ENHANCEMENT OF MECHANICAL PROPERTIES FOR SELF-REINFORCED HOT-PRESSED SILICON CARBIDE

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Abstract

The effect of Si_3N_4 - $MgSiN_2$ addition on the densification and mechanical properties of SiC composites was investigated with the aim of encouraging the development of "self-reinforcement" due to the elongation of grains or fibers during hot-pressing. Relative densities of the composites with SiC contents of less than 85.63 mol% (sintering aids: B_4C and Yb_2O_3) hot-pressed at 1800ºC for 1 h in Ar atmosphere under a uniaxial pressure of 62 MPa were close to the theoretical fully dense values; however, no unidirectionally-elongated grains were observed within the SiC matrix. For these compositions, fibrous grains were only found to be formed when the hot-pressing pressure was less than 50 MPa. However, for the composite with a SiC content of 85.63 mol% and 4.98 mol% Si_3N_4 - 4.98 mol% $MgSiN_2$ addition (hot-pressed at 1800ºC for 1.5 h under a pressure of 75 MPa, followed by hot-pressing at 1800ºC for 1 h under a pressure of 50 MPa) a maximum fracture toughness of 6.3 MPa $m^{1/2}$ was acheieved due to the presence of elongated grains.

1 Introduction

Silicon carbide (SiC) ceramics are known to possess excellent corrosion and oxidation resistance and, therefore, various potential applications exist which make use of these properties at elevated temperature, *e.g.*, structural and aerospace development materials, and semiconductor devices. However, the relatively low fracture toughness of monolithic SiC ceramic (typically 1~2 MPa·$m^{1/2}$) has resulted in significant attention being paid to the fabrication of ceramic matrix composites (CMCs) containing continuous fibers within the matrix.

On the other hand, the present authors have examined the reinforcement of CMCs by discontinuous fibers. Although their fracture toughness is relatively low (*e.g.*, 5 MPa·$m^{1/2}$) when compared to that of continuous fiber-reinforced composites (*e.g.*, 10~20 MPa·$m^{1/2}$), other significant advantages exist, such as precise control of the fiber amount, reduced fabrication costs, and simpler production of complex shapes. For example, the fracture toughness of hot-pressed SiC/SiC composites containing chopped Tyranno® Si-Al-C (SA) fibers (mean length: 394 μm) was shown to exhibit a maximum value of 5.8 MPa·$m^{1/2}$ [1]. However, one problem with such composites is that the homogeneous mixing of chopped fibers with SiC matrix powder is required in order to improve the fracture toughness. The production of elongated grains within the SiC matrix during hot-pressing, in order to produce a self-reinforced SiC composite, is another possible method to avoid the problem of homogeneous dispersion of fibers within the matrix. Previously, several of the present authors had noted that the development of elongated grains may occur during the hot-pressing of magnesium silicon nitride ($MgSiN_2$) - silicon nitride (Si_3N_4) composites [2]. On the basis of that work, we have examined the enhancement of fracture toughness for SiC due to the elongation of grains during hot-pressing.

2 Experimental procedures

The starting ultrafine SiC powder (Sumitomo Osaka Cement Co., Tokyo; specific surface area, 47.5 $m^2 \cdot g^{-1}$; crystalline phase, SiC(3C)) was mixed with Si_3N_4 (SN-10, Ube Industries, Ube; SSA, 10.9 $m^2 \cdot g^{-1}$; α-Si_3N_4>95%), $MgSiN_2$, B_4C (sintering aid) and Yb_2O_3 (sintering aid) powders. Whereas the SiC and Si_3N_4 powders were commercially available, the $MgSiN_2$ powder (SSA: 7.6 $m^2 \cdot g^{-1}$) was prepared by the authors, using Mg and Si as starting materials;

the mixture of Mg and Si powder (Mg/Si ratio of 2.0) was heated at 700°C for 90 min in Ar atmosphere to form Mg_2Si and then at 1350°C for 10 min in N_2 atmosphere to obtain $MgSiN_2$.

