Journal of the European Ceramic Society **19** (1999) 293–298

PII: S0955-2219(98)00150-2
0955-2219/99/$—see front matter

Reaction Synthesis and Mechanical Properties of TiB_2–AlN–SiC Composites

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(Received 10 January 1998; revised version received 15 May 1998; accepted 16 June 1998)

Abstract

TiB_2–AlN–SiC (TAS) ternary composites were prepared by reactive hot pressing at 2000°C for 60 min in an Ar atmosphere using TiH_2, Si, Al, B_4C, BN and C as raw powders. The phase composition was determined to be TiB_2, AlN and β-SiC by XRD. The distribution of elements Al and Si were not homogeneous, which shows that to obtain a homogeneous solid solution of AlN and SiC in the composites by the proposed reaction temperatures higher than 2000°C or time duration longer than 60 min are needed. The higher fracture toughness ($6{\cdot}35 \pm 0{\cdot}74\ MPa{\cdot}m^{1/2}$ and $6{\cdot}49 \pm 0{\cdot}73\ MPa{\cdot}m^{1/2}$) was obtained in samples with equal molar contents of AlN and SiC (TAS-2 and TAS-5) in the TAS composites. The highest fracture strength ($470 \pm 16\ MPa$) was obtained in TAS-3 sample, in which the volume ratio of $TiB_2/(AlN + SiC)$ was the nearest to 1 and there was finer co-continuous microstructure. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: titanium diboride, aluminum nitride, silicon carbide, reactive synthesis, ceramic composite.

1 Introduction

In the ternary system of TiB_2–AlN–SiC (TAS), there are three binary systems, i.e. TiB_2–AlN, TiB_2–SiC and AlN–SiC. In these binary systems, TiB_2–AlN composites are considered to be used as cathodes for aluminum electrosmelting[1] and TiB_2–SiC composites to be used as structural components.[2,3] Also, AlN–SiC composites have potential application at high temperatures and have been studied in considerable detail in the past 20 years.[4–14] AlN and SiC can form a solid solution in a very wide composition range at high temperatures above 1900°C, and this solid solution can spinodally decompose to AlN-rich and SiC-rich phases by annealed below 1900°C for a long time.[6] This characteristic has been used to modulate the microstructures and to improve the mechanical properties of AlN–SiC composites. Although a high flexural strength of 1000 MPa has been obtained in the AlN–SiC solid solution material with very fine grain size about 1 μm,[12] the fracture toughness of this kind of material is usually lower than $4MPa{\cdot}m^{1/2}$ (Ref. 11) except a value of $5{\cdot}5\ MPa{\cdot}m^{1/2}$ reported by Lee and Wei.[10]

Adding reinforcement such as particles, whiskers and fibers into ceramic matrix for improving the strength and toughness of the matrix material has been widely studied in various ceramic systems such as Si_3N_4,[15] sialon,[16] SiC[2,3] and Al_2O_3.[17] The mechanical properties of the abovementioned matrix composites are usually significantly improved when compared to those of their monolithics. However, to the authors' knowledge, study in this research area has not yet been proceeded for the AlN–SiC solid solution system.

In our previous work, TiB_2–SiC[18] and AlN–TiB_2[19] composites were prepared by reactive hot pressing according to the following reactions:

$$TiH_2 \longrightarrow Ti + H_2\uparrow$$

$$2Ti + Si + B_4C \longrightarrow 2TiB_2 + SiC \quad (1)$$

$$Ti + 2Al + 2BN \longrightarrow TiB_2 + 2AlN \quad (2)$$

In the present work, a reaction based on the above reactions is proposed to prepare TiB_2–AlN–SiC composites. The reaction is as follows:

$$mAl + nSi + xBN + 0{\cdot}25(2x - m)B_4C + 0{\cdot}25(4n + m - 2x)C \longrightarrow xTiB_2 + mAlN + nSiC \quad (3)$$

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in which x, m and n are coefficients of the products TiB_2, AlN and SiC, while $m/2 \leqq x \leqq (4n+m)/2$. This paper will report the preliminary results on phase composition, mechanical properties and microstructures of these composites manufactured by reactive hot pressing.

