Journal of the European Ceramic Society 22 (2002) 551–558

www.elsevier.com/locate/jeurceramsoc

Microstructure and mechanical properties of in situ produced Ti_5Si_3/TiC nanocomposites

Jianlin Li*, Dongliang Jiang, Shouhong Tan

State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, China

Received 30 October 2000; received in revised form 18 April 2001; accepted 28 April 2001

Abstract

The microstructure and mechanical properties of in situ produced Ti_5Si_3/TiC nanocomposites have been studied. Ti_5Si_3/TiC composites have been prepared by reaction hot pressing mixed powders of elemental Ti, Si and SiC. XRD, SEM, TEM were employed to characterize the structure of the composites. When no elemental Si is added, the resulting composite contains 65 vol.% Ti_5Si_3, with a small amount of carbon dissolved in it. The majority of the TiC particles are nanosized. A small fraction Ti_3SiC_2 grains, with an average size 100 nm, are located in the TiC particles while other elongated Ti_3SiC_2 grains in the Ti_5Si_3 matrix. The highest bending strength of the Ti_5Si_3/TiC composites is 510 MPa at room temperature, which is approximately 6 times that of the monolithic Ti_5Si_3 material. The fracture toughness of the composites exceeds that of pure Ti_5Si_3, and at 1100°C, the yield strength of Ti_5Si_3/35TiC reaches 800 MPa.

Keywords: Mechanical properties; Microstructure; Reaction hot pressing; TiC; Ti_5Si_3

1. Introduction

High melting point intermetallic compounds with low density and improved oxidation resistance have received wide attention as potential aerospace materials over the past 20 years. The current interest in their high temperature properties has initiated extensive research activities on the microstructure and mechanical behavior. Molybdenum disilicide ($MoSi_2$) has come to be recognized as the promising matrix. However, in the implied restrictive selection of $MoSi_2$ as the preferred high temperature composite matrix, it is tacitly assumed that a balance of all the engineering properties can be achieved either with fiber development or fiber coating and no further modifications of the matrix material is required. However, if such an approach proved difficult, or more broadly, we were not to limit the development strategy solely to $MoSi_2$, it would be useful to develop other silicides.[1–8]

In comparison to $MoSi_2$, much less is known about Ti_5Si_3, on which only a few investigations have been reported. Hence, data on microstructures, as well as mechanical properties, are very limited. Ti_5Si_3 exhibits low density (4.32 g/cm^{-3}) and high melting temperature (2130°C). Among the 5-3 silicides, only Ti_5Si_3 has satisfactory oxidation resistance.[9]

Monolithic Ti_5Si_3 has been fabricated by various methods, including arc melting of Ti and Si pieces, hot isostatic pressing or hot pressing of Ti_5Si_3 powders.[10–12] Rosenkranz et al. reported that Ti_5Si_3 was synthesized by reaction sintering in vacuum in the temperature range from 1400 to 1500°C. The Ti_5Si_3 conglomerations obtained were ground in argon atmosphere to powder, then compacted by the hot isostatic pressing technique.[9] In addition, shock compression of 5Ti and 3Si at 7.5 GPa pressure led to the formation of Ti_5Si_3.[13] Researchers have also investigated self-propagating exothermic reactions in the titanium silicon system induced by mechanical, shock loading, and thermal ignition of elemental powder mixtures.[14]

Monolithic Ti_5Si_3 material is, however, very brittle and its strength is also unsatisfactory. The brittleness is due to its complex hexagonal structure, with low symmetry and highly covalent bonding, which increases the Peierls stress. The size of the Burgers vector would also be large. A promising alternative method is to produce a Ti_5Si_3 matrix composite. To the authors' knowledge, a few reports about Ti_5Si_3 based composites are available.

* Corresponding author.
E-mail address: lijinlin2000@263.net (J. Li).

0955-2219/02/$ - see front matter
PII: S0955-2219(01)00304-1

Mitra reported that alloying of Ti_5Si_3 with 8 wt.% Al formed Al_2O_3 and $Al_{0.67}Si_{0.08}Ti_{0.25}$ as uniformly dispersed phases in the microstructure. This led to a noticeable improvement in room temperature hardness and toughness properties.[15]

TiC is compatible with Ti_5Si_3 and the thermal expansion coefficients ($7.7\times10^{-6}/^{\circ}C$ for TiC, $9.7\times10^{-6}/^{\circ}C$ for Ti_5Si_3) match well.[1] Therefore, TiC is a candidate reinforcement for the Ti_5Si_3 matrix. Mitra et al. also reported the microstructure and mechanical properties of the Ti_5Si_3/20TiC composite.[15] The composite was processed by reaction hot-pressing a mixture of TiH_2, Si and TiC powders. The fracture toughness of this Ti_5Si_3/TiC composite was improved. In fact, when TiC and Ti_5Si_3 coexist at high temperature, some C atoms would migrate from TiC to Ti_5Si_3 without changes in crystal structure. In other words, Ti_5Si_3 is converted to $Ti_5Si_3C_x$ while TiC to TiC_{1-x} when they are in equilibrium with each other. The phase relation in the Ti-Si–C system have been determined by Van Loo et al.[16]

In the current study, Ti_5Si_3-based composites were produced via an in situ process. The Ti_5Si_3/TiC nanocomposites were prepared by reaction hot-pressing mixed powders of Ti, Si and SiC, and the resulting microstructure and mechanical properties is reported.

