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Effect of silicon nitride addition on the thermal and mechanical properties of magnesium silicon nitride ceramics

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Abstract

The effect of silicon nitride (Si_3N_4) addition on the sintering of magnesium silicon nitride ($MgSiN_2$) powder has been examined using a hot-pressing technique. The $MgSiN_2$ powder compacts with 1, 4, and 9 mol% of Si_3N_4 addition [sintering aid: 1 mol% ytterbium oxide (Yb_2O_3)] were hot-pressed at a temperature between 1550 and 1800 °C for 90 min in a nitrogen (N_2) atmosphere under the pressure of 75 MPa. The relative density of a $MgSiN_2$ compact with 4 mol% of Si_3N_4 addition hot-pressed at 1600 °C for 90 min showed a maximum (98.6%), although the relative density was reduced by the addition of Si_3N_4 at other hot-pressing temperatures. The maximum fracture toughness (6.6 MPa·$m^{1/2}$) was achieved for the $MgSiN_2$ specimen with 4 and 9 mol% of Si_3N_4 addition hot-pressed at 1600 °C for 90 min. This value was 2.5 times higher than that of $MgSiN_2$ specimen without Si_3N_4 addition (2.6 MPa·$m^{1/2}$). The improvement of the fracture toughness appeared to be due to the elongation of the Si_3N_4 grains, which had occurred in the presence of a liquid phase during the hot pressing. The thermal conductivity of the $MgSiN_2$ specimen with 9 mol% of Si_3N_4 addition hot-pressed at 1750 °C for 90 min increased to 34.1 W m^{-1} K^{-1}, which is to our knowledge, the highest among the values so far reported for $MgSiN_2$ ceramics.

Keywords: Hot pressing; Mechanical properties; $MgSiN_2$; Si_3N_4; Thermal properties

1. Introduction

Magnesium silicon nitride ($MgSiN_2$) is one of the candidates for a material with high thermal conductivity, as well as aluminum nitride (AlN). In 1993, Groen et al.[1] fabricated $MgSiN_2$ ceramics using a closed Mo vessel to prevent thermal decomposition, and found that the maximum relative density of the resulting $MgSiN_2$ ceramic attained 99.4%, whereas the thermal conductivity was as low as 17 W m^{-1} K^{-1}. Later, Hintzen et al.[2] fabricated $MgSiN_2$ ceramics using a hot pressing technique and measured the thermal conductivities, which were low (15 W m^{-1} K^{-1}). On the other hand, Davies et al.[3,4] fabricated pressureless-sintered and hot-pressed $MgSiN_2$ compacts using Y_2O_3 as a sintering aid; thermal conductivities of the hot-pressed $MgSiN_2$ compacts with 1 mass% of Y_2O_3 addition are in the range of 20–21 W m^{-1} K^{-1}, although the relative density had a maximum of 99.9%. Regardless of the homogeneous dispersion of Y_2O_3 in the $MgSiN_2$ powder using a urea-based homogeneous precipitation method, the thermal conductivities of the resulting $MgSiN_2$ ceramics are still in the order of 20–21 W m^{-1} K^{-1}. Recently, some of the present authors[5] examined the effect of rare-earth oxide addition on the sintering of $MgSiN_2$ powder, and found that the thermal conductivity of a $MgSiN_2$ ceramic with 1 mass% of ytterbium oxide (Yb_2O_3) addition increases to 26.1 W m^{-1} K^{-1}. To our knowledge, this value is the highest among the values so far reported and may be close to the theoretical thermal conductivity of $MgSiN_2$; Bruls[6,7] has claimed that the maximum thermal conductivity is theoretically around 26–28 W m^{-1} K^{-1} at 300 K.

Apart from the above studies, Hayashi et al.[8] have investigated the effect of $MgSiN_2$ addition on the

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densification of silicon nitride (Si_3N_4) compact, and found that the thermal conductivity of a Si_3N_4 ceramic with $MgSiN_2$ addition (sintering aid: Yb_2O_3) is as high as 140 W m^{-1} K^{-1}. This fact suggests that the addition of Si_3N_4 to a $MgSiN_2$ ceramic could contribute to enhancing the thermal conductivity as well as the fracture toughness of $MgSiN_2$, because the Si_3N_4 ceramic possesses excellent mechanical and thermal properties.

