In-situ synthesized Ti_5Si_3/TiC composites by spark plasma sintering technology

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Sub-microstructured Ti_5Si_3/TiC composites were in-situ fabricated by through spark plasma sintering (SPS) technique using Ti and nanosized SiC powders without any additive. It was found that the composite could be sintered in a relatively short time (8 min at 1260°C) to 98.8% of theoretical density. After sintering, the phase constituents and microstructures of the samples were analyzed by X-ray diffraction (XRD) techniques and observed by scanning electron microscopy (SEM) and TEM. Fracture toughness at room temperature was also measured by indentation tests. The results showed that fracture toughness of Ti_5Si_3/TiC composite reached 4.2 ± 0.4 MPa.$m^{1/2}$, which is higher than that of monolith Ti_5Si_3 (2.5 MPa.$m^{1/2}$).

1. Introduction

Intermetallic compounds (such as silicides) with low density and oxidation resistance are being considered for a wide range of high temperature applications and much research effort has been devoted to their development in the last ten years. Among these silicides is the compound Ti_5Si_3, which has been the focus of considerable attention as an attractive materials for high temperature applications [1–3]. The advantages of Ti_5Si_3 are its extremely high melting temperature (2130°C) and low density (4.32 g/cm^3). However, as in the case of many intermetallic compounds, the current concern about this material focuses on its low fracture toughness (2.5 MPa $m^{1/2}$) below the ductile-brittle transition temperature [4].

Ti_5Si_3 can be synthesized by reacting mixed stoiciometric powders of Ti and Si at high temperature [5–7]. Monolithic Ti_5Si_3 has been successfully fabricated by various methods, including arc melting of Ti and Si pieces, hot pressing or hot isostatic pressing of Ti_5Si_3 powders [8–10]. Monolithic Ti_5Si_3 is very brittle and its high temperature strength is also unsatisfactory. A promising alternative method is to produce a Ti_5Si_3 matrix composite. Shon *et al*. reported that synthesizing of Ti_5Si_3 with 20 vol% ZrO_2 formed Ti_5Si_3-20 vol%ZrO_2 composites. This led to a noticeable improvement in room temperature fracture toughness [11]. Mitra *et al*. also reported the microstructure and mechanical properties of the Ti_5Si_3/20TiC composites [12]. TiC is a suitable candidate reinforcement for the Ti_5Si_3 matrix due to thermal expansion match well (7.7×10^{-6}°C^{-1} for TiC and 9.7×10^{-6}°C^{-1} for Ti_5Si_3). Li *et al*. reported that the Ti_5Si_3/TiC composites was fabricated by *in-situ* reaction hot-pressing [13]. A new process, spark plasma sintering (SPS) has recently been developed. Compared with traditional pressure sintering techniques such as hot-pressing, the advantages of the SPS method lies in its lower temperatures, a shorter sintering and soaking time. This method has been used for processing of ceramics and metallic materials, for example: TiC-SiC, Si_3N_4-SiC Ti_3SiC_2, (TiWCr)B_2 etc. [14–18]. It was been demonstrated that metals and ceramics could be rapidly sintered under a relatively lower temperature and short time.

The in-situ processing of ceramic composites is advantageous for obtaining composites with a finer and more homogeneous microstructure, high chemical and thermodynamic stabilities at high temperature, and better mechanical properties compared to conventional processes such as mechanical powder mixing [19]. In this work, TiC reinforced Ti_5Si_3 matrix composites were fabricated in on step by spark plasma sintering (SPS) from Ti and nano-sized SiC powders.

2. Experimental procedure

The Ti powder was 99% pure and had a sieve classification of –300 mesh, the SiC powder was 99% pure and

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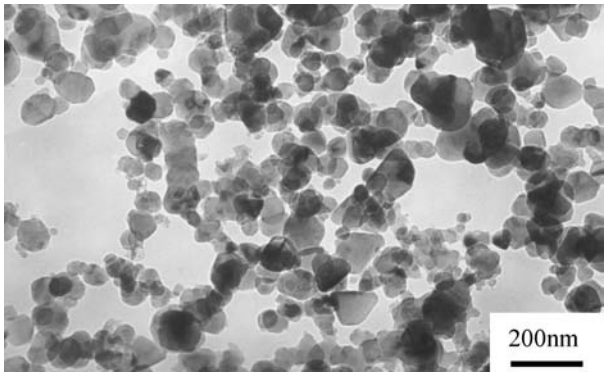

