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Synthesis and mechanical properties of in-situ hot-pressed Ti_3SiC_2 polycrystals

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Abstract

The synthesis of titanium silicon carbide (Ti_3SiC_2) from non-stoichiometric mixture of elemental Ti, Si, and active carbon or graphite powders (3Ti:1.2Si:2C) was investigated. The results show that higher-purity Ti_3SiC_2 can be attained using active carbon instead of graphite. The fracture toughness of the materials was improved by delamination, grain buckling and pull-out. An high flexural strength resulted for high-purity Ti_3SiC_2 polycrystals from room temperature to 1473 K.

Keywords: A. Hot pressing; C. Mechanical properties; Synthesis; Ti_3SiC_2

1. Introduction

Recent interest in the ternary compound Ti_3SiC_2 is due to a combination of ceramic and metal properties. The compound has a layered crystal structure, low specific gravity (4.53 g/cm^3), and a high melting temperature (>3273 K) [1,2]. Its hardness at 4 GPa is anomalously low for a carbide [3–8], and despite its excellent mechanical properties, it is readily machinable using regular high-speed tool steels; no cooling or lubrication is required.

The compound was first synthesized by Nickel et al. [1] using chemical vapor deposition (CVD). Attempts to synthesized single-phase Ti_3SiC_2 by combustion synthesis, reactive sintering and arc melting have yielded limited success [2,8–11]. Significant amounts of second phases were present in the reaction products when a stoichiometric blend (3Ti:Si:2C) of elemental reactants was used. The amount of second phases could be minimized or eliminated by altering the starting reactant ratio or by substituting carbide as the source for carbon [4,12]. Although TiC also was used as the starting powders in other investigations [12,13], we considered that using elemental Ti, Si and C powders as source should be more effective for the formation of Ti_3SiC_2, as compared to chemically stable SiC or TiC. However, the validity of such starting materials has not been confirmed yet by the few previous investigations [2,4,11,14]. Otherwise, we firstly adopted activated carbon instead of graphite or carbon to synthesized Ti_3SiC_2, because activated carbon has higher activity than graphite and carbon. The present work was, therefore, aimed at synthesizing high-purity Ti_3SiC_2 with near-full density by hot pressing mixtures of Ti, Si and activated carbon powders. The mechanical properties of the synthesized Ti_3SiC_2 polycrystals were investigated.

2. Experimental procedure

Commercial Ti (38 μm, >99.6 purity, Beijing Nonferrous metal Co., China), Si (5 μm, >99.5% purity, Beijing FangDa Co., China) and activated carbon or graphite (7 μm, >99.8% purity,) powders were used. The powder mixtures were ball-milled in ethanol, in a polyurethane container with agate balls for 72 h. The slurry was subjected to stirred-drying in a rotary evaporator at 60 °C, and the resulting mixture was reground in a mortar and screened through a 100-mesh sieve, The mixture powders were compressed at 100 MPa in 50 mm diameter disk, then the green compacts were hot-pressed in foil lined graphite dies at 1600 °C, for 2 h, 25 MPa, under flowing argon. The heating and

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cooling rates were 10 and 15 °C/min, respectively. The resultant products were examined by (XRD) D/EAX-3B X-ray diffractometer with CuK_α radiation. The XRD data were refined for lattice parameters and phase fractions by the Rietveld analysis. The density was determined by the Archimede's method. Microstructures were observed by scanning electron microscopy (SEM). Flexure strength was measured in a 3-point bending test with spans of 30 mm. The bending tests were performed at a crosshead speed of 0.5 mm/min using specimens of nominal dimensions 30×4×3 mm^3. The work of fracture was measured in a 4-point bending test with lower and upper spans of 30 and 10 mm, respectively. The bending tests were performed at a crosshead speed of 0.05 mm/min using specimens of nominal dimensions 30×4×3 mm^3. At least six samples were used at each test. The tensile surface was ground and polished to achieve a mirrorlike surface finish prior to mechanical testing. Young's modulus was measured by the strain gauge method.

3. Results and discussion

Fig. 1 shows XRD patterns of the products obtained by heating two different powders of the mixed Ti, Si, graphite and Ti, Si, activated carbon with a molar ratio 3:1.2:2, in an argon atmosphere at 1600 °C. The purity of the reaction product was reported to be very sensitive to the discrepancy from the stoichiometric composition [14]. The deficiency of Si usually favors the formation of TiC [13,14]. Loss of Si might occur by evaporation in the sample sintered in Ar, resulting in a product consisting of quite a large amount of TiC. So a composition with a slight excess of Si than suggested by stoichiometry was tried. Fig. 1 shows that using activated carbon instead of graphite or carbon, higher phase purity was obtained at 1600 °C for 2 h, due to the higher activity of activated carbon than graphite or carbon. From the Rietveld analysis of X-ray diffraction spectra, the Ti_3SiC_2 content of the powder synthesized was calculated to be about 87 wt.% for (a) and 98 wt.% for (b). The content of Ti_3SiC_2 (b) was much higher than (a). Ti_3SiC_2 had a hexagonal structure with space group of P63/mmc. Lattice parameters of $a=3.062$ Å and $c=17.662$ Å were calculated from the refinement. The lattice constants calculated in this work agree quite well with the result of Jeitschko et al. [15].