Compositions of the starting materials have been shown in **Table 1**. Note that B_4C and Yb_2O_3, *i.e.*, the sintering aids for SiC and $MgSiN_2$/Si_3N_4, respectively, were further added to the mixtures of SiC, Si_3N_4 and $MgSiN_2$. Approximately 1.5 g of each mixture was uniaxially pressed at 50 MPa and then cold-isostatically pressed at 100 MPa in order to obtain a disk with a diameter of 20 mm and thickness of ~2 mm. The resulting disk was hot-pressed at 1800°C for 1 or 2.5 h in Ar or N_2 atmosphere under a uniaxial pressure of 31~75 MPa.

Crystalline phases of each composite were identified using an X-ray diffractometer (XRD; Model RINT2000PC, Rigaku, Tokyo). The relative density of the composite was calculated by dividing the bulk density by true density. The fracture toughness, K_{IC}, of bar-like specimens (12 × 2 × 1.5 mm^3) was determined using the single-edge notched beam (SENB) technique in the three-point bend configuration (Model Y2500-PC, Yasuda Precision Instruments, Tokyo) with a span of 10 mm and a cross-head speed of 0.5 mm·min^{-1}. Moreover, the microstructure of hot-pressed composites was observed using a scanning electron microscope (SEM; Model S-4500, Hitachi, Tokyo); quantitative elemental analysis was conducted using an energy-dispersive X-ray microanalyzer (EDX).

3 Results and discussion

3.1 Effect of SiC content on the relative density and mechanical properties

Firstly, the effect of Si_3N_4 and $MgSiN_2$ addition on the relative density of SiC composites hot-pressed at 1800°C for 1 h in Ar atmosphere was examined by fixing the hot-pressing pressure at 62 MPa. The results have been presented in **Fig. 1**,

Table 1 Compositions of the starting materials

Sample No.	SiC mol%	Si_3N_4 mol%	$MgSiN_2$ mol%	B_4C mol%	Yb_2O_3 mol%
1	96.00	0	0	4.00	0
2	89.75	2.99	2.99	3.99	0.28
3	85.63	4.98	4.98	3.98	0.43
4	81.48	6.96	6.96	3.97	0.63
5	77.42	8.93	8.93	3.97	0.75
6	85.63	9.96	0	3.98	0.43
7	85.63	0	9.96	3.98	0.43

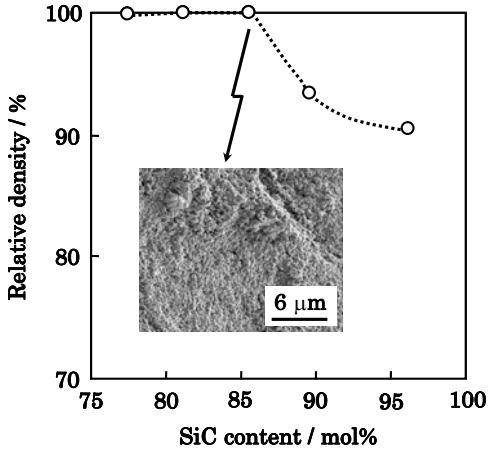

Fig. 1 Effect of SiC content on the relative density of composite hot-pressed at 1800°C for 1 h under a pressure of 62 MPa.

together with a typical SEM micrograph. The relative density of the composites increased with decreasing SiC content; almost full density was achieved when the SiC content was 85 mol% or less. The SEM micrograph of the composite containing 85.63 mol% of SiC showed that presence of closely packed grains with sizes of approximately 1 μm.

Thus, almost full density was found to be achieved when the SiC content was 85 mol% or less; this phenomenon was attributed to the decrease in SiC with poor sinterability and the increase in Si_3N_4 and $MgSiN_2$ contents. It should be noted that SEM examination of the hot-pressed composites revealed the absence of elongated grains within the matrix, regardless of the high relative density for some of the composites.