2. Experimental procedure

A reaction hot-pressing process was developed for fabricating the composites. Mixed powders of SiC, Ti and Si, with composition chosen to yield a TiC content from 14 to 35 vol.% in the product, were wet blended for 5 h with SiC media (Table 1). This was followed by drying, sieving and dry mixing for 5 h with SiC media. The Ti_5Si_3 /TiC samples were densitied by hot pressing the mixed powders at 1380°C for 1 h under a pressure of 35 MPa in Ar, using a BN-lined graphite die. The heating rate was 15°C/min. Pressure was applied only after the temperature reached 1200°C. In order to compare the mechanical properties of monolithic Ti_5Si_3 material with that of Ti_5Si_3/TiC composites, pure Ti_5Si_3 was also fabricated.

When the samples were polished, X-ray diffraction (XRD, CuK_α radiation: $\lambda = 0.154$ nm) was carried out to identify the phases present. Microstructural characterization was carried out using optical microscopy and scanning election microscopy (SEM). The grain size of matrix were obtained by quantitative analysis on polished surfaces etched in acid solution ($HF:HNO_3:H_2O$, 1:1:1) 10 s.[5] The porosity was also obtained by the quantitative analysis. Microstructural characterization was performed using transmission electron microscopy (TEM) and electron diffraction. TEM samples were studied using a JEM-200cx operating at 200 kV.

Table 1
Characteristics of powders used in this work

Powder	Purity (%)	Particle size	Sources
Ti	99.5	−300 mesh	Zhujiang Hard Alloy Factory, China
Si	99.5	−300 mesh	Zhujiang Hard Alloy Factory, China
SiC	99.5	7 μm	Notwon Chem. Co., Norway

Rectangular bars, 3×4×36 (mm), were prepared by grinding with a 400 grit diamond wheel. Three point bending tests were performed using a universal testing machine (Instron 1195) with a span of 30 mm at 20°C and 20 mm at elevated temperature (1250°C). The speed of crosshead was 0.5 mm/min. Three samples were used for each measurement. Indentation was employed to determine fracture toughness K_{IC} at room temperature using Vickers' diamond indentor. Four to six samples were used for each measurement. K_{IC} was calculated using the following formula:[17]

$$K_{IC} = P(\pi c)^{-3/2}\cot\beta$$

where $2c$ is the length of crack. P is the applied force (98 N) and $\beta = 68^{\circ}$.

3. Results and discussion

3.1. Microstructure

X-ray diffraction analysis (Fig. 1) was carried out to identify the phases present. The results indicate that Ti_5Si_3/TiC composites and Ti_5Si_3 can be produced via reactive hot pressing process. The reactions taking place are,

$$8Ti + 3SiC = 3TiC + Ti_5Si_3 \quad (1)$$

$$3Si + 5Ti = Ti_5Si_3 \quad (2)$$

Gibbs free energy change of reactions (1) or (2) is negative, the heat evolved in the exothermic reaction (1) is 742 kJ mol^{-1} and 497 kJ mol^{-1} in reaction (2).[18]

Ti_5Si_3/TiC composite with 35 vol.% TiC was fabricated by hot pressing the stoichiometric mixed powders of SiC and Ti according to reaction (1). Pure Ti_5Si_3 material was obtained by reaction (2). Other composites involved both reactions (1) and (2). Fig. 1(a) indicates that TiC is compatible with the Ti_5Si_3 matrix. All the other peaks are indexed on the basis of Ti_5Si_3 and TiC according to JCPDS cards except an unknown weak peak near 40 degree (2θ) in the pattern of the Ti_5Si_3/TiC composites [Fig. 1(a)]. This unknown weak peak was attributed to Ti_3SiC_2 phase. It is concluded that a small amount of Ti_3SiC_2 existed in the Ti_5Si_3/TiC composite.

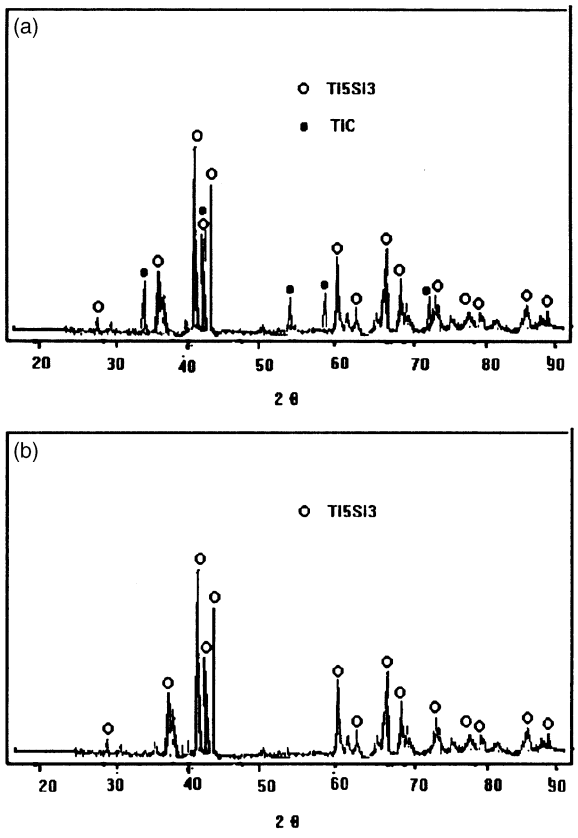

Fig. 1. XRD patterns of (a) Ti_5Si_3/TiC composite with about 35 vol.% TiC, (b) Ti_5Si_3.

