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Pressureless sintered SiC matrix toughened by *in situ* synthesized TiB_2: Process conditions and fracture toughness

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Abstract

This paper reports the fabrication of SiC toughened by *in situ* synthesized TiB_2 based on pressure-less sintering technique using TiO_2, B_4C, C and SiC as starting materials. The process conditions were investigated in detail, including the pre-sintering temperatures, carbon contents, differently sized TiO_2 powders, TiB_2 volume contents, final sintering temperature and time. These conditions were found to have great influence on the TiB_2 toughened SiC in terms of relative density, TiB_2 particle size and fracture toughness. Homogeneous dispersion of *in situ* synthesized TiB_2 secondary phase was confirmed to enhance the K_{IC} of the SiC matrix. The K_{IC} of SiC toughened by *in situ* synthesized TiB_2 (15 vol%) reaches 6.3 MPa $m^{1/2}$, which is among the highest values reported so far on TiB_2 reinforced SiC composites based on the pressure-less sintering technique using TiO_2 as Ti source.

Keywords: A. Sintering; B. Composites; C. Toughness and toughening; D. SiC

1. Introduction

Silicon carbide (SiC) is one kind of high-performance structural ceramic, famous for its low density, high strength and hardness, good oxidation resistance, high thermal conductivity and low thermal expansion coefficient, high strength even at high temperatures. But the low fracture toughness (K_{IC}) of SiC, 3–4 MPa $m^{1/2}$, make itself very sensitive to defects and therefore less reliable in application. Therefore, great attention has been paid to enhance the fracture toughness of SiC. In previous studies, it has been found that the incorporation of some secondary phases, serving as crack deflector, can greatly enhance the fracture toughness of SiC matrix [1–5]. For example, when 24.6 vol% TiC phases were introduced into SiC, the fracture toughness of the composite can reach 6.0 MPa $m^{1/2}$ [3]. Similarly, Endo et al. fabricated 20–40 vol% TiC reinforced SiC by hot-pressing method with enhanced fracture toughness up to 6.0 MPa $m^{1/2}$ [4].

Besides the TiC phase, TiB_2 in many cases has also been used to reinforce the SiC since TiB_2 is also an important structural ceramic due to its exceptional hardness, elastic modulus, high melting point, good corrosion resistance to chemicals and molten metal, etc. McMurty et al. reported that the inclusion of TiB_2 phases can effectively suppress the growth of SiC crystals and thus remarkably enhance the fracture toughness [2].

Compared with the pre-formed TiB_2 powders, the *in situ* synthesized TiB_2 phases have some advantages to reinforce the SiC as they can be facilely and homogeneously dispersed in the SiC matrix [6–12]. With respect to the toughening effect of *in situ* synthesized TiB_2 on SiC matrix, Zhang et al. reported that K_{IC} of 6.21 MPa $m^{1/2}$ can be obtained by hot pressing method when 30 vol% of TiB_2 was incorporated [9]. The K_{IC} of TiB_2 (30 vol%) reinforced SiC fabricated by hot isostatic pressing (HIP) method was 4.75 MPa $m^{1/2}$ [8]. It is worthy to note that toughening the SiC matrix using *in situ* synthesized TiB_2 *via* pressure-less sintering route [1,10–12] is also an attractive alternate to hot-pressing method [6–9], because the latter is expensive and not suitable to fabricate samples with sophisticated shapes. Using TiO_2 as Ti source and pressure-less sintering method, Blanc et al. reported that the K_{IC} of the TiB_2/SiC composite with 15 vol% of TiB_2 is around 3.9 MPa $m^{1/2}$ [11]. Very recently, based on the similar synthetic strategy but using Al_2O_3 and Y_2O_3 as sintering aids, the K_{IC} of

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about 4.3 MPa m$^{1/2}$ and 5.7 MPa m$^{1/2}$ were achieved with 12 vol% and 30 vol% of TiB_2, respectively [12].

As summarized in Table 1, currently there are several synthesis routes that can be followed to fabricate *in situ* synthesized TiB_2 toughened SiC. In comparison with other titanium sources employed in these synthetic routes, including Ti, TiC, TiH_2 and TiN, titanium dioxide (TiO_2) is cheap and extensively available. It would be very appealing to synthesize *in situ* TiB_2 from TiO_2. Despite above works dealing with the preparation of *in situ* synthesized TiB_2 reinforced SiC [10–12], up to now it is still lack of a systematic investigation on the process conditions and their influence on the fracture toughness of the composite ceramics. This work is thus intended to shed light on the process conditions with an aim to obtain TiB_2/SiC composites with enhanced fracture toughness. This work is supposed to provide an overall picture of *in situ* synthesized TiB_2 reinforced SiC using cheap TiO_2 as Ti source based on the pressure-less sintering technique.

