



Effect of atmosphere on the fabrication of $\text{Si}_2\text{N}_2\text{O}$ matrix composites

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Abstract

$\text{Si}_2\text{N}_2\text{O}$ matrix composites were fabricated by solid/gas reaction in air or N_2 atmosphere. The effects of atmosphere on the phase and microstructure of the composites were investigated. The reaction mechanism of $\text{Si}_2\text{N}_2\text{O}$ system was discussed by analysing the variation of the Gibbs free energy with temperature. The effect of N_2 and air on sintering of $\text{Si}_2\text{N}_2\text{O}$ matrix composites was discussed in relation to observed kinetics and thermodynamic calculations. The results showed that gradient structure of $\text{Si}_2\text{N}_2\text{O}$ matrix composites were obtained in N_2 atmosphere. While high N_2 concentration was useful for the formation of the pure $\beta\text{-Si}_3\text{N}_4$ ceramics, low N_2 concentration was proposed to form the pure $\text{Si}_2\text{N}_2\text{O}$ ceramics. However, in the air atmosphere, structure of the $\text{Si}_3\text{N}_4/\text{SiO}_2$ composites is homogeneous without the gradient structure appearing. Its composition is a little different as the O_2 concentration changes.

Keywords: $\text{Si}_2\text{N}_2\text{O}$ matrix composites, gradient structure, sintering atmosphere, solid/gas reaction

I. Introduction

As an advanced materials preparation technology, microwave sintering has attracted considerable attention in the field of fabrication of high temperature materials [1–5]. Technological innovation and theoretical breakthrough of wave-transparent composites are imperative for the development of microwave sintering technique.

Si_3N_4 ceramics is often used as kiln-furniture due to its good mechanical and dielectric and wave performance properties, while its thermal shock resistance still needs to improve at high temperatures [6,7]. As a unique compound in the $\text{SiO}_2\text{-Si}_3\text{N}_4$ system [8], silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) has excellent resistance to oxidation, creep, wear, molten non-ferrous metals and salts, and thermal shock [9–14], as well as low dielectric constant [15–17]. So it is a candidate for thermal insulation for microwave sintering. However, $\text{Si}_2\text{N}_2\text{O}$ is difficult to densify by solid phase sintering because of the low self-diffusion coefficients of Si, N, and O. Metal ox-

ides additives such as ZrO_2 [18], Al_2O_3 [19] and Y_2O_3 [20] are usually necessary to facilitate densification of $\text{Si}_2\text{N}_2\text{O}$ ceramics by liquid phase sintering. Transition metal oxides additives always lead to the degradation of the dielectric properties of $\text{Si}_2\text{N}_2\text{O}$ ceramics due to the aggregation of metal ions in the residual intergranular phases [21]. The addition of Li_2O , which can form the eutectic liquid at low temperature, is a desirable mean to improve the properties of $\text{Si}_2\text{N}_2\text{O}$ ceramics without its dielectric performance degradation. Although extensive studies have been conducted on the preparation of $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$ [17,18,22] ceramics by liquid phase sintering with different additives and processes, there has been no report on the influences of oxygen partial pressure (P_{O_2}) and nitrogen partial pressure (P_{N_2}) on the preparation process of $\text{Si}_2\text{N}_2\text{O}$ matrix composites.

In this study, multi-layer $\text{Si}_2\text{N}_2\text{O}$ matrix composites were fabricated with Li_2O as sintering additives. The effect of atmosphere on the phase and microstructure of the composites was investigated. In addition, the crystallization mechanism of $\text{Si}_2\text{N}_2\text{O}$ was also discussed with the help of thermodynamic calculations.

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II. Experimental procedure

Nano-sized amorphous Si_3N_4 powder (>99% purity, ~20 nm) was purchased from Shanghai Chao Wei Nanotechnology Co., Ltd, China. In order to increase oxygen content in the raw materials, the amorphous Si_3N_4 powder was oxidized at 1000 °C for 2 h. As starting materials, the pre-oxidized Si_3N_4 powders and sintering additives (2 wt.% Li_2CO_3 , 99% purity, Xilong Scientific Co., Ltd. China) were mixed and milled with Si_3N_4 balls media. After ball milling, the mixture was dried at 100 °C for 8 h under vacuum. The mixture was passed through a 100 mesh screen, and then the powder was compacted by uniaxial pressing to produce circular green body with diameter of 30 mm and thickness of 3 mm. The green compacts were sintered in a high temperature furnace and heated at a controlled rate of 8, 5 and 3 °C/min at 0–1000 °C, 1000–1500 °C and 1500–1600 °C, respectively, then held at 1600 °C under protecting atmosphere of N_2 or air for 2 h, followed by natural cooling to room temperature.