In the current work, the lowest content of Ti_3SiC_2 that could be detected by XRD is about 3–4 vol.%. Namely, the volume of Ti_3SiC_2 is about 3–4 vol.%. Much low content means that only the first intense peak (104) was detected.[19] It has been reported by Barsoum et al. that polycrystalline bulk samples of Ti_3SiC_2 were fabricated by reactively hot pressing Ti, graphite, and SiC powder, to yield the stoichiometry (3:1:2, Ti:Si:C), at 40 MPa and 1600°C for 4 h.[20] Ti_3SiC_2 is thermodynamically stable with TiC or Ti_5Si_3. According to the results of Ti–SiC diffusion-couple experiment in the work of Van Loo et al.,[16] several phases were in equilibrium: Ti(C, Si)/ $Ti_5Si_3C_x/Ti_5Si_3C_x + TiC_{1-x}/Ti_3SiC_2/SiC$ at 1250°C. Although the current experiment was conducted at 1380°C, the similar results suggest that Ti_5Si_3 possess a solid solution range in the binary Ti–Si diagram. Obviously, when Ti and SiC were consumed the phases in the composites would be $Ti_5Si_3C_x + TiC_{1-x} + Ti_3SiC_2$, and Ti_3SiC_2 would disappear if the reaction (1) was completed. However, a little amount of Ti_3SiC_2 phase would exist if the reaction (1) is not completed absolutely.

Williams et al. reported that interstitial additions, such as carbon, affected the structure of Ti_5Si_3 lattice.[21] In the current work, although some carbon could dissolve in Ti_5Si_3, TiC and Ti_5Si_3 are identified instead of $Ti_5Si_3C_x$ and TiC_{1-x} phases. Therefore the lattices of TiC and Ti_5Si_3 have not been changed obviously. Namely, only a few of carbon atoms might be in Ti_5Si_3 lattices.

On the other hand, three very weak peaks near 39 and 37° were observed in the pattern of Ti_5Si_3 [Fig.1(b)], which are related with $TiSi_2$. This result shows that there is a small amount of $TiSi_2$ in Ti_5Si_3 material. A similar result has been reported elsewhere.[14]

Fig. 2(a) is a backscattered SEM micrograph of Ti_5Si_3/35TiC composite. A small amount of pore is found because the hot pressing temperature (1380°C) was not high enough compared with Ti_5Si_3 melting point (2130°C). The porosity is about 3–4% for all Ti_5Si_3/TiC composites fabricated in this work. In a backscattered SEM micrograph, TiC particles should appear to be dark spots in bright Ti_5Si_3 matrix. In this figure, there are few obvious TiC dark spots in bright Ti_5Si_3 matrix. Therefore, TiC particles are well distributed in Ti_5Si_3 matrix and TiC particles should be fine. The total volume of TiC particles above 1 μm in size in Ti_5Si_3/35TiC composite is only about 10 vol.% by quantitative analysis, suggesting that a large number of TiC particles are nanosized. These nanosized TiC particles cannot be detected in the figure. Fig. 2(b) is the Si mapping of Fig. 2(a). It shows the Si element is well distributed, and this also means TiC particles should be fine and well distributed. Some elongated grains, which are proved to be Ti_3SiC_2 by XRD and EDS, can be seen in Fig. 2(c). The content of elongated Ti_3SiC_2 grains is about 2 vol.% by quantitative analysis.

As is known, Ti_3SiC_2 has a layered crystalline structure and is a natural layered material. So, the morphology of Ti_3SiC_2 grains often appeared to be plate. But the morphology of Ti_3SiC_2 grains is different via different fabrication processing. Sun et al. also reported that elongated Ti_3SiC_2 grains were prepared in their work due to the different growth rate on a different face.[20] It is assumed that the same mechanism works here.

Table 2 gives the grain size of the Ti_5Si_3 matrix. It appears that the fine TiC dispersions restrain the growth of Ti_5Si_3 matrix grains.

3.2. Submicrostructure

In order to study the microstructure of Ti_5Si_3/TiC composites, TEM analyses was carried out. TiC particles are from 100 to 400 nm in size, as shown in Fig. 3(a), and some nanosized Ti_5Si_3 grains can be observed in the graph. Some nanosized Ti_3SiC_2 grains are located in a large TiC grain [Fig. 3 (b)]. Fig. 3(c) is the electron diffraction pattern of (b). Fig. 3(d) shows elongated Ti_3SiC_2 grains in the Ti_5Si_3 matrix. TEM images [Fig. 3(d) and (e)] show that these elongated Ti_3SiC_2 grains have a natural layered structure.

