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Effect of TiO_2 addition on the properties of $Ti_3Si(Al)C_2$ based ceramics fabricated by reactive melt infiltration

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ABSTRACT

In this paper, $Ti_3Si(Al)C_2$ based ceramics were fabricated by reactive melt infiltration (RMI) of TiC/TiO_2 preforms with liquid silicon. The microstructure, phase composition, and mechanical properties of the $Ti_3Si(Al)C_2$ based ceramics have been investigated to understand the effect of phase composition of the preforms on the formation mechanisms of $Ti_3Si(Al)C_2$. The preforms with different content of TiO_2 infiltrated at 1500 °C with liquid silicon for 1 h were composed of $Ti_3Si(Al)C_2$, Al_2O_3, TiC, $TiSi_xAl_y$ and residual Al. The prior generated Al_2O_3 phases inhibited the dispersion of $Ti_3Si(Al)C_2$ phases, resulting in the drastically grain growth of $Ti_3Si(Al)C_2$. Subsequently, the microstructure with gradually increasing $Ti_3Si(Al)C_2$ grain size resulted in the decrease of the bending strength and fracture toughness of samples. When the content of TiO_2 reached 20 wt%, the bending strength reached the maximum, 326.6 MPa. The fracture toughness attained the maximum, 4.3 MPa $m^{1/2}$, when the content of TiO_2 was 10 wt%.

1. Introduction

The ternary carbide and nitride with general formula $M_{n+1}AX_n$ (n=1, 2 or 3) have attracted extensive attention, which possess a unique combination of ceramic and metal properties for its special nanolaminated microstructure and coexistence of three kinds of bonds [1,2]. As representative of the MAX phase, Ti_3AlC_2 and Ti_3SiC_2, possess excellent electrical and thermal conductivity, low hardness and high elasticity modulus at the room temperature just like the metal. Meanwhile, they keep unique properties of ceramics. Such as high temperature stability, low density, high melting, excellent thermal shock resistance and oxidation resistance. The Ti_3AlC_2 or Ti_2AlC contained composites have been synthesized through in-situ hot pressing and reaction hot-pressing process [3,4].

Reactive melt infiltration (RMI) is a versatile method to form ceramic based composites, in which melt is infiltrated into a porous ceramic preform driven by capillary force [5–7]. Sequentially, the infiltrated melt reacts with porous ceramic preforms to form composites with a certain microstructure expected. Meanwhile, the phase content in the final products is controllable by adjusting the ratio of the powders in the starting materials.

RMI is widely used in the fabrication of ceramics based composites, for example, ZrB_2-ZrC based composites [8–10] and fabrication of C_f/ZrC-SiC composites with Zr-8.8Si alloy [11]. It is also a preferred method in the fabrication of advanced ceramics such as Si-SiC [7,12] and MAX phase, which is extremely popular nowadays.

MAX phase based composites have been fabricated by a joint process of three-dimensional printing (3D printing) and reactive melt infiltration (RMI) in our previous work, in which the first step, porous preforms composed of TiC or/and TiO_2 were fabricated by three-dimensional printing [12,13]. In the second step, Al metal melt was infiltrated into the porous preforms to obtain the MAX phase based materials. The Ti-Al-O-C composites were fabricated by infiltration of Al melt into TiC/TiO_2 preform, which attained flexural strength of 320 ± 40 MPa, Young's modulus of 7.2 ± 0.4 GPa and Vicker's hardness of 2.5 ± 1.2 GPa [14,15]. In the similar way, Ti_3SiC_2 based composites were fabricated by liquid silicon infiltration (LSI) of TiC preform at 1700 °C, which attained flexural strength of 293 ± 17.8 MPa, Vicker's hardness of 184 ± 24 GPa and electrical resistivity of 27.8 ± 1 μΩ cm [16]. The effect of Al-Si alloy constitute on the production of Ti_3SiC_2 phase has been analyzed [17].

Compared with Ti_3SiC_2, $Ti_3Si(Al)C_2$ possesses a better oxidation resistance [18,19]. Al_2O_3 has high melting point and excellent oxidation resistance. The combination of $Ti_3Si(Al)C_2$ and Al_2O_3 may lead to the composite ceramics with both advantages. However, only a few reports concerning about the $Ti_3Si(Al)C_2/Al_2O_3$ composites can be found. The present work aims to fabricate $Ti_3Si(Al)C_2$ based ceramics by reactive Al-Si alloy (70 wt% Al, 30 wt% Si) melt infiltration of TiC/TiO_2 preforms. Al_2O_3 phase is expected to in-situ form by the reaction between Al and TiO_2. The effects of TiO_2 mass fraction on the microstructure, phase composition, and

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mechanical properties of the $Ti_3Si(Al)C_2$ based ceramics were studied.

2. Experimental

2.1. Material preparation

TiC powders (LongJin S melt Co. Ltd., ShangHai, China) with an average particle size of 1–2 μm and a nanoscale anatase TiO_2 powders (HuiJing Co. Ltd., ShangHai, China) with a mean particle size of 20 nm were used. Five kinds of mixed powders (1-X) wt% TiC-X wt%TiO_2 (X=10, 20, 30, 40, 50) were prepared, which were made up of TiC and TiO_2 powders. Firstly, the mixed powders were blended into distilled water with 0.5 wt% of dispersant sodium carboxymethyl cellulose ($RnOCH_2COONa$ BoDi Co. Ltd., TianJin, China). Sequentially, the slurry was ball-milled for 24 h, and then freeze-dried (LGJ-18S, SongYuanHuaXin Science and Technology Develop Co. Ltd., BeiJing, China). After that, the mixed powders were passed through a 200 μm sieve.