Phase compositions were identified by X-ray diffraction (XRD, Beijing Purkinje General Instrument Co. Lt, Cu-K α radiation), and the fractured surface of specimens was coated with Pt for SEM (FESEM; JEOL JSM-6700F, Japan) observation.

III. Results and discussions

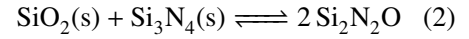
Figure 1 shows XRD patterns of the prepared samples. It can be seen that XRD pattern of the centre of the samples under N_2 atmosphere contains only sharp peaks of $\text{Si}_2\text{N}_2\text{O}$, while the surface XRD pattern for the same samples mainly consists of Si_3N_4 peaks. On the contrary, in the samples obtained under air atmosphere XRD patterns showed that the obtained composites mainly consisted of Si_3N_4 and minor amounts of SiO_2 .

During the sintering of amorphous silicon nitride in nitrogen, the formation of $\text{Si}_2\text{N}_2\text{O}$ is only observed

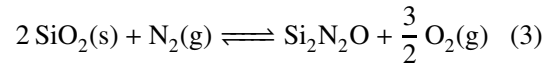
via presence of liquid phase whereby the liquid phase is generally provided by the intentionally added Li_2O and facilitates Si_3N_4 decomposition [23,24]. Possible material balances for formation and decomposition of $\text{Si}_2\text{N}_2\text{O}$ were considered and as the first approximation thermodynamics was used to calculate the standard Gibbs free energy at the time of the reaction equilibrium:

$$\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ \quad (1)$$

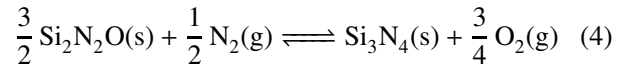
According to this:



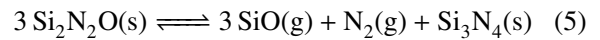
$$\Delta G_T^\circ(1) = 182.159 - 20.797T$$



$$\Delta G_T^\circ(2) = 903210 - 119.457T$$



$$\Delta G_T^\circ(3) = 631905 - 39.587T$$



$$\Delta G_T^\circ(4) = 1710359 - 676.027T$$

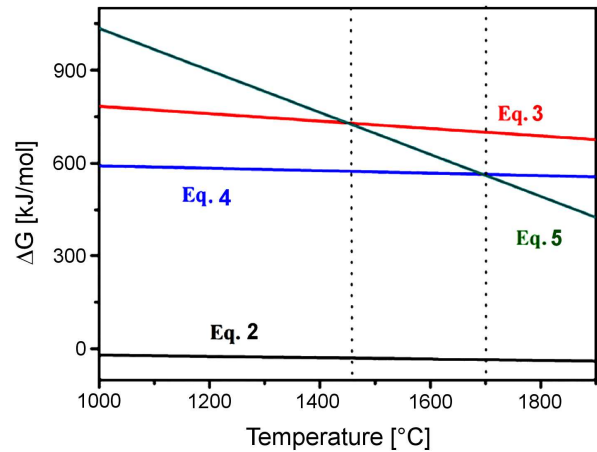


Figure 2. Variation of Gibbs free energy of formation for $\text{Si}_2\text{N}_2\text{O}$ according to the reactions presented by Eqs. 2-5 from 1000 to 1900 °C

Variations of the standard Gibbs free energy values (ΔG_T°) of the above reactions as a function of temperature are shown in Fig. 2. As can be seen, $\Delta G_T^\circ(1)$ is always lower than $\Delta G_T^\circ(2)$, which means that at these reaction temperatures, Eq. 2 takes place theoretically without considering the kinetic factors. If $\text{Si}_2\text{N}_2\text{O}$ is synthesized from Eq. 3, lot of SiO_2 in the raw materials should be nitrated into $\text{Si}_2\text{N}_2\text{O}$ with higher N_2 pressure. As it is known, it is difficult for Si_3N_4 to react with SiO_2 without the help of oxide additive that is in liquid phase at high temperature. Mitomo *et al.* [25] have been proved that Eq. 4 and Eq. 5 are reversible and the decomposition of $\text{Si}_2\text{N}_2\text{O}$ could be effectively suppressed by increasing N_2 pressure or choosing suitable powder bed (Si_3N_4 bed). Considering the ΔG_T° of

