Fabrication and Mechanical Properties of Textured Ti$_3$SiC$_2$ Systems Using Commercial Powder*1

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Ti$_3$SiC$_2$ is a typical M$_{n+1}$AX$_n$ (MAX) phase ceramic and exhibits both metal-like and ceramic-like properties. To improve these properties, texturing and Al$_2$O$_3$ addition were performed. The commercial Ti$_3$SiC$_2$ powder used contained approximately 10 mass% TiC phase. Textured Ti$_3$SiC$_2$ was prepared by slip casting in a strong magnetic field (MF) followed by spark plasma sintering (SPS) at 1623 K under a pressure of 40 MPa for 5 min. The Lotgering orientation factor of the (002) peaks of Ti$_3$SiC$_2$ prepared under an MF was 0.96, and the relative density of samples exceeded 99%. The bending strength and fracture toughness of Ti$_3$SiC$_2$ were improved by texturing. The textured Ti$_3$SiC$_2$ exhibited an excellent bending strength of 978 MPa, but Al$_2$O$_3$ addition, reduced the bending strength and fracture toughness. The textured Ti$_3$SiC$_2$ showed the plastic deformation at a temperature of approximately 1173 K. [doi:10.2320/matertrans.Y-M2018812]

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1. Introduction

Transition-metal ternary MAX phases have the form M$_{n+1}$AX$_n$, where M is an early transition metal such as Sc, Ti, Cr, Zr or Nb; A is an group element, such as Al, Si, Ga, or Ge; X is C or N, and n = 1~3. MAX phases have covalent bonds and metallic bonds, giving them a combination of metal-like properties, such as high electrical and thermal conductivities, and thermal shock resistance and ceramic-like properties such as good wear, corrosion, and oxidation resistance, high hardness, and high bending strength at high temperature. These properties make them possible candidates for use as electrodes and structural materials in industrial applications at high temperatures and/or in corrosive environments.

Sixty different MAX phases have now been reported. Ti$_3$SiC$_2$ is a typical MAX phase with some excellent properties. For example, its electrical conductivity is as high as 4.5 x 10$^5$ Ω$^{-1}$m$^{-1}$, similar to that of a metal. In the range of 1173 to 1673 K, a TiO$_2$ or SiO$_2$ protective film is formed, outstanding oxidation resistance. Under acid and alkali conditions, a SiO$_2$ film is formed that giving Ti$_3$SiC$_2$ acts as a passive film, giving Ti$_3$SiC$_2$ excellent corrosion resistance. Moreover, its hardness is as high as 4~8 GPa and it shows excellent machinability.

On the other hand, to improve the properties of ceramics, an orientation technique that arranges particles in a specific direction is very effective. The template method and hot forging method are methods of preparing textured bulk ceramics. Recently our group has proposed colloidal processing such as by slip-casting, gel-casting, tape-casting and electrophoretic deposition (EPD) under a strong magnetic field (MF). When the crystal structure of a particle is non-cubic, the magnetic susceptibility is different in the a, b and c directions. Owing to the difference, a magnetic torque arises upon the application of a magnetic field. Therefore, the particles rotate in a direction that stabilizes the magnetization energy and solidify in the resulting state. In this way, when the particles in a solvent are aggregated, the rotation of each particle is inhibited, if the particles are monodispersed in a suspension.

Sato et al. fabricated textured Ti$_3$SiC$_2$ with the addition of Al as a sintering aid using a slip-casting method in an MF followed by pressureless sintering, then measured the bending strength and fracture toughness of the sintered body at room temperature. An improvement in both was observed compared with those of samples prepared without an MF.

Similarly, Hu et al. also fabricated a textured Nb$_2$AlC$_3$ MAX phase by slip-casting in an MF followed by SPS. Both the bending strength and fracture toughness at room temperature were improved by texturing. As the reason for this, it was shown that a particle pullout effect and crack deflection effect were realized by texturing.