On the basis of such background, this paper describes the effect of Si_3N_4 addition on the thermal and mechanical properties of $MgSiN_2$ ceramics, together with presenting results on the densification and microstructural developments during hot pressing of the $MgSiN_2$ compact.

2. Experimental procedure

2.1. Starting materials, compaction and hot pressing

The starting $MgSiN_2$ powder was prepared by nitridation of magnesium silicide (Mg_2Si; Mg/Si = 2.0) powder at 1350 °C for 10 min in a nitrogen atmosphere. The resulting $MgSiN_2$ powder was mixed with 1–9 mol% of Si_3N_4 (SN-E10; Ube Industries, Co. Ltd., Ube, Japan; $\beta/(\alpha+\beta) > 95$ mass%, oxygen content < 2.0 mass%, carbon content < 0.2%) and 1 mol% of Yb_2O_3 (99.99% purity, Wako Pure Chemical Ltd., Osaka) using a zirconia mortar and pestle in the presence of *n*-hexane. After drying, approximately 1.5 g of the mixed powder was uniaxially pressed at 30 MPa to result in a compact with a diameter of 20 mm and a thickness of approximately 2 mm. Each compact was placed in a graphite die and hot-pressed at a temperature between 1550 and 1750 °C for 90 min in a nitrogen atmosphere under a pressure of 75 MPa. The heating rate was 30 °C min^{-1} up to 1100 °C and 10 °C min^{-1} up to the desired temperature with the compact being furnace-cooled following the hot pressing procedure.

2.2. Measurements

The relative density of the hot-pressed compact was calculated using the bulk and true densities; the bulk density was measured using Archimedes method, while the true density was determined picnometrically at 25.0 °C after pulverizing the hot-pressed compact. Crystalline phases present in the hot-pressed compact were characterized using an X-ray diffractometer (XRD) (model RINT2000, Rigaku Co., Tokyo) with monochromatic Cu$K\alpha$ radiation at 40 kV and 40 mA, and referenced using the Joint-Committee-on Powder-Diffraction Standards (JCPDS) cards.

The microstructure of the hot-pressed compact was investigated using a field-emission scanning electron microscope (FE-SEM) (model S-4500, Hitachi, Tokyo; accelerating voltage, 15.0 kV) after coating the surfaces by Pt-Pd in order to reduce charging effects. The oxygen and nitrogen contents in the hot-pressed compact were examined using an N/O determinator (model TC-436, Leco, St. Joseph, MI, USA). The Vickers hardness (H_v) was measured using an indentation load of 9.81 N for 15 s (model MVK-E, Akashi Corp., Tokyo). Ten or more different regions were evaluated for each ceramic in order to obtain an average value. The fracture toughness (K_{IC}) was measured using the single-edge notched beam (SENB) technique. The hot-pressed compact was cut with a diamond saw to prepare a bar-like specimen with a size of $15\times2.5\times3$ mm^3; the notch (approximately 0.7 mm depth) was introduced into the center of specimen. The thermal diffusivity was measured at room temperature, using a photo-flash technique (Compotherm, Germany) and a laser-flash technique (model TC-7000, Shinku-Riko, Tokyo). The thermal conductivity (κ) is expressed by:[9]

$$\kappa = a\rho C_v \quad (1)$$

where a is the thermal diffusivity, ρ is the density, and C_v is the specific heat at constant volume. The thermal conductivity was calculated on the basis of specific heats of $MgSiN_2$ (61.71 J mol^{-1} K^{-1})[10,11] and β-Si_3N_4 (90.68 J mol^{-1} K^{-1}).[11]

3. Results and discussion

3.1. Densification and microstructural developments

First, the effect of Si_3N_4 addition on the relative density of the $MgSiN_2$ compact was examined by fixing the hot pressing temperature at 1550 °C, as we previously fabricated the high-density $MgSiN_2$ compact with rare-earth oxide addition at this temperature. The densification of the $MgSiN_2$ compact may be affected by the hot-pressing pressure. We have previously reported that the relative density of a hot-pressed $MgSiN_2$ compact with 1 mass% (= 0.21 mol%) Yb_2O_3 addition is 93.3% at 31 MPa.[5] The relative density increased to 98.0% when the hot-pressing pressure was enhanced to 75 MPa (1 mol% of Yb_2O_3 addition).

