Formation and Microstructure of Silicide-Particle-Reinforced Si₃N₄ Composites with Crystallized Grain Boundary Phase of Yb₂Si₂O₇

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Silicide-particle-reinforced Si₃N₄ composites with a crystallized grain boundary phase of Yb₂Si₂O₇ were synthesized in-situ by hotpressing Si₃N₄ with the metal oxides M₂O₃ (silicide-forming oxides), which can react with Si₃N₄ to form silicide, and Yb₂O₃ as sintering additives. The reaction between Si₃N₄ and silicide-forming oxide (Ta₂O₅ or MoO₃) and Yb₂O₃ at high temperatures generated silicide (Ta₃Si or Mo₃Si₄) particles and a grain boundary phase, Yb₂Si₂O₇, simultaneously. The silicide particles mainly existed at the grain boundaries, but a small amount of Ta₃Si particles were detected from Si₃N₄ grains. Ta₃Si particle grew up to a polyhedron shape, but Mo₃Si₄ particle to a spherical shape. To obtain the crystallized grain boundary phase of RE₂Si₂O₇, the molar ratio of Yb₂O₃ to M₂O₃ should be adjusted to q/4 (q: the number of oxygen atoms in M₂O₃). However, because a small amount of oxygen was included in Si₃N₄ powder and existed on the surface of Si₃N₄ as SiO₂, the excess SiO₂ reacted with Si₃N₄ to generate a trace of Si₃N₄O grain. In the silicide–Yb₂Si₂O₇–Si₃N₄ composites, the grain boundary phases were crystalized, but thin amorphous films with a thickness of 1 nm were detected from the interfaces between the silicide particle, Si₃N₄ grain, and the grain boundary phase of Yb₂Si₂O₇. The dense silicide particles reinforced Si₃N₄ matrix composites can be obtained by using this in-situ synthesis method, and the flexural strength and fracture toughness of Ta₃Si–Yb₂Si₂O₇–Si₃N₄ composite were 1209 MPa, and 6.0 MPa·m¹/², respectively.

Key-words: Silicide, Ta₃Si, Mo₃Si₄, Yb₂Si₂O₇, Si₃N₄, Particle, Composite, Grain boundary phase, Crystallization

1. Introduction

Si₃N₄-based ceramics are promising materials for structural components because of their high strength, high toughness, low density, and excellent wear resistance. However, the use of Si₃N₄ at temperatures above 1300 °C in the oxidizing environments is difficult due to the severe oxidation. Generally, Si₃N₄ is fabricated by adding sintering additives such as MgO, Al₂O₃, and Y₂O₃, and thus grain boundary glassy phases were generated during sintering.1–6 When Si₃N₄ oxidizes at an elevated temperature, SiO₂ layer is formed on the surface, and subsequently react with sintering additives to form Y₃Si₂O₇ or MgSiO₄, respectively.1–6 The penetration of oxygen into the material and the segregation of the sintering-additive cations from the grain boundary glassy phase into the surface oxide scale cause severe oxidation and a rapid decrease in strength. To improve the oxidation resistance of Si₃N₄, the minimization of the amount of grain boundary glassy phase, the incorporation of non-oxide ceramic particles into the grain boundary glassy phase, and the crystallization of the grain boundary phase have been studied.7–22 By adding the rare-earth oxide (RE₂O₃) and SiO₂ to Si₃N₄ and adjusting the mole ratio of RE₂O₃ to SiO₂, the grain boundary phases of RE₂Si₂O₇ or RE₅Si₃O₇ were generated by the post-heat treatment after sintering.7–10,13–14 Si₃N₄ with the crystallized grain boundary phase of RE₂Si₂O₇ showed the best oxidation resistance and high-temperature behavior among the Si₃N₄ based materials.5–14,22 Although the oxidation behavior of Si₃N₄ can not be improved greatly by incorporating the Mo₃Si₄ particles into the grain boundary glassy phase, the mechanical properties of Si₃N₄ were greatly improved.21–23