XRD patterns of the composites with various SiC contents have been shown in **Fig. 2**. The only crystalline phase found in the composite with 96.00 mol% SiC content was SiC(3C) (Fig. 2(a)). Crystalline phases present in the composites with 89.75 mol% SiC content were SiC(3C), SiC(4H) and C (Fig. 2(b)). Composites with 85.63 and 81.48 mol% SiC contents were found to contain SiC(3C), $MgSiN_2$ and C (Fig. 2(c) and (d)), whereas the phases observed in composites with 77.42 mol% SiC content were SiC(3C), β-Si_3N_4, $MgSiN_2$ and C (Fig. 2(e)).

No reaction products are detected from the hot-pressed composites containing various SiC contents. Nevertheless, according to our previous work on $MgSiN_2$-Si_3N_4 composites [3], it is probable that small amounts (*i.e.*, below the detection limit of the XRD apparatus) of $Yb_2Si_3O_3N_4$ may have been formed by the reaction between the Si_3N_4 and Yb_2O_3 used as a sintering aid. In addition, it is likely that

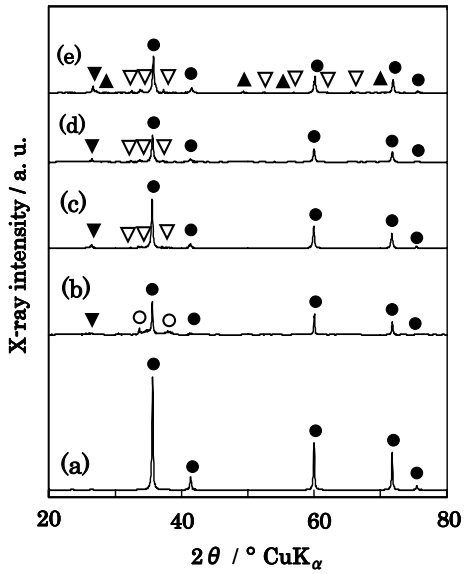

Fig. 2 XRD patterns of composites with SiC contents of (a) 96.00 mol%, (b) 89.75 mol%, (c) 85.63 mol%, (d) 81.48 mol% and (e) 77.42 mol% hot-pressed at 1800°C for 1 h under the pressure of 62 MPa.

●: SiC(3C) ○: SiC(4H) ▲: β-Si_3N_4
▽: $MgSiN_2$ ▼: C

amorphous material in the Mg-Si-C-N system may also be present at the grain boundaries. The carbon detected from the composite with 77.42 - 89.75 mol% SiC proves the occurrence of a reaction between the starting materials to form such amorphous materials in the Mg-Si-C-N system.

Following this, the flexural strength and fracture toughness of hot-pressed composites were investigated with the result being presented in **Fig. 3**. The maximum flexural strength and fracture toughness of the hot-pressed composites were 293 MPa at 85.63 mol% SiC content and 4.4 MPa·$m^{1/2}$ at 81.48 mol% SiC content, respectively.

The decrease in flexural strength and fracture toughness with increasing SiC content from 85 to 96 mol% was noted to closely correlate with the decrease in relative density. Although, as mentioned above, the flexural strength and fracture toughness of the hot-pressed composite exhibited maxima (*i.e*, 293 MPa and 4.4 MPa·$m^{1/2}$, respectively), these values decreased as the SiC content decreased from 85 down to 77 mol%. The decrease in flexural strength and fracture toughness with decreasing SiC content (*i.e*., with increasing amounts of $MgSiN_2$ and Si_3N_4), was explained by assuming that the amorphous materials in the Mg-Si-C-N system did

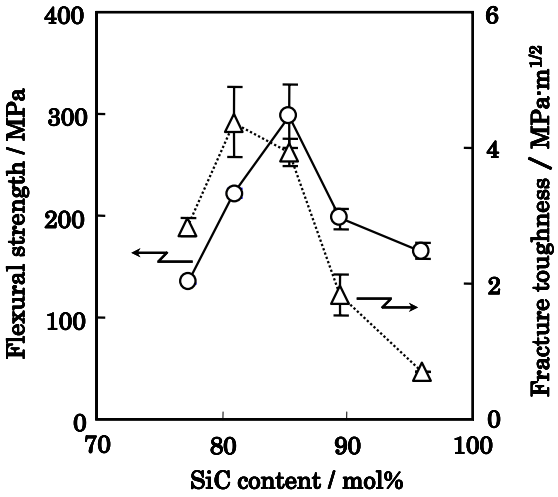

Fig. 3 Effect of SiC content on the flexural strength and fracture toughness of composite hot-pressed at 1800°C for 1 h under a pressure of 62 MPa.

not contribute to enhancing the mechanical properties of the composites.