Figure 1 TEM micrograph of SiC powders.

had a particle size in the range –100 nm, as shown in the Fig. 1. The mixed powder of Ti and SiC was wet blended for 6 h with SiC media. The mixed powders were put into a graphite die (15 mm in diameter). Graphite sheet was inserted between the die and the sample in order to avoid the reaction between the sample and the die during the sintering. The samples were sintered with Dr. Sinter® 2040spark plasma sintering system (Sumitomo Coal Mining Co., Tokyo, Japan) in vacuum (less than 4 Pa). The heating rate was controlled in the range of 100–200°C/min and the pressure was applied from 1000°C and maintained constant at 60 Mpa. The temperature was measured by means of an infrared pyrometer focused on to the sintered sample through a small hole in the die. The temperature was held at 1260°C for a few min before turning off the power.

After sintering, the surfaces of samples were ground to remove the graphite layer and analyzed by X-ray diffractometry (XRD) with CuKa radiation at 40 KV and 100 mA (D/max 2550 V). The phase distribution of the polished samples were performed using optical microscopy (Model BX51 M, Olympus Optical, Tokyo, Japan). The densities of consolidated specimens were obtained using the Archimedes immersion method with deionized water as the immersion medium. The theoretical densities of the specimens were calculated according to the rule of mixtures. Microstructural observation was conducted using a scanning electron microscope (SEM) and transmission electron microscopy (TEM). Indentation tests were performed with a diamond Vickers indenter. The indention parameters for fracture toughness (K_{IC}) at room temperature were made using a 20 kg loads with a dwell of 15 s.

3. Results and discussion

The XRD results for mixed powders and samples reacted in the SPS for 8 min at 1260°C are shown in Fig. 2. The results showed that the product consisted of Ti_5Si_3 as a major phase and the coexistence of TiC phase. It implied that Ti_5Si_3/TiC composite could be fabricated by SPS according to following reaction:

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

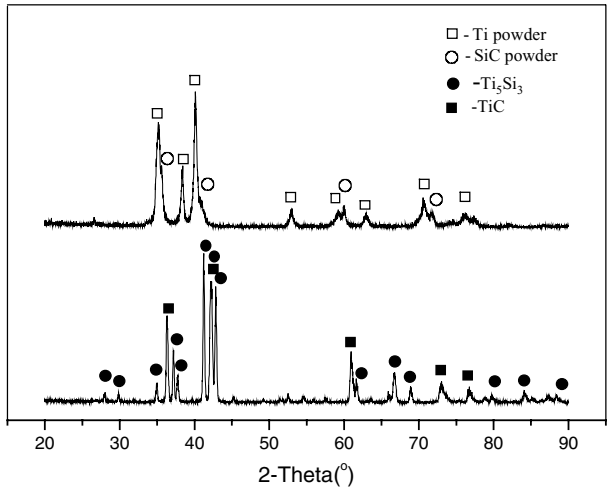

Figure 2 XRD patterns of (a) Ti/SiC powder; (b) Ti_5Si_3/TiC composite.

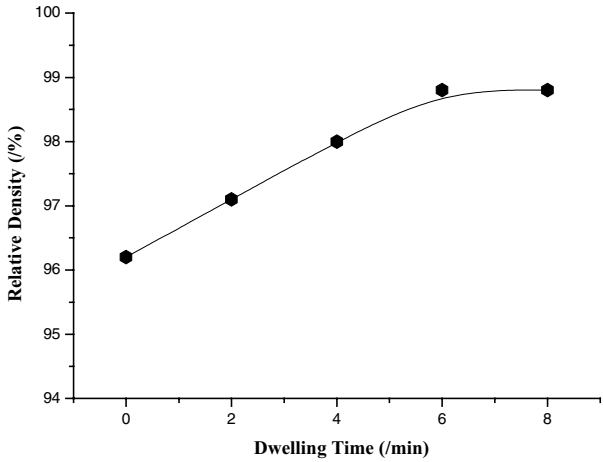

Figure 3 Relationship between the relative density and dwelling time by SPS.

Previous work has shown that the mixture of Ti, SiC and TiC(Ti:Si:C = 3:1:2)results in production of Ti_3SiC_2 according to following reaction [20]:

$$2Ti + SiC + TiC \rightarrow Ti_3SiC_2 \quad (2)$$

But in this work, the Ti_3SiC_2 ternary compound phase was not detected by XRD, so the content of Ti_3SiC_2 is about less 3 vol.%. It indicates that chemical reaction was followed according to reaction (1), and the reaction (2) was no obviously during sintering.

