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Synthesis and high temperature mechanical properties of Ti_3SiC_2/SiC composite

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A high density Ti_3SiC_2/20 vol % SiC composite was hot pressed under a uniaxial pressure of 45 MPa for 30 min in an Ar atmosphere at 1600 °C. The grain size of the Ti_3SiC_2/SiC composite was finer than that of monolithic Ti_3SiC_2, though the composite was hot pressed at a higher temperature, due to the dispersion of SiC particles in the Ti_3SiC_2 matrix. Room temperature fracture toughness of the composite and Vickers hardness were measured as 5.4 MPa $m^{1/2}$ and 1080 kg mm^{-2}, respectively. A higher flexure strength of the composite compared to that of monolithic Ti_3SiC_2 was measured both at room temperature and up to 1200 °C. At 1000 °C, the composite showed a lower oxidation rate than that of monolithic Ti_3SiC_2.

1. Introduction

The melting point, T_m, of Ti_3SiC_2 has been reported to be very high ($T_m > 3000$ °C [1, 2]). Furthermore, Ti_3SiC_2 shows a plastic behaviour [3, 4] and a high flexure strength similar to SiC [5, 6]. These results imply that the compound Ti_3SiC_2 could probably be used as a high temperature structural material. The mechanical properties of this compound have not been clarified yet.

The chemical vapour deposition (CVD) technique has been used to synthesize Ti_3SiC_2 [4]. The CVD technique is convenient for obtaining pure compounds on the laboratory scale, but it is difficult to develop this into a larger scale process since the efficiency of the process is not so high. A conventional powder process using Ti, TiC and Si powders has been developed to prepare a Ti_3SiC_2 sintered body containing a small amount of TiC and SiC, and the following properties have been reported [7]. The sintered body with 95% theoretical density (TD) was obtained by hot pressing at 1400 °C. It shows high fracture toughness, 6.9 MPa $m^{1/2}$, and high flexure strength, 560 MPa, at room temperature. The flexural strength does not change until 1000 °C, whereas large plastic deformation is observed at 1200 °C. Furthermore, the oxidation rate of the Ti_3SiC_2 sintered body is much higher than that of SiC.

In this paper, to improve high temperature flexural strength and resistance of oxidation of the Ti_3SiC_2 sintered body, the Ti_3SiC_2/SiC composite is synthesized by the hot pressing method, and high temperature mechanical properties of the composite are observed. The selection of SiC particles as a reinforcement material was based on the following considerations. First, SiC is stable at high temperature, and it possesses good resistance to oxidation. Second, well dispersed fine SiC particles would restrict abnormal grain growth of Ti_3SiC_2. The mechanical and thermal properties of the composites are compared with those of a monolithic Ti_3SiC_2 body reported previously [7].

2. Experimental procedure

Ti_3SiC_2 and a fine β-SiC powder (Ibiden Co., Gifu, Japan) were used as starting materials. The Ti_3SiC_2 aggregate was synthesized in vacuum at 1300 °C for 1 h from Ti, TiC and Si powders, as described in a previous paper [7]. Besides the main phases of Ti_3SiC_2, a small amount of TiC and SiC was detected by X-ray diffractometry (XRD). Ti_3SiC_2 and SiC were mixed in a ratio of 80 : 20 vol % by wet ball milling for 24 h. After drying, the mixture was preformed in a graphite mould, and then hot pressed under a pressure of 45 MPa at 1500 or 1600 °C in an Ar atmosphere for 30 min.