2. Experimental procedure

2.1. Materials

α-SiC powders (0.4 μm) were bought from Hongde Fine Powders Ltd., Weifang, China; TiO_2 powders (74 μm) and nano-sized TiO_2 (20 nm) were purchased from Fe Alloy Factory, Jinzhou, China; B_4C powders (3.5 μm) were obtained from Friction Materials 2nd Factory, Mudanjiang, China. The phenol resin and ethanol were purchased from the Sinopharm Chemical Reagent Co., Ltd. All the chemicals are used as received.

2.2. Synthesis procedure

The synthesis procedure includes five steps: mixing by ball-milling, drying, granulation, molding and pressure-less sintering. Typically, in order to prepare TiB_2 (15 vol%)-SiC, 80.0 g SiC, 23.0 g TiO_2, 9.0 g B_4C and 29.2 g phenol resin were ball milled in ethanol for 12 h. After drying, granulation and screening, batches of powders were compacted by cold uniaxial pressing at a pressure of 150 MPa into rectangular shape green compacts with approximate dimensions of 37.5 mm × 6 mm × h mm. The dried samples were pre-sintered at various temperatures in vacuum (<100 Pa) before being sintered at final temperatures for different durations in argon finally.

Table 1
Reactions for the *in situ* synthesis of TiB_2.

No.	Reactions	Ref.
1	$TiC + 2B \rightarrow TiB_2 + C$	[6]
2	$TiN + 2B \rightarrow TiB_2 + 0.5N_2$	[7]
3	$2Ti + Si + B_4C \rightarrow SiC + 2TiB_2$	[8]
4	$2TiH_2 + Si + B_4C \rightarrow 2TiB_2 + SiC + 2H_2$	[9]
5	$2TiO_2 + B_4C + 3C \rightarrow 2TiB_2 + 4CO$	[10–12]

2.3. Characterization

The microstructures of obtained TiB_2/SiC composite ceramics were examined by scanning electron microscopy (SEM, JSM-5600LV). The phase compositions were studied using D/Max-YX X-ray diffractometer. The porosity was measured by Archimedes' method. The mechanical properties were tested on mechanical testing machine (CMT5105).

The fracture toughness was measured by using the indentation method using Vicker's indenter, which is simple and has been used in many works on TiB_2 toughened SiC materials [6,8,11,12]. Therefore, this work employed this method to measure the facture toughness especially for direct comparison purpose. In this work, the equation used for calculation was proposed by Evans–Charles [11,13]:

$$K_{Ic} = 0.057 H_v a^{1/2} \left(\frac{E}{H_v}\right)^{2/5} \left(\frac{c}{a}\right)^{\frac{-3}{2}} \quad (1)$$

where E in Gpa is the Young's modulus (Young's moduli of SiC/TiB_2 composites were calculated from the Young's moduli of SiC (414 GPa) and TiB_2 (529 GPa), assuming a rule of mixture), The influence of porosity on the Young's modulus was further considered based on the model proposed by Pabst and Gregorová [14],

$$E = E_0 \times (1 - p) \times \left(1 - \frac{p}{p_c}\right) \quad (2)$$

where E and E_0 are the Young's modulus of porous (with porosity of p) and dense ceramics, respectively; p_c is the critical porosity at which the material looses integrity, is equal to 1. H_v in Gpa is the Vicker's hardness, a in μm is the half-length of Vicker's print and c in μm is the half-length of the crack.

3. Results and discussion

3.1. Optimization of the pre-sintering temperature and amounts of reactants

In the sintering process, the CO gas is released according to the reaction between TiO_2, B_4C and C, as shown in the reaction (R5) in Table 1. The release of CO is actually harmful to the densification of the TiB_2/SiC composite [10]. It is proposed that by means of pre-sintering treatment at relatively low temperatures in the vacuum (<100 Pa), it is possible to minimize this problem before sintering at the final temperature around 2000 °C (more details below). Although our previous calculation and experimental results showed that this reaction can take place at as low as 1100 °C under vacuum (<0.01 Pa) [15], the pre-sintering temperature of 1400 °C is chosen in view of both speeding up the reaction and saving energy under the condition employed in this work (see Section 2). As shown in