2 Experimental Procedure

The raw materials were powders of TiH_2 (purity 99·5%, particle size < 45 μm, Beijing Non-ferrous Research Institute), Al (particle size < 10 μm, Liaoning Aluminum Factory, China), Si (purity > 99%, particle size < 45 μm,), B_4C (purity 99%, particle size 5∼8 μm, The Second Factory of Abrasives of Mudanjiang, China), BN (purity > 99·3%, particle size ∼1 μm, Boron Nitride Factory of Gongyi City, China) and C (purity > 99%, particle size ∼1 μm, Shanghai Factory of Colloidal Carbon). The stoichiometric powders were mixed in alcohol with WC–Co balls for 4 h in a nylon pot and then dried. The powder compacts were uniaxially hot pressed in graphite die with BN coating at 2000°C under 25 MPa pressure for 60 min in an Ar atmosphere. After the products (50 mm in diameter × ∼6 mm thick) were removed from the die, the surfaces were ground and the density was determined by measuring dimensions and weight. X-ray diffraction (XRD) was used to identify the phase composition of the products. The three-point bending test was used to measure the fracture strength of the samples (3×4×36 mm, span 30 mm) cut from the hot pressed bodies by electrical discharge machining. The surfaces of sample were polished with 14, 7, 3·5 and 1·5μm diamond paste and the edges of the tensile surfaces were beveled. Fracture toughness was tested on bars (2×4×20 mm) by the SENB method (three-point bending, notch width < 0·2 mm, depth about 1·8 mm, just broken from the notch[20]). The crosshead speed was 0·5mm min^{-1} for strength and toughness tests. Each data of strength and toughness was the average of five values. A scanning electronic microscope (SEM) equipped with energy dispersive X-ray analysis (EDAX) was used to observe the microstructures and semiquantitatively analyze the phase chemistry of the composites.

3 Results and Discussion

Figure 1 is the molar phase composition diagram for the TiB_2–AlN–SiC composites that can be produced by reaction (3). Points 'S' and 'A' stand for reactions (1) and (2), and the corresponding binary composites are named as TS and TA, respectively. The TAS-1 to 6 phase composition points correspond to the ternary composites selected for study in this work. The calculations of phase composition and theoretical densities are listed in Table 1. The theoretical densities of the composites were calculated from the theoretical density of TiB_2 (4·52 g cm^{-3}), AlN (3·26 g cm^{-3}) and SiC (3·21 g cm^{-3}) according to the mixture rule.

The relative densities and mechanical properties of these composites are listed in Table 2. Each data was an average of five or six values. It can be seen that the addition of C will lower the relative density and fracture strength of the composites. It was considered that this may be due to the inhomogeneous distribution of the fine carbon powder in the mixed powder reactants. In the carbon rich region the extra carbon would displace nitrogen and form pores. About the mechanical properties, the values of the fracture toughness of the composites with the same molar contents of AlN and SiC (TAS-2 and TAS-5) were relatively higher than those of the other TAS composites, but the reason was unclear yet. The TS sample had the highest value of fracture toughness, the toughening mechanism was considered to be microcracking as discussed in our previous paper.[18] On the other hand, for TA sample as discussed in Ref. 19 the toughening mechanism of the composite was suggested to be thermal residual stress toughening and crack deflection toughening. The thermal expansion coefficients of TiB_2, SiC and AlN are 8·1, 4·0 and 4·03×10^{-6}°C^{-1} respectively. So there would be residual tensile stress in TiB_2 phase and compressive stress in SiC and AlN phases. These residual stresses should take a role in the toughening of the composites just as in AlN/TiB_2 and TiB_2/SiC composites.[18,19] However because the volume contents and the microstructures of these samples were different, the contribution of the residual stresses to the toughening effect would be also different. According to the volume contents of the component phases and the SEM micrographs (refer to Fig. 3) of the composites, in TS, TAS-1 and TAS-2 samples the continuous phase was TiB_2, on the other hand, in TA, TAS-4, TAS-5 and TAS-6 samples the continuous phase was AlN and SiC. A special one was TAS-3 sample in which the volume ratio of TiB_2/(AlN + SiC) was the nearest to 1 as well as TiB_2 and AlN + SiC were seemed to distribute co-continuously and both of TiB_2 and AlN + SiC phase were with fine particle sizes. This was considered to be the reason for TAS-3 sample showing the highest strength among all of these composites. However the fracture strength of the present composites was lower than the literature results, the main reason was considered to be the relatively low density of the composites.