The formation reaction of Ti_3SiC_2 from the mixed elemental powders, is considered to be highly related to the formation of the liquid phase in the Ti–Si system. The eutectic temperature in the Ti–Si system is 1603 K. At first, TiC forms between the Ti and C particles as shown in Eq. (1), because thermodynamically this reaction is favored among all possible reactions in the mixture.

$$\mathrm{Ti} + \mathrm{C} \rightarrow \mathrm{TiC} \quad (1)$$

Secondly, at a temperatures near the eutectic point (1603 K), an eutectic liquid phase appears between the Ti and Si particles as follows.

$$\mathrm{Ti} + \mathrm{Si} \rightarrow \mathrm{Ti\text{-}Si(l)} \quad (2)$$

Finally, Ti_3SiC_2 grains are formed at the interfaces between the eutetic liquid phases and the particles.

Table 1
Selected properties of the Ti_3SiC_2

Property	Value
Density (g/cm^3)	4.52
Vickers hardness (GPa)	4.32±0.16
Young's modulus (GPa)	303±7
Flexure strength (MPa)	376±8
Work of fracture (J/m^2)	1350±30

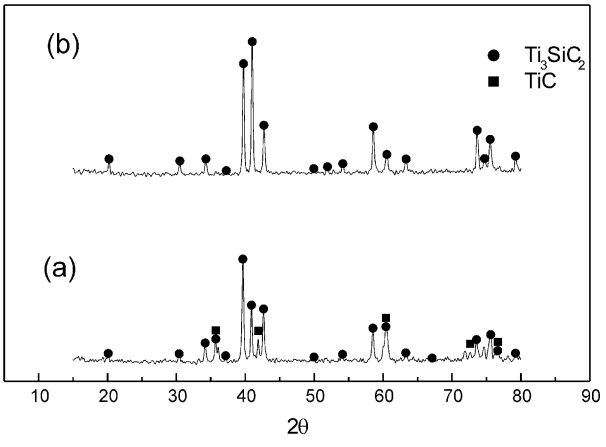


Fig. 1. X-ray diffraction patterns of the Ti_3SiC_2 samples fabricated by hot-pressing the elemental powders with molar ratio of 3Ti:1.2Si:2C (a) graphite and (b) active carbon.

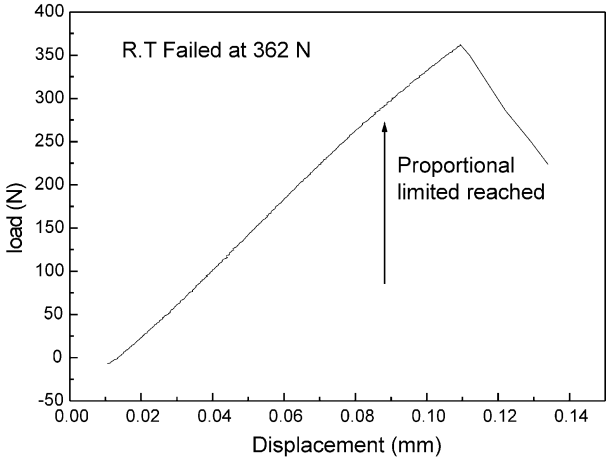


Fig. 2. Load/displacement curves by 4-point bending.

$$TiC + Ti\text{-}Si(l) \rightarrow Ti_3SiC_2 \quad (3)$$

The reaction (1) between Ti and C is highly exothermic, which can increase local temperatures inside the powder compacts. Therefore, the reactions (2) and (3) might be triggered even when the furnace temperature was below the eutectic point (1603 K).