Fig. 4 shows the HRTEM image of the grain boundary of TiC and Ti_5Si_3. No amorphous phase was found

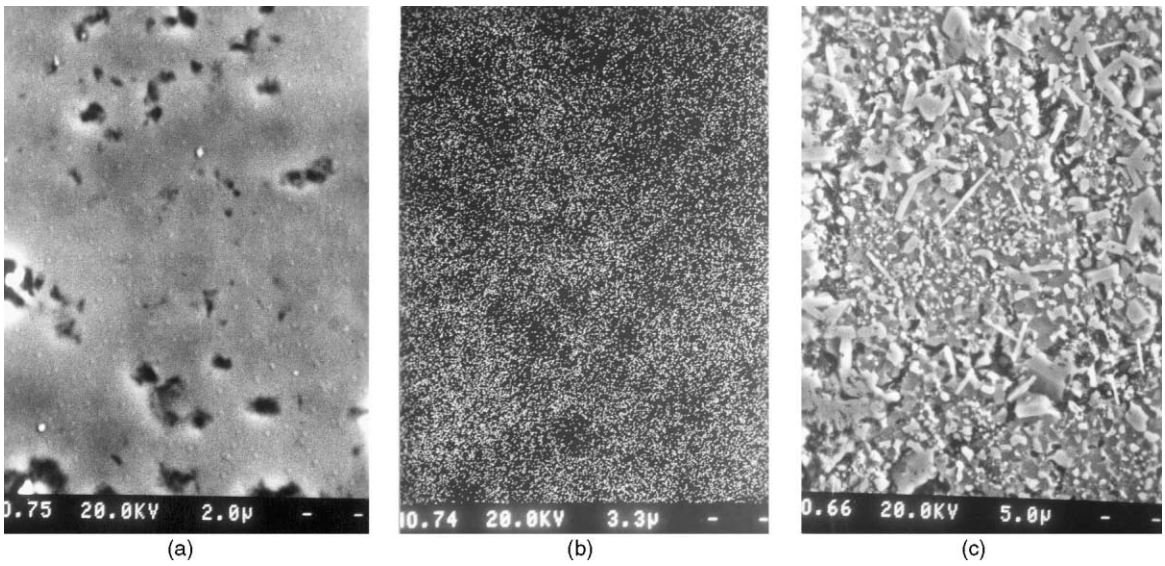

Fig. 2. (a) And (c), backscattered SEM micrographs of Ti_5Si_3/35TiC composite fabricated by reaction (1), (b) Si mapping of (a).

Table 2
Ti_5Si_3 matrix grain sizes of composites[a]

TiC content (vol.%)	0	14	22	35
Ti_5Si_3 grain size (μm)	25	18	10	4

[a] Considering a little amount of Ti_3SiC_2 in the composites, the TiC content is not accurate. The values are obtained through reactions (1) and (2).

at the grain boundary. HRTEM examination has shown that some monatomic steps at TiC/Ti_5Si_3 interface (arrows). Although a bit of carbon could dissolve in Ti_5Si_3, the change of lattice parameter of TiC or Ti_5Si_3 could not be identified in this image, in agreement with the XRD result. This means that the content of carbon in Ti_5Si_3 is much low and can be ignored. The XRD results and electron diffraction pattern and HRTEM all demonstrate the conclusion in the current work.

3.3. Mechanical properties at ambient temperature

The dependence of bending strength of the composites on TiC content is shown in Table 3. The bending strength of Ti_5Si_3/TiC composite, with about 35 vol.% TiC, reaches 510 MPa, nearly 6 times that of monolithic Ti_5Si_3. Ti_5Si_3/TiC composites achieved higher strength with higher TiC content. Another factor related to strength is Ti_5Si_3 matrix grain size (Table 2 shows the matrix grain size). The fine TiC dispersions restrain the growth of Ti_5Si_3 grains. Finer matrix grains are commonly associated with higher strength.[22]

Fig. 5(a) shows a SEM micrograph of fracture surface of pure Ti_5Si_3. The Ti_5Si_3 grains are coarse and fracture is highly transgranular. In view of the anisotropy of Ti_5Si_3 lattice, the low strength is in part attributable to the internal stress or microcrack induced by thermal expansion anisotropy. Although this suggestion yet is not proved, a crack was observed on the surface of a Ti_5Si_3 sample aged in air at room temperature for 30 days. Due to microcracks, the bending strength of pure Ti_5Si_3 is just 94 MPa. For Ti_5Si_3/TiC composites, a large fraction of TiC particles produced in hot pressing process are nanosized, and Ti_5Si_3 matrix grains are rather fine. Thus, for fine-grained Ti_5Si_3/TiC composites the microcracks induced by internal stress could be avoided and strength was improved.

In an earlier report,[16] the bending strength of hot-pressed Ti_5Si_3 was reported to be 255 MPa, much higher than that of hot-pressed Ti_5Si_3 in this work. However, the grain size of Ti_5Si_3 material reported in the report was in the range 5–10 μm, while it is 25μm in this work. The strength is strongly depends on matrix grain size. On the other hand, the strength with a grain size 10μm for Ti_5Si_3/22TiC in this work is 270 MPa, and Ti_5Si_3/35TiC composite with a size of 4μm is as higher as 510 MPa.

Fig. 5(b) shows a fracture micrograph of Ti_5Si_3/35TiC composite. It can be observed that Ti_5Si_3 grains of this composite are finer than that of pure Ti_5Si_3, and the fracture shows a mixture of transgranular and intergranular mode. In addition, the fracture surface of pure Ti_5Si_3 is relatively smooth while that of Ti_5Si_3/35TiC is rather rough, therefore, the fracture energy of Ti_5Si_3/TiC composite is bigger, and this is helpful to strength.

