Fabrication of textured Ti$_3$AlC$_2$ by spark plasma sintering and their anisotropic mechanical properties

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Textured, dense, polycrystalline Ti$_3$AlC$_2$ ceramics was fabricated by spark plasma sintering (SPS) of plate-like Ti$_3$AlC$_2$ powder synthesized by a reactive SPS-heat treatment of elemental Ti, Al and carbon black powders. The relative density was found to exceed 99% for samples sintered at 1573 K. The Lotgering orientation factor was determined to be $f(001) = 0.69$. The crack propagation behavior near the indentation marks formed by a force of 49 N was observed. On the surface parallel to the SPS-loading direction, the toughening mechanism of crack deflection was observed.

Key-words : MAX Phases, Ti$_3$AlC$_2$, Shell-like ceramic, Spark plasma sintering (SPS)

1. Introduction

Ternary layered compounds of transition metal carbides and nitrides, commonly known as MAX phase materials with the general formula of M$_{n+1}$AX$_n$ (M is an early transition metal, A is normally from the IIIA and IVA groups, and X is either C and/or N, and $n = 1–3$) offer a unique combination of metal and ceramic-like properties such as high strength, high thermal expansion modulus and high thermal/chemical stability combined with a dramatically improved machinability and excellent thermal shock resistance/damage tolerance characteristics. This unique combination of properties originates from their layered hexagonal structure and the anisotropy of the bonding strength; M$_{n+1}$X$_n$ layers having strong covalent bonding through single A-planes, and held together by the comparatively weaker M-A bonds.

To date, more than 60 M$_3$AX, seven M$_4$AX$_2$ (Ti$_3$SiC$_2$, Ti$_3$AlC$_2$, Ti$_3$GeC$_2$, V$_4$SiC$_3$, V$_4$AlC$_3$, and Ti$_4$GaC$_3$), and seven M$_2$AX$_3$ (Ti$_2$AlN$_3$, Ti$_2$AlC$_3$, Ti$_2$SiC$_2$, Ti$_2$GeC$_3$, Nb$_2$AlC$_3$, V$_2$AlC$_3$, and Ti$_2$GaC$_3$) MAX compounds have been identified. Among them, Ti$_3$AlC$_2$ has the best oxidation resistance at high temperatures due to the formation of a continuous Al$_2$O$_3$ surface layer. Therefore, it is a promising material for high-temperature structural applications. However, Ti$_3$AlC$_2$ suffers from a brittleness, the main drawback for such applications.

The structure of Nacre has received significant attention as a clue to improve the mechanical properties of the MAX-phase. Nacre composed of 95% calcium carbonate and 5% organic matter in volume has an excellent mechanical fracture resistance. The work of fracture is thousands of times greater than that of monolithic calcium carbonate. The high fracture resistance of Nacre is attributed to its laminar structure of aragonite layers weakly held together by interface layers. Recently, Hu et al. have successfully improved the toughness of Ti$_3$SiC$_2$ and Nb$_2$AlC$_3$ by a texture process. They showed that the crystal orientation could effectively activate the toughening mechanisms, such as pull-out and crack bridging along the c-axis, and thus effectively improve the toughness.

As the texture process, several approaches have been developed, including (1) the template grain growth (TGG) method, in which the alignment of a small fraction of large rod-like particles (the so-called seeds or templates) in a fine powder matrix was involved during forming by tape casting or extrusion, (2) the hot-working method, in which the imposition of an uniaxial stress on the loosely packed powder or green powder compacts was involved during sintering, or on the nearly sintered body during superplastic deformation, and (3) the magnetic field alignment method, in which a magnetic field to align the ceramic particles in a suspension was used during the consolidation process.

In this study, we attempted for the first time to fabricate dense, textured bulks of single-phase Ti$_3$AlC$_2$ by the hot working method using spark plasma sintering (SPS). In recent years, SPS has been widely investigated due to its inherent advantages, such as faster densification, shorter sintering time, lower sintering temperature, and higher energy activity in comparison to the conventional hot pressing technique. A plate-like Ti$_3$AlC$_2$ powder was also produced for obtaining a higher textured Ti$_3$AlC$_2$. A series of microstructural and mechanical characterizations were then performed.