To improve the mechanical properties of Ti$_3$SiC$_2$, the formation of composites with other metals and ceramics has been attempted. Miyamoto et al. fabricated Ti$_3$SiC$_2$ (containing TiC as an impurity) by mixing Ti, TiC, Si and Al$_2$O$_3$ powder followed by SPS. Both the bending strength and the fracture toughness at room temperature were improved by the addition of Al$_2$O$_3$. Uchida et al. used a powder with a small particle size, to fabricate textured Ti$_3$SiC$_2$, complexed with Al$_2$O$_3$ powder by slip-casting in an MF followed by SPS. Although the both of bending strength and fracture toughness at room temperature were improved by texturing and the addition of Al$_2$O$_3$, it was suggested that many oxides formed during the processing even in samples without the addition of Al$_2$O$_3$.

In this study, we use a commercial powder with a comparatively large particle size and a small amount of oxide to fabricate textured Ti$_3$SiC$_2$ with and without the addition of Al$_2$O$_3$ by slip-casting in an MF followed by SPS. The purpose of this study is to clarify the effect of texturing and the addition of Al$_2$O$_3$ on the mechanical properties of Ti$_3$SiC$_2$.

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2. Experimental Procedure

2.1 Preparation of suspension
The particle shape and dispersion state of the raw Ti3SiC2 powder (KANTHAL) were observed by SEM (JSM-6500F, JEOL Ltd.) by dispersing it in ethanol then drying it on a silicon wafer. Extra phases in the sample were identified using an X-ray diffractometer (Miniflex 600, Rigaku.) To determine the amount of oxygen in the row powder, the powder was heated and melted with sodium carbonate and boric acid in helium, and the oxygen was quantified from the amount of obtained carbon dioxide using an infrared detector (TC-436, LECO).

An ethanol suspension loading with 30 vol% Ti3SiC2 powder was prepared. Here, 1.5 mass% polyethylene imine (PEI, molecular weight 10,000, Wako Pure Chemical Industries, Ltd.) was added to the suspension as a dispersant, and the particles were dispersed in ethanol using an ultrasonic homogenizer (600 W) (GSD-600 AT, Sonic Technologies, Inc.) while stirring at room temperature with a magnetic stirrer.

To clarify the effect of Al2O3 (TM-DAR) (Taiyo Kagaku Kogyo Co., Ltd.), 5 vol% and 10 vol% Al2O3 dispersed Ti3SiC2 were prepared. Here, to investigate the dispersion effect of Al2O3 in the suspension, a suspension was prepared by two methods. First, Ti3SiC2 powder with a solid particle concentration of 40 vol% was placed in a beaker containing ethanol and PEI as a dispersant. Then Al2O3 was added, and ultrasonic treatment was carried out for 10 min. This suspension is denoted as Ti3SiC2/Al2O3. Second, to produce a sample in which Al2O3 was more dispersed, the solid particle concentration was set to 30 vol%. Here, Al2O3 was added before Ti3SiC2 powder and the suspension was subjected to ultrasonic treatment. This sample is denoted as Al2O3/Ti3SiC2. Then, to remove the air bubbles remaining in each suspension, a deformation of the suspension was carried out for about 1 h in vacuum.

2.2 Fabrication of textured body
Slip-casting was carried out by pouring the suspension into a φ25-mm-diameter acrylic cylindrical mold on a porous alumina mold with a membrane filter. The mold was placed in a helium-free superconducting magnet (JMTD-12T100NC5, JASTEC) to apply an MF of 12 T in the horizontal direction, while the sample was rotated at 30 rpm.27 As a reference, we also fabricated a sample by slip-casting without an MF. Samples were sintered by SPS (1050-SUMITOMO). The green body was sandwiched between carbon sheets and a carbon punch in a carbon die, and set in an SPS. The PEI dispersant was removed by vacuum heating at 973 K for 10 min, then the atmosphere was replaced with Ar, and the sample was heated at a rate of 323 K/min to 1623 K, which was then maintained for 5 min. The sintering was carried out under a pressure of 40 MPa.