Figure 2 shows the XRD pattern of specimen TAS-5. The XRD patterns of other TAS composites are similar to this one. It can be seen that in these composites the phase composition is TiB_2, AlN and β-SiC, but the existence of α-SiC (for example, 2H–SiC) can not be excluded only by XRD pattern. As discussed in our previous work,[18,19] when using reaction (1) to produce TiB_2/SiC composite, TiC and Ti_5Si_3 were the transient phases, the finishing temperature of the reaction was 1350°C and the final phase products were TiB_2 and β-SiC. When using reaction (2) to prepare AlN/TiB_2 composite, TiN and $TiAl_3$ were the transient phases, also there was a small amount of α-Al_2O_3 appeared in the reaction process, caused by the existence of B_2O_3 in BN powder and the absorption of oxygen by aluminum powder. However pure product of AlN and TiB_2 could be obtained at 1700°C. It was considered that the reaction mechanism of reaction (3) would be more complex, but the above reaction processes should be involved in the phase forming mechanism.

Figure 3 shows the SEM photos of these composites. In these photos, the white phase is TiB_2, the grey phase is AlN and SiC and it is difficult to distinguish AlN and SiC just by color. From Fig. 3(d)–(f), it can be seen that the pore distribution coincided with the densities of the composites. With the increasing of AlN and decreasing of TiB_2 in content (from point S to A on SA line in Fig. 1), the particle size of TiB_2 decreased and a co-continuous microstructure in TAS-3 sample was obtained as above mentioned. Figure 4 is the EDAX spectrums corresponding to points 179# and 180# in Fig. 3(e). The results of semiquantitative analysis of the numbered points in Fig. 3(e) by EDAX are listed in Table 3. It can be seen from Table 3 that the atomic composition of the metallic atoms (Ti, Al and Si) of the whole area in Fig. 3(e) is very near to the designed composition (see Table 1). In TiB_2 particles, the contents of Al and Si are very low, showing the low dissolubilities of AlN and SiC in TiB_2. However it is difficult to find an area in which that the atomic composition is 'pure' Al or Si. Points 179# and 180# are very near, but their compositions are very different. These results show that AlN and SiC are actually some solid solutions

Table 1. Calculation of phase composition and theoretical densities of TiB_2–AlN–SiC composites

Specimen	m, n *and* x *values*	*Phase composition*[a]			*Theoretical density* ($g\,cm^{-3}$)
		TiB_2	*AlN*	*SiC*	
TAS-1	$m=1, n=2,$ $x=4{\cdot}5$	60 64·82	13·33 11·78	26·67 23·41	4·065
TAS-2	$m=1, n=1,$ $x=2.5$	55·56 60·53	22·22 19·80	22·22 19·67	4·0129
TAS-3	$m=2, n=1,$ $x=3$	50 55·07	33·33 30·02	16·67 14·92	3·9464
TAS-4	$m=1, n=2,$ $x=0{\cdot}5$	14·29 17·00	28·57 27·79	57·14 55·22	3·4465
TAS-5	$m=1, n=1,$ $x=0{\cdot}5$	20 23·47	40 38·39	40 38·14	3·5367
TAS-6	$m=2, n=1,$ $x=1$	25 29·00	50 47·43	25 23·56	3·6137
TA	$m=2, n=0,$ $x=1$	33·33 37·94	66·67 62·06	0 0	3·7381
TS	$m=0, n=1,$ $x=2$	66·67 71·11	0 0	33·33 28·89	4·1415

[a]The data in the first line of phase composition correspond to the percents of molar contents (mol%) and the second line to those of volume contents (vol%).

Table 2. Properties of TiB_2–AlN–SiC composites

Specimen	*Relative density* (*TD*%)	*Fracture strength* (*MPa*)	*Fracture toughness* ($MPa{\cdot}m^{1/2}$)
TAS-1	97·73	380 ± 29	6·06 ± 0·68
TAS-2	96·25	309 ± 26	6·35 ± 0·74
TAS-3	95·84	470 ± 16	5·81 ± 0·62
TAS-4	84·00	244 ± 3	3·30 ± 0·11
TAS-5	92·93	294 ± 13	6·49 ± 0·73
TAS-6	93·75	304 ± 32	4·61 ± 0·18
TA	96·82	352 ± 40	5·21 ± 0·25
TS	99·21	332 ± 26	8·67 ± 0·52

