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Short communication

Fabrication of high-purity ternary carbide Ti_3AlC_2 by spark plasma sintering (SPS) technique

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Abstract

The effect of silicon on synthesis of Ti_3AlC_2 by spark plasma sintering (SPS) from TiC/Ti/Al powders was investigated. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for phase identification and microstructure evaluation. The results showed that addition of silicon can considerably accelerate the synthesis reaction of Ti_3AlC_2 and fully dense, essentially single-phase polycrystalline Ti_3AlC_2 could be successfully obtained by sintering 2TiC/1Ti/1Al/0.2Si powders at 1200–1250 °C under a pressure of 30 MPa. SEM micrographs showed the obtained Ti_3AlC_2 samples to be about 2–5 μm thick and 10–25 μm long platelets. The fracture toughness and flexural strength of Ti_3AlC_2 were 7.0 ± 0.2 MPa $m^{1/2}$ and 450 ± 10 MPa, respectively.

Keywords: A. Sintering; B. Grain size; C. Mechanical properties; Ti_3AlC_2

1. Introduction

The ternary-layered compound Ti_3AlC_2 has been the focus of investigations due to its unique combination of properties [1]. Like metals, it is thermally and electrically conductive, easy to machine with conventional tools, and resistant to thermal shock; like ceramics, it has high strength, high melting point and thermal stability. Moreover, Ti_3AlC_2 is also a damage-tolerant material [2]. Because of these unique properties, Ti_3AlC_2 is expected to be applied as high temperature structural material, machinable ceramics, kiln furniture, heat exchanger, and so on.

However, further research and application of Ti_3AlC_2 are halted for the difficulty to synthesize high-purity Ti_3AlC_2. Pietzka and Schuster [3] first synthesized Ti_3AlC_2 by sintering cold-compacted power mixtures of Ti, TiAl, Al_4C_3, and carbon under hydrogen for 20 h. Tzeonov and Barsoum [2] successfully prepared high-purity bulk Ti_3AlC_2 polycrystals by hot isostatic pressing (HIP) mixtures of titanium, graphite and Al_4C_3 powders. However, such methods were either very time-consuming or requiring high pressure and high temperature.

Recently, the spark plasma sintering (SPS) method has been developed for fabricating metals, ceramics, and composites [4–8]. Compared to hot-pressing and hot isostatic pressing (HIP), the SPS technique allows sintering at lower temperatures and shorter time. Zhou et al. adopted this technique to sinter Ti_3AlC_2 from different raw materials [9]. However, their method is two steps and relatively complex.

High-purity Ti_3AlC_2 polycrystals were recently successfully obtained by hot pressing of Ti/TiC/Al powders at 1300–1400 °C [10]. In the present study, we adopted the spark plasma sintering technique to fabricate and simultaneously density high-purity Ti_3AlC_2 by one-step process.

2. Experimental procedure

All the work was conducted by using powder mixtures of titanium (99.0% purity, 10.6 μm), Si (99.5% purity, 9.5 μm), Al (99.8% purity, 12.8 μm) and TiC (99.2% purity, 8.4 μm). A mixture with a designed composition was firstly mixed in ethanol for 24 h, then was filled into a 20 mm diameter graphite die and finally spark plasma sintered (SPS-1050, Lzumi Technology Co. Ltd., Japan). The samples were heated at a rate of 80 °C/min at 1150–1300 °C. The soaking time was 8 min.

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The sintered sample was polished and the density was measured by the Archimedes' method. The micro-hardness was measured using a Microhardness Tester (Leitz Wetzlar, Germany) at 1 N with a loading time of 30 s. The three-point bending flexural strength was measured on Instron-1195 machine with cross head speed of 0.5 mm/min and span of 20 mm. Single-edge notch beam (SENB) specimens with dimensions of 4 mm × 8 mm × 36 mm were used for the fracture toughness measurements. X-ray diffraction (XRD) was used to determine the phase composition. The lattice parameters were measured using silicon as the internal standard. The microstructures of the samples were observed by SEM (JSM-5610LV, JEOL Ltd., Japan).