2.3 Characterization
The degree of orientation was characterized from XRD patterns of the top surface of the sintered samples. The Lotgering orientation factor was calculated using the following equations:28

\[
f_L = \frac{P - P_0}{1 - P_0}
\]

\[
P = \frac{\sum I(00l)}{\sum I(hk0)}
\]

\[I: \text{Intensity} \quad P: \text{Value calculated from ICDD} \quad P_0: \text{Value calculated from ICDD}
\]

\[f_L = 0, \text{Randomly oriented} \quad f_L = 1, \text{Perfectly oriented}
\]

The reference \(P_0\) was calculated using the value on the ICDD card (No. 01-080-3343).

The sintered body was cut parallel to the slip-casting direction, its surface was polished with diamond slurry with 9 µm and 6 µm particle sizes, and then it was finished to a mirror surface using colloidal silica. The samples were chemically etched using a mixed with a stoichiometric ratio of HNO3:HF:H2O = 1:1:2. The microstructure of the etched surface was observed by SEM. The relative density of the sintered body was calculated from the true density of the powder measured in a pycnometer (Accupyc II 1340, Shimadzu) and the apparent density of the sintered body was measured using the Archimedes method.

A three-point bending test was carried out on the sintered bodies using disc-shaped specimens with dimensions of 2.0 mm × 1.5 mm × 18 mm so that the c axis of Ti3SiC2 was parallel to the 2.0 mm × 1.5 mm plane. All surfaces of each sample were polished. The bending test was carried out using mechanical testing equipment (Autograph, Shimadzu) at room temperature. For textured Ti3SiC2 without Al2O3, the temperature of the specimen during the bending test was raised varied from 973 to 1373 K. The bending test was conducted in air at room temperature and in Ar at a high temperature. The testing span was 16 mm, the crosshead speed was 0.05 mm/s, and the bending strength was calculated from the maximum load at which the sample broke.

A fracture toughness test was carried out using the SEVNBN method on samples with dimensions of 2.0 mm × 4.0 mm × 18 mm and a V notch in the direction of loading. The depth of the notch was 0.5 mm and the radius of curvature of the notch tip was 10–20 µm. The test conditions were the same as those of the bending test at room temperature. The fracture surface after the test was observed by SEM.

3. Results and Discussion

3.1 Sintering behavior
An SEM image of the Ti3SiC2 powder is shown in Fig. 1(a) and the powder after ultrasonic treatment is shown in Fig. 1(b). The particle size of the powder was approximately 2 to 4 µm, and no significant aggregation of the particles was observed. The XRD results for the powder are shown in Fig. 2(d). The results suggested that about 10 mass% TiC was present, and 1.4 mass% O was detected in the powder by chemical analysis.

For each sintered body, the surface perpendicular to the slip-casting direction was defined as the top surface, and the surface parallel to the slip-casting direction was defined as the side surface. The XRD diffraction results for the top plane are shown in Fig. 2(a)–(c). In the samples subjected to an
MF, the intensities of the (00l) peaks were very high compared with those of the samples without an MF.

Calculation of the Lotgering factor using eq. (1) showed that \( f_{(00l)} \) for Ti\(_3\)SiC\(_2\) subjected to an MF was 0.96, whereas \( f_{(00l)} \) for textured Ti\(_3\)SiC\(_2\)/10 vol\% Al\(_2\)O\(_3\) was 0.91. The decrease with the addition of Al\(_2\)O\(_3\) was because the Al\(_2\)O\(_3\) particles inhibited the rotation of the Ti\(_3\)SiC\(_2\) particles during the slip casting in an MF and the grain growth of Ti\(_3\)SiC\(_2\) during the sintering. In addition, \( f_{(000l)} \) for 10 vol\% Al\(_2\)O\(_3\)/Ti\(_3\)SiC\(_2\) that had been treated to disperse the Al\(_2\)O\(_3\) was also 0.91, and no difference resulting from the use of different dispersion methods was recognized. On the other hand, \( f_{(000l)} \) for Ti\(_3\)SiC\(_2\) without an MF was only 0.60, because the particles were oriented by the uniaxial pressure during the SPS process.\(^{29}\) Peaks of TiC remained even after sintering.