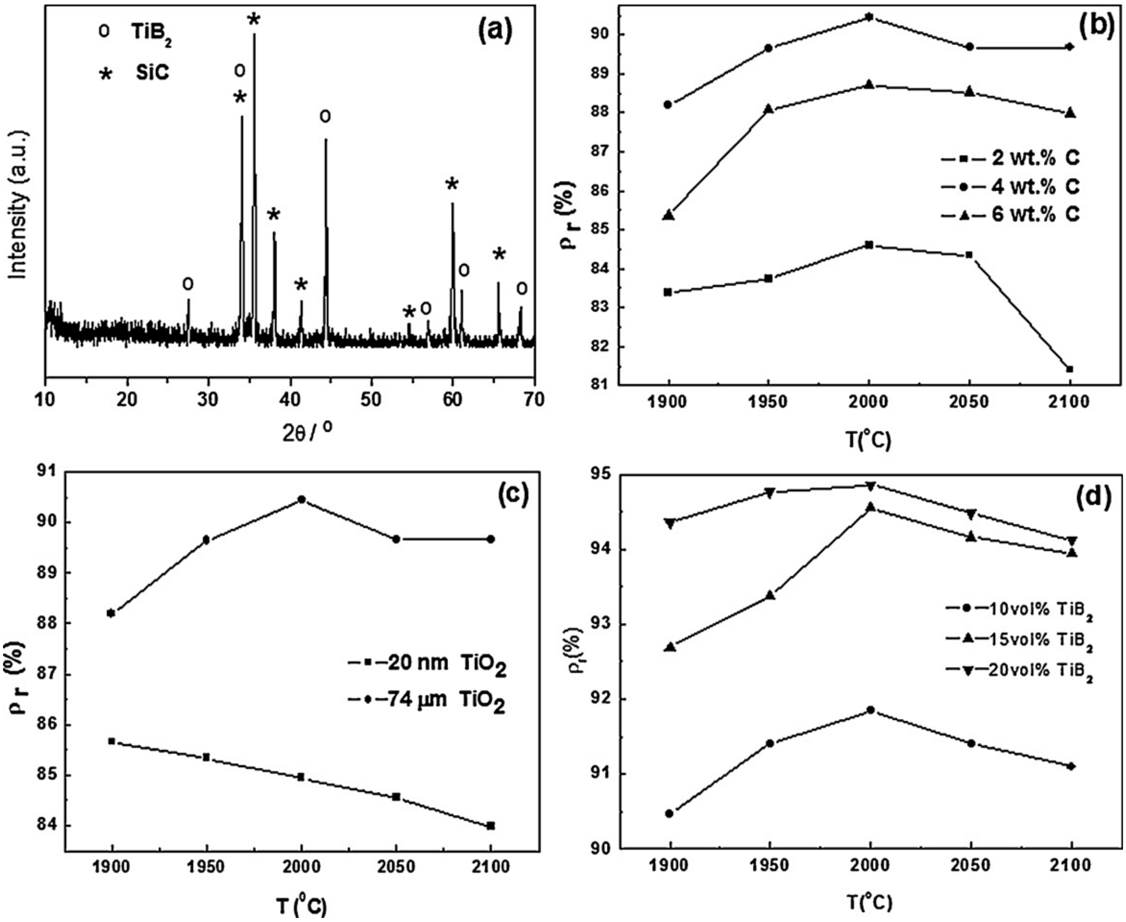

Fig. 1. (a) XRD pattern of pre-sintered samples obtained at 1400 °C, variation of relative densities of TiB_2/SiC composites sintered at different temperatures with (b) varying amounts of carbon with 5 vol% TiB_2 (micro-sized TiO_2, 74 μm), (c) differently sized TiO_2 powder with 5 vol% TiB_2 (carbon content of 4 wt.%), and (d) TiB_2 volume contents with carbon content of 4 wt.% using micron-sized TiO_2.

Fig. 1a, the XRD pattern of the TiB_2/SiC composite is free of impurities except the TiB_2 and SiC phases, indicating the completion of transformation of TiO_2 into TiB_2 under such conditions.

In addition, the amount of carbon, derived from phenolic resin, is an important factor influencing both the reaction (Eq. (R5) in Table 1) and the sintering process. It is well known that the carbon can activate the SiO_2 or SiO_xC_y species formed on the SiC surface *via* carbothermal reduction reactions [16]. Therefore, besides the carbon necessary to complete the reaction (R5) in Table 1, an extra amount of carbon can promote the sintering the SiC in the final sintering step. Herein, the effect of the extra carbon on the densification of composite ceramics is investigated. As shown in Fig. 1b, irrespective of the sintering temperature, an extra carbon of 4.0 wt.% favors the formation of more dense ceramic composite. On the one hand, upon the addition of too much carbon, e.g., 6.0 wt.%, some of them will enrich in the grain boundaries. As a result, the contacts and following sintering of SiC crystals will be impeded. On the other hand, too less of carbon might compromise the activation effects of SiC surface, which is not advantageous to the sintering either. In the following discussion, the amount of extra carbon is thus set to be at 4.0 wt.% unless indicated otherwise.

In this work, two kinds of TiO_2 powders with different sizes were studied. It turns out that the nanosized TiO_2 is disadvantageous to the formation of highly densified TiB_2/SiC composite (Fig. 1c). This could be explained that the higher decomposition rate of nanosized TiO_2 at high temperatures or the agglomeration during the preparation could lead to these low densities. The micron-sized TiO_2 powders are therefore selected for the preparation of TiB_2/SiC composites.

