Properties of novel silicon nitride-based materials

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Abstract Our research on the mechanical and thermal properties of magnesium silicon nitride (MgSiN\textsubscript{2})-silicon nitride (Si\textsubscript{3}N\textsubscript{4}) composite specimens has been reviewed in this paper. The specimen was fabricated by hot-pressing the compressed powder at a temperature between 1550\degree C and 1700\degree C for 90 min under a pressure of 75 MPa in a nitrogen atmosphere, using 1 mol\% ytterbium oxide (Yb\textsubscript{2}O\textsubscript{3}) addition as a sintering aid. Mechanical and thermal properties of MgSiN\textsubscript{2} specimen without Si\textsubscript{3}N\textsubscript{4} addition were as follows: Vickers hardness, 18.3 GPa; flexural strength, 371 MPa; fracture toughness, 2.2 MPa-m\textsuperscript{1/2}; and thermal conductivity, 22.7 W-m\textsuperscript{-1.K}\textsuperscript{-1}. In order to improve these properties, MgSiN\textsubscript{2} composite was fabricated with the addition of 0–89 mol\% Si\textsubscript{3}N\textsubscript{4}. The fracture toughness of MgSiN\textsubscript{2} specimen could be enhanced by the addition of Si\textsubscript{3}N\textsubscript{4}, e.g., 6.6 MPa-m\textsuperscript{1/2} (4 mol\% Si\textsubscript{3}N\textsubscript{4} addition) and 8.7 MPa-m\textsuperscript{1/2} (49 mol\% Si\textsubscript{3}N\textsubscript{4} addition). An increase in fracture toughness of MgSiN\textsubscript{2}-Si\textsubscript{3}N\textsubscript{4} specimen was attributed to the elongation of Si\textsubscript{3}N\textsubscript{4} grains. Moreover, the thermal conductivity of MgSiN\textsubscript{2}-Si\textsubscript{3}N\textsubscript{4} specimen increased to 32.7 W-m\textsuperscript{-1.K}\textsuperscript{-1} for 29 mol\% Si\textsubscript{3}N\textsubscript{4} addition.

Keywords magnesium silicon nitride • silicon nitride • composite • densification • microstructure • mechanical properties • thermal properties

Introduction

Many researchers pay much attention to the new ceramics with excellent mechanical, electrical, thermal and optical properties. Some of the non-oxide ceramics have much possibility to fulfill these requirements rather than oxide ceramics, chiefly due to strong covalent bonding. On the basis of such respect, our research has been focused on the development of dense magnesium silicon nitride (MgSiN\textsubscript{2}) specimen, partly because this compound is regarded as the replacement of 2Al\textsuperscript{3+} in the AlN by Mg\textsuperscript{2+}/Si\textsuperscript{4+}, and partly because the magnesium and silicon recourses are abundant in the earth crust.

Slack [10] is a first researcher who predicted the high thermal conductivity of MgSiN\textsubscript{2}. On the basis of his prediction, Groen et al. [3] and Hintzen et al. [5] fabricated the dense MgSiN\textsubscript{2} ceramics by pressureless-sintering and hot-pressing techniques, respectively; however, the thermal conductivities did not exceed 20 W-m\textsuperscript{-1.K}\textsuperscript{-1} in both cases.

As these cases indicate, the fabrication of dense MgSiN\textsubscript{2} ceramic started with the attention to develop a novel inorganic material having high thermal conductivity. Such properties may not be obtained until dense MgSiN\textsubscript{2} ceramic with controlled microstructure is fabricated using an advanced sintering technique. On the other hand, Hayashi et al. [4] investigated the effect of MgSiN\textsubscript{2} addition on the densification of silicon nitride (Si\textsubscript{3}N\textsubscript{4}) powder, and found that the thermal conductivity of Si\textsubscript{3}N\textsubscript{4} ceramic with MgSiN\textsubscript{2} addition (sintering aid; Yb\textsubscript{2}O\textsubscript{3}) is as high as 142 W-m\textsuperscript{-1.K}\textsuperscript{-1}. This
fact suggests that the addition of Si₃N₄ to the MgSiN₂ ceramic must also contribute to enhancing the thermal conductivity as well as the fracture toughness of MgSiN₂ because the monolithic Si₃N₄ ceramic possesses excellent mechanical and thermal properties. On the basis of such background, this paper reviews our research on the fabrication of MgSiN₂-Si₃N₄ composite specimens with controlled microstructure, and mechanical/thermal properties of the resulting specimens.