Figure 3 shows the SEM images of Ti\(_3\)SiC\(_2\) after etching. From the side surface of the sample subjected to an MF, it was confirmed that each particle was aligned, in contrast to the case of no MF. From the top surface, it was confirmed that plate-like grains were regularly stacked. Moreover, Al\(_2\)O\(_3\) particles (gray regions in the drawing) were mainly dispersed at the grain boundaries of Ti\(_3\)SiC\(_2\) in the Al\(_2\)O\(_3\) added sample.

The apparent density of the sintered body subjected to an MF was 4.44 g/cm\(^3\), obtained using the Archimedes method, and the sample without an MF had an apparent density of 4.43 g/cm\(^3\). The true density, obtained using a pycnometer, was 4.49 g/cm\(^3\), meaning that the relative density of each sample was more than 99%.

![Fig. 1 SEM images of (a) as-received raw Ti\(_3\)SiC\(_2\) powder and (b) powder in dispersed state.](image1)

![Fig. 2 XRD patterns of top surfaces of (a) Ti\(_3\)SiC\(_2\) without an MF, (b) Ti\(_3\)SiC\(_2\) subjected to an MF, (c) Ti\(_3\)SiC\(_2\)/10 vol\%Al\(_2\)O\(_3\) with an MF, and (d) Ti\(_3\)SiC\(_2\) powder.](image2)

![Fig. 3 SEM images of surfaces of etched Ti\(_3\)SiC\(_2\) after SPS (a) side surface of sample with an MF, (b) top surface of sample with an MF, (c) side surface of sample without an MF, (d) side surface of Ti\(_3\)SiC\(_2\)/5 vol\%Al\(_2\)O\(_3\) with an MF, and (e) side surface of Ti\(_3\)SiC\(_2\)/10 vol\%Al\(_2\)O\(_3\) with an MF.](image3)
3.2 Mechanical properties

The results of the bending test at room temperature and the fracture toughness test are shown in Fig. 4. The reported values are also shown in Table 1. Focusing on bending strength, even for the sample without an MF, the obtained value was larger than the reported value for Ti$_3$SiC$_2$. In general, the bending strength depends on the particle size, vacancies and the existence of a second phase. One of the reasons why the samples exhibited high strength is considered to be that the relative density was almost 100%. On the other hand, it is thought that TiC, the second phase in the microstructure of Ti$_3$SiC$_2$, contributed to the bending strength. Zhang et al. prepared a Ti$_3$SiC$_2$/TiC sintered body and reported the effect of the TiC content.30) As the amount of TiC increased, the bending strength also increased by about 100 MPa as compared with that when TiC was not added. The maximum bending strength was 730 MPa when the amount of TiC was 30 vol%. It has been proposed that the residual stress caused by the difference in the thermal expansion coefficients of Ti$_3$SiC$_2$ and TiC improved the bending strength. In our experiment, about 10 mass% TiC was present as a second phase in the Ti$_3$SiC$_2$ structure in the form of a powder, which remained after sintering. This was one of the reasons for the high strength.

The strength (978 MPa) of Ti$_3$SiC$_2$ subjected to an MF was larger than that (843 MPa) of Ti$_3$SiC$_2$ without an MF because of texturing. Figure 5 shows a crack in the Ti$_3$SiC$_2$ specimen subjected to an MF. The zigzag propagation of cracks was observed.