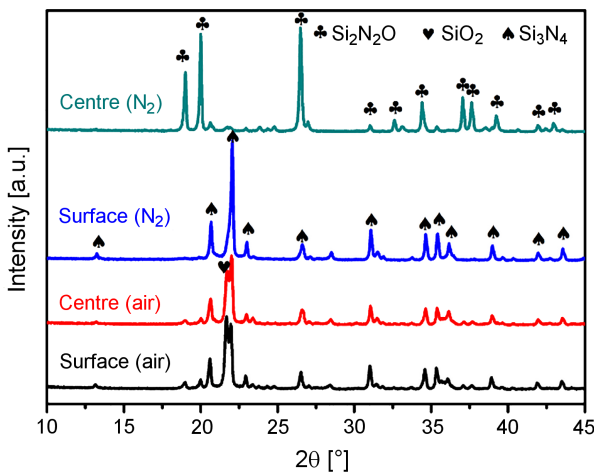


Figure 1. XRD patterns of $\text{Si}_2\text{N}_2\text{O}$ matrix composites sintered under different atmosphere for 2 h

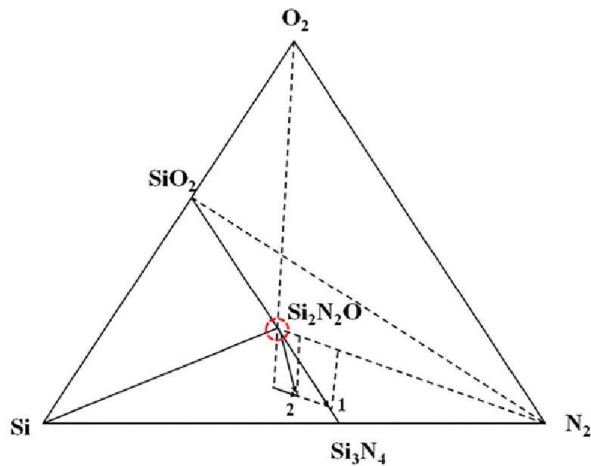


Figure 3. Ternary phase diagram of Si-N-O system at $T < 1827\text{ }^{\circ}\text{C}$ and 1 atm pressure (arrows show the composition evolution of the $\text{Si}_2\text{N}_2\text{O}$ with N_2 pressure: 1) at equilibrium, 2) when the pressure of N_2 is decreased

Eqs. 2–5 shown in Fig. 2, the formation of $\text{Si}_2\text{N}_2\text{O}$ via Eq. 2 is more thermodynamically favourable than Eq. 4 and Eq. 5. Whether they can occur also has a great relationship with the partial pressure of the various gases in the reaction system. Therefore, it is necessary to further study the relationship between the partial pressure in the system and the product phase.

Generally, the reaction between $\text{SiO}_2(\text{s})$ and $\text{N}_2(\text{g})$ is passive nitride process when nitrogen partial pressure (P_{N_2}) is high and it changes to active nitride process when P_{N_2} becomes lower. The transition condition of passive to active process is affected by the atmosphere temperature and gas flowing rate [26]. Ehlert *et al.* [27] had also found that the outer surface $\beta\text{-Si}_3\text{N}_4$ was formed according to Eq. 5 from the decomposition of $\text{Si}_2\text{N}_2\text{O}$. Being in the flowing nitrogen gas atmosphere, the decomposition of $\text{Si}_2\text{N}_2\text{O}$ occurred as the applied N_2 pressure is very high according to Eq. 4. Thus $\beta\text{-Si}_3\text{N}_4$ phase layer was formed on the outer surface, according to Eq. 4 and Eq. 5; in other words, the gradual evaporation of $\text{SiO}(\text{g})$ and N_2 would eventually lead to the decomposition of $\text{Si}_2\text{N}_2\text{O}$ and formation of $\beta\text{-Si}_3\text{N}_4$ layer.