To achieve the in-situ generation of Mo₃Si₄ particles and the crystallization of the grain boundary phase, MoO₃ and Yb₂O₃ have been added to Si₃N₄ as sintering additives, and a Mo₃Si₄ particle reinforced Si₃N₄ composite with a crystallized grain boundary phase of Yb₂Si₂O₇ has been developed.24–25 The reaction between MoO₃ and Si₃N₄ at high temperatures not only generated the Mo₃Si₄ particle but also supplied SiO₂ source for the formation of Yb₂Si₂O₇. It is thought that a series of silicide-particle-reinforced Si₃N₄ composites with a crystallized grain boundary phase of RE₂Si₂O₇ can be synthesized if other metal oxides (silicide-forming oxides) and rare-earth oxides are added to Si₃N₄. As the silicide, there are tens of kinds, and tantalum silicide shows the highest melting point among them.26

In this present study, tantalum silicide-particle-reinforced Si₃N₄ composite with a crystallized grain boundary phase was fabricated, and the microstructure was analyzed. For comparison, Mo₃Si₄–Yb₂Si₂O₇–Si₃N₄ composites were also fabricated. In addition, the fabrication route for other silicide (M₃Si₄)–particle-reinforced Si₃N₄ composites with the crystallized grain boundary phase of RE₂Si₂O₇ was discussed.

2. Experimental procedure

2.1 Design of the reaction

Si₃N₄ (SN–E10, UBE Industries Co., Ltd.), rare-earth oxide (Yb₂O₃, RU–P, Shin-Etsu Chemical Co., Ltd.), and silicide-forming oxide powders (Ta₂O₅ or MoO₃, Pure Chemi-
cal Co., Ltd.) were used for fabricating the composites. Because Mo$_x$Si$_y$ or Fe$_x$Si$_y$ particles were generated when MoO$_3$ or Fe$_2$O$_3$ was added to Si$_3$N$_4$, the following equation is considered to be occurring during sintering in this study:

$$a \text{RE}_2\text{O}_3 + b \text{M}_2\text{O}_3 + c \text{Si}_3\text{N}_4 = a\text{RE}_2\text{Si}_3\text{O}_7 + pb\text{M}_4\text{Si}_p + 2c \text{N}_2$$

(1)

where RE is a rare-earth element, and M is a metal element, which can react with silicon to form a silicide ($\text{M}_x\text{Si}_y$). For Eq. (1), the mole ratio of RE$_2$O$_3$ to M$_2$O$_3$ can be determined by the equilibrium of oxygen as given by the following equation regardless of the type of silicide:

$$a/b = q/4$$

(2)

where $q$ is the number of oxygen atoms in silicide-forming oxide. For the additives of Yb$_2$O$_3$ and Ta$_2$O$_5$, the molar ratio of Yb$_2$O$_3$ to Ta$_2$O$_5$ was 1.25. However, because the MoO$_3$ would be decomposed to form Mo$_2$O$_3$ and O$_2$, the molar ratio of Yb$_2$O$_3$ to MoO$_3$ should be calculated from the reaction between Si$_3$N$_4$, MoO$_3$, and Yb$_2$O$_3$, and it was found to be 0.5. According to the calculated results, 2.93 mol% Yb$_2$O$_3$ and 2.34 mol% Ta$_2$O$_5$ ($\text{Yb/Ta}=1.25$), 2.83 mol% Yb$_2$O$_3$ and 5.66 mol% MoO$_3$ ($\text{Yb/Mo}=0.5$) powders were mixed with Si$_3$N$_4$, and ball-milled in ethanol for 24 h. After ball milling, the powder mixtures were dried at 230°C, and then were hot-pressed in a graphite die at 1800°C with an applied pressure of 30 MPa in flowing N$_2$ atmosphere for 1 h.