The fracture toughness of Ti_5Si_3/TiC composites at room temperature is also shown in Table 3. Compared with the increment of strength, the toughness of composites is also slightly improved. The value 3 MPa $m^{1/2}$ for Ti_5Si_3 is consistent with the results reported by Mitra et al.,[15] but is higher than other reports.[9,10] As the CTE value of TiC is less than that of Ti_5Si_3, residual tangential tensile strains are induced at particle/matrix interfaces,

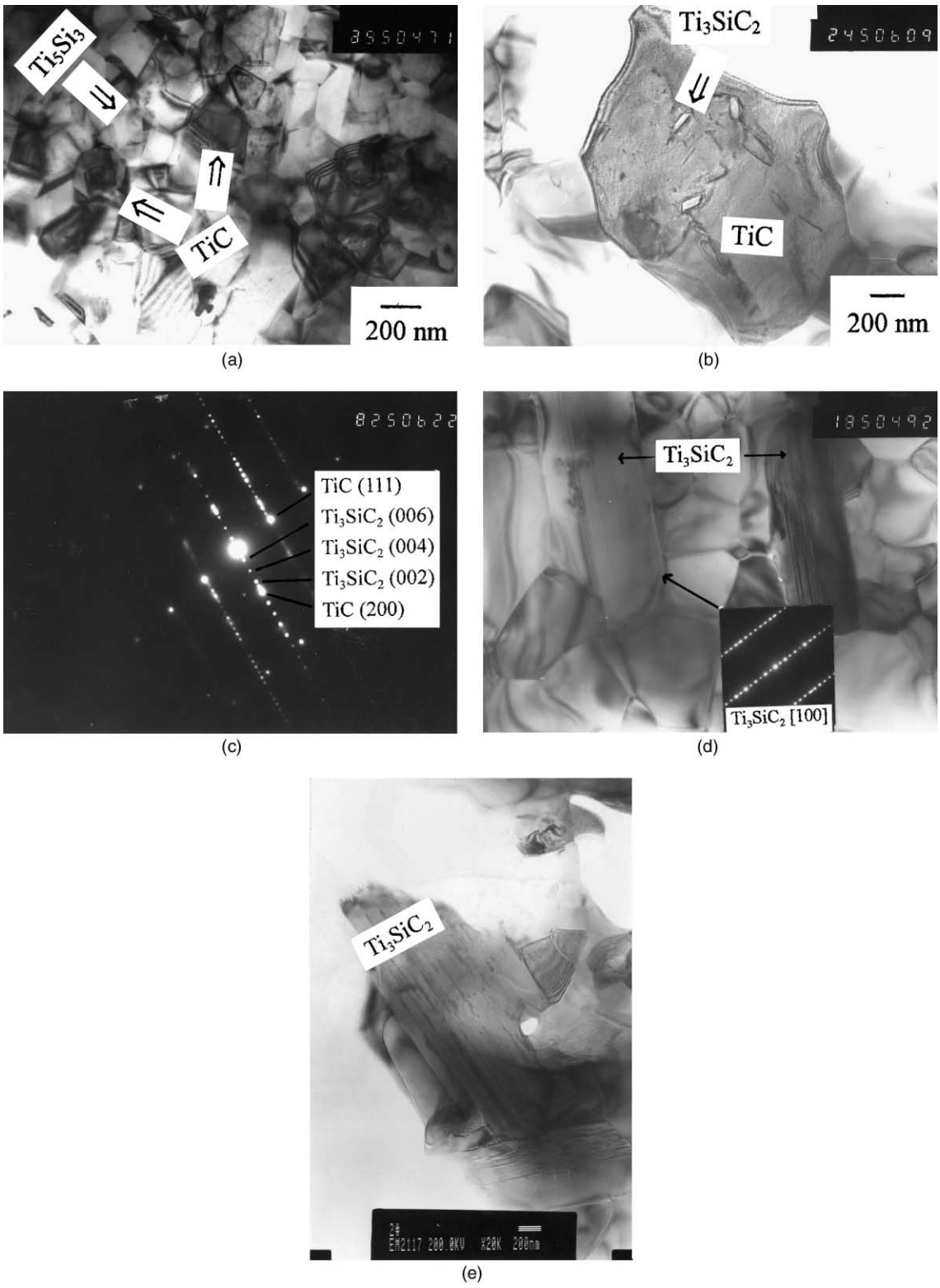

Fig. 3. TEM images show, (a) some fine TiC grains, (b) a large TiC grain, in which there are some nanosized Ti_3SiC_2 grains, (c) electron diffraction pattern of (b), (d) and (e) elongated Ti_3SiC_2 grains in the Ti_5Si_3 matrix.

and this implies that cracks would be deflected toward the particles. Fig. 6 shows the trajectory of an indentation crack extension. In view of the TiC grains being fine, the residual stress is low and there is little ability to affect the extension of the crack. The trajectory is seen to slightly zigzag. The increment of toughness is in part attributable to crack deflection caused by residual stress.

Mitra reported that the toughness of Ti_5Si_3/20TiC composite was 4.1 MPa $m^{1/2}$,[15] higher than that of in situ produced Ti_5Si_3/22TiC composite and close to that of the Ti_5Si_3/35TiC composite prepared in this work (Table 3). The main difference is due to the difference of TiC particle size. TiC that Mitra used had an average particle size of about 1.0 μm, rather larger than that of in situ produced TiC particles in this work.