2. Experimental procedure

Ti$_3$AlC$_2$ powder was fabricated by the solid reaction method. Powders of Ti (38 μm, 99.9% purity, Kojundo Chemical Laboratory Co., Ltd., Japan), Al (30 μm, 99.9% purity, Kojundo Chemical Laboratory Co., Ltd., Japan) and carbon black (30 nm, Mitsubishi Chemical Corp., Japan) were used as the starting materials with the optimized mole ratio of 3Ti/1.1Ti/1.8Al. The elemental powders were put in a polypropylene bottle and ball-milled for 12 h. The obtained mixture was then placed in a graphite die (30 mm diameter) and uniaxially pressed at 35 MPa to form a green compact prior to the SPS process (SPS-1050, SPS Syntex, Inc., Japan). A heating rate of 80 K/min, the reaction temperature in the range of 1573–1773 K and a holding time...
of 10 min were chosen. The reacted compact was then roughly pulverized using a stamp mill (Ito Seisakusho Co., Ltd., Japan) and further milled in a Si3N4 jar using a planetary-type ball mill (Pulverisette 6, Fritsch GmbH, Germany) for 20 h. Ethanol was used as the medium and the milling speed was set at 250 min⁻¹ in order to prepare the plate-like powders. After drying in air, the powder was sieved with a 400-mesh screen. The constituent phases were determined using X-ray diffraction (XRD; RINT-2500, Rigaku Co., Japan), and the powder morphology was characterized using a scanning electron microscope (SEM; JSM-6500F, JEOL Ltd., Japan). Next, the dense, textured Ti3AlC2 bulk was fabricated by SPS of the synthesized Ti3AlC2 powder at the heating rate of 80 K/min, a holding temperature of 1473 and 1573 K below the decomposition temperature of 1633 K and a holding time of 3 min. A compressive stress of 80 MPa was continuously applied during the SPS process.

The density of the synthesized specimen was determined by Archimedes method with distilled water as the immersion medium [relative density was calculated using the theoretical density of Ti3AlC2 (4.25 g/cm³)]. The textured dense sample was characterized by XRD and SEM.

The Vickers hardness tests were performed on the surfaces parallel and perpendicular to the SPS-loading direction with a 10 N load; ten measurements were conducted per one sample. Finally, the crack propagation behavior near the indentation marks formed by a force of 49 N was observed by SEM.

3. Results and discussion

Figure 1 shows the XRD patterns of the reacted compacts prepared by heating of the mixture of elemental powders (3Ti/1.1Al/1.8C) in the temperature range of 1473 to 1773 K for 10 min. At 1473 K, three phases of Ti2AlC, TiC and Ti3AlC coexist. The Ti3AlC phase disappears at 1573 K and the Ti3AlC2 phase appears at 1673 K. When the mixture was heated at 1773 K, the intensity of the Ti3AlC2 phase increased. The decomposition of Ti3AlC2 into TiC was observed at temperatures above 1773 K. Therefore, the temperature of 1773 K was chosen to synthesize the Ti3AlC2 powder. Figure 2 shows the XRD pattern of the powder obtained by pulverization and milling of the reacted compact prepared at 1773 K. In addition to the peaks of the Ti2AlC2 phase, small peaks of the Ti3AlC and TiC phases were also detected. The mass percentages of the Ti2AlC2, Ti3AlC and TiC phases were then calculated by the following equations:

\[
W_a = \frac{I_a}{(I_a + 0.220I_b + 0.084I_c)} 
\]  
\[
W_b = \frac{I_b}{(4.545I_a + 0.220I_b + 0.382I_c)} 
\]  
\[
W_c = \frac{I_c}{(11.905I_a + 2.619I_b + I_c)} 
\]  

where \(W_a\), \(W_b\) and \(W_c\) represent the mass percent of Ti2AlC, Ti3AlC and TiC, respectively. \(I_a\), \(I_b\) and \(I_c\) represent the integrated peak intensities of Ti2AlC (002), Ti3AlC (002) and TiC (112), respectively. According to these equations, the Ti2AlC2, Ti3AlC and TiC contents were estimated to be 86, 10 and 4%, respectively. Figure 3 shows the plate-like morphology of the pulverized/milled Ti3AlC2 powder; a facile cleavage along the basal plane could contribute to realization of this plate-like morphology.