For the equilibrium of Eqs. (1) and (2), there is assumption that the raw powders do not contain impurities. However, 1.2 mass% of oxygen was actually included in the commercial Si$_3$N$_4$ powder, and some of them existed on the surface of Si$_3$N$_4$ as silicon oxide. Therefore, the amount of SiO$_2$ will be too much for the crystallization of the grain boundary phase when the powders of rare-earth oxide and silicide-forming oxide are mixed as indicated in Eq. (2). To improve the crystallization of the grain boundary phase, it is necessary to consider the influence of SiO$_2$ included in the Si$_3$N$_4$ powder, and to increase the molar ratio of the rare-earth oxide to the silicide-forming oxide relative to Eq. (2). To confirm this, the molar ratio of Yb$_2$O$_3$ to MoO$_3$ has been increased from 0.5 to 0.75, and 2.89 mol% Yb$_2$O$_3$ and 3.85 mol% MoO$_3$ powders ($\text{Yb/Mo}=0.75$) were mixed to Si$_3$N$_4$ to prepare the powder mixture. The mixed powder was sintered under the same condition as the above-mentioned.

2.2 Microstructural characterization and mechanical properties

The phases were identified by X-ray diffractionometry (XRD; Model MXP 18, MacScience Co., Ltd., Yokohama), and the microstructures were characterized by scanning electron microscopy (SEM; Model JSM-5800LV, JEOL, Tokyo) equipped with energy-dispersive X-ray spectrometry (EDS; Model Link ISIS, Oxford Instruments, Oxford, U.K.) and transmission electron microscopy (TEM). For SEM observations, the sintered composites were cut and polished, and some of the polished samples were plasma-etched using a carbon tetrafluoride (CF$_4$) gas. TEM specimens were prepared by diamond cutting, mechanical grinding, dimpling, and ion-thinning. Electron-transparent foils were examined in a TEM (Model JEM-2000FX, JEOL) equipped with EDS (Model Link ISIS, Oxford Instruments, Oxford, U.K.), and high-resolution structural images were obtained by high-resolution transmission electron microscopy (HRTEM; Model JEM-4000, JEOL) operating at 400 kV. In the present study, a 3 nm diameter electron probe was used for the EDS analysis. Before the EDS analysis, the samples were coated with carbon.

The densities of the sintered composites were measured using Archimedes method. The sintered plates were cut into 3 mm × 4 mm × 40 mm rectangular cross-sectioned bars for four-point bending strength measurement, with an outer span of 30 mm and an inner span of 10 mm, at a crosshead speed of 0.5 mm/min. Vickers microhardness indentation testing was used to investigate the microhardness and to evaluate the fracture toughness of the composites. A 196 N indentation load was used to measure the microhardness, and the fracture toughnesses of the composites were calculated from the crack-lengths and microhardness values, according to JIS R 1607.

3. Results and discussion

3.1 In-situ formation of silicide ($\text{M}_x\text{Si}_y$)–Yb$_2$Si$_3$O$_7$–Si$_3$N$_4$ composites

The powder mixture of Si$_3$N$_4$, Yb$_2$O$_3$, and Ta$_2$O$_5$ was hot-pressed at 1800°C for 1 h in flowing N$_2$ atmosphere. Figure 1 shows the XRD pattern of the sintered Si$_3$N$_4$ composite. The phases of $\beta$-Si$_3$N$_4$, $\alpha$-Si$_3$N$_4$, Yb$_2$Si$_3$O$_7$, Si$_3$N$_4$, and Ta$_2$Si were identified from the sintered composite (denoted as Ta$_2$Si–Yb$_2$Si$_3$O$_7$–Si$_3$N$_4$ composite). $\beta$-Si$_3$N$_4$, Yb$_2$Si$_3$O$_7$, Si$_3$N$_4$, and Ta$_2$Si were generated during sintering, but a small amount of $\alpha$-Si$_3$N$_4$ still remained in the composite. Because the peaks of Si$_3$N$_4$ were overlapped with the peak of $\alpha$-Si$_3$N$_4$ at $d$ = 0.336 nm (2$\theta$ = 26.5°) and the peak of Yb$_2$Si$_3$O$_7$ at $d$ = 0.444 nm (2$\theta$ = 20°), it is difficult to determine the Si$_3$N$_4$O from the XRD pattern accurately.