Serving as the secondary phase to reinforce SiC, the content of TiB_2 is no doubt a key factor and thus needs to be investigated and optimized in order to obtain the TiB_2/SiC composite with enhanced fracture toughness. In this work, the effects of different amounts of *in situ* synthesized TiB_2 on both the relative densities and microstructures of TiB_2/SiC composite ceramics were studied. The influence of TiB_2 volume contents on the densities of sintered TiB_2/SiC composites was shown in Fig. 1b and d. It can be seen that the relative densities of TiB_2/SiC composite are highly dependent on the volume contents of TiB_2. The higher the TiB_2 volume contents are, the higher densities of the sintered TiB_2/SiC composites can be achieved. Although it has been recently reported that the utilisation of sintering aids, e.g., $Al_2O_3 + Y_2O_3$, was found to be able to further increase the relative density to around 97% [12], the highest relative density

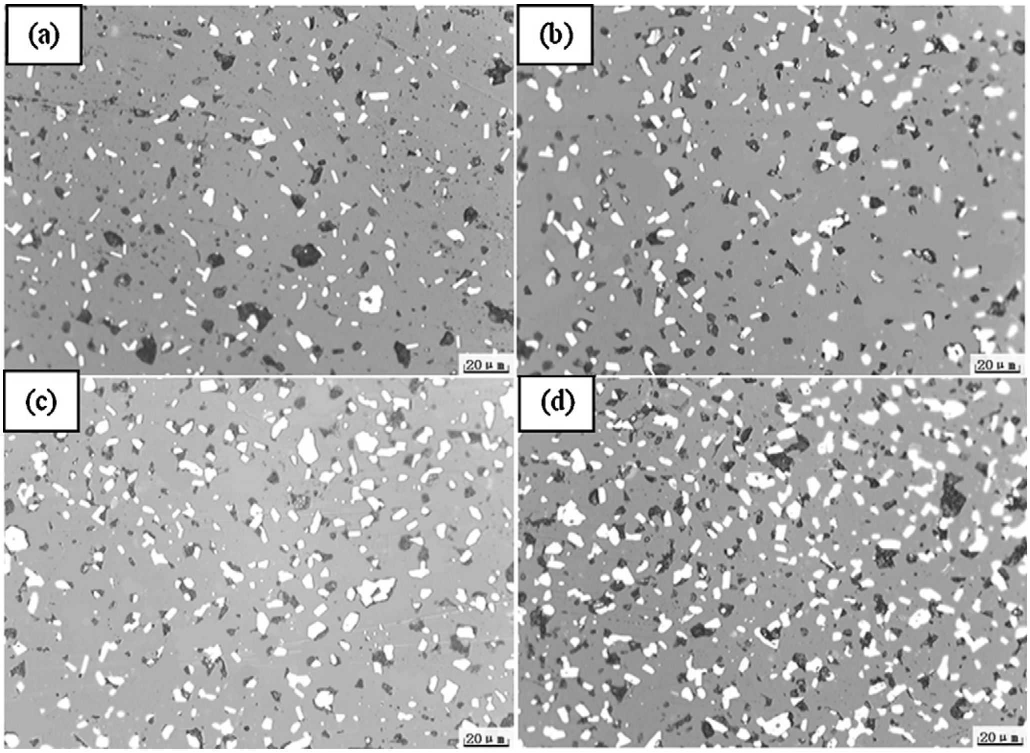

Fig. 2. Influence of TiB_2 volume contents on the microstructures of TiB_2/SiC composites sintered at 2000 °C with (a) 5 vol%, (b) 10 vol%, (c) 15 vol% and (d) 20 vol%.

up to 95% (20 vol% of TiB_2) obtained in this work is comparable with results reported by others using the same method [10]. Therefore, with increasing amounts of the TiB_2, very fine, active *in situ* synthesized TiB_2 particles are demonstrated to be able to promote the sintering and therefore help densify the TiB_2/SiC composites.

The dependence of microstructures on the TiB_2 volume contents was shown in Fig. 2. With the increase in TiB_2 volume contents, the particle sizes (equivalent circle diameter) of *in situ* synthesized TiB_2 particles increased from ~2.6 μm at 5.0 vol% to 3.9 μm at 20.0 vol%. The higher probability of contact and shorter distance between TiO_2 or *in situ* generated TiB_2 at high TiB_2 volume contents are responsible for such increase in TiB_2 particle sizes. It is worthy to note that TiB_2 phases are all homogeneously dispersed in the SiC matrix irrespective of the volume contents of TiB_2 phases in the range from 5.0 to 20.0 vol%. The existence of TiB_2 particle sized voids (black holes) is probably due to the falling of the TiB_2 particles during the preparation of sample for SEM measurements. Some finer voids are also observable due to the evolution of CO gas during the reaction as discussed above.