**Experimental procedure**

The starting MgSiN₂ powder was prepared by the nitridation of magnesium silicide (MgSi; Mg/Si = 2.0) powder at 1350°C for 10 min in a nitrogen atmosphere. The resulting MgSi₃N₄ powder was mixed with 0 to 89 mol% Si₃N₄ (SN-E10; Ube Industries, Ube; α:β ratio > 95%, oxygen content < 2.0%, carbon content < 0.2%) and 1 mol% Yb₂O₃ (99.99% purity, Wako Pure Chemical, Osaka) in the presence of n-hexane. After drying, approximately 1.5 g of the mixed powder was uniaxially pressed at 30 MPa to fabricate a compact with a diameter of 20 mm and a thickness of 2 mm. Each compact was hot-pressed at a temperature between 1550°C and 1700°C for 90 min in a nitrogen atmosphere under a pressure of 75 MPa.

The relative density of hot-pressed specimen was calculated using the bulk and true densities; the bulk density was measured using the Archimedes method, while the true density was determined pycnometrically at 25.0°C after pulverizing the hot-pressed specimen. Crystalline phases in the hot-pressed specimen were examined using an X-ray diffractometer (XRD) (Model RINT2000, Rigaku, Tokyo) with monochromatic CuKα radiation at 40 kV and 40 mA. The magnesium and silicon contents in the hot-pressed specimen were determined using an energy dispersive X-ray spectroscope (EDX; Model EMAX5770, Horiba, Kyoto), whereas the oxygen and nitrogen contents were examined using an N/O determinator (Model TC-436, Leco, St. Joseph, MI, USA).

The microstructure of hot-pressed specimen was investigated using a field-emission scanning electron microscope (FE-SEM; Model S-4500, Hitachi, Tokyo). The Vickers hardness (Hᵥ) was measured using an indentation load of 9.81 N for 15 s (Model MVK-E, Akashi, Tokyo). Moreover, the fracture toughness (Kᵥc) of a specimen with sizes of 15 × 2.5 × 3 mm² was measured using a single-edge notched beam technique; the specimen was fabricated by cutting the sintered specimen. The thermal diffusivity was measured at room temperature, using a laser-flash technique (Model TC-7000, Shinku-Riko, Tokyo). On the basis of thermal diffusivity data, the thermal conductivity was calculated using specific heats of MgSiN₂ (61.71 J·mol⁻¹·K⁻¹) [1, 2] and β-Si₃N₄ (90.68 J·mol⁻¹·K⁻¹) [1].

**Results and discussion**

We first examined the properties of high-purity MgSiN₂ powder prepared by the reaction of MgSi with nitrogen. Typical density and specific surface area of the MgSiN₂ powder were 3.102 g·cm⁻³ and 16.8 m²·g⁻¹, respectively. The primary particle size, calculated on the basis of these data, was 0.12 μm, while the crystal size calculated on the basis of the broadening of XRD reflection was 0.042 μm (42 nm). The chemical composition of this MgSiN₂ powder was examined [14], together with the data on carbothermic reduction of magnesium metasilicate (MgSiO₃) [15] and solid-state reaction of Mg₂N₂ with Si₃N₄ [3]. The magnesium and silicon contents were in accordance with those of theoretical contents, independent of the preparation technique. On the other hand, the oxygen contents in the MgSiN₂ powders were varied, according to the preparation technique: 0.61% (present technique; direct nitridation) < 2.54% (carbothermal reduction [15]) < 3.7% (solid-state reaction [3]). As the above data indicate, the amount of oxygen in the present powder is comparatively low. The contamination of oxygen seems to be minimized by the nitridation of MgSiN₂ from MgSi, except for the case that the small amount of oxygen is inevitably included in the starting magnesium and silicon powders used for the preparation of MgSi.