To understand the reaction between Si$_3$N$_4$, Yb$_2$O$_3$, and Ta$_2$O$_5$, the powder mixture was calcined at 1500°C for 1 h in flowing N$_2$ atmosphere. After calcination, the powder mixture was analyzed by XRD, and the formation of SiO$_2$ was confirmed. It is thought that Ta$_2$O$_5$ reacts with Si$_3$N$_4$ to generate Ta$_2$Si and the intermediate product of SiO$_2$ as shown in Eq. (3) during sintering. However, the intermediate product SiO$_2$ reacts with Yb$_2$O$_3$, and generated the eutectic liquid phase of Yb$_2$Si$_3$O$_7$ at the grain boundary as shown in Eq. (4). This liquid phase enhanced the densification and the growth of Si$_3$N$_4$ grains. Therefore, the reaction between Yb$_2$O$_3$, Ta$_2$O$_5$, and Si$_3$N$_4$ can be expressed as Eq. (5). It is obviously that the formation of the eutectic liquid phase of Yb$_2$O$_3$–SiO$_2$ and then the crystallization of the grain boundary phase Yb$_2$Si$_3$O$_7$ were supported by mixing Ta$_2$O$_5$ and Yb$_2$O$_3$ powders stoichiometrically.

$$19\text{Si}_3\text{N}_4 + 18\text{Ta}_2\text{O}_5 = 12\text{Ta}_2\text{Si} + 45\text{SiO}_2 + 38\text{N}_2$$

(3)
Yb2O3 + 2SiO2 = Yb2Si2O7 
45Yb2O3 + 36Ta2O3 + 38Si3N4 = 45Yb6Si13O12 + 24Ta3Si + 76N2

For the pure raw materials, the reaction between Si3N4, Yb2O3, and Ta2O5 would be occur as the Eq. (5). However, because Si3N4 powder contained a small amount of oxygen, which existed on the surface of Si3N4 as SiO2, the equilibrium of reactions would be changed. In this study, although the rare-earth oxide and silicide-forming oxide were mixed stoichiometrically as given by Eq. (2), the amount of SiO2, which is necessary for the crystallization of the grain boundary phase, was too much owing to the purity of Si3N4 powder, and the excess SiO2 reacted with Si3N4 to form Si3N4O as the following equation.

Si3N4 + SiO2 = 2Si3N4O

The reaction among Si3N4, Ta2O5, and Yb2O3 at high temperatures generated TaSi particles and the grain boundary phase of Yb2Si3O5 simultaneously, but a trace of Si3N2O was also generated.

Figure 2 shows the XRD patterns of the hot-pressed Mo2Si1−Yb2Si3O5−Si3N4 composites. The peaks of β-Si3N4, α-Si3N4, Yb2Si3O5, Si3N4O, and Mo2Si1 were detected. When the additive of Mo2Si1 was added instead of Ta2O5, the phase of Mo2Si1 was identified (denoted as Mo2Si1−Yb2Si3O5−Si3N4 composite). During sintering, an in-situ reaction occurred among Si3N4, Mo2Si1 and Yb2O3, and Mo2Si1 and Yb2Si3O5 were generated as given by the following equation.