3.2 Effect of hot-pressing pressure on the relative density and mechanical properties

In Section 3.1, the effect of SiC content on the relative density and mechanical properties was examined by fixing the hot-pressing pressure at 62 MPa. Since the degree of densification may be strongly influenced by the hot-pressing pressure, the effect of hot-pressing pressure (31~62 MPa) on the relative density of SiC composites was examined in this section with results being shown in **Fig. 4**. Note that the SiC content was selected to be 85.63 mol%, due to its potential to produce a dense composite with high fracture toughness (4.4 MPa·$m^{1/2}$) as shown in Section 3.1. The relative density was found to increase with hot-pressing pressure; almost fully-dense SiC composites could be fabricated when the hot-pressing pressure was greater than 50 MPa.

The influence of hot-pressing temperature on fracture toughness was also examined with the results being shown in **Fig. 5**, together with a typical SEM micrograph. The fracture toughness of the composite with 85.63 mol% SiC content increased with increasing pressure and attained a maximum of 5.5 MPa·$m^{1/2}$ at 50 MPa. On further increases in hot-pressing pressure to 62 MPa, however, the fracture toughness was reduced. A SEM investigation indicated the presence of elongated grains within the SiC matrix.

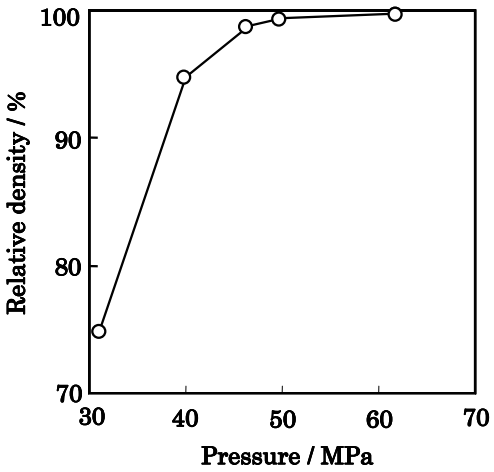

Fig. 4 Effect of hot-pressing pressure on the relative density of composite hot-pressed at 1800°C for 2.5 h. (Chemical composition of the composite: 85.63 mol% SiC, 4.98 mol% Si_3N_4, 4.98 mol% $MgSiN_2$, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3).

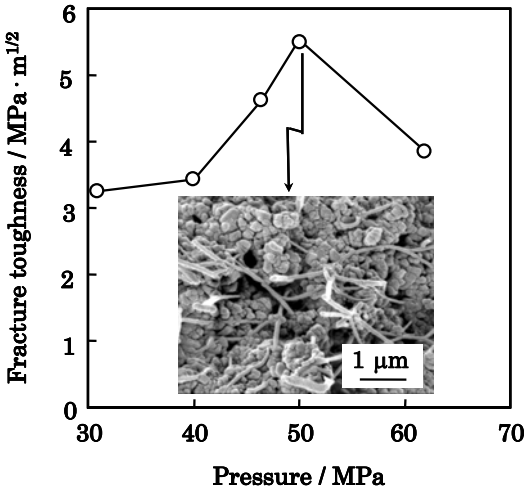

Fig. 5 Effect of hot-pressing pressure on the fracture toughness of composite hot-pressed at 1800°C for 2.5 h. (Chemical composition of the composite: 85.63 mol% SiC, 4.98 mol% Si_3N_4, 4.98 mol% $MgSiN_2$, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3).