Although the optimum amount of Yb_2O_3 (sintering aid) for the densification of the $MgSiN_2$ compact was estimated to be 1 mass% (= 0.21 mol%) in our previous paper,[5] a larger amount of Yb_2O_3 addition for the densification of the $MgSiN_2$ compact seemed to be needed due to the addition of Si_3N_4, because the covalent Si_3N_4 is not densified without a sintering aid. Actually, preliminary experiments revealed that 0.5 mol% of Yb_2O_3 addition was not enough but that 1 mol% of Yb_2O_3 addition was necessary for the densification of a $MgSiN_2$ compact with 4 mol% of Si_3N_4 addition.

Fig. 1 shows the changes in the relative density of the hot-pressed $MgSiN_2$ compact with increasing amount of Si_3N_4 addition, together with typical SEM micrographs of the fracture surfaces. Note that the amount of Yb_2O_3 addition and hot-pressing pressure were fixed to be 1 mol% and 75 MPa, respectively. Although the relative density of the hot-pressed $MgSiN_2$ compact was 98.0% for 0 mol% of Si_3N_4 addition, it was reduced down to approximately 94.6% for 1 mol% of Si_3N_4 addition. The relative density was slightly reduced on further increases in amount of Si_3N_4.

The SEM micrograph of the hot-pressed $MgSiN_2$ compact with 0 mol% of Si_3N_4 addition showed that the corner-rounded grains with sizes of approximately 1 μm were closely packed. On the other hand, SEM micrographs of the hot-pressed $MgSiN_2$ compacts with 4 and 9 mol% of Si_3N_4 addition revealed that elongated grains were present among the corner-rounded grains, and that the number of such grains increased with increasing Si_3N_4 addition from 4 to 9 mol%. The elongated grains, which resulted from the addition of Si_3N_4, are assumed to be Si_3N_4, because they did not exist until the $MgSiN_2$ compact was hot-pressed in the presence of Si_3N_4. These elongated grains seem to be formed in the presence of liquid phase during the hot pressing.

The effect of hot-pressing temperature on the relative density of $MgSiN_2$ compact with 4 mol% of Si_3N_4 addition is shown in Fig. 2, together with typical SEM micrographs of the fracture surfaces. Although the relative density was 94.3% at the hot-pressing temperature of 1550 °C, it increased to 98.6% at 1600 °C; on further increase in hot-pressing temperature, however, the relative density gradually decreased and became 96.4% at 1700 °C. Above 1700 °C, the $MgSiN_2$ compacts with Si_3N_4 addition became brittle, owing to the partial thermal decomposition of $MgSiN_2$. The SEM micrographs showed that the elongated grains present in the $MgSiN_2$ matrix tended to be oriented, normal to the pressing direction at the hot-pressing temperature of 1600 °C, and that these elongated grains stuck together to the $MgSiN_2$ matrix at 1700 °C.

A significant elongation of grains occurs as the hot-pressing temperature increases from 1550 from 1600 °C (Figs. 1 and 2). Moreover, sticking of grains to the matrix takes place with a further increase in hot-pressing temperature up to 1700 °C. These phenomena may be attributed to the accelerated mass transfer in the presence of liquid phase during the hot-pressing, i.e., the anisotropic crystal growth (elongation of grains) and progress in chemical reaction at the interfaces (sticking of grains to the matrix). Thus the bonding of $MgSiN_2$ matrix with Si_3N_4 grains seems to be enhanced, due to the accelerated mass transfer during the hot-pressing. Regardless of the enhancement of such bonding, a gradual decrease in the relative density with hot-pressing temperature from 1600 to 1700 °C may be ascribed to

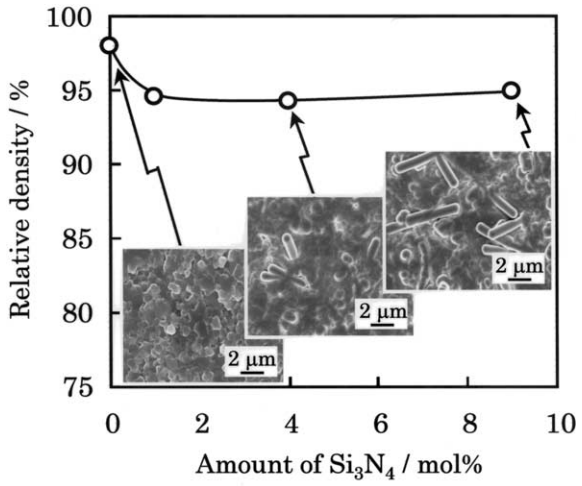

Fig. 1. Effect of the Si_3N_4 and 1 mol% Yb_2O_3 addition on the relative density of $MgSiN_2$ compact hot-pressed at 1550 °C for 90 min at 75 MPa, together with typical SEM micrographs of the fracture surfaces.