3.2. *Influence of the sintering conditions on the microstructures*

After pre-sintering at 1400 °C, it is necessary to sinter the TiB_2/SiC composite at final temperatures to complete the densification process. It can be seen from Fig. 1b and d that the densities of TiB_2/SiC composite are highly dependent on the final sintering temperatures studied. Independent of the carbon and TiB_2 contents, the optimal sintering temperature at 2000 °C leads to the most densified composite ceramics. With the increase in sintering temperatures ranging from 1900 °C to 2100 °C, the obvious growth of the TiB_2 particles can be observed in Fig. 3a and b. *Via* pressure-less sintering method, it is hard to completely remove these pores even after sintering at higher temperatures up to 2100 °C, which can be seen from the existence of some fine voids in Fig. 3a and b. This phenomenon was also observed by others in the TiB_2 reinforced SiC *via* pressure-less sintering method [12].

The average particle sizes of TiB_2 at 20.0 vol% increased from about 2.3 μm to 4.5 μm when the sintering temperatures were increased from 1950 to 2100 °C (Fig. 3c). Moreover, the grain size of the matrix discriminated by etching method was found to decrease with the increasing amount of TiB_2, suggesting the inhibiting effect of the *in situ* formed TiB_2 on the grain size of the SiC matrix (Fig. 3d). This is in consistent with the results reported by others: the *in situ* synthesized TiB_2 can suppress growth of SiC matrix during the sintering process [2,12]. It is proposed that the TiB_2 *in situ* formed in the grain boundaries function as the SiC growth inhibitor, but the fine TiB_2 particle might also activate the SiC and therefore promote the sintering the SiC matrix by increasing the defects and inducing the distortion in the crystalline lattice, which in both cases have been confirmed by TEM observations (Fig. 4a and b). As shown in Fig. 4, very fine TiB_2 particles at the SiC boundaries or in the SiC grains can be observed. These observations also agree well with the results that the high relative densities can be achieved at higher TiB_2 volume contents, as shown in Fig. 1d.

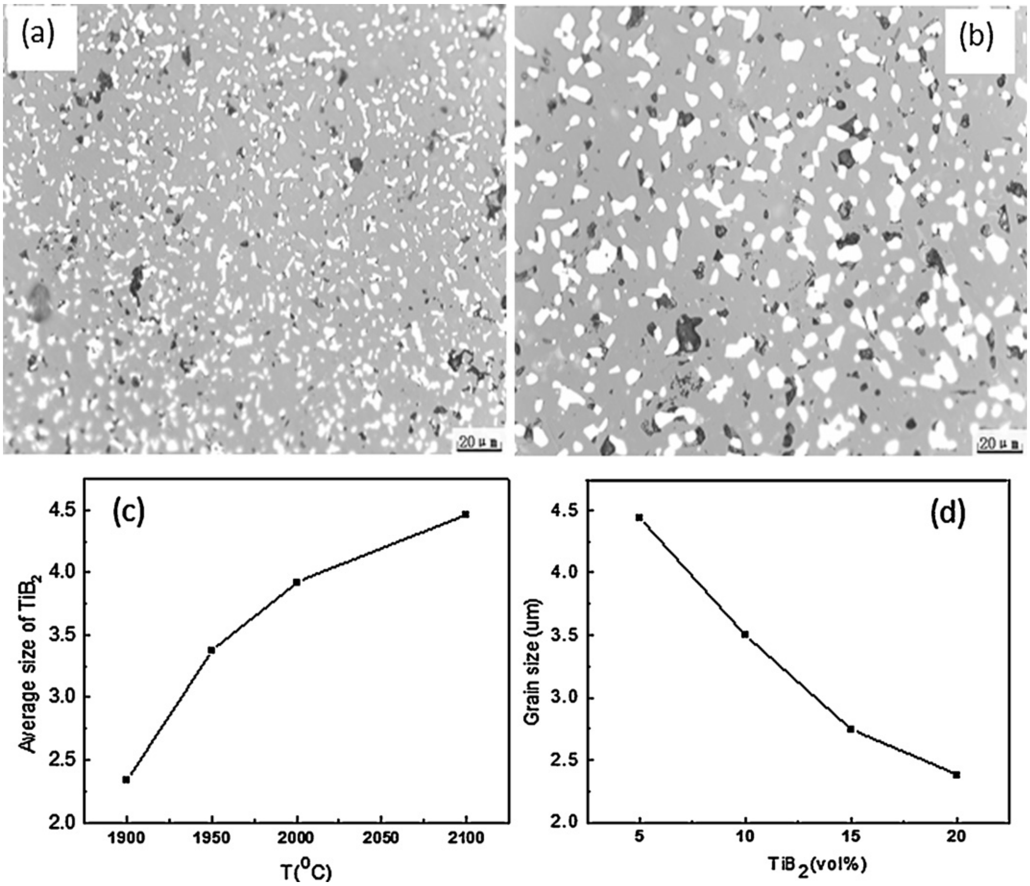

Fig. 3. Influence of sintering temperatures on the microstructures of TiB_2/SiC composites (20 vol% TiB_2) at (a) 1900 °C and (b) 2100 °C with the holding time of 0.5 h. (c) Plot of the average particle sizes of TiB_2 (20 vol%) against varying sintering temperature held for 0.5 h. (d) Plot of the grain size of the SiC matrix against TiB_2 contents sintered at 2000 °C for 0.5 h.