The increase in fracture toughness for hot-pressed composites with increasing hot-pressing pressure up to 50 MPa was found to be correlated to the relative density. As the SEM micrograph in Fig. 5 indicates, the presence of elongated grains would appear to enhance the fracture toughness. The decrease in fracture toughness, regardless of the increase in hot-pressing pressure up to 62 MPa, was attributed to the restricted elongation of grains as SEM micrographs for these composites indicated a reduced number of elongated grains (not shown here).

In order to make clear the elongation behavior of grains, crystalline phases were checked using XRD with the results being presented in **Fig. 6**. For hot-pressing pressures between 31 and 62 MPa, only two kinds of crystalline phases were noted, *i.e.*, SiC(3C) and SiC(2H); the X-ray intensity of the SiC(4H) phase decreased with increasing hot-pressing pressure from 31 to 62 MPa.

As mentioned earlier, SEM observation indicated that the number of elongated grains decreased with increasing hot-pressing pressure. Thus, the formation of elongated grains can be correlated to the transformation of SiC(3C) to SiC(4H). Regarding the grain morphology of SiC(4H), Tanaka [3] reported that elongated and plate-like grains tend to form when SiC contains a large number of stacking faults.

Furthermore, EDX investigation was carried out in order to make clear which component ions may assist the elongation of grains. Results have been shown in **Fig. 7**. EDX results indicated that Mg was detected within the grains, together with Si, with SEM observation indicating that the fibrous grains possessed a mean length of approximately 5 μm.

The detection of Mg within the grains suggested

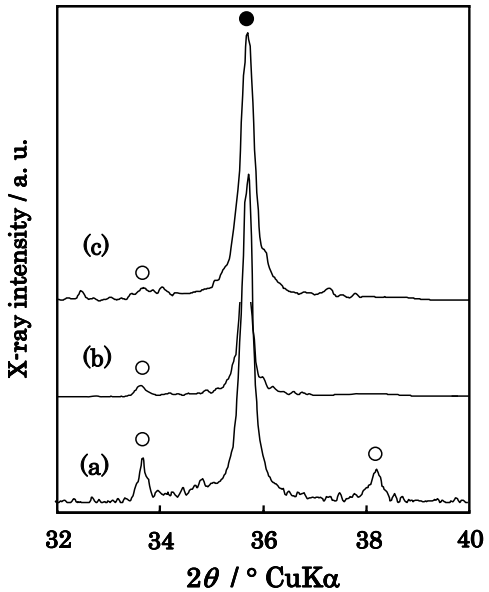

Fig. 6 XRD patterns of the composites hot-pressed at 1800°C for 2.5 h under a pressure of (a) 31 MPa, (b) 46.5 MPa and (c) 62 MPa.
●: SiC(3C) ○: SiC(4H)
(Chemical composition of the composite: 85.63 mol% SiC, 4.98 mol% Si_3N_4, 4.98 mol% $MgSiN_2$, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3).

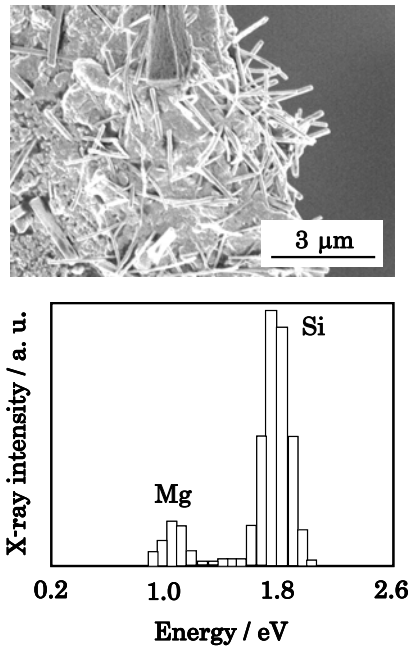

Fig. 7 EDX analysis of the composite hot-pressed at 1800ºC for 2.5 h under a uniaxial pressure of 46.5 MPa, together with typical SEM micrograph. (Chemical composition of the composite: 85.63 mol% SiC, 4.98 mol% Si_3N_4, 4.98 mol% $MgSiN_2$, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3.

the presence of $MgSiN_2$ and/or reaction products. Previously, Inomata *et al*. [4] reported that a eutectic liquid in the Si_3N_4-$MgSiN_2$ system may form at approximately 1520°C. Thus, it is probable that $MgSiN_2$ formed a eutectic liquid with Si_3N_4, which aided the uniaxial elongation of grains, in addition to enhancing densification. Both $MgSiN_2$ and Si_3N_4 addition, therefore, appear to be effective for the formation of fibrous grains and for the enhancement of fracture toughness.

