Effect of Particle Size Distribution on Microstructure and Mechanical Properties of TiB$_2$-SiC-Si Composites

Cuiping Zhang$^{1,2, a *}$, Tian You$^{1,2, b}$, Ling Zhao$^{1,2, c}$, Qian Xia$^{1,2, d}$, Zhaobo Qin$^{1,2,e}$, Yongyang Liu$^{1,2, f}$, Hongqiang Ru$^{1,2, g}$, Wei Wang$^{1,2, h}$ and Xinyan Yue$^{1,2, i}$

$^1$ School of Materials Science and Engineering, Northeastern University, Shenyang, Liaoning 110004, China
$^2$Key Laboratory for Anisotropy and Texture of Materials (MOE), Northeastern University, Shenyang, Liaoning 110004, China
$^a$zhangcp@smm.neu.edu.cn, $^b$1041306845@qq.com, $^c$371921216@qq.com,
$^d$782582415@qq.com, $^e$315155343@qq.com, $^f$821593190@qq.com,
$^g$ruh@smm.neu.edu.cn, $^h$wangw@atm.neu.edu.cn, $^i$yuexy@atm.neu.edu.cn

Abstract. TiB$_2$-SiC-Si ceramic composites were fabricated based on molten silicon infiltration method. The influence of particle size distribution of TiB$_2$ on the microstructure and mechanical properties of TiB$_2$-SiC-Si ceramic composites was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron universal testing machines, etc. The results showed that the composite consisted of TiB$_2$, SiC and Si phases. The microstructure analysis showed that: the content of residual Si could be controlled less than 16 vol.% in the composite by particle size distribution. When the particle size distribution of TiB$_2$ was 42:32:26, the TiB$_2$-SiC-Si composite showed the optimum properties. The open porosity, volume density, Vickers-hardness, flexural strength and fracture toughness were 0.51%, 3.63 g/cm$^3$, 17 GPa, 275 MPa and 5.7 MPa·m$^{1/2}$, respectively.

1. Introduction

Due to its high hardness, high melting point and high chemical stability, etc., titanium diboride (TiB$_2$) has found applications in various areas, such as military industries, mechanics, chemical engineering and aeronautics [1-4]. Currently, nearly all TiB$_2$ based ceramics are produced by hot-pressing and pressureless sintering, with low fracture toughness and high fabrication costs hampering its applications [5-7]. Introduction of the second phase (SiC, TiC, etc.) can improve the fracture toughness of TiB$_2$ [8-11]. Nevertheless, some problems have to be solved in the production, such as deformation, cracks and high fabrication costs. Therefore, there is a demand in developing a simple and low-temperature-sintering approach to fabricating TiB$_2$ composite without deformation in shapes and compromise in properties.

In recent years, researchers have developed a new process for preparing TiB$_2$-SiC composites based on the mechanism of reactive sintering SiC, which has the advantages of simple process, short sintering time, far lower sintering temperature and cost than hot pressing and pressureless sintering TiB$_2$, net size sintering and easy preparation of large and complex shape products [12,13]. However, the content of free Si in TiB$_2$-SiC composite prepared by this process is as high as 30 vol.% [14], which has a great impact on the properties and use of the material. Therefore, in this study, TiB$_2$ particle size distributions was used to reduce the content of free Si of the composites. Further, the...
effects of TiB₂ particle size distributions on the phase, microstructure, density and mechanical properties of TiB₂-SiC composites were discussed.

2. Materials and methods

2.1. Preparation of TiB₂-SiC-Si composites.

The commercial TiB₂ powders (Shandong Pengcheng Special Ceramics Co., China, 99 % purity) with various particle size distributions given in Table 1 and phenolic resin solution with a ratio of TiB₂-10% C (mass percent) were mechanically mixed using ethanol as a liquid medium for 24 h, then dried at 40 °C. The dried powder mixtures were crushed using mortar and then sieved through a 250 μm sieve. The powder mixtures were uniaxially pressed at 180 MPa for a dwell time of 5 s. The compacted specimens (36 mm×6 mm×6 mm) were infiltrated with silicon lumps (99.9 % purity, 5-10 mm) in a resistance heated graphite furnace under vacuum (50 Pa) at 1600 °C for 60 min, using a heating rate of 5 °C/min.

