties, and oxidation behaviors of Ti₃Si(Al)C₂/SiC composites. The main contributions of this work are: (1) bulk Ti₃Si(Al)C₂/SiC composites were in situ synthesized at relatively low temperatures; (2) no impurity phase like TiC co-exists with SiC; and (3) the effects of SiC on the microstructure and properties of the Ti₃Si(Al)C₂/SiC composites can be well understood.

2. Experimental

2.1. Material preparation

Previous studies [22,23] demonstrated that Ti₃SiC₂ and SiC could simultaneously be formed from elemental powders of Ti, Si, and graphite at relatively low temperatures, which indicated that Ti₃SiC₂/SiC composites could be synthesized in situ. Thus, we used elemental powders of Ti (99%, 300 mesh), Si (99%, 400 mesh), graphite (98%, 200 mesh), and Al (99.5%, 200 mesh) as initial materials. Al was added to eliminate TiC and to form a Ti₃Si_{0.95}Al_{0.05}C₂ matrix. The contents of SiC in Ti₃Si(Al)C₂/SiC composites were adjusted by controlling the amounts of Si and graphite. Table 1 lists the target compositions of Ti₃Si(Al)C₂ and Ti₃Si(Al)C₂/SiC composites with different amounts of SiC. The SiC contents in the final bulk composites determined by X-ray diffraction were also depicted and compared in Table 1. Bulk Ti₃Si(Al)C₂ and Ti₃Si(Al)C₂/SiC composites were prepared by in situ hot pressing/solid–liquid reaction process [24], wherein both SiC and Ti₃Si(Al)C₂ matrices were synthesized in situ. In this process, elemental powders of Ti, Si, Al and graphite were precisely weighed according to the target compositions

and mixed in a polyurethane mill for 15 h in a wet medium. After drying at room temperature, the mixtures were screened through a 60-mesh sieve and then were put in a ϕ 50 mm graphite mold coated with a layer of boron nitride (BN) and cold pressed. The green compacts were then hot pressed at 30 MPa under a flowing Ar atmosphere at 1560 °C for 60 min (this temperature is suitable to warrant the simultaneous formation of Ti₃Si(Al)C₂ and SiC), and subsequently annealed at 1400 °C for 30 min.

2.2. Characterization of Ti₃Si(Al)C₂/SiC composites

The densities of the as-prepared composites were determined by Archimedes method. The phase compositions were identified by X-ray diffraction using powders drilled from the bulk samples. The XRD data were collected by a step-scanning diffractometer with Cu K α radiation (Rigaku D/max -2400, Japan). To determine the true SiC contents in the Ti₃Si(Al)C₂/SiC composites, quantitative phase analysis was conducted. The data used for quantitative analysis had an accuracy better than 0.02°. Two methods, i.e. the Internal Standard method [25] and the Rietveld method [26] were used to calculate the SiC contents. In the Internal Standard method, the mass fraction of SiC was calculated using the equation:

$$\frac{I_{SC}}{I_{TSC}} = K \frac{W_{SC}}{W_{TSC}} = K \frac{W_{SC}}{1 - W_{SC}} \quad (1)$$

where I_{SC} and I_{TSC} are the intensities of selected lines in the diffraction pattern of SiC and Ti₃Si(Al)C₂, respectively; W_{SC} and W_{TSC} , the mass fractions of SiC and Ti₃Si(Al)C₂ phase, respectively; K is a constant which depends on the nature of SiC and Ti₃Si(Al)C₂ as well as the geometry of the instrumentation, and can be calibrated using different weight ratios of SiC to Ti₃Si(Al)C₂ as mixtures. In the Rietveld method, crystal structure and peak profile parameters are refined in several stages. The complete profile of the powder diffraction pattern is refined by employing a DBWS code [27] in Cerius² computational program for materials research (Molecular Simulation Inc., USA). The intensity is represented by:

$$I_{\text{Rietveld}}(2\theta) = b(2\theta) + S \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A_K \quad (2)$$

Table 1

The target SiC contents compared with those calculated by two different methods in Ti₃Si(Al)C₂/SiC composites

| The target SiC contents in Ti ₃ Si(Al)C ₂ /SiC composites | | The calculated SiC contents by the Internal Standard method | | The calculated SiC contents by the Rietveld method | |
|---|------|---|------|--|------|
| vol.% | wt.% | vol.% | wt.% | vol.% | wt.% |
| 0 | 0 | 1.2 | 0.9 | 4.1 | 3.0 |
| 5 | 3.6 | 6.9 | 5.0 | 9.4 | 6.9 |
| 10 | 7.4 | 9.6 | 7.1 | 11.9 | 8.8 |
| 20 | 15.2 | 18.9 | 14.3 | 18.7 | 14.1 |
| 30 | 23.5 | 31.4 | 24.6 | 29.2 | 22.8 |

where $b(2\theta)$ is the background intensity; S , scale factor; L_K , contains the Lorentz polarization and multiplicity factors; ϕ , profile function; P_K , preferred orientation function; A_K , absorption factor; and F_K , structure factor. The index K represents Miller indices for the Bragg reflections. In the Rietveld method, the mass fraction of a phase q , W_q , is given by [26,28]:

$$W_q = \frac{S_q M_q V_q}{\sum (S_i M_i V_i)} \quad (3)$$

where S is the Rietveld scale factor for the phase q ; M , molar mass; and V , volume of the unit cell. The advantages of the Rietveld method include, viz. the calibration constants are computed rather than measured by experiments; all the peaks in the pattern play a part in the analysis; the use of a continuous fitting function provides a much improved background fit, and finally, the effects of preferred orientation and extinction are reduced.