3. Results and discussion

Fig. 1 shows the XRD patterns of different composition sintered at 1250 °C. Sample (a) had a starting composition of 2TiC + Ti + 1.0Al, sample (b) had 20 mol% more Al than sample (a). The main phases of sample (a) were Ti_3AlC_2 and TiC. The diffraction peaks of TiC in sample (b) were much weaker than those of TiC in sample (a), which also indicated that addition of Al favors the formation of Ti_3AlC_2. However, in both samples, the content of TiC impurity is considerable.

Ti_3AlC_2 is known to have the same structure and similar properties of Ti_3SiC_2 [1,2]. Moreover, a liquid Al–Si alloy containing 0–44% Si forms at 1000 °C in the Al–C–Si–Ti quaternary system [11]. Thus, the addition of Si to the initial powder mixture may improve the synthesis of Ti_3AlC_2 via a solid–liquid reaction. So different Si amounts were added in order to obtain high-purity Ti_3AlC_2.

Fig. 2 shows the XRD patterns of samples obtained by sintering different compositions of $Ti_3Al_{1.2-x}Si_xC$, where $x = 0.05$, 0.1, 0.2 and 0.3, respectively. For the sample with the addition of 0.05 mol Si, the product was high pure; only a very weak peak of TiC ($2\theta = 36.0°$) was identified. For samples with of 0.10 and 0.20 mol Al addition, reaction product was pure Ti_3AlC_2. Nevertheless, in the 0.30 mol Al sample, a new phase (Ti_2AlC) appeared. Therefore, $Ti_3Al_{1.0}Si_{0.2}C$ composition was chosen for further experiments.

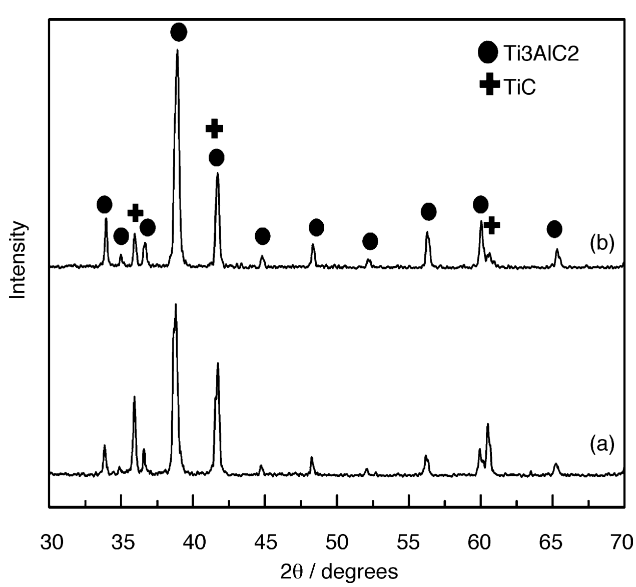

Fig. 1. XRD patterns of sample (a) with the starting composition of 2TiC + Ti + 1.0Al, and (b) with the starting composition of 2TiC + Ti + 1.2Al sintered at 1250 °C.