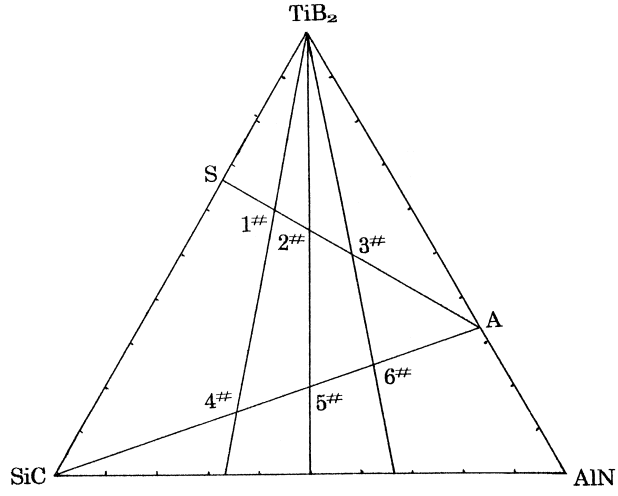


Fig. 1. Molar phase composition diagram.

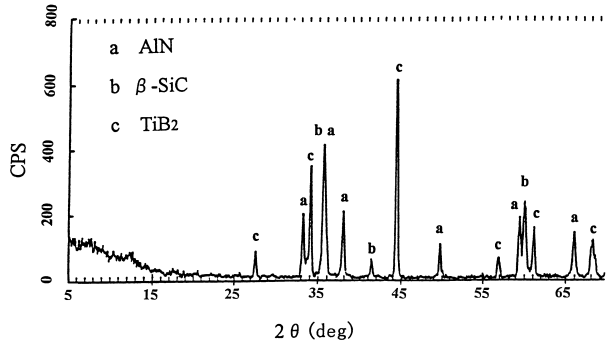
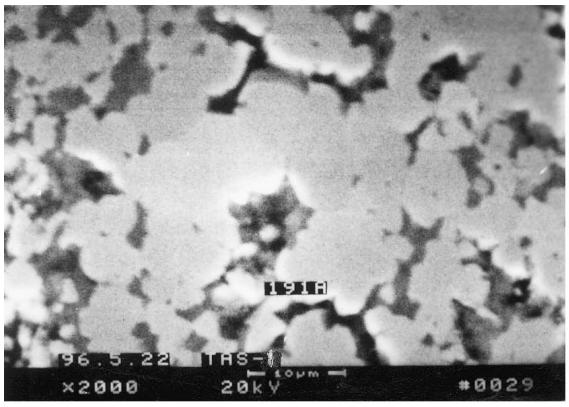
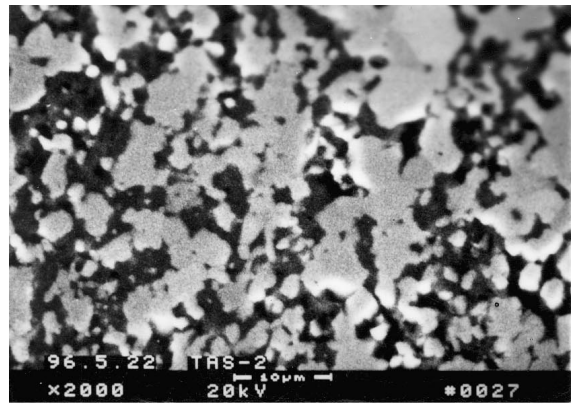


Fig. 2. XRD pattern (CuKα)of specimen TAS-5.



(a)



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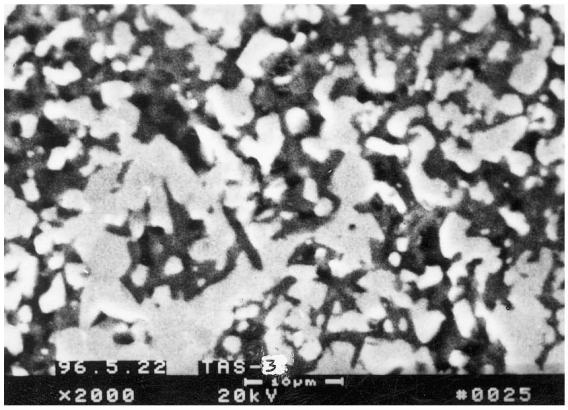