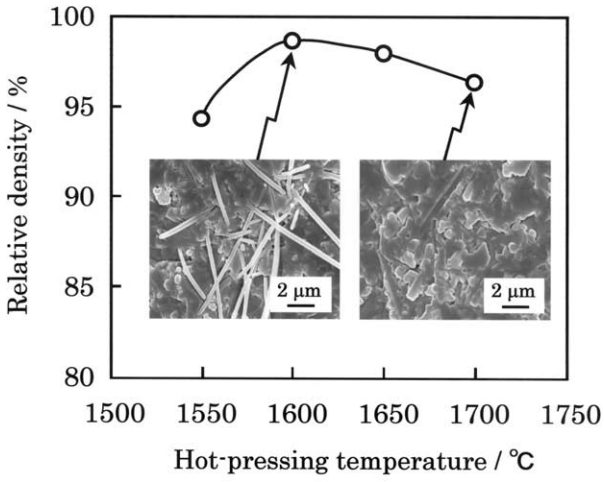

Fig. 2. Effect of hot-pressing temperature (for 90 min and at 75 MPa) on the relative density of the $MgSiN_2$ compact with 4 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition, together with typical SEM micrographs of the fracture surfaces.

the partial evaporation of the components on and near the surfaces. Details will be explained later together with the XRD data.

The effect of hot-pressing temperature on the relative density of $MgSiN_2$ compact with 9 mol% of Si_3N_4 addition is shown in Fig. 3. The relative density increased from 94.7 to 96.9% with increasing hot pressing temperature from 1550 up to 1750 °C. The SEM micrographs showed that the elongated grains stuck to the $MgSiN_2$ matrix at 1700 °C, and that plate-like grains with average sizes of approximately 4 μm prevailed at 1750 °C.

Typical X-ray diffraction patterns for the $MgSiN_2$ compact with 9 mol% of Si_3N_4 addition hot-pressed at 1550 and 1750 °C for 90 min are shown in Fig. 4. The

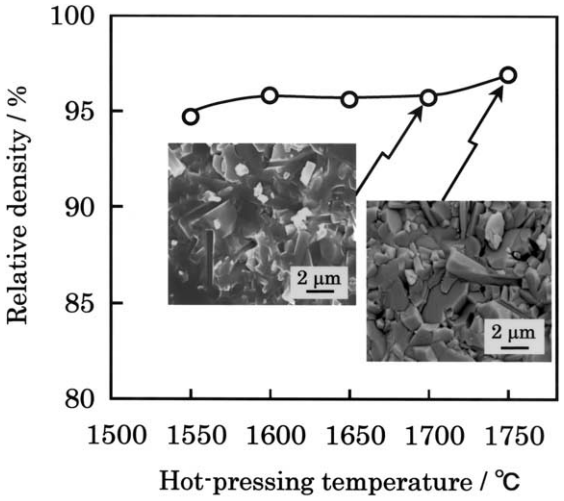

Fig. 3. Effect of hot-pressing temperature (for 90 min and at 75 MPa) on the relative density of the $MgSiN_2$ compact with 9 mol% of Si_3N_4 addition (1 mol% Yb_2O_3 addition as a sintering aid), together with typical SEM micrographs of the fracture surfaces.

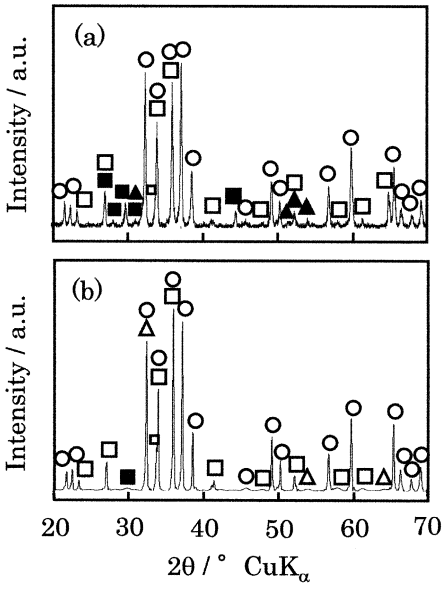

Fig. 4. XRD patterns for the $MgSiN_2$ compacts with 9 mol% of Si_3N_4 and 1 mol% Yb_2O_3 addition hot-pressed at (a) 1550 °C and (b) 1750 °C for 90 min. ○: $MgSiN_2$, □: β-Si_3N_4, ■: $Yb_2Si_3O_3N_4$, △: YbN, ▲: $Yb_2Si_3O_5N_2$.