3.3 Effect of $MgSiN_2$ - Si_3N_4 composition on the relative density and mechanical properties

We further examined the effect of Si_3N_4-$MgSiN_2$ addition on the chemical composition, as the densification and fracture toughness of the composite may be affected by the amount of liquid phase formed during hot-pressing, in addition to examining the relative sinterability of $MgSiN_2$ and Si_3N_4 [5]. Firstly, the relative density of composites containing 9.96 mol% Si_3N_4 addition was 87.3%, whereas that containing 9.96 mol% $MgSiN_2$ addition was 95.1%. On the other hand, the relative density of the composite containing 4.98 mol% Si_3N_4 - 4.98 mol% $MgSiN_2$ addition was 99.7%.

On the basis of this information, the effect of Si_3N_4-$MgSiN_2$ addition on the composite fracture toughness was further examined with the results being shown in **Fig. 8**. The fracture toughness of the composite exhibited a maximum (5.5 $MPa{\cdot}m^{1/2}$) at 4.98 mol% Si_3N_4-4.98 mol% $MgSiN_2$.

Crystalline phases for these composites were checked using XRD with the results being presented in **Fig. 9**. Note that the SiC content was fixed to be 85.63 mol%. Crystalline phases present in the composite containing 9.96 mol% Si_3N_4 addition were SiC(3C) and C (Fig. 9(a)). Crystalline phases noted in the composite with 4.98 mol% Si_3N_4-4.98 mol% $MgSiN_2$ were SiC(3C), SiC(4H), YbN and C (Fig. 9(b)), whereas those of the composite with 9.96 mol% $MgSiN_2$ addition were SiC(3C), YbN and C.

The formation of YbN may be expressed as follows:

$$3MgSiN_2 + 2Yb_2O_3 \rightarrow Yb_2Si_3O_5N_2 + 2YbN + Mg_3N_2 + (1/2)O_2 \quad (1)$$

Other reaction products, *i.e.*, $Yb_2Si_3O_5N_2$ and Mg_3N_2, were not detected, either due to their poor crystallinity or else due to the amount being below the detectable limit of the XRD apparatus. This reaction process was believed to be correlated to the higher fracture toughness and formation of elongated grains.

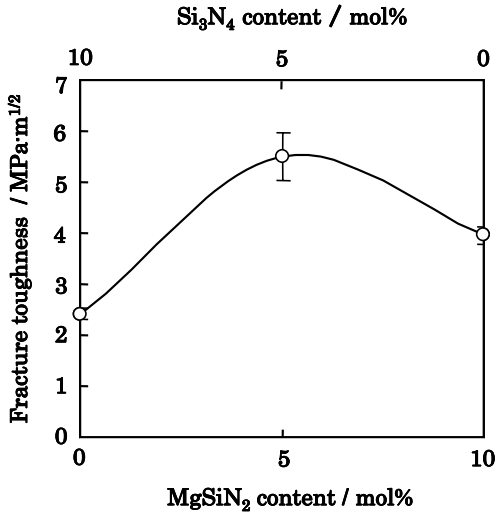

Fig. 8 Effect of Si_3N_4 and $MgSiN_2$ addition on the fracture toughness of composite hot-pressed at 1800°C for 2.5 h under a pressure of 50 MPa. (Chemical composition of the composite: 85.63 mol% SiC, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3).

