Synthesis and high temperature mechanical properties of \( \text{Ti}_3\text{SiC}_2/\text{SiC} \) composite

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A high density \( \text{Ti}_3\text{SiC}_2/20 \text{ vol } \% \text{ SiC} \) 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 \( \text{Ti}_3\text{SiC}_2/\text{SiC} \) composite was finer than that of monolithic \( \text{Ti}_3\text{SiC}_2 \), though the composite was hot pressed at a higher temperature, due to the dispersion of SiC particles in the \( \text{Ti}_3\text{SiC}_2 \) 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 \( \text{Ti}_3\text{SiC}_2 \) 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 \( \text{Ti}_3\text{SiC}_2 \).

1. Introduction

The melting point, \( T_m \), of \( \text{Ti}_3\text{SiC}_2 \) has been reported to be very high (\( T_m > 3000 °C \) [1, 2]). Furthermore, \( \text{Ti}_3\text{SiC}_2 \) shows a plastic behaviour [3, 4] and a high flexure strength similar to \( \text{SiC} \) [5, 6]. These results imply that the compound \( \text{Ti}_3\text{SiC}_2 \) 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 \( \text{Ti}_3\text{SiC}_2 \) [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 \( \text{Ti}_3\text{SiC}_2 \) 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 \( \text{Ti}_3\text{SiC}_2 \) sintered body is much higher than that of \( \text{SiC} \).

In this paper, to improve high temperature flexural strength and resistance of oxidation of the \( \text{Ti}_3\text{SiC}_2 \) sintered body, the \( \text{Ti}_3\text{SiC}_2/\text{SiC} \) 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 \( \text{Ti}_3\text{SiC}_2 \). The mechanical and thermal properties of the composites are compared with those of a monolithic \( \text{Ti}_3\text{SiC}_2 \) body reported previously [7].

2. Experimental procedure

\( \text{Ti}_3\text{SiC}_2 \) and a fine \( \beta\)-\( \text{SiC} \) powder (Ibiden Co., Gifu, Japan) were used as starting materials. The \( \text{Ti}_3\text{SiC}_2 \) 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 \( \text{Ti}_3\text{SiC}_2 \), a small amount of TiC and SiC was detected by X-ray diffractometry (XRD). \( \text{Ti}_3\text{SiC}_2 \) 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 \( 2.5 \times 3.5 \times 30 \text{ mm}^3 \) 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 \( 1 \times 10^{-3} \text{ Pa} \). Another group of specimens with dimensions of \( 2.1 \times 2.8 \times 30 \text{ mm}^3 \) 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$_3$SiC$_2$ 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$_3$SiC$_2$/SiC composite.

Fig. 1 shows scanning electron microscope (SEM) micrographs of the thermally etched surface of the composite and monolithic Ti$_3$SiC$_2$. 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$_3$SiC$_2$. 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$_3$SiC$_2$ in the composite hot pressed at 1600 °C is smaller than that of monolithic Ti$_3$SiC$_2$ hot pressed at 1400 °C. It is believed that grain growth of the Ti$_3$SiC$_2$ 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$_3$SiC$_2$, 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$_3$SiC$_2$ 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$_3$SiC$_2$ during the hot pressing process at 1600 °C, to SiC and TiC. The SEM observation mentioned above suggests the decomposition of Ti$_3$SiC$_2$, 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$_3$SiC$_2$ sintered body [7]. The reason for

<table>
<thead>
<tr>
<th>Hot pressing temperature (°C)</th>
<th>Density (g cm$^{-2}$)</th>
<th>Per cent theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolithic 1400</td>
<td>4.29</td>
<td>95.1</td>
</tr>
<tr>
<td>Composite 1500</td>
<td>3.75</td>
<td>91.4</td>
</tr>
<tr>
<td>1600</td>
<td>4.03</td>
<td>96.3</td>
</tr>
</tbody>
</table>

*Direction to the hot pressing axis.

Figure 1 Microstructure of polished surface of (a) monolithic Ti$_3$SiC$_2$ and (b) Ti$_3$SiC$_2$/SiC composite, which were thermally etched at 1200 °C for 20 min in vacuum.