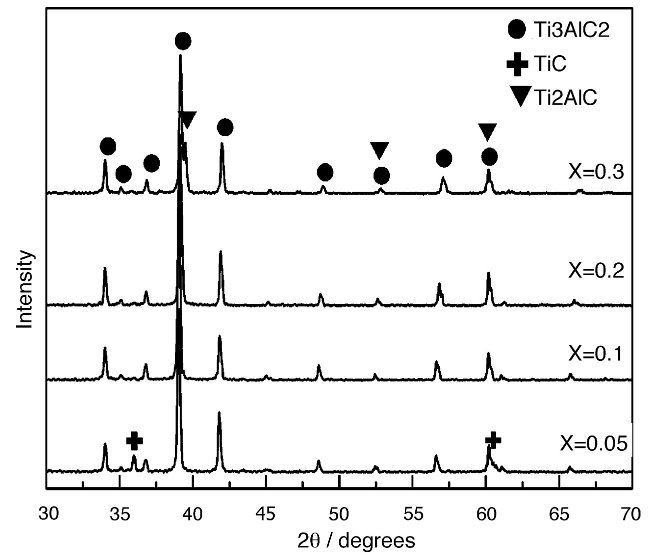

Fig. 2. XRD patterns of sample with the starting composition of $Ti_3Al_{1.2-x}Si_xC$, where $x = 0.05$, 0.1, 0.2, and 0.3, sintered at 1250 °C.

Fig. 3 shows the XRD patterns of samples obtained by sintering $Ti_3Al_{1.0}Si_{0.2}C$ at different temperatures. When sintered at 1150 °C, the content of Ti_3AlC_2 in the product was very high, only very weak TiC ($2\theta = 36.0°$) and Al_3Ti ($2\theta = 47.3°$) peaks were identified. By sintering at 1200 and 1250 °C, essentially single-phase Ti_3AlC_2 was obtained. When sintered at 1300 °C, TiC appeared again, and Ti_3AlC_2 weakened. The densities of Ti_3AlC_2 samples sintered at 1200 and 1250 °C were measured to be 4.19 and 4.21 g/cm^3, respectively, i.e. 98.6% and 99.1% of the theoretical density.

Fig. 4 shows SEM micrographs of the fracture surfaces of Ti_3AlC_2 sintered at 1250 °C from different compositions. In sample (a), there was a small amount of fine particle TiC. The

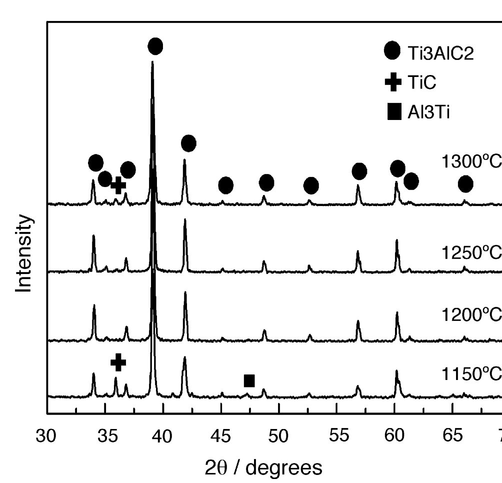

Fig. 3. XRD patterns of sample with the starting composition of $Ti_3Al_{1.0}Si_{0.2}C$, sintered at 1150–1300 °C.