The hot pressed samples were cut into two different dimensions using a diamond saw. The surfaces of the specimens were ground and then polished using diamond pastes. One group of specimens with dimensions of $2.5 \times 3.5 \times 30$ mm^3 was used for flexure strength measurement by the four-point bending method, with a 14 mm outer span and a 7 mm inner span at 0.5 mm min^{-1} crosshead speed. Room temperature measurement was conducted in air. Measurements at 1000 and 1200 °C were carried out under a vacuum of 1×10^{-3} Pa. Another group of specimens with dimensions of $2.1 \times 2.8 \times 30$ mm^3 was used for fracture toughness measurement by the single edge precracked beam (SEPB) method using the four-point bending method with a 2 mm inner span and a 13 mm outer span at 0.5 mm min^{-1} crosshead speed. A precrack was introduced by an indentation and a precracker (Maruto Co., Japan). The test was carried out at room temperature in air. In these measurements, one point consisted of four to five time measurements.

Bulk density was measured by the Archimedean method. Vickers hardness was measured after an indentation of 98 N for 15 s. For the evaluation of oxidation resistance, the composite sample, both with a Ti_3SiC_2 sintered body and SiC for comparison, were kept at 1000 °C in flowing air for a given time, and weight gain was measured by an electric balance.

3. Results and discussion

Table I lists the density of the composite compared with that of the monolithic body as reference. Although the monolithic phase could be densified to 95% TD by hot pressing at 1400 °C, the relative density of the composite only reached 91.4% TD by hot pressing at 1500 °C. To obtain a more dense body, a higher hot pressing temperature is necessary for the Ti_3SiC_2/SiC composite.

Fig. 1 shows scanning electron microscope (SEM) micrographs of the thermally etched surface of the composite and monolithic Ti_3SiC_2. The well polished surface of the samples was thermally etched at 1200 °C for 20 min in vacuum. From the energy dispersive X-ray microanalysis (EDX), medium columnar and grey contrast grains, labelled four, are Ti_3SiC_2. Very fine and agglomerated grains, labelled three, are SiC. Furthermore, fairly large, bright contrast particles, labelled one, may be TiC. The dark contrasting particle surrounding this TiC is SiC, labelled two. The grain size of Ti_3SiC_2 in the composite hot pressed at 1600 °C is smaller than that of monolithic Ti_3SiC_2 hot pressed at 1400 °C. It is believed that grain growth of the Ti_3SiC_2 crystal into columnar and/or plate-like grains is limited by the fine SiC particles distributed in the composite. XRD analysis of the specimens hot pressed at 1600 °C revealed Ti_3SiC_2, SiC and TiC phases. The amount of TiC in the composite (8 vol %) is found to be ten times greater than that of the raw material from the quantitative XRD analysis. Goto and Hirai [4] reported that the formation region of Ti_3SiC_2 decreased with increasing CVD temperature, and the stable compounds at 1600 °C were SiC and TiC. Thus, some TiC would be induced by the decomposition of a part of Ti_3SiC_2 during the hot pressing process at 1600°C, to SiC and TiC. The SEM observation mentioned above suggests the decomposition of Ti_3SiC_2, since the large TiC particles are always attached to SiC particles.

Table II shows Vickers hardness of the composite hot pressed at 1600 °C. It is higher than that of the monolithic Ti_3SiC_2 sintered body [7]. The reason for

TABLE I Density of monolithic Ti_3SiC_2 and Ti_3SiC_2/SiC composite

	Hot pressing temperature (°C)	Density	
		($g cm^{-3}$)	Per cent theoretical
Monolithic	1400	4.29	95.1
Composite	1500	3.75	91.4
	1600	4.03	96.3

TABLE II Vickers hardness of Ti_3SiC_2/SiC composite

Measuring surface	Direction of indentation diagonal line[a]	Vickers hardness ($kg mm^{-2}$)	Standard deviation
Vertical[a]	–	890	45
Parallel[a]	Vertical	1080	40
Parallel[a]	Parallel	960	43

[a] Direction to the hot pressing axis.