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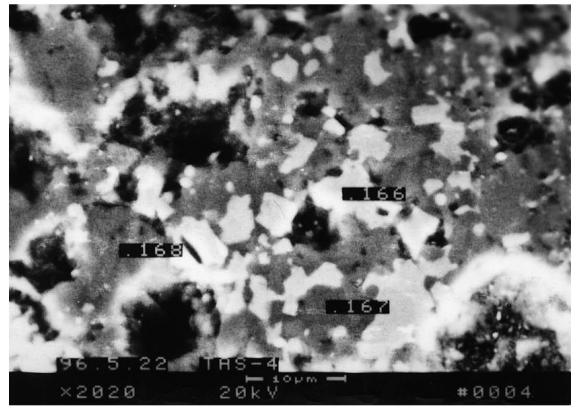
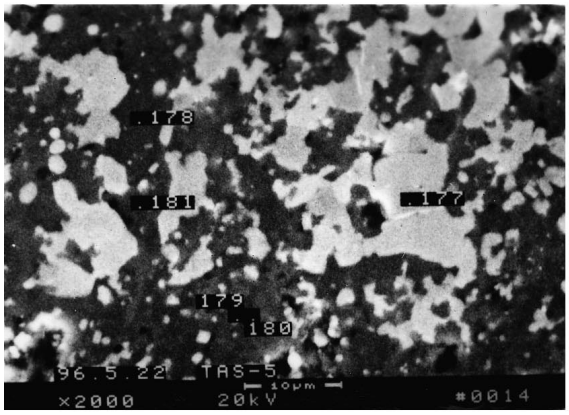
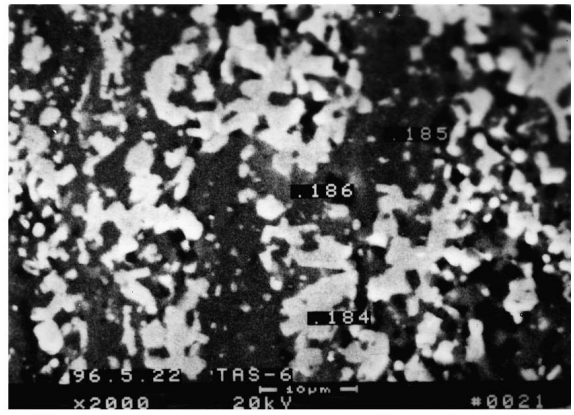


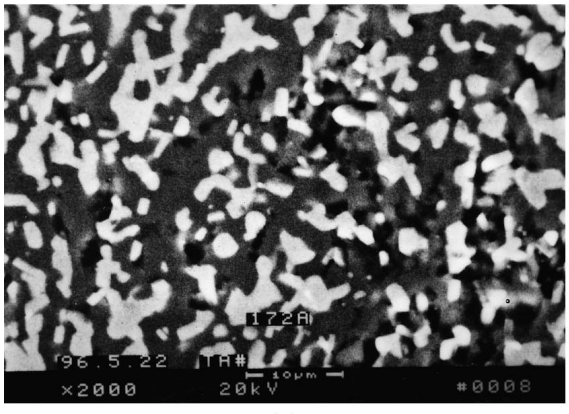
(d)



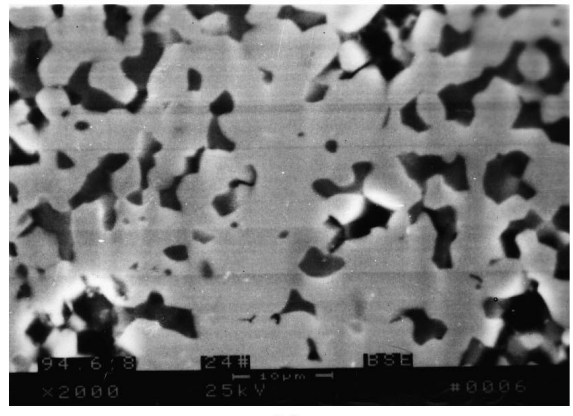
(e)



(f)



(g)



(h)

Fig. 3. SEM photographs of the composites. In these photographs, the white phase is TiB_2, the grey phase is AlN and SiC, the dark region is pores: (a) TAS-1; (b) TAS-2; (c) TAS-3; (d) TAS-4; (e) TAS-5; (f) TAS-6; (g) TA; (h) TS.