Additionally, the sintering time was found to be important for the final sintering step. As shown in Fig. 5, the optimum sintering time at 2000 °C for TiB_2/SiC composites with different TiB_2 volume contents is 0.5 h in terms of relative densities. Either too long or short sintering time is not advantageous to the formation of dense TiB_2/SiC composites. On the one hand, excessive grain growth induced by lengthy sintering might envelop the porosities and cause the decrease in the relative densities. On the other hand, too short sintering time cannot fully densify the composite. Therefore, the sintering

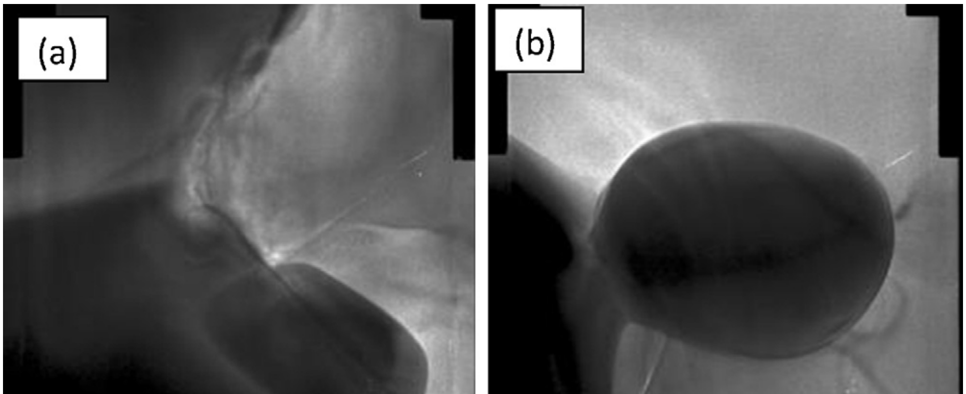

Fig. 4. Bright field images of (a) an intergranular TiB_2 particle (darker particles) and (b) two intragranular TiB_2 particles in SiC matrix.

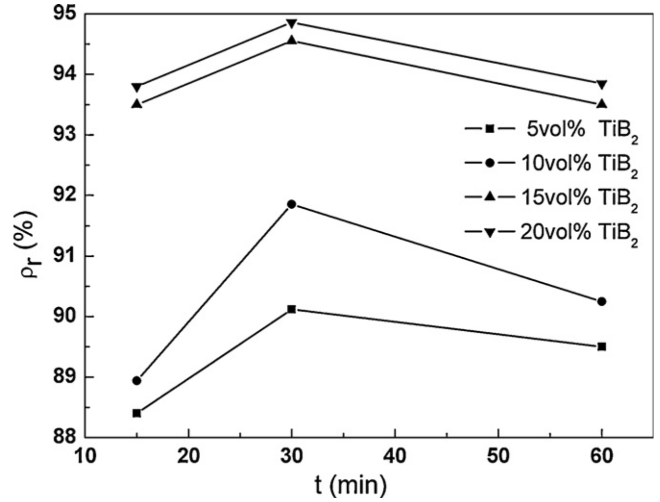

Fig. 5. The relationship between relative densities of TiB_2/SiC composites and the holding time at 2000 °C.

temperature and the holding time to sinter the TiB_2/SiC composite are set to be at 2000 °C and 0.5 h, respectively.

3.3. Fracture toughness of the TiB_2/SiC composites

Similar to the observation of TiC reinforced SiC [3,4], in the case of TiB_2, it has been reported that the fracture toughness was not only higher than single phase of both SiC and TiB_2 [9,11,17], but also was found to increase with the volume contents of TiB_2 [9,11]. In this work, when the volume contents of TiB_2 were increased from 5.0 vol% to 20.0 vol% as shown in Fig. 6a, the fracture toughness was found to correspondingly increase from 4.9 MPa $m^{1/2}$ to 5.9 MPa $m^{1/2}$. By incorporating the TiB_2 into the SiC matrix, the cracks can be deflected considerably. Consequently, their propagation can be suppressed in the TiB_2/SiC composites, which is otherwise not realizable in the monolithic SiC. On the one hand, with the increases in the TiB_2 volume contents, the frequency of interaction of crack tip with the TiB_2 particles increases, so does the fracture toughness (Fig. 6a). On the other hand, it was reported that the facture toughness was inversely proportional to the grain sizes of the matrix [18]. As shown in Fig. 3d, the grain sizes were found to decrease with the increase in the TiB_2 contents. Therefore, the increase in the TiB_2 volume contents is also believed to be helpful to the enhancement of fracture toughness.