By making use of this MgSiN₂ powder, we examined the fabrication conditions of dense MgSiN₂ ceramic, using Yb₂O₃ as a sintering aid. This Yb₂O₃ was selected for the sintering aid, because the thermal conductivity of MgSiN₂ ceramic with 1 mass% of Yb₂O₃ addition showed a maximum (26.6 W·m⁻¹·K⁻¹) among the rare-earth oxides (Y₂O₃, La₂O₃, Nd₂O₃, Sm₂O₃, Gd₂O₃, Er₂O₃, and Yb₂O₃) examined previously [12].

The relative density of MgSiN₂ specimen hot-pressed at 1550°C for 90 min attained 98.0%. Mechanical properties of this ceramic were as follows: Vickers hardness, 18.3 GPa; flexural strength, 371 MPa; and fracture toughness, 2.2 MPa·m⁰.⁵². These mechanical properties are similar to those reported by Groen et al. [3], e.g., (i) Vickers hardness of 14–16 GPa, (ii) flexural strength of 230–280 MPa, and (iii) fracture toughness of 3.1–4.4 MPa·m⁰.⁵². Relating to the mechanical properties of Si₃N₄ ceramic or a typical material for engine components, Vickers hardness is 17.7–20 GPa, whereas the flexural strength and fracture toughness are 980 MPa and 7–8 MPa·m⁰.⁵², respectively [13]. Thus Vickers hardness is almost comparable to that of the Si₃N₄ ceramic, but both flexural strength and fracture toughness are somewhat lower than the case of Si₃N₄ ceramic.

On the basis of research by Hayashi et al. [4], who succeeded in the enhancement of thermal conductivity of Si₃N₄ ceramic to 142 W·m⁻¹·K⁻¹ owing to the addition of MgSiN₂, we examined the fabrication conditions of dense MgSiN₂ specimens with Si₃N₄ addition.

As a typical case, the effect of hot-pressing temperature on the relative density of MgSiN₂ specimen with 4 mol% Si₃N₄ addition is shown in Fig. 1 [11]. Although the relative density of this specimen was 94.3% at 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.

Typical FE-SEM micrographs of the fracture surfaces of hot-pressed MgSiN₂ specimens with 4 mol%
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Si$_3$N$_4$ addition are shown in Fig. 2 [11]. The elongated grains were randomly present in the MgSiN$_2$ matrix at 1600°C (Fig. 2a), whereas the elongated grains stuck together to the MgSiN$_2$ matrix at 1700°C (Fig. 2b).

The above elongation and sticking 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 chemical reaction at the interfaces (sticking of grains to the matrix). The elongation of grains must be related to the reaction process among MgSiN$_2$, Si$_3$N$_4$, and Yb$_2$O$_3$ during the hot pressing. Then the crystalline phases of these MgSiN$_2$ specimens were examined using XRD. The crystalline phases at 1600°C were MgSiN$_2$ (JCPDS Card No. 25-530), β-Si$_3$N$_4$ (JCPDS Card No. 33-1160), Yb$_5$Si$_3$O$_4$N$_6$ (JCPDS Card No. 32-1423) and Yb$_5$Si$_3$O$_5$N$_2$ (JCPDS Card No. 31-1454). The reaction of MgSiN$_2$ with Yb$_2$O$_3$ may, therefore, occur as follows:

(1) 3MgSiN$_2$ + Yb$_2$O$_3$ → Yb$_2$Si$_3$O$_4$N$_4$ + Mg$_3$N$_2$

(2) 3MgSiN$_2$ + 2Yb$_2$O$_3$ → Yb$_2$Si$_3$O$_4$N$_4$ + 2YbN + Mg$_3$N$_2$ + ½O$_2$

Although Mg$_3$N$_2$ was not detected by XRD, it seems to partly be decomposed and/or evaporated during the hot pressing. In addition to these solid-state reactions, Si$_3$N$_4$ may react with Yb$_2$O$_3$ to form Yb$_2$Si$_3$O$_4$N$_4$ and Yb$_5$Si$_3$O$_5$N$_2$:

(3) Si$_3$N$_4$ + Yb$_2$O$_3$ → Yb$_2$Si$_3$O$_4$N$_4$

(4) 3Si$_3$N$_4$ + 5Yb$_2$O$_3$ → 3Yb$_2$Si$_3$O$_4$N$_2$ + 4YbN + N$_2$

The densification of MgSiN$_2$ specimen with Si$_3$N$_4$ and Yb$_2$O$_3$ addition seems to occur along with the formation of liquid phase. With respect to the liquid composition, Inomata et al. [6] pointed out that an eutectic liquid in the Si$_3$N$_4$-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$_3$N$_4$ [8, 9] but also the densification due to rearrangement of the grains. The relative density of MgSiN$_2$ specimen with 4 mol% Si$_3$N$_4$ addition decreases with hot-pressing temperature above 1600°C, which suggests that the thermal decomposition may proceed from surfaces to the inside of MgSiN$_2$ specimen during the hot pressing.