75Yb2O3 + 150Mo2Si1 + 80Si3N4
= 75Yb6Si13O12 + 30Mo2Si1 + 160N2

On the basis of the same reason as for the Ta2Si1−Yb2Si3O5−Si3N4 composite, the peaks of Si3N2O were also observed from the Mo2Si1−Yb2Si3O5−Si3N4 (M/Mo = 0.5) composite (Fig. 2 (a)), which was sintered with the additives of 2.83 mol% Yb2O3 and 5.66 mol% Mo2Si1. However, the peaks at d = 0.336 nm (2θ = 26.5°) and d = 0.444 nm (2θ = 20°) decreased for the Mo2Si1−Yb2Si3O5−Si3N4 (M/Mo = 0.75) composite (Fig. 2 (b)), which was sintered with the additives of 2.89 mol% Yb2O3 and 3.85 mol% Mo2Si1. As discussed above, because the peaks of Si3N2O overlapped with those of α-Si3N4 and Yb2Si3O5 at d = 0.336 nm and d = 0.444 nm, it is difficult to judge whether the peaks originated from Si3N2O. However, because these two peaks decreased with increasing molar ratio of Yb2O3 to Mo2Si1, it is obvious that an increase in the molar ratio of Yb2O3 to Mo2Si1 can obstruct the generation of Si3N2O.

On the other hand, the residual α-Si3N4 phase was also found from the Mo2Si1−Yb2Si3O5−Si3N4 composites, but the amounts of the residual α-Si3N4 in the Mo2Si1−Yb2Si3O5−Si3N4 composites were less than that in the Ta2Si1−Yb2Si3O5−Si3N4 composite. When the holding time was extended from 1 h to 4 h during sintering at 1800°C for Mo2Si1−Yb2Si3O5−Si3N4 (M/Mo = 0.5) composite, no peaks of α-Si3N4 were detected from the XRD pattern. It is thought that the amount of the residual α-Si3N4 would depend on the sintering additives, sintering temperature and holding times at the sintering temperature.

For the previous Mo2Si1−Yb2Si3O5−Si3N4 composite, which sintered at 1850°C in 19.6 MPa N2 atmosphere, although the addition of Mo2Si1 was more than that in this study, the generation of Si3N2O was hardly observed.24 Because silicon oxide was not detected form the Mo2Si1−Yb2Si3O5−Si3N4 composite sintered by using the gas-pressure sintering method,24 it is thought that the excess SiO2 would be consumed easily for the formation of the amorphous phase at the grain boundary pocket and the amorphous films between the Mo2Si1 particles, the grain boundary phase of Yb2Si3O5, and Si3N4 grains for promoting the sintering of Si3N4. However, excess SiO2 would react with Si3N4 to generate the Si3N2O grains under the hotpressing sintering condition in this present study.

3.2 Microstructure of silicide (M(Si))−Yb2Si3O5−Si3N4 composites

Figure 3 shows a SEM micrograph and a TEM micrograph of a Ta2Si1−Yb2Si3O5−Si3N4 composite. The microstructure of the sintered composite consisted of randomly oriented elongated Si3N4 grains, polyhedron-shaped TaSi particles, and grain boundary phases of Yb2Si3O5. The white particles shown in Fig. 3 (a) and the black ones shown in Fig. 3 (b) were polyhedron-shaped and spherical TaSi particles. Some of large aggregations were found in the Fig. 3 (a). According to the EDS analysis result, these large grains were Si3N2O.

Figure 4 shows a TEM micrograph, along with EDS analysis results for Ta2Si1−Yb2Si3O5−Si3N4 composite. Figures 4 (b), (c) and (d) are EDS spectra obtained from the points 1, 2, and 3 in Fig. 4 (a), respectively. The elongated grain (labeled "1") contains only silicon and nitrogen; the black particle (labeled "2") contains silicon and tantalum, and the grain boundary phase (labeled "3") contains ytterbium, silicon, and oxygen. Clearly, the elongated grain is Si3N4, the black polyhedron-shaped particle is Ta2Si1, and the grain boundary phase is Yb2Si3O5. Figure 5 shows another TEM micrograph, along
with the EDS analysis result. Figure 5(b) is EDS spectrum obtained from the point 1 in Fig. 5(a). Because the EDS spectrum obtained from point 2 is similar with Fig. 4(b), it was omitted from the Fig. 5. The black circle particle (labeled “1”) which existed in the Si₃N₄ grain contains only silicon and tantalum, was Ta₃Si particle. It is obvious that some of Ta₃Si particles with a spherical shape were generated in Si₃N₄ grains. The polyhedron-shaped Ta₃Si particles with an average size of 0.3 μm resided at the grain boundary phases, but the spherical Ta₃Si particles with an average diameter of 30 nm resided in Si₃N₄ grains. 