The weight percents of TiC and Ti_5Si_3 in the composite obtained according to reaction (1) are 36% and 64%, respectively, and the volume percents are 35% and 65%, respectively. The theoretical densities of the specimens were calculated according to the rule of mixtures. Fig. 3 shows the relationship between the relative density of the samples and dwelling time under SPS condition. The relative density of samples increased with dwelling time and the maximum relative density at 8 min reached 98.8%.

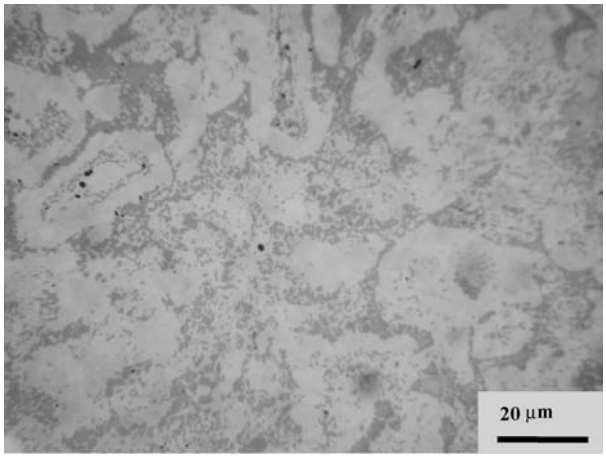

Figure 4 Optical microscope observation of Ti5Si_3/TiC composite sintered by SPS at 1260°C for 8 min.

Fig. 4 is a optical micrograph of the polished surface of Ti_5Si_3/TiC composite prepared by SPS at 1260°C, 60 Mpa for 8 min without any sintering aid. The gray phase is the Ti_5Si_3, and the dark phase is TiC in the Fig. 4. As shown, the composites are two-phase particulate composites consisting of uniformly distributed TiC particles in the Ti_5Si_3 matrix, and this also means TiC particles should be fine.

Typical fracture surface of the Ti_5Si_3/TiC composite (with a relative density of 98.8%), prepared via SPS is shown in Fig. 5(a). The fracture surface of the Ti_5Si_3/TiC composite was investigated and done spot analyses by energy dispersive spectroscopy, and the results showed fine grains were TiC, and coarse grains were Ti_5Si_3. It can be noted that fracture mode of small TiC grains is intergranular, while that of Ti_5Si_3 grains is transgranular mainly. Therefore, the contributions to toughening by crack bridging and crack deflection due to the second phase grains might be very fine. In addition, Ti_3SiC_2 has a layered crystalline structure and the morphology of grains often appears to be plate. While, layered crystalline structure grains is not found in the Fig. 5, which indicating the absence of Ti_3SiC_2 grains. So this conclusion is accordant with X-ray analysis. In order to further study microstructure of Ti_5Si_3/TiC composite fabricated by SPS, TEM analysis was carried out. Fig. 6 shows the TEM images of Ti_5Si_3/TiC composite. Some interesting features can be noted. First, most of TiC grains confirmed by electron diffraction pattern were very fine and less than 500 nm, but Ti_5Si_3 grains are very coarse and grain size is about 1 μm. Second, it can be easily seen that fine TiC grains are fairly homogeneously dispersed around Ti_5Si_3 grains.

TiC grains fabricated by SPS in this work had an average size of about less 500 nm, but TiC grains produced by hot pressing in our early work had an average size of about 200–300 nm [13]. However, the grain size of Ti_5Si_3 is no obviously difference. The SPS process in this work takes less 15 min from start to finish, which is much less than that of hot pressing process (at 1380°C for 1 h), but grain size are not more fine. The difference of TiC grains size is possible explanation for existing electric field of impulse current of SPS in this work. The diffusion and reaction speed are accelerated by the electric field, and these effects of electric field are beneficial for reaction and grain growth. In addition, the nanosized SiC was used as reactant in this work, which redound to improvement of reaction speed.

