International Journal of Refractory Metals & Hard Materials 70 (2018) 19–31

Contents lists available at ScienceDirect

International Journal of Refractory Metals & Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Effects of different sintering methods on the properties of SiC-TiC, SiC-TiB_2 composites

Mahdi Khodaei[a], Omid Yaghobizadeh[b,*], Hamid Reza Baharvandi[a], Alireza Dashti[b]

[a] Composite Materials & Technology Center, Malek-e-Ashtar University of Technology, Tehran, Iran
[b] Department of Materials Engineering, Imam Khomeini International University (IKIU), Qazvin, Iran

ARTICLE INFO

Keywords:
SiC-TiB_2
SiC-TiC
Fracture toughness
Flexural strength
Hardness
Microstructure
Crack deflection

ABSTRACT

Properties such as high hardness, low density, high melting temperature and high modulus of elasticity have made SiC suitable for a wide range of high-temperature and cutting tool applications. Although disadvantages like being difficult to sinter and low fracture toughness have limited its uses. TiB_2 and TiC are among the most common dispersed phases in a SiC matrix. Many previous investigations have demonstrated that the addition of TiB_2 and TiC can yield composites with superior mechanical properties. Sintering method is an important parameter affecting the derived properties of SiC-TiB_2 and SiC-TiC composites. In this paper the effects of different sintering methods on the physical, mechanical and sintering ability of SiC-TiB_2 and SiC-TiC composites were studied.

1. Introduction

Silicon carbide (SiC) generally exhibits two crystalline structures of cubic β and α polytypes with hexagonal and rhombohedral structures respectively. 6H is the most common α type [1,2]. Silicon carbide (SiC) is considered as a high-performance structural ceramic and is famous for properties such as low density (3.1 g/cm^3), high strength (550 MPa), great hardness (2800 kg/mm^2), good oxidation resistance, high thermal conductivity (120 W/m K), low thermal expansion coefficient ($4 * 10^{-6}$/°C) and high strength even at high temperatures [3–5]. The existing covalent bonds results in a very hard and strong material. As a result of the above-mentioned properties, according to some papers SiC can be used as a reinforcement in Al_2O_3 [6,7] and TiB_2 [8] matrix.

SiC forms a protective silicon oxide coating at 1200 °C while being exposed to air and is able to be used up to 1600 °C. The high thermal conductivity coupled with low thermal expansion and high strength gives this material exceptional thermal shock resistance. Silicon carbide ceramics with little or no grain boundary impurities maintain their strength to very high temperatures, approaching 1600 °C with no strength loss. On the other hand, the low fracture toughness of SiC (3–4 MPa $m^{1/2}$), makes it very sensitive to defects and less reliable in application [9]. Therefore, considerable attention has been paid to improve these properties of SiC bodies as its relatively low fracture toughness limits the uses [10].

It is well known that the introduction of transition metal borides and carbides as reinforcing phases can improve the fracture toughness of SiC ceramics. In order to improve the properties of SiC, some secondary phases such as TiC, B_4C and TiB_2, SiC [11,12], were also used to fabricate SiC-based materials. Additionally, the high percentage of covalent bonds and low self-diffusivity makes it impossible for SiC to be fully sintered and reach a high density without using sintering aids. For example, pure SiC with near theoretical density can only be achieved by hot pressing at 2500 °C and 50 MPa [2]. So far many efforts have been made to find an appropriate sintering additive for the solid-state or liquid phase-assisted sintering of SiC. Prochazka and Scanlan [13] achieved 96.4% SiC density by a solid-state sintering with B–C addition but the process required a high temperature of 2100 °C. another research showed that the additives such as B and C enhance densification and promote β to α transformation as well as increasing the amount of plate-like α-SiC in a β-SiC matrix. But there are problems at temperatures higher than 2000 °C. Therefore it would be interesting to consider other additives capable of suppressing β to α transformation and developing the mechanical properties [14].