crystalline phases at 1550 °C were $MgSiN_2$,[12] β-Si_3N_4,[13] $Yb_2Si_3O_3N_4$,[14] and $Yb_2Si_3O_5N_2$,[15] whereas those at 1750 °C were $MgSiN_2$, β-Si_3N_4, $Yb_2Si_3O_3N_4$ and YbN.[16]

We have reported the reaction of $MgSiN_2$ with Yb_2O_3 as follows:[5]

$$3MgSiN_2 + Yb_2O_3 \rightarrow Yb_2Si_3O_3N_4 + Mg_3N_2 \quad (2)$$

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

Although Mg_3N_2 was not detected by XRD, it may have been partly decomposed and evaporated on and near the surfaces. Moreover, it is probable that the Mg_3N_2 reacts with Si_3N_4 to form $MgSiN_2$ during the hot pressing.

In addition to these solid-state reactions, Si_3N_4 may react with Yb_2O_3 to form $Yb_2Si_3O_3N_4$ and $Yb_2Si_3O_5N_2$:

$$Si_3N_4 + Yb_2O_3 \rightarrow Yb_2Si_3O_3N_4 \quad (4)$$

$$3Si_3N_4 + 5Yb_2O_3 \rightarrow 3Yb_2Si_3O_5N_2 + 4YbN + N_2 \quad (5)$$

The densification of the $MgSiN_2$ compact with Si_3N_4 and Yb_2O_3 addition is assumed to occur along with the formation of three kinds of phases, i.e., liquid phase, $Yb_2Si_3O_3N_4$, and $Yb_2Si_3O_5N_2$. With respect to the liquid composition, Inomata et al.[17] have pointed out that a eutectic liquid in the Si_3N_4–$MgSiN_2$ system forms at approximately 1520 °C. Such liquid phase helps not only the elongation of grains due to transformation of the α- to β-phase of Si_3N_4[18,19] but also the densification due to rearrangement of the grains. Furthermore, it should be noted that the increased amount of the liquid phase with temperature changes the elongated grain morphology to the plate-like grain morphology, and that the plate-like grains grow to be as large as approximately 4 μm.

The relative density of the $MgSiN_2$ compact with 4 mol% of Si_3N_4 addition decreases with hot-pressing temperature above 1600 °C, which suggests that the evaporation of the components may occur from surfaces of the hot-pressed $MgSiN_2$ compact. On the other hand, the relative density of the $MgSiN_2$ compact with 9 mol% of Si_3N_4 addition slightly increases with hot-pressing temperature. This phenomenon suggests that the evaporation of such components may be suppressed by the presence of Si_3N_4.

3.2. Mechanical and thermal properties

The mechanical and thermal properties of the $MgSiN_2$ compact with Si_3N_4 addition were examined. Fig. 5 shows the changes in the Vickers hardness of the $MgSiN_2$ specimen with Si_3N_4 addition, as a function of the hot-pressing temperature. The Vickers hardness values of the $MgSiN_2$ specimens with 4 and 9 mol% of Si_3N_4 addition were around 18 GPa, independent of the hot-pressing temperature. Present Vickers hardness values seem more to be slightly lower than those of the pure $MgSiN_2$ specimen (20.7 GPa)[5] and Si_3N_4 specimen (approximately 20 GPa).[19] The Vickers hardness may be affected by the relative density and amorphous/crystalline phases present in the hot-pressed $MgSiN_2$ specimen. Relative densities of the $MgSiN_2$ specimens with 4 and 9 mol% of Si_3N_4 addition are around 95% or higher and,