The microstructure of the composites was examined in a S-360 scanning electron microscope (Cambridge Instruments Ltd., UK) equipped with an energy-dispersive spectroscopy (EDS) system. To expose the $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ and SiC grains, samples were mechanically polished and etched by an $\text{HNO}_3\text{:HF:H}_2\text{O}$ (1:1:2) solution before SEM observation.

Vickers hardness was tested on the polished surfaces under various loads of 0.98, 1.96, 2.94, 4.90, and 9.80 N with a dwell time of 15 s. Three-point bending tests were performed to measure the flexural strength, elastic modulus, and fracture toughness. The specimens for elastic modulus and flexural strength tests were rectangular bars of $3 \text{ mm} \times 4 \text{ mm} \times 36 \text{ mm}$ in size. The elastic modulus was obtained using the ratio of load increment to the deflection increment [29]. Single-edge notched beam (SENB) specimens with a size of $4 \text{ mm} \times 8 \text{ mm} \times 36 \text{ mm}$ were used to measure the fracture toughness. The notch was made 4 mm in depth and $\sim 0.15 \text{ mm}$ in width. The crosshead speed was 0.5 mm min^{-1} for flexural strength and elastic modulus tests, and 0.05 mm min^{-1} for fracture toughness measurements.

Friction and wear tests were performed under nonlubrication conditions with point contact wear mode using a ball on a flat sliding block specimen. All wear tests were conducted with a reciprocating machine (UMT-2 Multi-Specimen Test System, CETR, USA) at room temperature with a relative humidity of 40–55%. The ball was 4 mm in diameter and made of 52,100 bearing steel. A load of 10 N was applied downward through the ball against the flat specimen mounted on a reciprocating drive. The total sliding distance was 30 m at a sliding velocity of 30 mm s^{-1} for 1000 s. Before and after tests, all the samples were ultrasonically cleaned, dried, and weighed. The wear coefficient (W) is given by:

$$W = \frac{\Delta m}{PL} \quad (4)$$

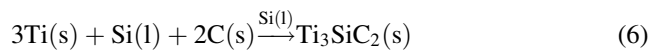
where Δm (kg) is the weight loss; P (N) is the applied load; and L (m) is the total sliding distance.

The isothermal oxidation kinetics of the $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ -based composites were investigated at 1100°C in air for 20 h and compared with that obtained from Ti_3SiC_2 . Specimens with dimensions of $3 \text{ mm} \times 4 \text{ mm} \times 15 \text{ mm}$ were ground to 1000 grit SiC, polished using diamond paste, chamfered and degreased in acetone. The samples were suspended with a Pt wire in a vertical Setsys16/18 thermal balance (SETARAM, France). The continuous mass gains were automatically recorded as a function of time.

3. Results

3.1. Synthesis, phase compositions, and microstructure

The reaction route for the synthesis of Ti_3SiC_2 from elemental powders of Ti, Si, and C, was investigated in many of the previous studies [22–24,30]. Briefly, intermediate phases such as Ti_5Si_3 , TiC, TiSi_2 , and SiC form during heating depending on the initial compositions of the powder mixture and temperature. Generally, Ti_3SiC_2 forms at $1400\text{--}1500^\circ\text{C}$ in Si-rich Ti, Si, and C powder mixtures according to the following reactions [31]:



The impurity phase such as TiC can be eliminated by partial substitution of Si with Al [20,21]. Higher synthesis temperature (above 1500°C) or surplus in C in the initial powder mixture favors the formation of SiC [22,30,31]. The reaction can be simply described as:



Based on these facts, we synthesized $\text{Ti}_3\text{SiC}_2/\text{SiC}$ composites at 1560°C utilizing extra Si and graphite to control the SiC content. In addition, 5 at.% of silicon in the Ti_3SiC_2 matrix was substituted with Al to make sure that no TiC existed in the final composites. Thus, the true composition of the matrix is $\text{Ti}_3\text{Si}_{0.95}\text{Al}_{0.05}\text{C}_2$ and is denoted as $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ hereafter for brevity.

Fig. 1 shows the X-ray diffraction patterns of $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2/\text{SiC}$ composites with different amounts of SiC. The crystalline phases were identified as $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ and $\beta\text{-SiC}$. No peaks from impurity phases such as TiC and Ti_5Si_3 could be detected via XRD. The intensity ratios of $\beta\text{-SiC}$ (1 1 1) ($I_{\text{SC}(111)}$) to $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$ (1 0 4) ($I_{\text{TSC}(104)}$) increase with the increment of SiC contents. To determine the true SiC contents in $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2/\text{SiC}$ composites, quantitative phase analysis was conducted using both the Internal Standard method and the Rietveld method. In the Internal Standard method, the constant K value of 1.46 was calibrated using the intensity ratios $I_{\text{SC}(111)}/I_{\text{TSC}(104)}$ versus the added $\beta\text{-SiC}$ amount in a series of SiC– $\text{Ti}_3\text{Si}(\text{Al})\text{C}_2$