In fact the addition of secondary phases, serving as crack deflector, can enhance the K_{Ic} of SiC matrix. For example, when 24.6 vol% of TiC phase was introduced into SiC body, the K_{Ic} of the composite reached 6.0 MPa $m^{1/2}$ [15]. Endo et al. fabricated 20–40 vol% TiC reinforced SiC using hot-pressing process and achieved K_{Ic} up to 6.0 MPa $m^{1/2}$ [16].

In many researches TiB_2 has also been used as dispersed phase in SiC matrix. Titanium diboride is one of the transitional metals with

* Corresponding author.
E-mail address: O.Yaghobizadeh@edu.ikiu.ac.ir (O. Yaghobizadeh).

http://dx.doi.org/10.1016/j.ijrmhm.2017.09.005
Received 21 August 2017; Accepted 15 September 2017
Available online 22 September 2017

covalent bonds. This material has found extensive application in advanced ceramics due to its superior properties including hardness, elastic modulus, high melting point, resistance to molten metal, etc. many researchers like Mc Murty et al. reported that the synthesis of TiB_2 in the SiC matrix can suppress the growth of SiC crystals which effectively leads to a higher fracture toughness [17]. The introduction of second phases such as TiB_2 can prevent the growth of SiC grains. Therefore, the addition of TiB_2 to matrix, diminishes the sintering temperature, develops the mechanical properties and modifies the microstructure of the final composite.

One of the intricacies of introducing a second phase in matrix is the proper distribution of the second phase in the final powders. In this regard, the in situ synthesized reinforcing phases are so appropriate as they can be facilely and homogeneously dispersed in the SiC matrix.

Because of the diverse uses of silicon carbide and the development of this substance in the presence of seconds phases such as TiB_2 and TiC, the current research is intended to investigate the effect of different sintering methods (spark plasma sintering, hot press and the pressureless sintering) on the physical and mechanical properties of SiC–Second phase composites (TiB_2, TiC).

2. Sintering methods of SiC–Second phase composites

Various techniques have been applied to fabricate SiC–TiB_2 and SiC–TiC composites according to the related reports. These two-phase systems are sometimes developed through carbothermal reactions of transition metal oxides and subsequent milling [18]. The following carbothermal reaction of TiO_2, B_4C and C at about 2000 °C followed by milling, is the industrial process of preparing fine TiB_2 [19,20].

$$TiO_2 + 0.\ 5B_4C + 1.\ 5C \rightarrow TiB_2 + 2CO \quad (1)$$

As another example TiB_2 was synthesized through heating at 1500 °C [21] or sintering SiC with boron and carbon through a carbothermal reaction [11]. Many papers have also reported the in-situ formation of TiB_2 particulates from TiO_2, B_4C and C, which were mixed with SiC powders [19]. Moreover Miyamoto et al. [22] pressed a mixture of Ti, B and SiC powders under a mechanical pressure of 3 GPa to synthesize TiB_2 in a SiC bed based on the following reaction:

$$Ti + 2B \rightarrow TiB_2 \quad (2)$$

Guolong Zhao et al. fabricated TiB_2–SiC composite through the hot pressing process in vacuum at 1700 °C. They used TiB_2 and SiC as the starting materials [23]. In another research, Guolong Zhao et al. also fabricated this composite using Ti, Si and B_4C powders and Ni powders as the sintering additive through the following reaction [21]:

$$Si(s) + 2Ti(s) + B_4C \rightarrow 2TiB_2(s) + SiC(s) \quad (3)$$

Yutaka Shinoda et al. made nanocrystalline SiC ceramics with Al_2O_3 and TiO_2 additives using spark plasma sintering. According to the paper, TiC phase was formed as a result of TiO_2 additive and SiC grains reaction. The effect of TiO_2 was doped by adding Al_2O_3 [24]. Hanqin Lianga et al. [25] introduced TiC particles in to the SiC matrix using TiO_2 particles as a Ti source according to the following reaction at 1800 °C:

$$TiO_2(s) + SiC(s) \rightarrow TiC(s) + 3Si(s) + 2CO\ (g) \quad (4)$$

Daniel Ahmoye et al. [26] used TiO_2 powders, carbon powders, and sintering aids Y_2O_3 and Al_2O_3 at temperatures ranging from 1825 °C to 1900 °C as follows:

$$TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO\ (g) \quad (5)$$

Hyun-Gu An et al. fabricated SiC-TiC composite, using SiC powders, TiC powders and sintering aids Y_2O_3 and Al_2O_3 [27]. In what follows we will outline the sintering behavior and the properties of SiC–TiB_2 and SiC-TiC composites made through different sintering methods (e.g., spark plasma sintering, hot press and pressureless sintering). The materials used to fabricate these composites were synthesized using the above-mentioned techniques.

2.1. Hot press method

Many papers have reported the application of hot press (HP) method to sinter SiC–TiB_2 and SiC–TiC composites. In the following paragraphs the findings of some related studies are presented.

Toshihiko Tani [28] and his colleagues mixed SiC and TiN powders with boron and hot-pressed the mixture at 2000 °C in an argon atmosphere. The boron molar content in the mixture was considered more than twice that of TiN. The following reaction took place during the HP process between 1100 °C and 1700 °C:

$$TiN + 2B \rightarrow TiB_2 + 0.5\ N_2 \quad (6)$$

The synthesis of TiB_2 was followed by the densification of SiC matrix with the aid of the excess boron. According to the results, fracture toughness has increased along with the increase of TiB_2 content compared with the HPed monolithic SiC body. The composite with 20 vol% of TiB_2 showed an 80% improvement in the fracture toughness (at 20 °C in air). On the other hand a similar flexural strength of about 490 MPa at 20 °C in air and 750 MPa at 1400 °C in vacuum was reported. To improve the in situ enhancement of toughness of SiC-30 wt%, 50 wt%, and 70 wt% TiB_2 composites, K-S Cho et al. [29] carried out the above-mentioned process based on liquid phase sintering and subsequent annealing. The starting materials and the properties of monolithic SiC and SiC-TiB_2 composite are shown in Table 1. This group of composites was synthesized using B-SiC, TiB_2 powders and additives Al_2O_3 and Y_2O_3 through the HP process at 1850 °C. The fabricated samples were finally annealed at 1950 °C.

Table 1
properties of monolithic SiC and SiC–TiB_2 Composites.

Composition (wt%)				Annealing time at 1950 °C(h)	Ralative density (%)	Crystalline phase		TiB_2 grain size (μm)	Fracture toughness (MPa $m^{1/2}$)	Flexural strength (MPa)
SiC	TiB_2	Al_2O_3	Y_2O_3			Major	Trace			
90	–	7	3	0	99.4	β–SiC	YAG[a], α–Al_2O_3	–	3.6 ± 0.4	611 ± 42
60	30	7	3	0	97.4	β–SiC, TiB_2	YAG, α–Al_2O_3	1.71	4.4 ± 0.5	571 ± 39
				6	96.8	α–SiC, TiB_2	YAG	2.44	6.7 ± 0.4	550 ± 33
				12	95.5	α–SiC, TiB_2	YAG	2.59	6.4 ± 0.4	501 ± 39
40	50	7	3	0	97.2	β–SiC, TiB_2	YAG, α –Al_2O_3	2	4.5 ± 0.4	504 ± 33
				6	97	α–SiC, TiB_2	YAG	4.13	7.3 ± 0.5	389 ± 32
				12	96.4	α–SiC, TiB_2	YAG	5.56	7.1 ± 0.4	290 ± 29
20	70	7	3	0	98.3	β–SiC, TiB_2	YAG, α–Al_2O_3	3.70	4.1 ± 0.5	593 ± 38
				6	97.3	α–SiC, TiB_2	YAG	5.94	6.8 ± 0.6	332 ± 32
				12	97	α–SiC, TiB_2	YAG	6.89	6.9 ± 0.5	231 ± 31

[a] $Al_5Y_3O_{12}$ (yttrium aluminium garnet).