The density of the textured Ti3AlC2 ceramic, fabricated by the SPS treatment of the plate-like Ti3AlC2 powder (Fig. 3), increases from 96.2 to 99.5% as the temperature increases from 1473 to 1573 K. Therefore, the temperature of 1573 K was chosen to synthesize the textured Ti3AlC2 ceramic. Figure 4 shows the XRD patterns of the top and side surface of textured Ti3AlC2, the surface parallel and perpendicular to the SPS-loading direction. The intermediate phases of TiC and Ti2AlC observed in the powder disappeared and only the Ti3AlC2 peaks were detected. This suggests that during the SPS, the Ti2AlC phase reacts with TiC to form the single-phase Ti3AlC2 as is the case of the pressureless calcining process. On the top surface, the (00l) peaks of Ti3AlC2 were detected (Fig. 4(a)), whereas on the side surface, few (00l) peaks of Ti3AlC2 were detected [Fig. 4(b)]. This result shows that the c-planes of the Ti3AlC2 grains are oriented perpendicular the SPS-loading direction. Figure 5 shows the polished and etched (a) top and (b) side surfaces. As seen in Fig. 5, the plate-like Ti3AlC2 grain with an

![Fig. 2. X-ray diffraction pattern of the synthesized Ti3AlC2 powder.](image)

![Fig. 3. SEM image of synthesized, plate-like Ti3AlC2 powder.](image)
average size of 3.2 µm in length and 0.7 µm in thickness was unidirectionally laminated, parallel to the SPS-loading direction. The measured density of the sintered sample was 4.23 g/cm³, 99.5% of the theoretical value. The degree of orientation, \( f \), was estimated by the Lotgering orientation factor defined as:

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

where

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

and \( P_0 \) represents the same quantity for the non-oriented sample. The \( f \) factor varies from zero for a non-oriented sample to one for a completely oriented sample. In this study, \( P_0 \) was calculated from the peak data of the JCPDS card, No. 52-0875. The degree of orientation calculated from the above equation was 0.69.

Table 1 summarizes the Vickers hardness determined in this study and from reported studies. As seen in the textured Ti₃AlC₂, both hardness values of the textured Ti₃AlC₂ are higher than that of previous studies. The dislocations of the MAX-phases are reported to be mobile and multiply at room temperature. Therefore, it is assumed that the Hall-Petch effect from the peak data of the JCPDS card, No. 52-0875. The degree of orientation calculated from the above equation was 0.69.

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![Fig. 4. X-ray diffraction patterns of the surfaces (a) perpendicular and (b) parallel to the SPS-loading direction.](image)

![Fig. 5. The polished and etched surfaces (a) perpendicular and (b) parallel to the SPS-loading direction.](image)

![Fig. 6. Vickers indentation marks on the surfaces (a) perpendicular and (b) parallel to the SPS-loading direction.](image)

| Vickers hardness /GPa | Sintering method | Synthesis temperature /K | Relative density /% | Grain width /µm | Grain length /µm |
|-----------------------|-----------------|--------------------------|--------------------|-----------------|-----------------|
| This work 5.9 (Top surface) | SPS | 1573 | 9.95 | 3.2 | 0.7 |
| Wang et al.27 | 2.7 | HP | 1773 | 99.1 | — | — |
| Tzenov et al.28 | 4.1 | HP | 1673 | 98.8 | 20–30 | — |
| Wan et al.29 | 3.5 | HP | 1793 | 98.9 | 28.4 | 6.5 |
| Wan et al.29 | 2.2 | HP | 1893 | 98.6 | 74.9 | 19.1 |
Ti$_3$AlC$_2$ surface parallel to the SPS-loading direction. Observed around the Vickers indentation marks on the texturedders. The toughening mechanism of the crack delamination within individual grains or along the basal plane was observed, which could determine the difference in the diagonal length. The toughening mechanism of the crack deflection was also observed on a submicron scale, which is largely beneficial for enhancement of the fracture toughness.

4. Conclusion

A dense, textured Ti$_3$AlC$_2$ ceramic has been fabricated by the SPS of the plate-like Ti$_3$AlC$_2$ powder synthesized by a reactive SPS-heat treatment of elemental Ti, Al and carbon black powders. The toughening mechanism of the crack deflection was observed around the Vickers indentation marks on the textured Ti$_3$AlC$_2$ surface parallel to the SPS-loading direction.

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