Although there are some elongated Ti_3SiC_2 grains in the samples, they do not show much toughening effects due to the too low content.

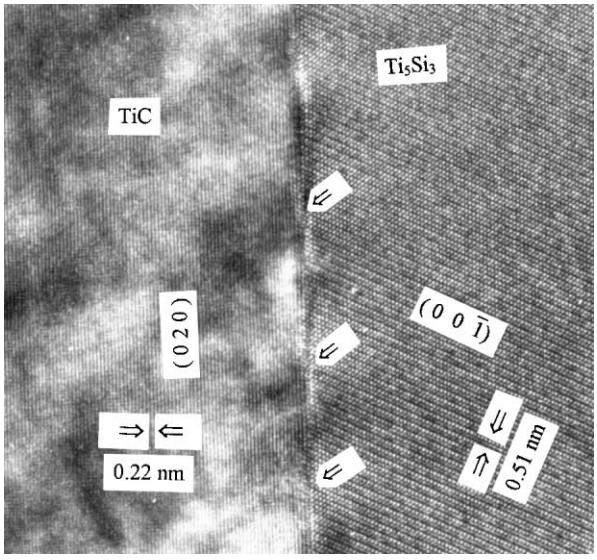

Fig. 4. HRTEM image of the grain boundary of TiC and Ti_5Si_3 showing some monatomic steps (marked with arrows). The lattice parameters are not changed compared with that of pure TiC or Ti_5Si_3.

Table 3
Bending strength and fracture toughness of Ti_5Si_3/TiC composites

TiC content/vol.%	0	14	22	35
Bending strength/MPa	94±15	220±30	270±35	510±40
Fracture toughness/MPa $m^{1/2}$	3±0.2	3±0.2	3.2±0.16	4.2±0.2

3.4. Strength of Ti_5Si_3 /35TiC composite at elevated temperature

Ti_5Si_3 exhibits a brittle to ductile transition at about 1000°C. At higher temperature, the strength of Ti_5Si_3 decreases sharply due to the thermally activated dislocation. [9] The Ti_5Si_3 exhibited a yield strength (compression) value of 1115 MPa at 1100°C and 500 MPa at 1250°C. In this work, the strength of Ti_5Si_3/35TiC composite was tested from 900 to 1250°C. Fig. 7 shows the dependence of yield strength (0.2% offset) on temperature.

At 1050°C or lower, Ti_5Si_3/35TiC composite shows brittle fracture. The bending strength of the composite has the same value until 1050°C. Although the DBTT (brittle to ductile transition temperature) of Ti_5Si_3 is about 1000°C (strain rate $10^{-4}s^{-1}$), [9] the high strain rate (4×10^{-4} s^{-1} in this work) raises the DBTT.[23] Thus, the Ti_5Si_3/35TiC composite shows brittle fracture although its slip systems may be activated at 1050°C. At 1100°C and above, it shows plastic behavior. At 1100°C, yield occurs when the applied stress is 800 MPa. In addition, the yield stress is 320 MPa at 1250°C.

At a lower temperature, the brittle composite fractures due to crack extension with a low elastic strain. At 1100°C, the dependence of stress on crosshead displacement shows a linear curve [Fig. 8(b)]. The plastic deforming stage is not obvious, and crack extension leads to the fracture. The DBTT of TiC is 800–1000°C,[24] therefore, TiC is expected to be soft enough to relieve

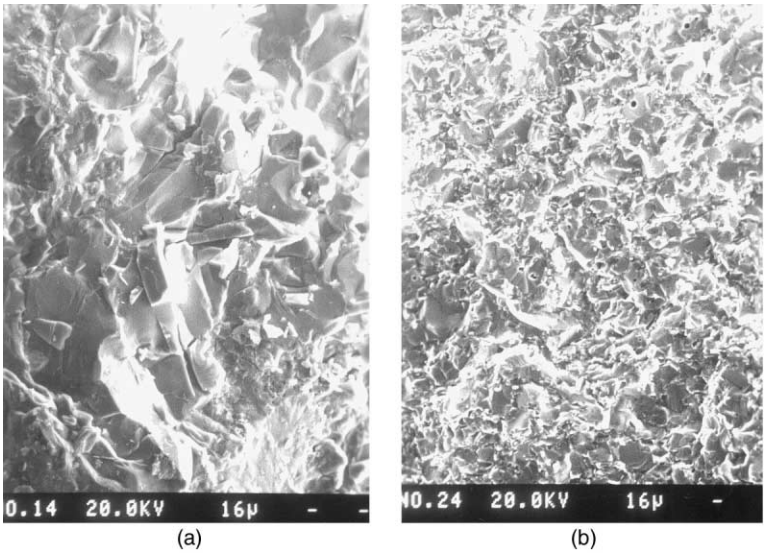

Fig. 5. SEM micrographs of the fracture surface of (a) pure Ti_5Si_3, (b) Ti_5Si_3/35 $_{TiC\ composite}$.

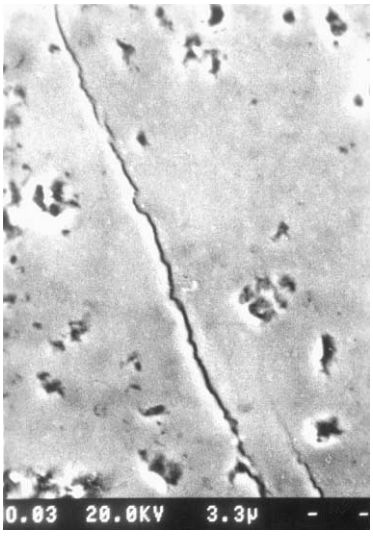

Fig. 6. Indentation crack extension in the Ti_5Si_3/35 TiC composite.