As shown above in Fig. 3c, higher final sintering temperatures results in larger TiB_2 particle sizes. The influence of the sintering temperatures on the fracture toughness was further studied, with the results shown in Fig. 6b. Clearly, the K_{IC} increases with the sintering temperatures in the range from 1900 °C to 2100 °C with 15 vol% TiB_2. It was reported that the grain coarsening in particle sizes of the secondary phase leads

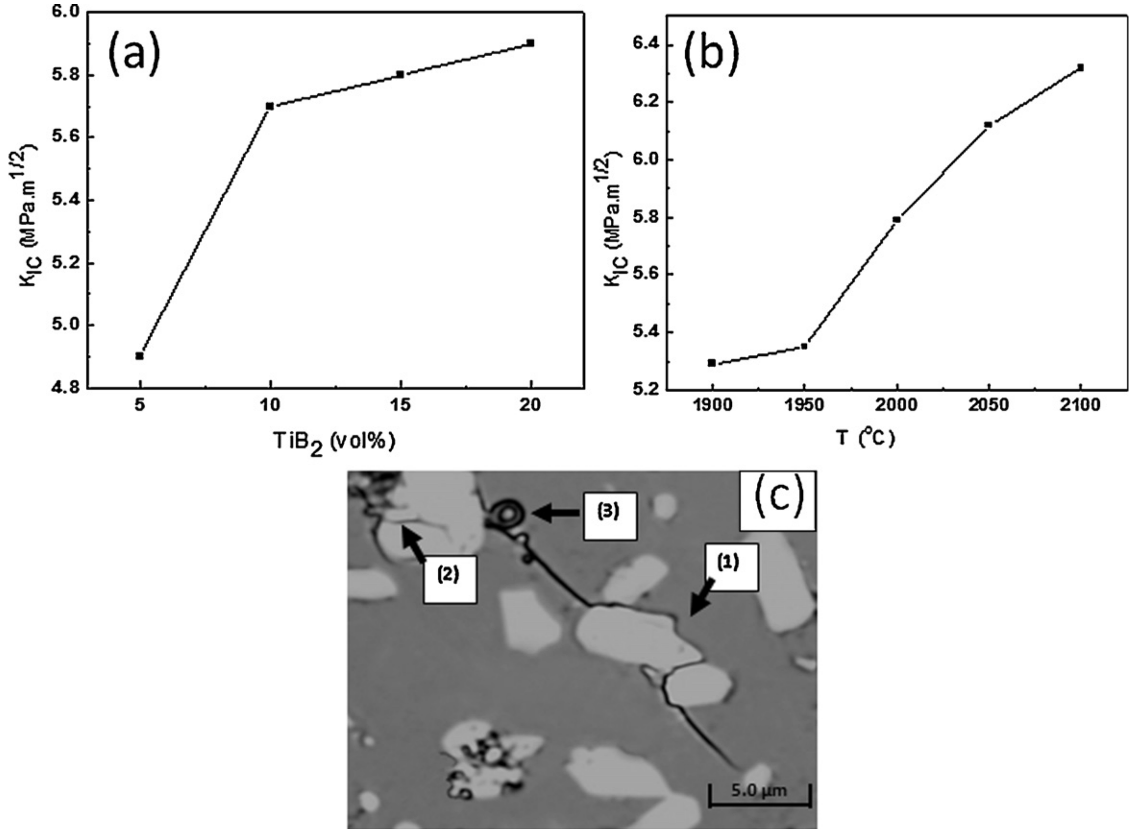

Fig. 6. Influence of TiB_2 volume contents (a) and sintering temperature on fracture toughness of TiB_2 (15 vol%)/SiC composites (b). (c) Optical micrographs of typical cracks paths induced by Vickers indentation: (1) crack deflection around TiB_2 particles, (2) TiB_2 particle sheared by a crack (cross over) and (3) the double crack deflection around TiB_2 particles.

to the increased fracture toughness, owing to the enhanced crack deflection [19]. In Fig. 6c, three kinds of cracks can be identified, including those around, cross over and double deflection around the TiB_2 particles. This explains the significantly enhanced K_{IC} compared with monolithic SiC.

When the TiB_2 (15.0 vol%)/SiC composite was sintered at 2100 °C, the highest K_{IC} can reach 6.3 MPa $m^{1/2}$, which nearly double the value of monolithic SiC, typically around 3–4 MPa $m^{1/2}$ and is among the highest values reported so far on TiB_2 reinforced SiC composites based on the pressure-less sintering technique using TiO_2 as Ti source [8,9,11,12]. Such high fracture toughness obtained in this work is ascribed to the systematically optimized synthetic conditions, including the amounts of reactants (TiO_2, carbon), pre-sintering conditions and final sintering conditions as well.