2.2. Microstructure and mechanical properties.

The volume density and open porosity of TiB₂-SiC-Si composites were measured via Archimedes principle using distilled water. Six samples were tested for each composite and the average values were reported. The phase was analyzed via X-ray diffraction (XRD) using CuKα radiation at 40 kV and 30 mA. The microstructure was examined using a scanning electron microscope (SEM). The elemental concentration profile of the microstructure was determined using energy dispersive X-ray spectroscopy (EDS). The volume percent of components in TiB₂-SiC-Si composites were determined using the quantitative image analysis software (Image-Pro Plus, Media Cybernetics company) on at least 10 SEM micrographs for each composite [15]. The samples for the micro-structural characterization were prepared using standard metallographic procedures that included a last stage of polishing by 1 μm diamond paste.

The Vickers-hardness was tested on the polished surface using a Vickers-hardness tester at a load of 1 kg for a dwell time of 10 s in accordance with 450SVD. Ten indentations were made on each sample. The three-point bending (TPB) samples, with a dimension of 25 mm×5 mm×6 mm, were prepared and polished to a surface finish using 1 μm diamond paste. The TPB was performed using a three-point bending with a span of 20 mm attached to a hydraulic universal testing machine (WE-10 A, Mts Systems Co. Ltd., China). In the TPB tests the cross head was set at a rate of 0.05 mm/min. The fracture toughness was measured by single edge notched beam method (specimen size = 25 × 5 × 6 mm, notch width=0.2 mm, notch depth=2 mm, bend span=20 mm, load speed=0.05 mm/min). Five bars were tested for each measurement of flexural strength and fracture toughness, respectively.

3. Results and discussion

3.1. Density of TiB₂-C green preforms

Table 2 shows the volume density and open-porosity of TiB₂-C porous green preforms with various particle size distributions. It can be seen from Table 2 that, the volume density of 2# and 4# green preforms with various powder mixtures is higher than that of 5# green preforms with monosized
powder. Not surprisingly, an inverse result was observed for the open-porosity, the open-porosity of 2# and 4# green preforms with various powder mixtures is lower than that of 5# green preforms with monosized powder. It illustrated that the porosity of TiB$_2$-C porous green preforms can be effectively decreased by optimizing the particle size distributions of TiB$_2$-powder. Generally, the volume density and open porosity of the green preforms are related to the particle size of the powder itself and the particle packing mode. Mixing one or more powders of smaller particle size into a powder of a certain size to occupy the gap of arranged large particles and form the closest packing, and the resulting green preforms can usually obtain higher volume density and lower open porosity[16].

### Table 2. The volume density and open-porosity of TiB$_2$-C green preforms with various particle size distributions.

| Number | Particle size distribution of TiB$_2$ coarse:medium:fine | Volume density (g/cm$^3$) | Open-porosity (%) |
|--------|--------------------------------------------------------|---------------------------|-------------------|
| 1#     | 46:23:31                                               | 2.81±0.01                 | 21.9±0.5          |
| 2#     | 66:15:19                                               | 2.85±0.02                 | 21.6±0.2          |
| 3#     | 51:26:23                                               | 2.65±0.02                 | 26.6±0.4          |
| 4#     | 42:32:26                                               | 2.89±0.01                 | 20.3±0.4          |
| 5#     | 100:0:0                                                | 2.78±0.02                 | 24.8±0.3          |

![XRD patterns](image)

**Figure 1.** XRD patterns of TiB$_2$-SiC-Si composites with various particle size distributions: (a) (1#) 46:23:31, (b) (2#) 66:15:19, (c) (3#) 51:26:23, (d) (4#) 42:32:26 and (e) (5#) 100:0:0.