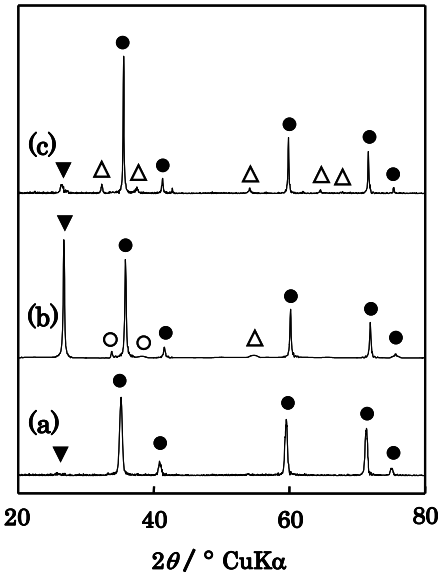

Fig. 9 XRD patterns of the composites containing: (a) 9.96 mol% Si_3N_4 addition, (b) 4.98 mol% Si_3N_4-4.98 mol% $MgSiN_2$ addition and (c) 9.96 mol% $MgSiN_2$ addition hot-pressed at 1800°C for 2.5 h under the pressure of 50 MPa.
●: SiC(3C) ○: SiC(4H) △: YbN ▼: C
(Chemical composition of the composite: 85.63 mol% SiC, 3.98 mol% B_4C and 0.43 mol% Yb_2O_3)

3.4 Enhancement of mechanical properties

On the basis of the results obtained so far, a two-step hot-pressing procedure for the composite (SiC: 85.63 mol%; Si_3N_4: 4.98 mol%; $MgSiN_2$: 4.98 mol%) was conducted in order to enhance the fracture toughness. The heating schedule has been illustrated in **Fig. 10**. The hot-pressing was conducted at 1800°C for 60 min under a 50 MPa pressure for the promotion of elongated grain growth. Hot-pressing was then carried at 1800°C for 90 min under a 75 MPa pressure for the promotion of densification.

The relative density of this hot-pressed composite was found to reach 99.8%. Reflecting such high relative density, the flexural strength of the composite was 389 MPa, whereas the fracture toughness attained a maximum of 6.3 MPa·$m^{1/2}$.

4 Conclusions

The effect of Si_3N_4-$MgSiN_2$ addition on the densification and microstructure development of SiC composites was examined in order to encourage "self-reinforcement" due to the uniaxial elongation of grains during hot-pressing. The following results were obtained:

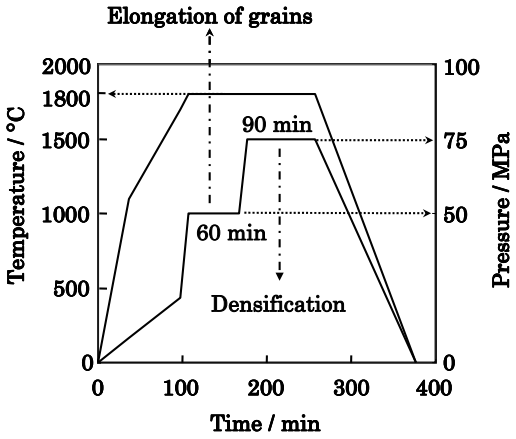

Fig. 10 Hot-pressing schedule of the composite for the fabrication of self-reinforcement hot-pressed SiC composite.

(i) Relative densities of the composites with SiC contents of less than 85.63 mol% (sintering aids: B_4C and Yb_2O_3) hot-pressed at 1800ºC for 1 h in Ar atmosphere under a pressure of 62 MPa were almost full; no elongated grains were observed in the SiC matrix. However, fibrous grains were found to be formed when the hot-pressing pressure was less than 50 MPa.

(ii) A composite containing 85.63 mol% SiC content and 4.98 mol% Si_3N_4 - 4.98 mol% $MgSiN_2$ addition was hot-pressed at 1800ºC for 1.5 h under a pressure of 75 MPa, followed by hot-pressing at 1800ºC for 1 h under a pressure of 50 MPa. The fracture toughness attained a maximum of 6.3 MPa $m^{1/2}$ due to the presence of elongated grains.

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