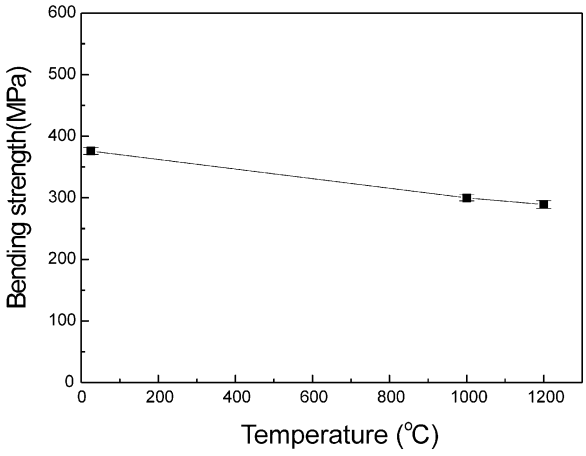
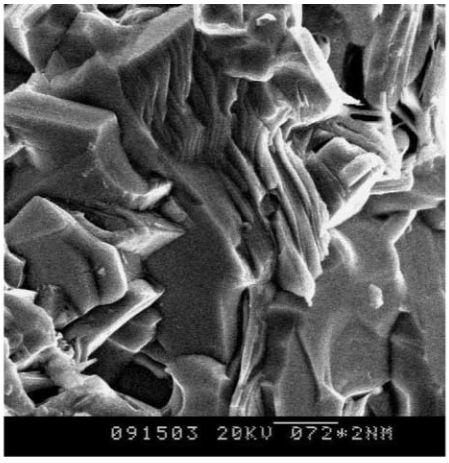
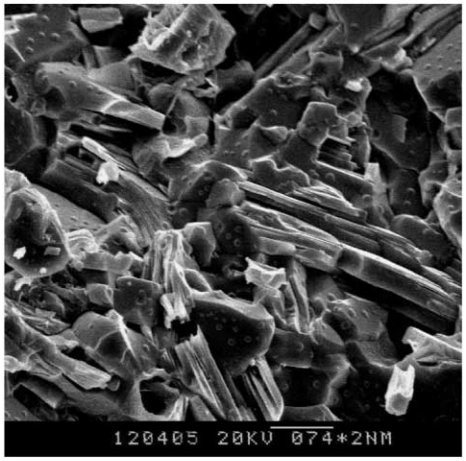


Fig. 3. Relationship between bending strength and temperature.

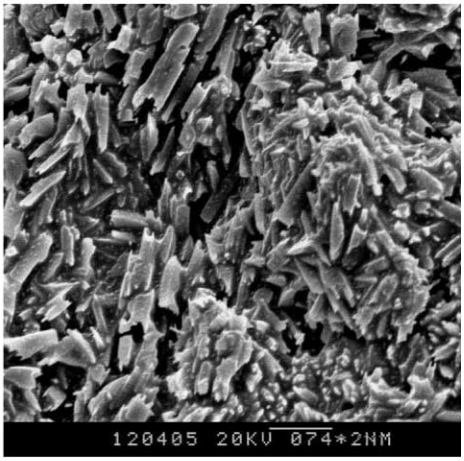
The mechanical properties were measured using the hot-pressed sample from the starting powders containing a slight excess of Si relative to Ti_3SiC_2. Table 1 shows selected properties of the sample synthesed with active carbon instead of carbon. The flexural strength was 376 MPa, which was higher than the values reported by Barsoum [4], Li et al. [16] and Tong et al [13]. The characteristic load-deflection curve for specimens at room-temperature is given in Fig. 2. It is evident that the Ti_3SiC_2 exhibits non-linear load-deflection behavior at 280 N, which indicates that the Ti_3SiC_2 possesses plastic deformation above 280 N at ambient temperature. The work of fracture is 1350 J/m^2, which is higher than the values reported by Tamer El-Raghy et al. [1] and of monolithic SiC and Si_3N_4. Young's modulus measured by the strain gauge method is 303 GPa, i.e. comparable to be value obtained by Barsoum and El-Raghy [4], who used the resonance method, and Li et al. [16], who also used the strain gauge method.



(a)



(b)



(c)

Fig. 4. Fracture morphology of samples tested at different temperatures: (a) at room temperature; (b) at 1273 K; (c) at 1473 K.

To investigate the effect of temperature on strength, samples of Ti_3SiC_2 were tested from room temperature to 1273 K. Fig. 3 shows the temperature dependence of strength for Ti_3SiC_2. Up to 1473 K, the samples kept high strength (about 289 MPa). Fig. 4 shows fracture morphologies of samples tested at different temperatures. SEM observation of fractures confirmed the unique behavior of the studied materials in comparison with the one shown by brittle ceramics. The fracture surface is very developed for Ti_3SiC_2 materials with many layers, steps and grain buckling [Fig. 4(a)]. Ti_3SiC_2 appeared to be a damage-tolerant material able to contain the extent of damage via a number of multiple energy-absorbing mechanisms herein identified namely: delamination, grain buckling, grain pull-out, which could improve fracture toughness of the materials. Brittleness and predominately intergranular failure were observed at room temperature, while at high temperature, failure was intergranular and transgranular. Low ductility and intergranular fracture in Ti_3SiC_2 at room temperature are due to an insufficient number of operative slip systems, which results in incompatible deformation at the grain boundaries. The ductility and fracture morphology changed with increase in temperature.

4. Summary

High-purity Ti_3SiC_2 polycrystals can be conveniently fabricated by reactive hot-pressing of mixed elemental powders. A slight excess of Si is beneficial to synthesize Ti_3SiC_2, active carbon resulting more effective than graphite for the formation Ti_3SiC_2. Ti_3SiC_2 showed excellent mechanical properties from room temperature to 1473 K.

Acknowledgements

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