#### 3.2. Phase composition of TiB$_2$-SiC-Si composites.

Figure 1 shows the XRD patterns of TiB$_2$-SiC-Si composites with various particle size distributions. According to the XRD results (Figure 1), the infiltrated composites consisted of three phases, namely original TiB$_2$ particles, free Si and SiC formed as a product of phenolic resin and Si reaction. In our system, one thing is certain: the complete consumption of C initially introduced in the powder mixtures, evidenced by the absence of C in the TiB$_2$-SiC-Si composites in XRD patterns (Figure 1).
This from another point of view indicates that: (i) the porosities of the preforms, fabricated with various particle size distributions, are appropriate and provide enough channels for molten Si infiltration; (ii) the molten silicon has appropriate fluidity, and the quantity of infiltrated silicon is enough to react with the introduced C in this study at 1600 °C under vacuum for a dwell time of 60 min.

Furthermore, by careful examination it can be observed that the relative intensities of Si main diffraction peaks (2θ=28.5 ° & 47.4 °) of 2# and 4# composites were lower, while that of 1#, 3# and 5# composites were higher, indicating that the amount of Si of 2# and 4# composites is lower and that of 1#, 3# and 5# composites is higher. A detailed explanation will be given in the next section.

3.3. Microstructure of TiB$_2$-SiC-Si composites.

Figure 2 shows the SEM micrographs of TiB$_2$-SiC-Si composites with various particle size distributions. In conjunction with the energy-dispersive spectrometer (EDS) and XRD results, it can be concluded that the light gray particles are TiB$_2$ particles, the black regions are SiC phases and the continuous gray regions are free Si, as marked in Figure 2(a). It can be seen from Fig. 2 that, the content of free Si (gray regions) of 2# and 4# composites is lower than that of 1# and 5# composites, while the content of TiB$_2$ (light gray regions) of 2# and 4# composites is higher than that of 1# and 5# composites. The results are confirmed by the results (Table 3) of quantitative image analysis of SEM micrographs. The content of free Si of 2# and 4# composites is 16.8% and 15.6% respectively, while that of 1# and 5# composites is as high as 23.0% and 22.9% respectively. In contrast, the content of TiB$_2$ of 2# and 4# composites is as high as 55.6% and 53.9% respectively, while that of 1# and 5# composites is only 50.0% and 50.7% respectively. It illustrated that the content of free Si of TiB$_2$-SiC-Si composites can be effectively decreased by optimizing the particle size distributions of TiB$_2$.

![Figure 2](image_url)

**Figure 2.** SEM micrographs of TiB$_2$-SiC-Si composites with various particle size distributions: (a) (1#) 46:23:31, (b) (2#) 66:15:19, (c) (3#) 51:26:23, (d) (4#) 42:32:26 and (e) (5#) 100:0:0.

It is reported that the pores in TiB$_2$-SiC-Si composites were partially occupied by in-situ reaction formed SiC because conversion of C to SiC due to reaction with molten silicon is associated with 2.33 times volume expansion [17] and remaining pores got filled with residual silicon. Therefore, the content of free Si in TiB$_2$-SiC-Si composites was determined by two factors: (i) the content of free carbon in the raw materials, and (ii) the porosity of green preforms. Firstly, the content of free Si was determined by the percentage of free carbon in the raw materials. In this paper, the content of free carbon in the raw materials is 10 wt%, which are constant in all the preforms and will contribute the
same to the amounts of liquid Si in the final TiB₂-SiC-Si composites. Secondly, the content of free Si was influenced by the porosity of green preforms because the remaining pores were filled with free Si during the infiltration process. According to Table 2, the porosity of 2# and 4# porous green preforms is lower than that of 1# and 5# green preforms. Therefore, the content of free Si filled in the remaining pores of 2# and 4# green preforms is lower. As a result, the content of free Si in the 2# and 4# composites decreased. It resulted in the relative intensities of Si main diffraction peaks ($2\theta$=28.5 ° & 47.4 °) decreased. Not surprisingly, an inverse trend was observed for the TiB₂ content, which increased in the 2# and 4# composites.