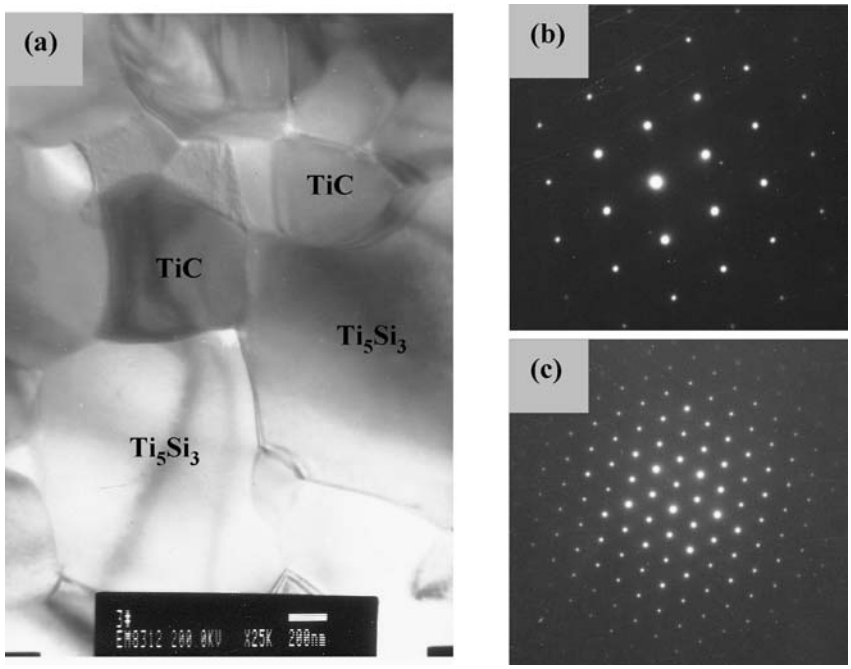

Figure 5 (a) TEM micrographs showing the grain size and distribution of TiC in the Ti_5Si_3/TiC composites; (b) electron diffraction pattern of TiC; (c) electron diffraction pattern of Ti_5Si_3.

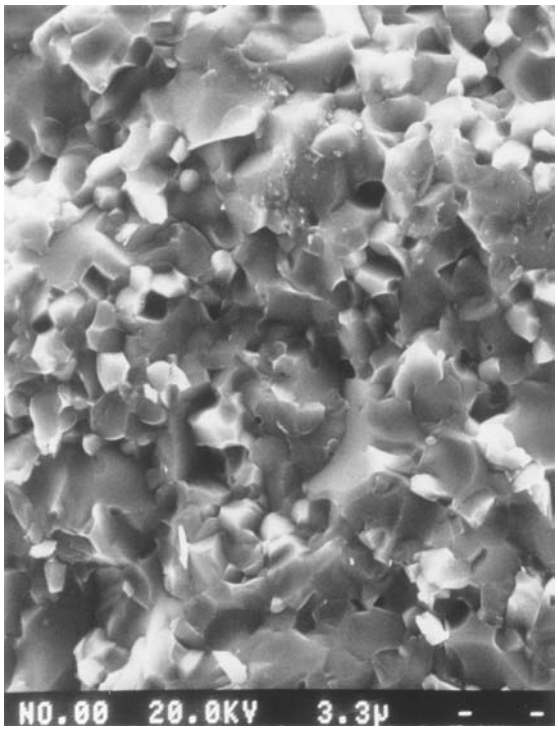

Figure 6 SEM micrographs of fracture surface of Ti_5Si_3/TiC composites.

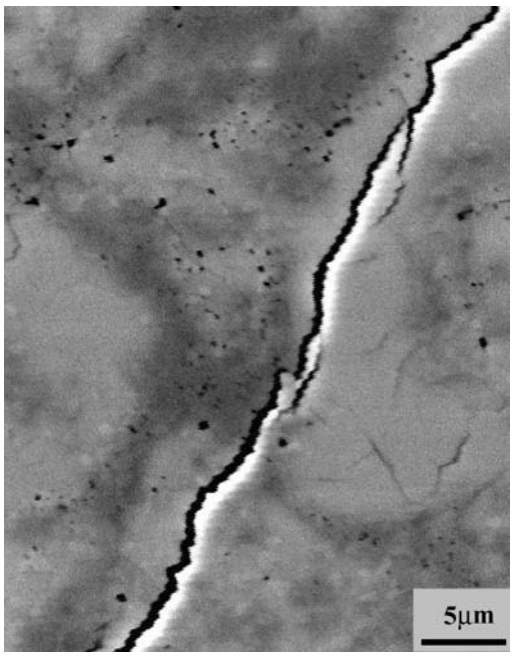

Figure 7 Scanning electron micrographs of a crack path induced by a Vickers' indentor in Ti_5Si_3/TiC composites.