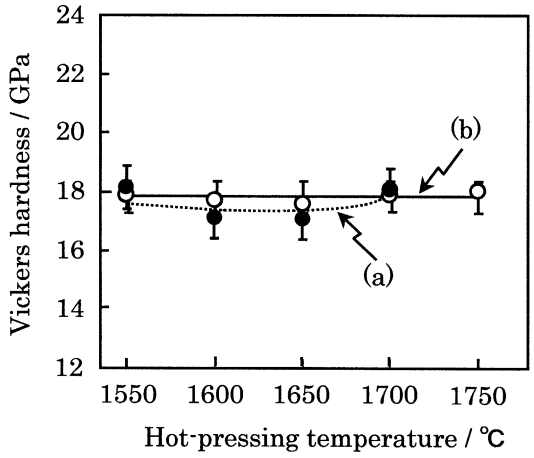

Fig. 5. Changes in the Vickers hardness of $MgSiN_2$ compact with (a) 4 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition and (b) 9 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition as a function of the hot-pressing temperature. Hot-pressing time and pressure: 90 min, 75 MPa.

therefore, the Vickers hardness seems to be lowered by the presence of reaction products, i.e., $Yb_2Si_3O_3N_4$, $Yb_2Si_3O_5N_2$, YbN, and amorphous materials.

The effect of the amount of Si_3N_4 addition on the average fracture toughness of the $MgSiN_2$ specimen is shown in Fig. 6, as a function of the hot-pressing temperature. The fracture toughness of the $MgSiN_2$ specimen without Si_3N_4 addition was 2.6 $MPa{\cdot}m^{1/2}$.

Fracture toughness values of the $MgSiN_2$ specimens with 4 and 9 mol% Si_3N_4 addition were highest at the hot-pressing temperature of 1600 °C, which may be based on the elongation of Si_3N_4 grains due to α- to β-phase transformation. The formation of elongated grains contributes to grain pull-out or crack branching, thereby enhancing the fracture toughness.[18] Decreases in fracture toughness with a further increase in hot-pressing temperature appear to be attributed to the change from elongated shapes into plate-like shapes and to the enhancement of bonding between $MgSiN_2$ matrix and elongated Si_3N_4 grains (see Fig. 3).

The effect of the Si_3N_4 addition on the thermal conductivity of the $MgSiN_2$ specimen is shown in Fig. 7. The thermal conductivities of the $MgSiN_2$ specimens with 9 mol% of Si_3N_4 addition hot-pressed at 1550 to 1650 °C were nearly the same as those with 4 mol% of Si_3N_4 addition. However, further increase in hot-pressing temperature resulted in enhancement of the thermal conductivity up to 34.1 $W\ m^{-1}\ K^{-1}$ at 1750 °C.

The thermal conductivity is affected not only by the relative density and grain size (see Figs. 2 and 3) but also by the oxygen content. For example, a typical nitrogen/oxygen content determination of the $MgSiN_2$ specimen with 9 mol% of Si_3N_4 addition hot-pressed at 1750 °C for 5 h revealed that the nitrogen content was 33.91 mass% (theoretical content: 34.84 mass%), whereas the oxygen content was only 0.51 mass%. To our knowledge, the resulting thermal conductivity of 34.1 $W\ m^{-1}\ K^{-1}$ is the highest among the values so far reported for $MgSiN_2$ ceramics.

Assuming that the Si_3N_4 grains are well-dispersed and, for the most part, not touching each other, the theoretical thermal conductivity of the $MgSiN_2$ specimen with Si_3N_4 addition may be obtained using the Maxwell–Eucken equation:[20]

$$\frac{\kappa_{M\text{-}S}}{\kappa_M} = \frac{2\kappa_M + \kappa_S + 2\Phi(\kappa_S - \kappa_M)}{2\kappa_M + \kappa_S - \Phi(\kappa_S - \kappa_M)} \quad (6)$$

where $\kappa_{M\text{-}S}$, κ_M, and κ_S are the thermal conductivities of the $MgSiN_2$ specimen with Si_3N_4 addition, $MgSiN_2$ matrix, and Si_3N_4 grains, respectively and Φ the volume fraction of Si_3N_4 grains. Incorporating the κ_M (assuming 26.1 $W\ m^{-1}\ K^{-1}$) and κ_S (assuming 140 $W\ m^{-1}\ K^{-1}$) into