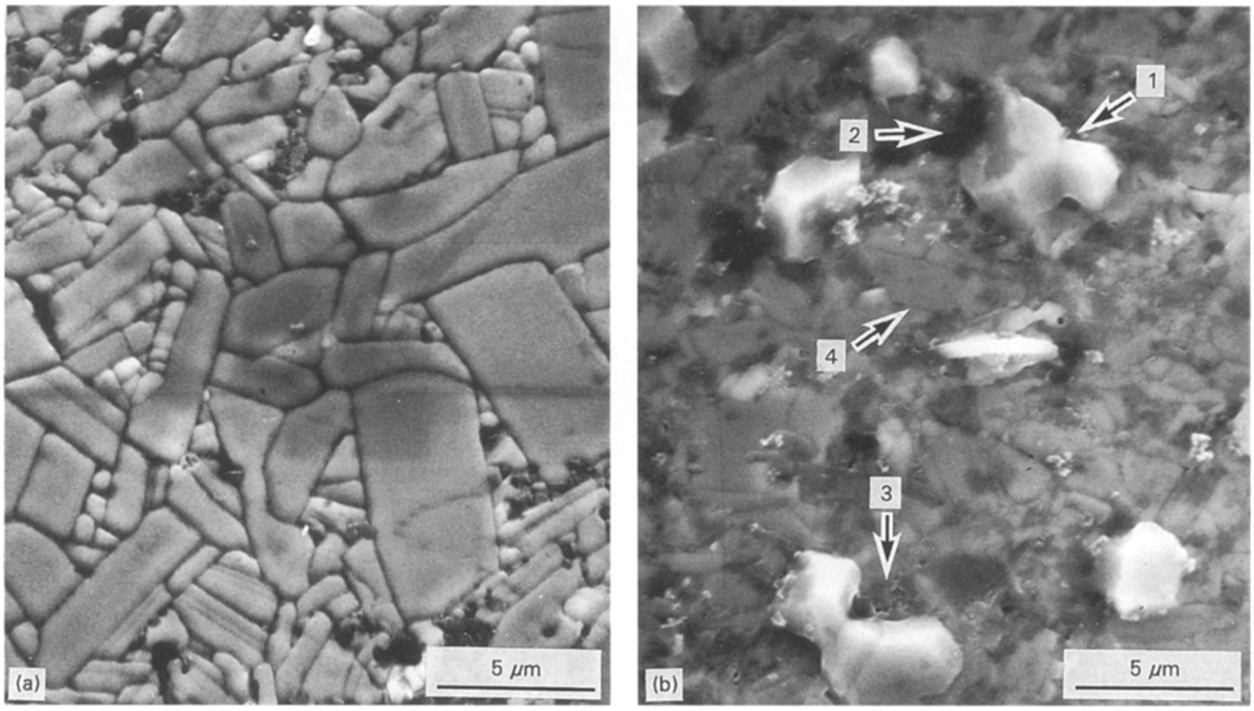

Figure 1 Microstructure of polished surface of (a) monolithic Ti_3SiC_2 and (b) Ti_3SiC_2/SiC composite, which were thermally etched at 1200 °C for 20 min in vacuum.

the hardness increase is attributed to the addition of SiC. Anisotropy of Vickers hardness in a plane parallel to the hot press direction is observed. The degree of anisotropy is smaller than that for monolithic Ti_3SiC_2, due to the restriction of growth of columnar Ti_3SiC_2 grains in the composite.

The fracture toughness and flexure strength of the Ti_3SiC_2/SiC composite hot pressed at 1600 °C are shown in Fig. 2, and are compared with those of monolithic Ti_3SiC_2 [7]. A slightly higher flexure strength than that of the monolithic bodies has been measured in the Ti_3SiC_2/SiC composite at all testing temperatures as a result of the addition of SiC particles. Especially at 1200 °C, although half of the flexure strength at room temperature has been measured in the composite, this value is bigger than that of monolithic bodies. It is clear that the addition of SiC particles greatly restrains plastic deformation of the sintered body. From observation of the fracture surface by SEM, some rounded particles are observed; thus it is supposed that a small amount of glassy phase exists in the grain boundary of Ti_3SiC_2/SiC. The presence of a glassy phase could be the reason for the decrease in flexure strength at 1200 °C.