Figure 6 shows HRTEM micrographs of the interfaces between Si₃N₄, Ta₃Si, and Yb₂Si₂O₇. The grain boundary phase was completely crystallized to Yb₂Si₂O₇ phase (Fig. 6(a)). However, some of thin amorphous films with a thickness of ~1 nm were detected from the interfaces between Si₃N₄, Ta₃Si, and Yb₂Si₂O₇. Because the thickness of the amorphous film was very thin, the chemical composition could not be analyzed by the energy-dispersive spectrometry (EDS) analysis, but it is thought that it was Si–N–O–Yb.
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Figure 6. HR-TEM images showing the interfaces between Ta₃Si particle, grain boundary phase of Yb₂Si₂O₅, and Si₃N₄ grain: (a) Si₃N₄ grain and grain boundary phase of Yb₂Si₂O₅ at a triple grain junction, (b) Ta₃Si-Si₃N₄ interface, (c) Ta₃Si-Si₃N₄-Ta₃Si interface, and (d) Si₃N₄-Si₃N₄ interface.

glass. Basically, Ta₃Si particles were generated at the grain boundary phase as a single crystal, but a small number of polycrystalline Ta₃Si particles were generated as shown in Fig. 6(c) and a thin amorphous film was also detected at the interface between two Ta₃Si particles. Because the formation of the grain boundary phase and the thin amorphous films at the interfaces between Si₃N₄, Ta₃Si, and Yb₂Si₂O₅ need a supply of SiO₂, it is necessary to mix SiO₂ formation additives, which can react with Si₃N₄ to form SiO₂ during sintering, with Si₃N₄ at an amount more than that needed for only the formation of Yb₂Si₂O₅. By considering the consumption of SiO₂ for the formation of such thin amorphous films, the molar ratio of RE₂O₃ to M₂O₅ (a/b) should be lower than q/4 for sintering the pure Si₃N₄ powder. However, because the Si₃N₄ powder contained a small amount of SiO₂, the molar ratio of RE₂O₃ to M₂O₅ (a/b) should be larger than q/4 for sintering the commercialized Si₃N₄ powder. Therefore, it is necessary to know the amount of SiO₂ in the Si₃N₄ powder accurately to decide the best dosage of the SiO₂ formation additives for sintering silicide (M(Si₃N₄))-particle-reinforced Si₃N₄ composites with the crystallized grain boundary phase.

Figure 7 shows SEM micrographs of the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ composites. Figures 7(a) and (c) show the microstructure of the polished surfaces, and Figs. 7(b) and (d) show the microstructure of the polished surfaces with plasma-etching. The microstructures of the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ composites consisted of randomly oriented elongated Si₃N₄ grains, spherical Mo₅Si₃ particles (white particles shown in Figs. 7(a) and (c)), and grain boundary phases. Because the etching speeds for Mo₅Si₃ and Si₃N₄ were different, the spherical voids were attributable to Mo₅Si₃ particles that were pulled out during plasma etching (Figs. 7(b) and (d)). Some exaggeratedly grown grain aggregations are found from the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ (Mₜ/Mₚ = 0.5) composite shown in Fig. 7(a). These large grain aggregations were analyzed by EDS, and were found to be Si₃N₂O grains. However, no Si₃N₂O grains were observed from the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ (Mₜ/Mₚ = 0.75) composite (Fig. 7(c)). For the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ (Mₜ/Mₚ = 0.75) composite, the XRD pattern suggested the possibility of the existence of Si₃N₂O, but the existence of Si₃N₂O cannot be detected during SEM observation using EDS. Although it is difficult to say that the generation of Si₃N₂O can be completely obstructed by increasing the molar ratio of Yb₂O₃ to MoO₂ from 0.5 to 0.75 due to the limitation of the SEM observation and EDS analysis, it is clearly that the generation of Si₃N₂O can be greatly controlled by increasing the molar ratio of Yb₂O₃ to MoO₂.