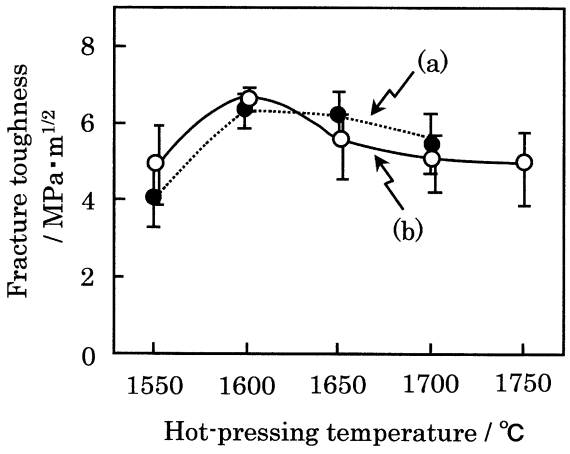

Fig. 6. Changes in the fracture toughness of $MgSiN_2$ compact with (a) 4 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition and (b) 9 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition as a function of the hot-pressing temperature. Hot-pressing time and pressure: 90 min, 75 MPa.

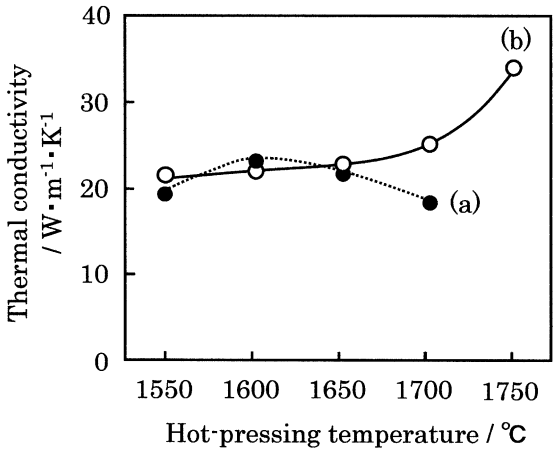

Fig. 7. Changes in the thermal conductivity at room temperature of $MgSiN_2$ compact with (a) 4 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition and (b) 9 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition as a function of the hot-pressing temperature. Hot-pressing time and pressure: 90 min, 75 MPa.

Eq. (6), the $\kappa_{M\text{-}S}$ is found from calculation to be 33.5 W m^{-1} K^{-1}. This value agrees well with the present maximum value (34.1 W m^{-1} K^{-1}) for the $MgSiN_2$ specimen with 9 mol% of Si_3N_4 addition hot-pressed at 1750 °C for 90 min. Such thermal conductivity of the $MgSiN_2$ specimen with Si_3N_4 addition may be enhanced by the higher relative density (96.9%), larger grain size (approximately 4 μm), and lower oxygen content (0.51%).

4. Conclusion

The effect of Si_3N_4 addition on the sintering and properties of magnesium silicon nitride ($MgSiN_2$) compacts has been examined using a hot-pressing technique. $MgSiN_2$ compacts with 1, 4, and 9 mol% of Si_3N_4 addition [sintering aid: 1 mol% of ytterbium oxide (Yb_2O_3)] were hot-pressed at a temperature between 1550 and 1800 °C for 90 min in a nitrogen (N_2) atmosphere under a pressure of 75 MPa. The results obtained were as follows:

1. The relative density of $MgSiN_2$ compact with 4 mol% of Si_3N_4 and 1 mol% Yb_2O_3 addition hot-pressed at 1600 °C for 90 min attained a maximum (98.6%). Although the relative densities of $MgSiN_2$ compacts with 9 mol% of Si_3N_4 and 1 mol% of Yb_2O_3 addition were approximately 95% in the hot-pressing temperature range between 1550 and 1650 °C, it increased to approximately 97% with hot pressing temperature up to 1750 °C.
2. The fracture toughness values of $MgSiN_2$ specimens with 4 and 9 mol% of Si_3N_4 addition hot-pressed at 1600 °C for 90 min were approximately 6.6 MPa·$m^{1/2}$ which is 2.5 times higher than the value (2.6 MPa·$m^{1/2}$) of a hot-pressed $MgSiN_2$ compact without Si_3N_4 addition. SEM micrographs showed the presence of elongated grains in these specimens. These elongated grains were formed by the presence of liquid phase during the hot pressing. The improvement of the fracture toughness was assumed to be due to the elongated Si_3N_4 grains.
3. The thermal conductivity of the $MgSiN_2$ specimen with 4 mol% of Si_3N_4 addition hot-pressed at 1600 °C for 90 min was 23.4 W m^{-1} K^{-1}. On the other hand, the thermal conductivity of the $MgSiN_2$ specimens with 9 mol% of Si_3N_4 addition hot-pressed at 1750 °C for 90 min increased to 34.1 W m^{-1} K^{-1}.

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