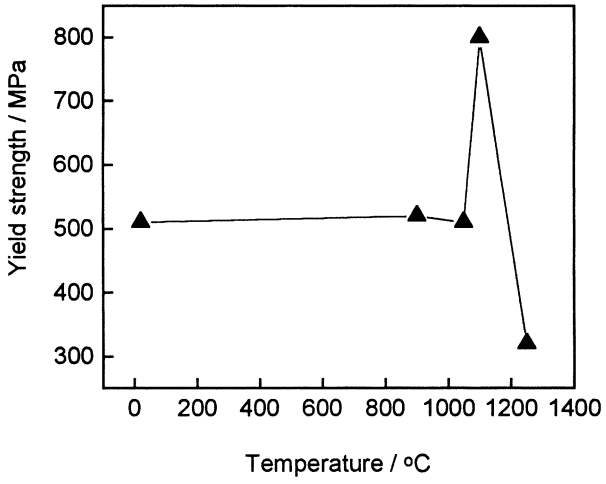

Fig. 7. Strength of the Ti_5Si_3/35 TiC composite at different temperatures. One sample was used for measurement at 1100 and 1250°C, respectively.

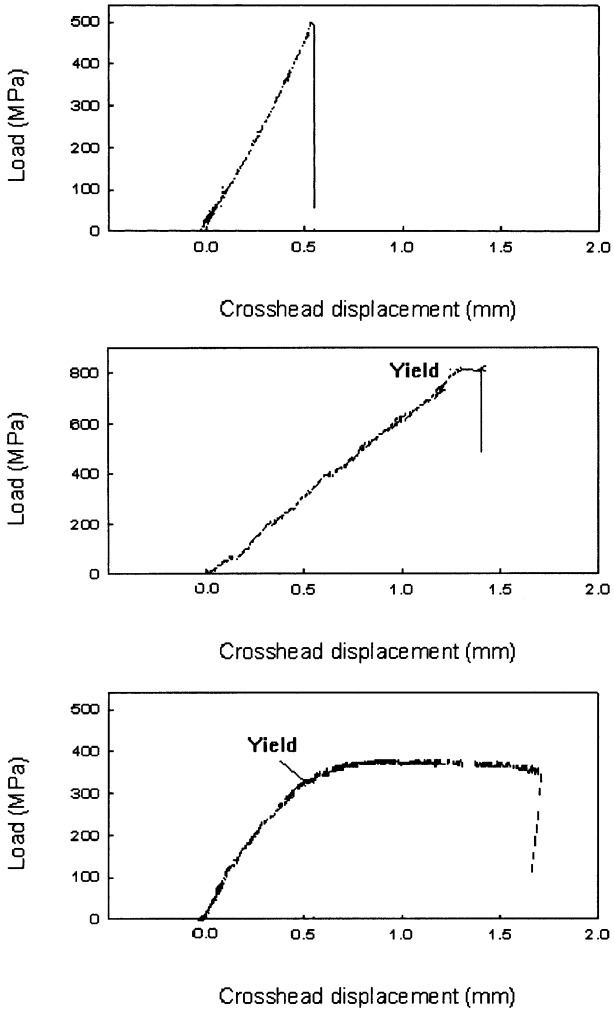

Fig. 8. Load and crosshead displacement curves for the Ti_5Si_3/35TiC composite at different temperatures: (a) 1050°C, (b) 1100°C and (c) 1250°C.

stress at 1100°C. In the bending test, crack tip can be blunted and stress is relieved because of dislocations gliding of TiC near the crack tip. In addition, the Young' s modulus of Ti_5Si_3 is just slightly decreased;[9] therefore, strength of the composite increases rapidly. Meredithand et al. reported a similar appearance when he studied the dependence of the strength of 95% Al_2O_3 material on temperature.[25] At 1000°C, the strength of 95% Al_2O_3 was almost 50% higher than that of the same material at room temperature. Meredithand et al. attributed the strength increment of this material to the decrement in stress near the crack tip caused by the soft glass phase. It seems that the two materials 95% Al_2O_3 and Ti_5Si_3/35TiC exhibit the same mechanism.

At 1250°C, dislocation gliding is responsible for the strength of the composite, as shown in Fig. 8(c). At this temperature, strength of the composite decreased sharply. TiC has a cubic lattice and Ti_5Si_3 has a hexagonal structure, and they have different slip systems and Burger vectors. TiC particles between Ti_5Si_3 grains may act as barriers to sliding dislocation and distortion of Ti_5Si_3 grains, but the test temperature 1250°C is rather higher than the DBTT of TiC or Ti_5Si_3, therefore, when dislocations arrive at grain boundaries, neighboring grains would not inhibit their mobility effectively. Hence, the Ti_5Si_3/TiC composite deforms plastically at 1250°C and strength decreased to 320 MPa, as shown in Fig. 8(c).