In the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ composites, fine spherical shaped Mo₅Si₃ particles, with an average diameter of 0.2 μm, resided in the grain boundary phase. Compared with that of the Ta₃Si particles, the shape of the Mo₅Si₃ particle changed greatly. Though the Ta₃Si and Mo₅Si₃ had the same tetragonal structure, Ta₃Si grow up to form the polyhedron particle and the Mo₅Si₃ to form the spherical particle. On the other hand, the growth speed of Si₃N₄ grains were faster in the Ta₃Si-Yb₂Si₂O₅-Si₃N₄ composite than in the Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ composite as shown in Fig. 3 and Fig. 7. Because the addition of Ta₂O₅ could accelerate the growth of Si₃N₄ grain, it is thought that the Ta₃Si particle could be trapped easily in Si₃N₄ grain compared with the Mo₅Si₃ particle.

Table 1 shows the mechanical properties of Ta₃Si-Yb₂Si₂O₅-Si₃N₄ and Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ composites. For the Ta₃Si-Yb₂Si₂O₅-Si₃N₄ (Mₜ/Tₚ = 1.25) and Mo₅Si₃-Yb₂Si₂O₅-Si₃N₄ (Mₜ/Mₚ = 0.5) composites, the densities were 3.49, and
ta the dense silicide-particle-reinforced Si respectively. By using this present in-situ synthesis method, Ta were achieved, respectively. The flexural strengths of the denser Si with high mechanical properties can be fabricated, but aatively higher strength was obtained. To obstruct the formation of Mo almost no influence on the sintering behavior, and a dense Mo composite. To understand the influence of the molar ratio of the amount of MoO, the molar ratio of Yb to MoO is small, there was almost no influence on the sintering behavior, and a dense MoSi–YbSi2O5–Si3N4 (M(Yb/Mo) = 0.75) composite with relatively higher strength was obtained. To obstruct the formation of Si3N2O, the molar ratio of Yb2O3 to MoO2 was raised from 0.5 to 0.75 in this study, but it is thought that further researches are needed for clarifying the influence of the mole ratio of Yb2O3 to MoO2 or the dosage of MoO2 on the sintering behavior, the crystallization of grain boundary phase, and the mechanical properties of the composite.

4. Conclusion
Silicide (M, Si)-particle-reinforced Si3N4 composites with a crystallized grain boundary phase were synthesized by sintering Si3N4 with the additives of rare-earth oxide (RE2O3: Yb2O3) and silicide-forming metal oxides (M2O3: MoO3, Ta2O5). To obtain the crystallized grain boundary phase of RE2SiO5, the mole ratio of RE2O3 to M2O3 should be adjusted to q/4 (q: the number of oxygen atoms in silicide-forming oxide). However, because a small amount of oxygen was included in the Si3N4 powder and existed on the surface of Si3N4 as SiO2, the SiO2 needed to generate Yb2Si2O5 was too much, where as the additives of Yb2O3 and M2O3 were mixed with the molar ratio of q/4, and Si2N4O was generated. To obstruct the generation of Si3N2O, it is necessary to reduce the amount of added silicide-forming metal oxide with respect to the calculated mixing value. When the mol ratio of Yb2O3 to MoO2 was increased from 0.5 (the calculated mixing value) to 0.75, the molar ratio of Yb2O3 to MoO2 was increased from 0.5 (the calculated mixing value)