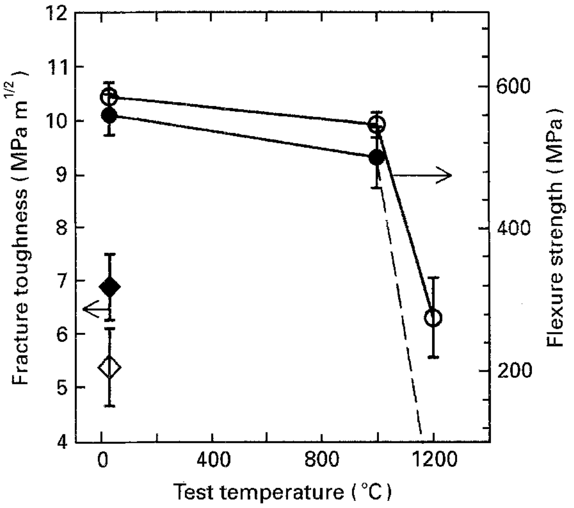

Figure 2 Fracture toughness, K_{IC} (◇, ◆) and flexure strength (○, ●) of monolithic Ti_3SiC_2 (solid) and Ti_3SiC_2/SiC composite (open) tested at room temperature and high temperatures.

The fracture toughness of Ti_3SiC_2/SiC is slightly lower than that of monolithic Ti_3SiC_2, as shown in Fig. 2. Fig. 3 shows crack propagation patterns of monolithic Ti_3SiC_2 and Ti_3SiC_2/SiC composite hot pressed at 1600 °C. In the composite, the crack propagates through the sample fairly straight. In contrast, the crack is deflected by large columnar or plate-like grains in monolithic Ti_3SiC_2. Thus, the decrease in the number of columnar or plate-like grains is the reason for the decrease in fracture toughness of the composite. One more reason for low fracture toughness in Ti_3SiC_2/SiC is attributed to the presence of agglomerated SiC particles, as observed in Fig. 1(b). These grains are seen to be poorly sintered.

The weight gain of monolithic Ti_3SiC_2 and Ti_3SiC_2/SiC composite at 1000 °C in flowing air is presented in Fig. 4. From the figure, the Ti_3SiC_2/SiC composite possesses better resistance to oxidation than monolithic Ti_3SiC_2. Both on the surface of Ti_3SiC_2 and Ti_3SiC_2/SiC composite after oxidation, TiO_2 was detected by XRD. On the basis of SEM observation, this TiO_2 film is porous and cannot protect the sample from oxidation, although the oxygen diffusion constant in TiO_2 is low, as in SiO_2, at 1000 °C [8]. Since a slow oxidation rate in SiC results in the formation of a deme SiO_2 film, the weight gain in the composite was caused by the oxidation of Ti_3SiC_2. Having a small amount of Ti_3SiC_2 in the