Vickers hardness of the MgSiN$_2$ specimen with 4 mol% Si$_3$N$_4$ addition was examined, as a function of the hot-pressing temperature. Although the Vickers hardness of the MgSiN$_2$ specimen with 4 mol% Si$_3$N$_4$ addition was 18.2 GPa at 1550°C, no appreciable changes in Vickers hardness were observed, regardless of an increase in hot-pressing temperature from 1650°C up to 1700°C.

Effect of the Si$_3$N$_4$ addition on the fracture toughness of MgSiN$_2$ specimen is shown in Fig. 3, as a function of the hot-pressing temperature [11]. On the other hand, the fracture toughness of MgSiN$_2$ specimen with 4 mol% Si$_3$N$_4$ addition increased to 6.6 MPa-m$^{1/2}$ with hot-pressing temperature up to 1600°C. On further increases in hot-pressing temperature, however, the fracture toughness was slightly reduced down to 5.1−5.5 MPa-m$^{1/2}$.

Fracture toughness of the MgSiN$_2$ specimens with 4 mol% Si$_3$N$_4$ addition was the highest at the hot-pressing temperature of 1600°C, which may be related to the elongation of Si$_3$N$_4$ grains due to α- to β-phase transformation. The formation of elongated grains contributes to de-bonding during the crack propagation, thereby enhancing the fracture toughness [9]. Decreases
in fracture toughness with a further increase in hot-pressing temperature may be attributed to the changes of elongated shapes into plate-like shapes and to the enhancement of bonding between MgSiN$_2$ matrix and elongated Si$_3$N$_4$ grains.

In order to make clear the effect of Si$_3$N$_4$ addition, we furthermore investigated the mechanical and thermal properties of MgSiN$_2$ specimens with Si$_3$N$_4$ addition to 89 mol%. Figure 4 shows the changes in relative density of the hot-pressed MgSiN$_2$ specimen with increasing amount of Si$_3$N$_4$ [7]. Although the relative density of MgSiN$_2$ specimen without Si$_3$N$_4$ addition was 98.0%, it was reduced down to 94% for the case of 49 mol% Si$_3$N$_4$. Nearly full density was, however, achieved with a further increase in amount of Si$_3$N$_4$ to 69 mol% or more. Although the relative density showed a minimum for the case of 49 mol% Si$_3$N$_4$, it should be noted that the relative densities always exceed 94%.

Figure 5 shows a typical FE-SEM micrograph of the hot-pressed MgSiN$_2$ specimen with 49 mol% Si$_3$N$_4$ and 1 mol% Yb$_2$O$_3$ addition [7]. The hot-pressed MgSiN$_2$ specimen was composed of the polyhedral grains with sizes of approximately 1 µm and elongated grains. The hot-pressed MgSiN$_2$ specimen without Si$_3$N$_4$ addition was composed of the grains with sizes of 1 µm. The elongated grains formed by the incorporation of Si$_3$N$_4$ are assumed to be Si$_3$N$_4$, because they did not exist until the MgSiN$_2$ specimen was hot-pressed by the incorporation of Si$_3$N$_4$. These elongated grains seem to be formed in the presence of liquid phase during the hot pressing.

Figure 6 shows the changes in flexural strength of the MgSiN$_2$ specimen with increasing amount of Si$_3$N$_4$ [7]. The flexural strength of MgSiN$_2$ specimen without Si$_3$N$_4$ addition was 371 MPa. The flexural strength of MgSiN$_2$ specimen increased with increasing amount
of Si$_3$N$_4$ and attained 1000 MPa (1 GPa) for the case of 89 mol% Si$_3$N$_4$.