4. Conclusions

This paper demonstrated that the fabrication of *in situ* synthesized TiB_2 toughened SiC can be realized *via* a pressure-less sintering technique using B_4C, C and SiC and cheap TiO_2 as starting materials. Detailed studies of the process conditions reveal that: (a) pre-sintering at temperatures of 1400 °C secures the complete transformation of TiO_2 into TiB_2. (b) The optimum carbon content apart from reaction consumption is 4.0 wt.%. (c) Compared with nano-sized TiO_2 powders, micron-sized TiO_2 powders favor the formation of more dense TiB_2/SiC ceramic composite. (d) The optimum final sintering condition is at 2000 °C with the holding time of 0.5 h. The TiB_2 phases of 5.0–20.0 vol% in volume contents can be homogeneously incorporated into the SiC matrix. The TiB_2 particles tend to coarsen in sizes with the increases in the volume contents of TiB_2 and the sintering temperatures as well. TiB_2 (15.0 vol%)/SiC composite sintered at 2100 °C showed the highest K_{IC} up to 6.3 MPa $m^{1/2}$.

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References

[1] M.H. Janney, Mechanical properties and oxidation behavior of a hot pressed SiC-15 vol% TiB_2 composite, Am. Ceram. Soc. Bull. 66 (1987) 322–324.

[2] C.H. McMurty, W.D. Boecker, S.G. Seshadri, J.S. Zanghi, J. Garnier, Microstructure and materials properties of SiC–TiB_2 particulate composites, Am. Ceram. Soc. Bull. 66 (1987) 325–329.

[3] G.C. Wei, P.F. Becher, Improvements in mechanical properties in SiC by addition of TiC particles, J. Am. Ceram. Soc. 67 (1984) 571–574.

[4] H. Endo, M. Ueki, H.J. Kubo, Microstructure and mechanical properties of hot-pressed SiC–TiC composites, J. Mater. Sci. 26 (1991) 3769–3774.

[5] I. Akin, M. Hotta, F.C. Sahin, O. Yucel, G. Goller, T. Goto, Microstructure and densification of ZrB_2–SiC composites prepared by spark plasma sintering, J. Eur. Ceram. Soc. 29 (2009) 2379–2385.

[6] Y. Ohya, M.J. Hoffmann, G. Petzow, Sintering of in situ synthesized SiC–TiB_2 composites with improved fracture toughness, J. Am. Ceram. Soc. 75 (1992) 2479–2483.

[7] T. Tani, S. Wada, SiC matrix composites reinforced with internal synthesized TiB_2, J. Mater. Sci. 25 (1990) 157–160.

[8] D.G. Zhu, S.K. Liu, X.D. Yin, L. Yang, C.C. Xiao, H.M. Zhou, J.Y. Zhang, In situ HIP synthesis of TiB_2/SiC ceramic composites, J. Mater. Process. Technol. 89–90 (89) (1999) 457–460.

[9] G.J. Zhang, X.M. Yue, Z.Z. Jin, J.Y. Dai, In situ synthesized TiB_2 toughened SiC, J. Eur. Ceram. Soc. 16 (1996) 409–412.

[10] T. Tani, S. Wada, Pressureless-sintered SiC–TiB_2 composite through internal synthesis method, J. Mater. Sci. Lett. 9 (1999) 22–23.

[11] C. Blanc, F. Thevenot, D. Goeuriot, Microstructural and mechanical characterization of SiC-submicron TiB_2 composites, J. Eur. Ceram. Soc. 19 (1999) 561–569.

[12] D. Bucevac, S. Boskovic, B. Matovic, V. Krstic, Toughening of SiC matrix with in situ created TiB_2 particles, Ceram. Int. 36 (2010) 2181–2188.

[13] P. Chantikul, G.R. Anstis, B.R. Lawn, D.B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness-II strength method, J. Am. Ceram. Soc. 64 (1981) 39–543.

[14] W. Pabst, E. Gregorová, New relation for the porosity dependence of the effective tensile modulus of brittle materials, J. Mater. Sci. 39 (2004) 3501–3503.

[15] P. Lu, X.Y. Yue, H.Q. Ru, L. Yu, Effect of TiB_2 in situ synthesized on presintering process and reaction of B_4C and Al during fabricating B_4C–TiB_2–Al composite, J. Mater. Sci. 44 (2009) 3483–3487.

[16] K. Guerfi, S. Lagerge, M.J. Meziani, Y. Nedellec, G. Chauveteau, Influence of the oxidation on the surface properties of silicon carbide, Thermochim. Acta 434 (2005) 140–149.

[17] G.J. Zhang, Y. He, Z.Z. Jin, Study on SiC matrix composites toughened by in situ synthesized TiB_2, J. Chin. Ceram. Soc. 23 (1995) 34–140 (in Chinese).

[18] V.D. Krstic, Effect of microstructure on fracture of brittle materials: unified approach, Theor. Appl. Fract. Mech. 45 (2006) 212–226.

[19] R.W. Rice, S.W. Freiman, P.F. Becher, Grain-size dependence of fracture energy in ceramics: I. Experimental, J. Am. Ceram. Soc. 64 (1981) 345–350.