Table 1. Mechanical Properties of Ta3Si–Yb2Si2O5–Si3N4 and Mo3Si–Yb2Si2O5–Si3N4 Composites

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Microhardness (GPa)</th>
<th>Flexural strength (MPa)</th>
<th>Fracture toughness (MPa·mⁱ/²)</th>
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<tr>
<td>Ta3Si–Yb2Si2O5–Si3N4 (M(Yb/Ta) = 1.25)</td>
<td>3.49</td>
<td>16.0</td>
<td>1209</td>
<td>6.0</td>
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<td>Mo3Si–Yb2Si2O5–Si3N4 (M(Yb/Mo) = 0.5)</td>
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<td>16.3</td>
<td>1004</td>
<td>5.6</td>
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<tr>
<td>Mo3Si–Yb2Si2O5–Si3N4 (M(Yb/Mo) = 0.75)</td>
<td>3.39</td>
<td>16.4</td>
<td>1059</td>
<td>5.3</td>
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</tbody>
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3.42 g/cm³, and 99.9% and 99.8% of the theoretical density were achieved, respectively. The flexural strengths of the Ta3Si–Yb2Si2O5–Si3N4 (M(Yb/Ta) = 1.25) and Mo3Si–Yb2Si2O5–Si3N4 (M(Yb/Mo) = 0.5) composites were 1209, and 1004 MPa, and the fracture toughness were 6.0, and 5.6 MPa·mⁱ/², respectively. By using this present in-situ synthesis method, the dense silicide-particle-reinforced Si3N4 matrix composites with high mechanical properties can be fabricated, but a denser Si3N4 composite can be obtained by adding Ta2O5. The Ta3Si–Yb2Si2O5–Si3N4 composite showed the higher mechanical properties compared with the Mo3Si–Yb2Si2O5–Si3N4 composite. To understand the influence of the molar ratio of Yb2O3 to MoO2 on the mechanical properties, the density and flexural strength of the Mo3Si–Yb2Si2O5–Si3N4 (M(Yb/Mo) = 0.75) composite were also measured, and were 3.39 g/cm³ (99.9% of theoretical density), 1059 MPa, respectively. Although the amount of MoO2 added was small, there was almost no influence on the sintering behavior, and a dense Mo3Si–Yb2Si2O5–Si3N4 (M(Yb/Mo) = 0.75) composite with relatively higher strength was obtained. To obstruct the formation of Si3N2O, the molar ratio of Yb2O3 to MoO2 was raised from 0.5 to 0.75 in this study, but it is thought that further researches are needed for clarifying the influence of the mole ratio of Yb2O3 to MoO2 or the dosage of MoO2 on the sintering behavior, the crystallization of grain boundary phase, and the mechanical properties of the composite.

Fig. 7. SEM micrographs of the Mo3Si–Yb2Si2O5–Si3N4 composites: (a) and (b) sintered with the additives of 2.83 mol% Yb2O3 and 5.66 mol% MoO2 (M(Yb/Mo) = 0.5), and (c) and (d) sintered with the additives of 2.89 mol% Yb2O3 and 3.85 mol% MoO2 (M(Yb/Mo) = 0.75); arrows show the Si3N2O grains.
to 0.75, the generation of Si2N2O was obstructed. In the silicide-Yb2Si2O5-Si3N4 composites, the grain boundary phases were crystallized, but the thin amorphous films with a thickness of 1 nm were detected from the interfaces between silicide particle, Yb2Si3O5, and Si3N4 grain.

Because there are numerous kinds of the silicide and the rare-earth oxide, the desired silicide particles and desired crystallized grain boundary phases can be designed by choosing the combination of the silicide-forming metal oxides and rare-earth oxides as sintering additives of Si3N4 for further improving the mechanical properties and oxidation resistance.

References