Vickers microhardness measurements were made on polished sections of the Ti_5Si_3/TiC composite using a 20 kg load. The calculated hardness value of Ti_5Si_3/TiC composite was 13.6 GPa. Indentation fracture toughness (K_{IC}) values were calculated using the following expression [21]:

$$K_{IC} = 0.016(E/H)^{1/2}.P/c^{3/2}$$

Where c is the average crack length, E is Elastic modulus, H is the hardness, and P is the load. The modulus was estimated by the rule of mixtures for the 0.35 volume fraction of TiC and the 0.65 volume fraction of Ti_5Si_3 using E(TiC) = 680 Gpa [22] and $E(Ti_5Si_3) = 225$ Gpa [23]. The calculated fracture toughness of Ti_5Si_3/TiC composite is about 4.2 ± 0.4 MPa.m$^{1/2}$, which is higher than that for monolith Ti_5Si_3 (2.5 MPa.m$^{1/2}$). A SEM picture of the indention radial cracks in the Ti_5Si_3/TiC composite is shown in Fig. 7, which indicates that crack branching and crack deflection might be playing an important role in the toughening behavior.

4. Summary

In this work, an in situ reaction of Ti and nanosized SiC powder was prepared Ti_5Si_3/TiC composite via SPS. In situ produced TiC particles in this work are fine and uniformly distributed around the Ti_5Si_3 grains. The fracture toughness of composites at room temperature reaches 4.2 $\pm$ 0.4 MPa.m$^{1/2}$, which is higher than that for monolith Ti_5Si_3 materials.

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References

1. T. SANDWICK and K. RAJAN, *J. Electr. Mater.* **19** (1990) 1193.
2. D. M. SHAH, D. BERCZIK, D. L. ALTON and R. HECHT, *Mater. Sci. Eng.* **A152** (1992) 45.
3. P. J. COUNIHAN, A. CRAWFORD and N. N. THADHANI, *ibid.* **A267** (1999) 26.
4. A. K. BHATTACHARYA, *J. Am. Ceram. Soc.* **74** (1991) 2707.
5. B. K. YEN, T. AIZAWA, J. KIHARA, *ibid. Sci.* **81** (1998) 1953.
6. B. R. KRUEGER, A. H. MUTZ and T. VREELAND, *Metall. Trans. A.* **23** (1992) 55.
7. S. C. DEEVI and N. NARESH, *Mater. Sci. Eng.* **A192/193** (1995) 604.
8. K. S. MIN, AREDELL, A. J. ECK and F. C. DHEN. *J. Mater. Sci.* **30** (1995) 5479.
9. L. L. WANG and Z. A. MUNIR, *Metall. Mater. Trans. B.* **26B** (1995) 595.
10. L. ZHANG and J. WU, *Acta Mater.* **46** (1998) 3535.
11. I. J. SHON, H. C. KIM, D. H. RHO, Z. A. MUNIR, *Mater. Sci. Eng.* **A269** (1999) 129.
12. R. MITRA, *Metall. Mater. Trans. A.* **29A** (1998) 1629.
13. J. L. LI, D. JIANG, S. TAN, *J. Eur, Ceram. Soc.* **22** (2002) 551.
14. L. J. WANG, W. JIANG and L. D. CHEN, *Mater. Lett.* **58** (2004) 1401.
15. L. J. WANG, W. JIANG, L. D. CHEN and S. Q. BAI, *J. Am. Ceram. Soc.* **87** (2004) 1157.
16. J. WAN, M. J. GASCH, A. K. MUKHERJEE, *ibid.* **86** (2003) 526.
17. L. J. WANG, W. JIANG and L. D. CHEN, *J. Mater. Sci.* **39** (2004) 4515.

18. H. KAGA, E. M. HEIAN and Z. A. MUNIR, *J. Am. Ceram. Soc.* **84** (2003) 2764.
19. P. GREIL, *Adv. Mater.* **14** (2002) 709.
20. Z. F. ZHANG, Z. M. SUN, H. HASHIMOTO, and T. ABE, *Scripta. Mater.* **45** (2001) 1461.
21. G. R. ANTIS, P. CHANTIKUL, B. R. LAWN, D. B. MARSHALL,. *J. Am. Ceram. Soc.* **64** (1981) 533.
22. K. S. CHO, Y. W. KIM, H. J. CHOI, J. G. LEE, *J. Mater. Sci.* **31** (1996) 6223.
23. A. K. BHATTACHARYA, *J. Am. Ceram. Soc.* **74** (1991) 2707.

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