### Table 3. Components of TiB₂-SiC-Si composites with various particle size distributions.

| Number | Particle size distribution of TiB₂ | Components of TiB₂-SiC-Si composites (volume percent) [%] |
|--------|----------------------------------|----------------------------------------------------------|
|        | coarse:medium:fine               | TiB₂          | SiC          | Si           |
| 1#     | 46:23:31                         | 50.0±1.3      | 27.0±1.1     | 23.0±0.2     |
| 2#     | 66:15:19                         | 55.6±0.1      | 27.6±1.1     | 16.8±1.0     |
| 3#     | 51:26:23                         | 43.0±0.4      | 35.5±1.8     | 21.5±1.4     |
| 4#     | 42:32:26                         | 53.9±0.8      | 30.5±0.1     | 15.6±0.9     |
| 5#     | 100:0:0                          | 50.7±0.1      | 26.4±0.9     | 22.9±1.1     |

Furthermore, it can be seen from Figure 2 that, the number of large-sized SiC regions is higher in 3# composites. It is reported in our previous work [18] that, the increase of SiC zones' size occurs by coalescence of neighboring zones during the infiltration. In 3# composites, the open porosity of green preforms is higher, the opportunity for neighboring zones contact also increased, which enhanced the coalescence of neighboring zones. Therefore, the number of large-sized SiC zones increased.

### Table 4. The volume density and open-porosity of TiB₂-SiC-Si composites with various particle size distributions.

| Number | Particle size distribution of TiB₂ | Volume density (g/cm³) | Open-porosity (%) |
|--------|----------------------------------|------------------------|-------------------|
| 1#     | 46:23:31                         | 3.59±0.01              | 0.69±0.02         |
| 2#     | 66:15:19                         | 3.63±0.02              | 0.45±0.02         |
| 3#     | 51:26:23                         | 3.38±0.03              | 0.99±0.03         |
| 4#     | 42:32:26                         | 3.62±0.01              | 0.51±0.04         |
| 5#     | 100:0:0                          | 3.60±0.02              | 0.70±0.05         |

### 3.4. Density of TiB₂-SiC-Si composites.

Table 4 shows the volume density and open-porosity of TiB₂-SiC-Si composites, as a function of particle size distributions. It can be seen from Table 4 that, the volume density of 2# and 4# composites is higher than the other composites. According to the rule of mixtures [19], the densities of TiB₂-SiC-Si composites are directly relative to the vol% and densities of their constituents. The density of TiB₂, SiC and Si are 4.52 g/cm³, 3.21 g/cm³ and 2.33 g/cm³, respectively. On the one hand, the vol% of TiB₂ of 2# and 4# composites is higher than the other composites (Table 3), which resulted in the higher volume density of 2# and 4# composites. On the other hand, the vol% of Si of 2#
and 4# composites is lower than the other composites (Table 3), which also resulted in the higher volume density of 2# and 4# composites.

Furthermore, it also can be seen from Table 4 that, all the open-porosities of TiB2-SiC-Si composites with different particle size distributions were below 1 %. As discussed above, the pores in TiB2-SiC-Si composites were partially occupied by in-situ reaction formed SiC because conversion of C to SiC due to reaction with molten silicon is associated with 2.33 times volume expansion and remaining pores got filled with residual silicon [17]. Consequently, all the open-porosities of TiB2-SiC-Si composites with different particle size distributions were lower than 1 %. The open porosity of 2# and 4# composites is lower than the other composites (Table 4). According to Table 2, the porosity of the 2# and 4# green preforms is lower than the other green preforms, which resulted in the lower remaining pores of 2# and 4# composites. Therefore, the open porosity of 2# and 4# composites is lower than that of the other composites.