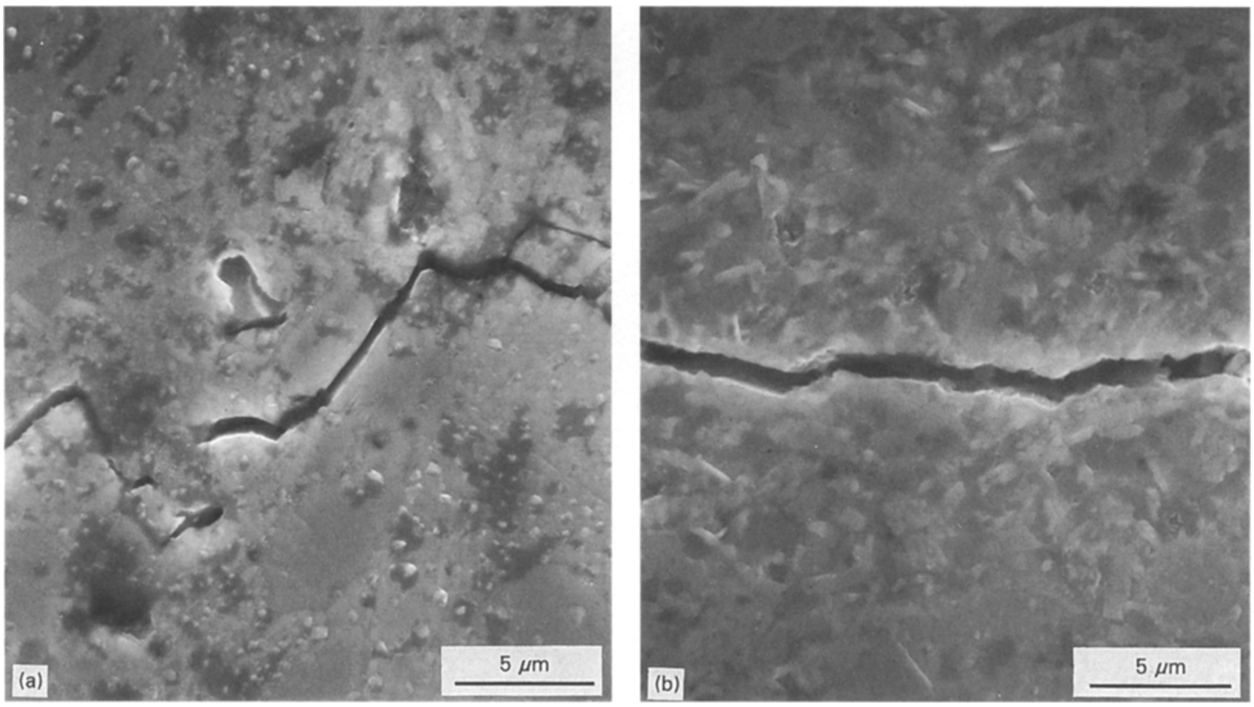

Figure 3 Crack propagation patterns in (a) monolithic Ti_3SiC_2 and (b) Ti_3SiC_2/SiC composite.

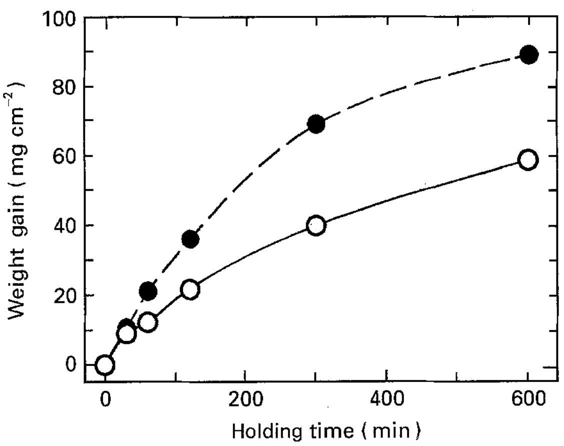

Figure 4 Weight gain of monolithic Ti_3SiC_2 (○) and Ti_3SiC_2/SiC composite (●) as a function of holding time at 1000 °C.

composite is thought to be the reason for the lower weight gain in the composite compared with monolithic Ti_3SiC_2 as shown in Fig. 4.

4. Conclusions

In this study, the following conclusions are obtained.

1. Ti_3SiC_2/20 vol % SiC mixture was hot pressed at 1600 °C to obtain a high density composite (96% TD). Due to a high hot pressing temperature, 8 vol % TiC was found in the body as a result of decomposition of Ti_3SiC_2.

2. As an effect of SiC addition, the flexure strength of the composite at room and high temperature increased compared to that of monolithic Ti_3SiC_2. Especially, plastic deformation at 1200 °C was greatly restricted in the composite. The fracture toughness and Vickers hardness of the composite were measured as 5.4 MPa m$^{1/2}$ and 1080 kg mm^{-2} at room temperature, respectively.

3. The oxidation resistance of the composite was better than that of the monolithic body.

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