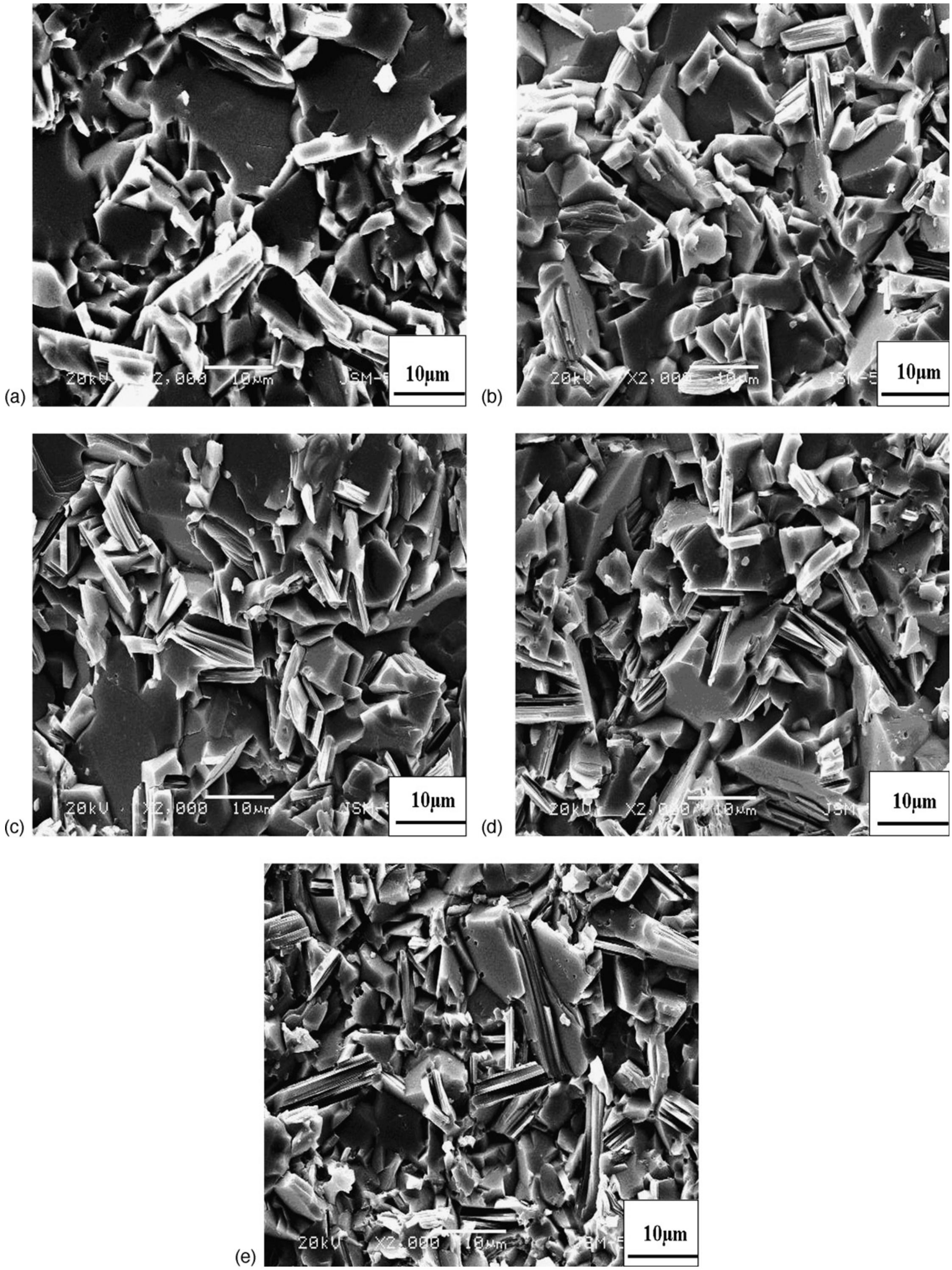

Fig. 4. SEM micrographs of the fracture faces of Ti_3AlC_2 material synthesized from the starting composition of $Ti_3Al_{1.2-x}Si_xC$: (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$, and (e) $x = 0.3$ sintered at 1250 °C.

well-developed Ti_3AlC_2 grains and the produce disappearance of TiC can be observed with increasing Si content of from 0.05 to 0.2 mol. Ti_3AlC_2 grains were platelets about 2–5 μm thick and 10–25 μm long in sample (d). Ti_3AlC_2 decreased in size, while a new phase Ti_2AlC appeared in sample (e).

Fig. 5(a) shows the backscattered electron image of the polished surface of $Ti_3Al_{1.0}Si_{0.2}C$ sintered at 1250 °C. The chemical analysis results listed in Table 1 revealed the atomic ratio of Al to Si in the sintered product (=4.35) to be smaller than in the starting mixture (=5). The measured crystal lattice parameters are $a = 0.3060$ and $c = 1.8308$ nm, i.e. slightly smaller than the results given by Tzenov [2] and Pietzka [3], since the atomic semi diameter of silicon is slightly smaller than that of aluminum.