3.5. Mechanical properties of TiB2-SiC-Si composites.

The hardness, flexural strength and fracture toughness of TiB2-SiC-Si ceramic composites are important mechanical properties and crucial for their applications. As shown in Table 5, the Vickers-hardness, flexural strength and fracture toughness of 4# composites is higher than that of the other composites. Some possible mechanisms for the improvement are discussed as follows.

| Number | Particle size distribution of TiB2 | Vickers hardness (GPa) | Flexural strength (MPa) | Fracture toughness (MPa·m1/2) |
|--------|----------------------------------|-----------------------|------------------------|-----------------------------|
| 1#     | 46:23:31                         | 13 ± 2                | 255 ± 49               | 5.0 ± 0.3                   |
| 2#     | 66:15:19                         | 14 ± 1                | 265 ± 32               | 4.6 ± 0.7                   |
| 3#     | 51:26:23                         | 13 ± 3                | 243 ± 72               | 4.7 ± 0.8                   |
| 4#     | 42:32:26                         | 17 ± 2                | 275 ± 40               | 5.7 ± 1.8                   |
| 5#     | 100:0:0                          | 11 ± 2                | 262 ± 33               | 5.2 ± 0.6                   |

Firstly, the Vickers-hardness of 4# composites is higher than that of the other composites. This was related to that, the hardness of TiB2 (34 GPa) [20] is higher than that of Si (7 GPa) [21]. Based on the rule of mixtures [19], the hardness of TiB2-SiC-Si composites should increase with increasing volume percent of TiB2 and decreasing volume percent of free Si. Therefore, the higher volume percent of TiB2 and the lower volume percent of free Si (Figure 2 and Table 3) resulted in the hardness of 4# composites increased.

Secondly, the decrease of free Si content of 4# composites can improve the flexural strength of TiB2-SiC-Si composites for two reasons. (i) With the decrease of free Si content, more and more TiB2 particles are bonded by SiC instead of by free Si (Figure 2). It improve the bonding strength of the interface, which is beneficial to the flexural strength of the composites. (ii) The amount of large size Si pools reduce with the decrease of free Si content (Figure 2 and Table 3). The large size Si pools are crack sources [22] and deteriorate the strength of the composites. Therefore, the decrease of large size Si pools can improve the flexural strength of 4# composites.

Thirdly, the porosity had a significant effect on the hardness and flexural strength. It has been observed that the hardness and flexural strength of ceramics can be estimated using the following empirical expression, respectively [23]:

\[ H = H_0 \exp(-cP) \]
\[ \sigma = \sigma_0 \exp(-nP) \]  

(2)

where \( \sigma_0 \) is the hardness of the fully dense composites, \( P \) is the volume fraction of the porosity, \( c \) is an empirical constant, \( \sigma_0 \) and \( n \) are two constants determined experimentally. According to Eqs. (1) and (2), the lower the porosity, the higher the hardness and flexural strength of ceramics. Therefore, the lower open-porosity of 4\# composites (Table 4) results in the higher hardness and flexural strength.

The porosity was detrimental to the flexural strength for two reasons: (i) pores reduced the cross-sectional areas across which a load was applied, and (ii) they also acted as stress concentrators, e.g., for an isolated spherical pore, an applied tensile stress would be amplified by a factor of 2.

Lastly, the flexural strength of a material is also dependent on its microstructure. The flexural strength was reported to be related to the flaw size [24]:

\[ \sigma = \frac{1}{Y} \frac{K_{IC}}{\sqrt{a}} \]  

(3)

where \( \sigma \) is the flexural strength, \( a \) is the flaw size, \( K_{IC} \) is the fracture toughness, and \( Y \) is the \( K \)-calibration. It can be seen that the flexural strength decreased with increased flaw size. The flaws in the present study were derived from the residual stress, developed during cooling at weak interfacial sites because of thermal expansion mismatch between TiB\(_2\) and silicon [25]. The flaws generated at the interface propagate to a maximum up to one grain size [26]. Therefore, the lower coarse TiB\(_2\) content (42\%) of 4\# composite may lead to shorter flaws and result in higher flexural strength. On the contrary, the presence of large SiC zones in 3\# composite (Figure 2) may lead to longer flaws and result in lower flexural strength.