On the other hand, the strength decreased as the amount of Al$_2$O$_3$ increased, in contrast to the previous reports.22,25) Also, the strength of Al$_2$O$_3$/Ti$_3$SiC$_2$ in the case that Al$_2$O$_3$ was added first and then dispersed was higher than that of Ti$_3$SiC$_2$/Al$_2$O$_3$ with Al$_2$O$_3$ added later, but lower than that in the case of no Al$_2$O$_3$ addition. However, the bending strength was higher than the reported value for Ti$_3$SiC$_2$/Al$_2$O$_3$. The increase in the bending strength due to the presence of TiC may have been negated by the addition of Al$_2$O$_3$, thus, systematic experiments on Ti$_3$SiC$_2$ without an impurity phase are necessary to clarify the effect of adding Al$_2$O$_3$. As shown in Figs. 3(d) and (e), by comparing with the particle size (0.1 µm) of the added Al$_2$O$_3$ powder, it was recognized that Al$_2$O$_3$ was agglomerated in the microstructure of Ti$_3$SiC$_2$, which may have reduced the strength of Ti$_3$SiC$_2$.

Focusing on the values of fracture toughness, similarly to the flexural strength, Ti$_3$SiC$_2$ subjected to an MF (7.3 MPa m$^{1/2}$) had a higher fracture toughness than Ti$_3$SiC$_2$ without an MF (6.6 MPa m$^{1/2}$). Because the orientation of the Ti$_3$SiC$_2$ improved and the grain boundaries were aligned by applying an MF, crack deflection occurred, and the absorption of a large amount of energy up to fracture is considered to have been a factor a factor improving the toughness. Upon the addition of Al$_2$O$_3$, the fracture toughness decreased.

The values of the bending strength of Ti$_3$SiC$_2$ without the addition of Al$_2$O$_3$ subjected to an MF at each temperature are shown in Fig. 6(a) together with previously reported values. Similarly to in the previous studies, the strength decreased as the temperature increased, but the values of the bending strength in this study were higher than those reported previously at each temperature. Photographs of the sample after the tests are shown in Fig. 6(b)–(d). At 1273 K or more, the samples were greatly deformed. The stress-strain curves of sample obtained at each temperature in Fig. 7. From room temperature to 800°C, the load was proportional to the strain.

![Fig. 4](image-url) (a) Bending strength and (b) fracture toughness (K$_{IC}$) versus amount of Al$_2$O$_3$ in Ti$_3$SiC$_2$/Al$_2$O$_3$.

![Fig. 5](image-url) SEM image of crack propagation in Ti$_3$SiC$_2$ with an MF.
of the sample, and brittle fracture occurred instantaneously at the maximum load. A slight curve appeared from approximately 1173 K. Zheng et al. reported the temperature dependence of the flexural strength of Ti$_3$SiC$_2$ prepared by SPS, and demonstrated that deformation occurred by basal plane sliding, intergranular cracking, grain buckling and the formation of kink bands, the peeling of layers, particle withdrawal, caused the deformation mechanism of Ti$_3$SiC$_2$ at 1173 K.\(^{31}\) In our experiment, it appears that deformation occurred at 1173 K in the same way, but in this system TiC exists as a second phase, meaning that precise and detailed observation of the deformation mechanism is required.

4. Conclusion

Textured Ti$_3$SiC$_2$ was prepared by slip casting in an MF and by SPS. Its degree of orientation was calculated to be 0.96 and the relative density was 99%. TiC from the commercial powder used in the preparation remained in the sample after sintering. The bending strength and fracture toughness at room temperature were higher than previously reported values for Ti$_3$SiC$_2$, and both were found to be improved by texturing. The mechanical properties were deteriorated by the addition of Al$_2$O$_3$, but even for the samples without Al$_2$O$_3$, the bending strength was higher than that in previous works; it is necessary to consider the effect of adding Al$_2$O$_3$ including the effect of TiC contained as a second phase. Furthermore, a high-temperature bending test on Ti$_3$SiC$_2$ subjected to an MF was carried out.

It was found that the strength decreased with increasing temperature, and plastic deformation was observed at approximately 1173 K.

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REFERENCES