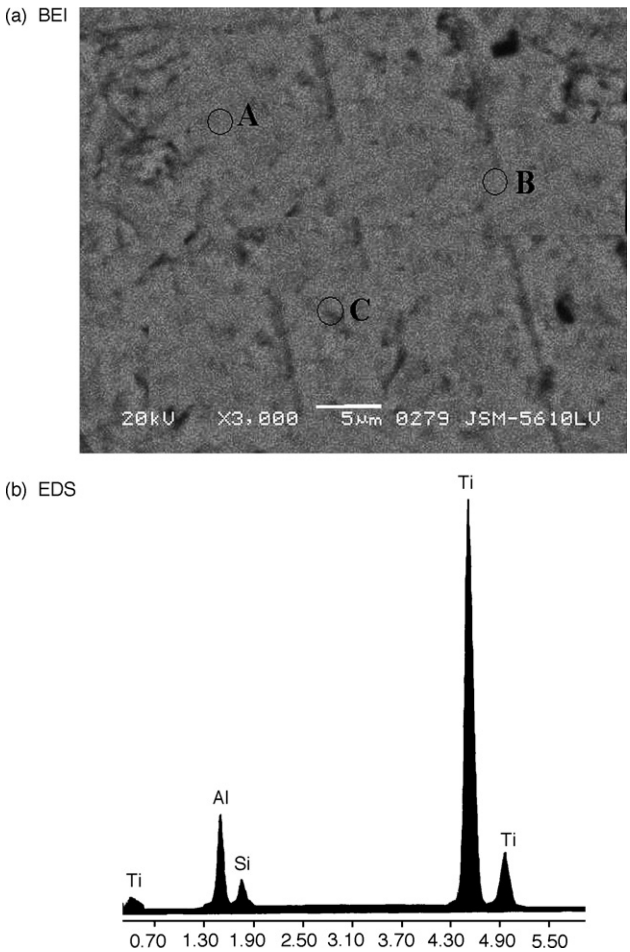

Fig. 5. Microstructure of polished surfaces of $Ti_3Al_{1.0}Si_{0.2}C$ sintered at 1250 °C.

Table 1
Atomic ratios of Ti, Al and Si of $Ti_3(Al/Si)C_2$

at.%	Ti	Al	Si	Al/Si
A	71.49	23.08	5.43	4.25
B	71.85	22.86	5.29	4.32
C	72.16	22.67	5.17	4.38
The whole	72.07	22.71	5.22	4.35

The micro-hardness of the $Ti_3Al_{1.0}Si_{0.2}C_2$ sample was 4.8 GPa which is consistent with a previous work [2], its fracture toughness was 7.0 ± 0.2 MPa $m^{1/2}$, a value higher than traditional brittle ceramics like SiC, Si_3N_4, and Al_2O_3, possibly deriving from its layered nature, and the flexural strength was 450 ± 10 MPa, one higher value than the one reported by Tzenov and Barsoum [2]. Since brittleness is the most obvious shortcoming of structural ceramics, the high fracture toughness and flexural strength of Ti_3AlC_2 indicate this material to be a very promising candidate for application as structural material.

4. Conclusions

High-purity Ti_3AlC_2 can be prepared using a one-step method by the spark plasma sintering technique. It was demonstrated that proper additions of silicon accelerate the crystal growth of Ti_3AlC_2. High-purity polycrystalline bulk Ti_3AlC_2 could be fabricated at the relatively low temperature of 1200–1250 °C by spark plasma sintering by using powder mixtures of composition TiC:Ti:Al:Si = 2:1:1:0.2 in molar ratio. The fracture toughness and flexural strength of Ti_3AlC_2 were 7.0 ± 0.2 MPa $m^{1/2}$ and 450 ± 10 MPa, respectively.

Acknowledgment

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