4. Conclusions

In this study dense TiB\(_2\)-SiC-Si ceramic composites were fabricated by infiltrating silicon into TiB\(_2\)-C porous green preforms with various particle size distributions. The results showed that the composite consisted of TiB\(_2\), SiC and Si phases. The microstructure analysis showed that: the content of residual Si could be controlled less than 16 vol.\% in the composite by particle size distribution. The mechanical properties of TiB\(_2\)-SiC-Si ceramic composites were improved by optimizing particle size distribution due to composition and microstructure changes. Then the particle size distribution of TiB\(_2\) was 42:32:26, the TiB\(_2\)-SiC-Si composite showed the optimum properties. The open porosity, volume density, Vickers-hardness, flexural strength and fracture toughness were 0.51\%, 3.63 g/cm\(^3\), 17 GPa, 275 MPa and 5.7 MPa·m\(^{1/2}\), respectively.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 51602041 and 51772048), National Key R&D Program of China (2017YFB0310300), Equipment pre research project (41422010903, 41422010905), the Fundamental Research Funds for the Central Universities (N170204014, N160204006) and also the Liaoning Province Doctor Startup Fund Program (201601021).

References

[1] Munro R G 2000 J. Res. Natl. Inst. Stand. Technol. 105 709
[2] Wen G, Li S B, Zhang B S and Guo Z X 2001 Acta Mater. 49 1463
[3] Ji W, Zhang J, Wang W, Wang H, Zhang F, Wang Y and Zheng Y F 2015 J. Eur. Ceram. Soc. 35 879
[4] Bao K, Wen Y, Khangkhamao M and Zhang S 2017 J. Am. Chem. Soc. 100 2266
[5] Cui H Z, Liu W and Cao L L 2015 J. Eur. Ceram. Soc. 35 3381
[6] Basu B, Raju G B and Suri A K 2006 Int. Mater. Rev. 51 354
[7] Wang D, Wang H, Sun S, Zhu X and Tu G 2014 Int. J. Refract. Met. H. 45 95
[8] Cymerman K, Oleszak D, Rosinski M and Michalski A 2018 Adv. Powder Technol. 29 1795
[9] Bhaumik S K, Divakar C, Singh A K and Upadhyaya G S 2000 Mat. Sci. Eng. A-Struct. 279 275
[10] Wang H, Sun S, Wang D and Tu G 2011 Powder Technol. 217 340
[11] Fu Z Z and Koc R. 2016 Ceram. Int. 42 12231
[12] Zhang C P, Ru H Q, He R P, Sun W K, Zhu J H, Wang W and Yue X Y 2016 Key Eng. Mater. 697 539
[13] Tian W B, Kita H, Hyuga H and Kondo N 2011 J. Alloy. Compd. 5 1819
[14] Zhang C P, Gao X W, Ru H Q, Sun W K, Zhu J H and Zong H 2017 J. Inorg. Mater. 32 502
[15] Hilliard J E, Cahn J W 1961 Trans. Metall. Soc. AIME 221 344
[16] Hayun S, Weizmann A, Dariel M P and Frage N 2009 Int. J. Appl. Ceram. Tec. 6 492
[17] Yurkov A L 1989 Refract. Ind. Ceram.+. 30 731
[18] Zhang C P, Ru H Q, Wang W, Yue X Y and Zhao J 2014 J. Am. Ceram. Soc. 97 3286
[19] Callister W D 1985 Materials Science and Engineering: An Introduction (New York: John Wiley & Sons)
[20] Zou B, Huang C, Song J, Liu Z, Liu L and Zhao Y 2012 Int. J. Refract. Met. H. 35 1
[21] Hayun S, Dilman H, Dariel M P and Frage N 2009 Mater. Chem. Phys. 118 490
[22] Hayun S, Darie M P, Frage N and Zaretsky E 2010 Acta Mater. 58 1721
[23] Chaim R and Hefetz M 2004 J. Mater. Sci. 39 3057
[24] Engel U and Heinz H 1978 J. Mater. Sci. 13 2003
[25] Dowling N E 1999 Int. J. Fatigue 19 85
[26] Barsoum M W 1997 Fundamentals of Ceramics (New York: McGraw-Hill)