An increase in flexural strength of the MgSiN$_2$ specimen with increasing amount of Si$_3$N$_4$ to 49 mol% may be related to the elongation of Si$_3$N$_4$ grains on the basis of the α- to β-phase transformation. Moreover, a further increase in flexural strength due to the incorporation of 49 mol% or more Si$_3$N$_4$ addition seems to be ascribed to the increase in relative density.

Figure 7 shows the changes in fracture toughness of MgSiN$_2$ specimen with increasing amount of Si$_3$N$_4$ [7]. The fracture toughness of MgSiN$_2$ specimen without Si$_3$N$_4$ addition was 2.2 MPa-m$^{1/2}$. The fracture toughness of the MgSiN$_2$ specimen increased with increasing amount of Si$_3$N$_4$ and attained 8.7 MPa-m$^{1/2}$ for 49 mol% Si$_3$N$_4$ addition. On further increase in amount of Si$_3$N$_4$ however, the fracture toughness was slightly reduced.

The highest fracture toughness of MgSiN$_2$ specimen with 49 mol% Si$_3$N$_4$ addition also seems to be ascribed to the elongation of Si$_3$N$_4$ grains. As mentioned before, the formation of elongated grains contributes to debonding during the crack propagation [9], thereby enhancing the fracture toughness. Decreases in fracture toughness with a further increase in amount of Si$_3$N$_4$ may be explained in terms of the shortening of elongated grains, due to the reaction of Si$_3$N$_4$ with MgSiN$_2$ matrix. The thermal conductivity of MgSiN$_2$ specimen increased with increasing amount of Si$_3$N$_4$ addition and attained 32.7 W-m$^{-1}$K$^{-1}$ for 29 mol% Si$_3$N$_4$ addition. On further increase in amount of Si$_3$N$_4$, however, the thermal conductivity was slightly reduced.

The thermal conductivity is affected not only by the relative density and grain size but also by the oxygen content. With reference to the oxygen content, the oxygen content of the MgSiN$_2$ specimen with 4 mol% Si$_3$N$_4$ addition hot-pressed at 1600°C for 90 min was only 0.4 mass%. Thus the changes in thermal conductivity of the MgSiN$_2$ specimen with Si$_3$N$_4$ addition must be chiefly related to the changes in microstructure. Further examination is, however, needed in order to make clear this phenomenon.

**Conclusion**

Our research on the mechanical and thermal properties of magnesium silicon nitride (MgSiN$_2$)-silicon nitride (Si$_3$N$_4$) composite specimens has been reviewed in this paper. MgSiN$_2$ compacts with 1–89 mol% of Si$_3$N$_4$ and 1 mol% ytterbium oxide (Yb$_2$O$_3$; sintering aid) addition were hot-pressed at a temperature between 1550°C and 1700°C for 90 min in a nitrogen (N$_2$) atmosphere under the pressure of 75 MPa. The results obtained were summarized as follows:

1. Mechanical and thermal properties of MgSiN$_2$ specimen without Si$_3$N$_4$ addition but with 1 mol% Yb$_2$O$_3$ addition (sintering aid) hot-pressed at 1550°C for 90 min were as follows: Vickers hardness, 18.3 GPa; flexural strength, 371 MPa; fracture toughness, 2.2 MPa-m$^{1/2}$; and thermal conductivity, 22.7 W-m$^{-1}$K$^{-1}$.

2. The fracture toughness of MgSiN$_2$ specimen with 4 mol% of Si$_3$N$_4$ and 1 mol% Yb$_2$O$_3$ addition hot-pressed at 1600°C for 90 min was 6.6 MPa-m$^{1/2}$, which was three times higher than the value of the hot-pressed MgSiN$_2$ specimen without Si$_3$N$_4$ addition (2.2 MPa-m$^{1/2}$). The maximum fracture toughness of MgSiN$_2$ specimen (8.7 MPa-m$^{1/2}$) was obtained by the addition of 49 mol% Si$_3$N$_4$. The enhancement of fracture toughness seemed to be attributed to the elongation of Si$_3$N$_4$ grains. The thermal conductivity of MgSiN$_2$ specimen increased with increasing amount of Si$_3$N$_4$ addition and attained 32.7 W-m$^{-1}$K$^{-1}$ for 29 mol% Si$_3$N$_4$ addition.

**References**