4. Conclusion

Ti_5Si_3/TiC nanocomposites can be prepared by reaction hot pressing the mixed powders of SiC, elemental Si and Ti. The in situ produced TiC particles are fine. A few of the nanosized Ti_3SiC_2 grains are located in TiC grain while other elongated Ti_3SiC_2 grains are in the Ti_5Si_3 matrix. At room temperature, the highest bending

strength of Ti_5Si_3/TiC composites is 510 MPa, nearly 6 times that of monolithic Ti_5Si_3 material. The fracture toughness of composites also exceeds that of pure Ti_5Si_3. At elevated temperature, yield strength of the Ti_5Si_3/35TiC composite maintains at 500 MPa at 1050°C. At 1100°C, strength of this composite is as high as 800 MPa. The strength increment of the Ti_5Si_3/35TiC composite is attributed to the decrement of stress near the crack tip reduced by soft TiC particles.

References

1. Vasude, van, A. K. and Petrovic, J. J., Comparative overview of molybdenum disilicide composites. *Mater Sci. Eng.,* 1992, **A155**, 1–17.
2. Srinivasan, S. R., Ductile to brittle transition in $MoSi_2$. *Mater. Res. Symp. Proc.,* 1993, **288**, 1099–1104.
3. Shah, D. M., Appraisal of other silisides as structural materials. *Mater Sci. Eng.,* 1992, **A155**, 45–57.
4. Ward-Close, C. M., Minor, R. and Doorbar, P. J., Intermetallic matrix composites a review. *Intermetallics,* 1996, **4**, 217–229.
5. Lee Jong, I. K., Normanl, H. and Li, M. T., In situ processing and properties of SiC/ $MoSi_2$ nanocomposites. *J. Am. Ceram. Soc.,* 1998, **81**(2), 421–424.
6. Aikin, R. M., Structure and properties of in situ reinforced $MoSi_2$. *Ceram. Eng. Sci. Proc.,* 1991, **12**(9–10), 1643.
7. Shah, D. M. and Anton, D. L., Evaluation of refractory intermetallics with A15 structure for high temperature structural applications. *Mater. Sci. Eng.,* 1992, **A153**, 402–407.
8. Petrovic, J. J., ZrO_2-reinforced $MoSi_2$ matrix composite. *Ceram. Eng. Sci. Proc.,* 1991, **12**(9–10), 1633.
9. Rosenkranz, R., Frommeyer, G. and Smarsly, W., Microstructures and properties of high melting point intermetallics Ti_5Si_3 and $TiSi_2$ composites. *Mater. Sci. Eng.,* 1992, **A152**, 288–294.
10. Min, K. S., Aredell, A.J, Eck, S. J. and Chen, F. C., A small-specimen investigation of fracture toughness of Ti_5Si_3. *J. Mater. Sci.,* 1995, **30**(12), 5479–5483.
11. Wang, L. L. and Munir, Z. A., Kinetic analysis of the combustion synthesis of molybdenum and titanium silicides. *Metall. Mater. Trans. B,* 1995, **26B**, 595–602.
12. Zhang, L. and Wu, J., Ti_5Si_3 and Ti_5Si_3-based alloys: alloying behavior, microstructure and mechanical property evaluation. *Acta Mater.,* 1998, **46**(10), 3535–3546.
13. Deevi, S. C. and Naresh, N., Reaction synthesis of high temperature silisides. *Mater. Sci. Eng.*, 1995, **A152/153**, 604–611.
14. Yen, B. K., Aizawa, T. and Kihara, J., Reaction synthesis of titanium silisides via self propagating reaction kinetics. *J. Am. Ceram. Soc.*, 1998, **81**(7) 1953–1956.
15. Mitra, R., Microstructure and mechanical behavior of reaction hot-pressed titanium silicide and titanium silicide-based alloys and composites. *Metall. Mater. Trans. A.,* 1998, **29A**, 1629–1640.
16. Wakekamp, W. J. J., Van Loo, F. J. J. and Metselaar, R., Phase relation in Ti–Si–C system. *J. Eur. Ceram. Soc.,* 1991, **8**, 135–139.
17. Evans, A. G., *ISIJ International,* 1989, **29**, 244.
18. Barin, I. and Knacke, O., *Thermochemical Properties of Inorganic Substances*. Spring Verlag, New York, 1973.
19. Barsoum, M. W. and El-Raghy, T., Synthesis and characterization of a remarkable ceramic: Ti_3SiC_2. *J. Am. Ceram. Soc.,* 1996, **97**(7), 1953–1956.
20. Sun, Z. M., *et al.*, Ti_3SiC_2 material fabricated by a fluctuant-method. *Mater. Res. Innovat.,* 1999, **2**, 227–231.
21. Williams, J. J. and Kramer, M. J., *et al.*, Effects of interstitial additions on the structure of Ti_5Si_3. *J. Mater. Res.,* 2000, **15**(8), 1773–1779.
22. Niihara, K., New design concept of structural ceramics — ceramic nanocomposite. *J. Ceram. Soc. Jpn.,* 1991, **99**(10), 974–982.
23. Tan, H. L., Atomistic simulation. *Acta Mechanica Sinica,* 1994, **10**(2), 151–162.
24. Chang, H., Plasticity enhancement of elevated temperature $MoSi_2$ toughen by the addition of TiC. *Mater. Res. Symp. Proc.,* 1992, **273**, 253–255.
25. Zhang, Q. C., *Mechanical properties of ceramics materials*. Science Press, Beijing, 1987, pp. 87.