The well-mixed powders were cold-pressed into bars to obtain TiC/TiO_2 preforms with different mass fraction of TiO_2, and dimensions of samples were 70 mm × 15 mm × 13 mm. Sequentially, the preforms were placed into Al_2O_3 crucible which was fully filled by SiC powders, then put into Al_2O_3 cube furnace, heat-treated at 1400 °C in flowing argon for 1 h. By heat-treatment, certain mechanical strength can be obtained and the damage of preforms before reaction melt infiltration can be avoided. After heat-treatment, the preforms were infiltrated with $Al_{70}Si_{30}$ alloy (Huawei Ruike Co. Ltd., BeiJing, China) at 1500 °C for 2 h in flowing argon.

To prepare testing samples, the preforms infiltrated were polished to a 5 μm and then cut by electro-discharge machining (EDM). The samples were prepared for fracture toughness and flexural strength measurements with dimensions of 26 mm × 5 mm × 2.5 mm and 36 mm × 4 mm × 3 mm, respectively. The final samples fabricated with preforms composed of (1-X) wt%TiC-X wt%TiO_2 (X=10, 20, 30, 40, 50) were designated as TO10, TO20, TO30, TO40, and TO50.

2.2. Characterizations

The samples were crushed into powders and analyzed by X-ray diffraction (XRD) with CuKα radiation at 40 kV and 100 mA. The element composition and microstructure of the infiltrated samples were characterized by back-scattered electron image (BSE) and scanning electron microscope (SEM, S-4700, Hitachi, Tokyo, Japan). The fracture toughness was measured by single-edge-V-notched beam method (SEVNB) on a universal testing machine (CMT 4304, Sans, Shenzhen, China) at a loading rate of 0.05 mm/min with a loading span of 20 mm. However, the flexural strength was measured by three-point bending method on the machine at a loading rate of 0.5 mm/min with a loading span of 30 mm.

3. Results and discussion

3.1. Open porosity and density

The open porosity and density of the samples heat-treated are listed in Table 1. With the increase of the addition content of TiO_2, the open porosity of the as heat-treated samples increased from 50.95% to 58.73%, while the density decreased from 2.37 g/cm^3 to 1.88 g/cm^3.

During the process of reactive melt infiltration, $Al_{70}Si_{30}$ alloy melt was infiltrated into the porous TiC/TiO_2 preforms driven by capillary force to obtain the MAX phase based materials. The open porosity and density of the as fabricated samples are listed in Table 2. The open porosity of the preforms decreased to less than 5% after reactive melt infiltration, indicating that the pores of preforms after reactive melt infiltration were well penetrated and filled. With increasing of the amount of TiO_2, the open porosity of the as fabricated samples increased from 1.43% to 3.72%, while the density decreased from 3.82 g/cm^3 to 3.28 g/cm^3.

Table 1
Open porosity and density of samples before heat-treatment varying with the content of TiO_2 (in the starting material).

TiO_2 mass fraction (%)	Open porosity (%)	Volume density (g/cm^3)
10	50.95	2.37
20	52.15	2.28
30	54.35	2.14
40	56.24	2.02
50	58.73	1.88

Table 2
Open porosity and density of samples after reactive melt infiltration varying with the content of TiO_2 (in the starting material).

TiO_2 mass fraction (%)	Open porosity (%)	Volume density (g/cm^3)
10	1.43	3.82
20	2.11	3.62
30	2.93	3.46
40	3.12	3.28
50	3.72	3.28

3.2. Phase composition and microstructure

XRD patterns of samples TO10, TO20, TO30, TO40, TO50 and pure TiC preforms infiltrated by $Al_{70}Si_{30}$ alloy are shown in Fig. 1. The main generated phases were $Ti_3Si(Al)C_2$, Al and Al_2O_3, meanwhile the residual TiC and $TiSi_xAl_y$ could be detected. No residual TiO_2 was found in any samples. The weight ratio of $Al_{70}Si_{30}$ alloy and preforms was 3:1, and the reaction between Al and TiO_2 is shown in Eq. (1-1). It is notable that TiO_2 in the preforms reacted completely.

With the increase of TiO_2 content, the intensity of $Ti_3Si(Al)C_2$ diffraction peaks increased, but the intensity exhibited a slight dropping conversely as the content of TiO_2 reached 50 wt%. The intensity of Al_2O_3 diffraction peaks showed an increasing trend. The Al_2O_3 phase was generated according to Eq. (1-1), which can explain the change tendency of Al_2O_3 diffraction peaks. The intensity of Al diffraction peaks kept almost no change before the content of TiO_2 reached 50 wt%, at which the intensity of Al diffraction peaks increased obviously. The intensity of TiC diffraction peaks decreased with increasing TiO_2 content.

In order to compare the phase content in different samples, the

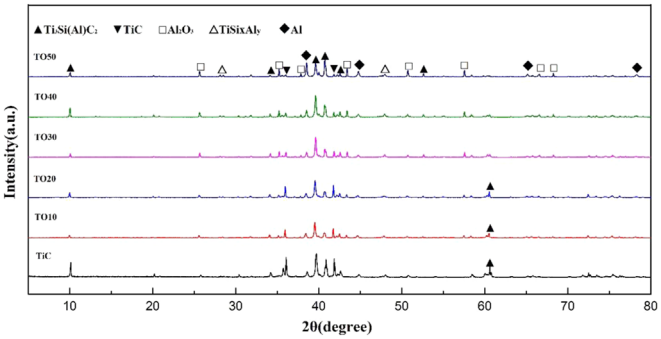

Fig. 1. XRD patterns of samples TiC, TO10, TO20, TO30, TO40, and TO50.