Table 3. Atomic compositions of the numbered points in Fig. 3(e) by EDAX

Point number	*Atomic composition (at%)*		
	Ti	*Al*	*Si*
177	96·31	1·94	1·75
178	1·04	81·02	17·94
179	5·99	34·94	59·07
180	1·68	61·95	36·37
181	5·48	51·74	42·77
The whole area	21·46	37·63	40·92

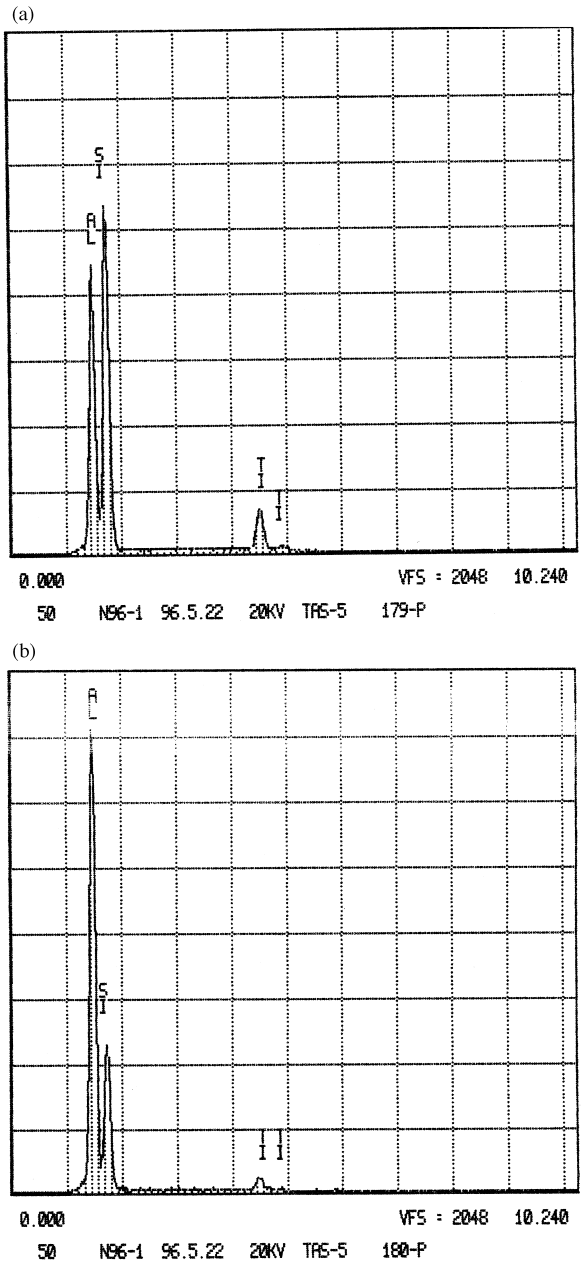


Fig. 4. EDAX spectrums of points 179# and 180# in Fig. 3(e): (a) point 179#; (b) point 180#.

and the distributions of Al and Si are not uniform. It means that temperatures higher than 2000°C or time duration longer than 60 min are necessary for obtaining a homogeneous solid solution of AlN and SiC by reaction (3).

4 Conclusion

TiB_2–AlN–SiC composites were prepared by reactive hot pressing using TiH_2, Al, Si, B_4C and C as raw materials. The phase composition of the obtained products is TiB_2, AlN and β-SiC. AlN and SiC are actually some solid solutions of each other. The inhomogeneity of the distributions of Al and Si shows that temperatures higher than 2000°C or time duration longer than 60 min are necessary for receiving a homogeneous solid solution of AlN and SiC in TiB_2–AlN–SiC composites by the proposed reaction. The relative densities and fracture strength were lowered by the addition of C and it was suggested to be the inhomogeneous distribution of the fine carbon powder in the reactants. The higher fracture toughness ($6{\cdot}35 \pm 0{\cdot}74\,MPa{\cdot}m^{1/2}$ and $6{\cdot}49 \pm 0{\cdot}73\,MPa{\cdot}m^{1/2}$) was obtained in samples with equal molar contents of AlN and SiC (TAS-2 and TAS-5) in the TAS composites. The highest fracture strength (470 ± 16 MPa) was obtained in TAS-3 sample, in which the volume ratio of TiB_2/(AlN + SiC) was the nearest to one and there was finer co-continuous microstructure.

Acknowledgements

This work was partly supported by the National Natural Science Foundation of China (NSFC) on grant no.59502008 and State Key Laboratory of New Ceramics and Fine Processing in Tsinghua University.

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