Ternary phase diagram of the Si-N-O system at $T < 1827\text{ }^{\circ}\text{C}$ is shown in Fig. 3. We found that the N_2 and O_2 partial pressures have a very important effect on the final

phase composition of the system. At the junction point (pure $\text{Si}_2\text{N}_2\text{O}(\text{s})$, the equilibrium point) there is a partial pressure of $P_{\text{O}_2} = 2.5 \times 10^{-30}$ Pa and $P_{\text{N}_2} = 1.4 \times 10^{-2}$ Pa. When the partial pressure of N_2 deviates from the equilibrium point, the $\text{Si}_2\text{N}_2\text{O}(\text{s})$ original composition must move along the line $\text{Si}_3\text{N}_4\text{-Si}_2\text{N}_2\text{O}$ (Fig. 3). $\text{Si}_2\text{N}_2\text{O}$ tends to be present in the high O element content region. In fact, for kinetic reasons, for example the higher N_2 pressure, $\text{Si}_3\text{N}_4(\text{s})$ phase was observed due to the decomposition of $\text{Si}_2\text{N}_2\text{O}$. Si_3N_4 could be formed when N_2 partial pressure is above the 1.4×10^{-2} Pa and oxygen partial pressure is below the 2.5×10^{-30} Pa.

The P_{O_2} in the centre position of the sintered body could not be measured. Therefore, we do not know whether P_{O_2} was higher than 2.5×10^{-30} Pa or not in this region of specimen. As a result, it is not confident which reaction occurs for the formation of $\text{Si}_2\text{N}_2\text{O}$ in the centre position of specimen. The $\text{SiO}_2(\text{s,l})$ phase in reaction provides a viscous glass phase for the reaction in Eq. 2 and Eq. 3 to generate $\text{Si}_2\text{N}_2\text{O}$. This liquid formation is strongly influenced by Li_2CO_3 which decreases the melting temperature by forming a Li-Si melt [28]. It enhances the dissolution of Si_3N_4 , and promotes the formation of $\text{Si}_2\text{N}_2\text{O}$ solid solution. No $\text{Si}_2\text{N}_2\text{O}$ phase was generated in the surface region, because the P_{O_2} was too low to precipitate $\text{SiO}_2(\text{s,l})$ in the flowing nitrogen gas atmosphere, which can react with Si_3N_4 and N_2 . Hence, Eq. 2 or Eq. 3 could not occur under these conditions. Even if $\text{Si}_2\text{N}_2\text{O}$ could be produced, it would decompose under flowing nitrogen gas atmosphere. Accordingly, in the surface region, only Si_3N_4 phase was detected. Therefore, it is not difficult to understand that the mixed phase includes Si_3N_4 and SiO_2 under air atmosphere rather than appear a multilayer structure.

Figure 4 shows the micrographs of the samples sintered under the air atmosphere. The inner and surface regions both showed a bimodal grain size distribution. In the inner region, as shown in Fig. 4b, grain size of $\beta\text{-Si}_3\text{N}_4$ was coarser than that in the surface region with the small amount of glass phase. However, in the surface region, elongated $\beta\text{-Si}_3\text{N}_4$ grains and glass phase matrix can be obviously observed, as shown in Fig. 4c. Accordingly, the influence of atmosphere on the microstructure is obvious under the N_2 atmosphere.

The gradient structure of the prepared samples under the N_2 atmosphere is shown in Fig. 5. Apparently

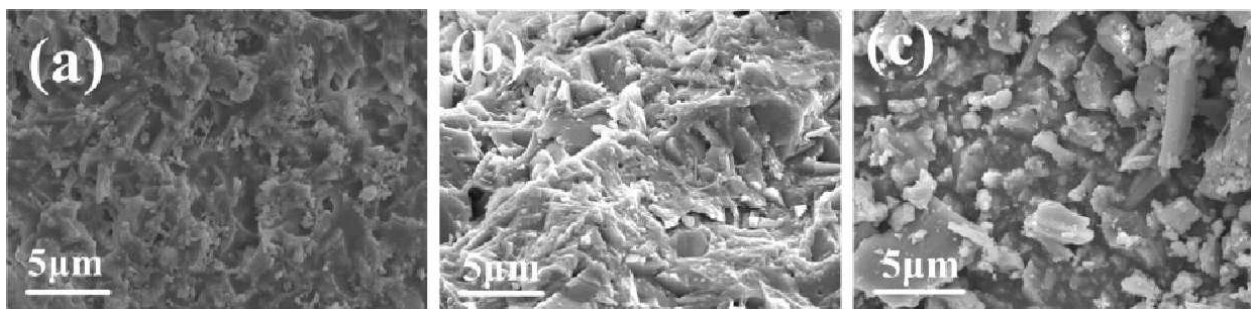


Figure 4. SEM images of prepared samples in the air atmosphere (a) the cross section of the samples; (b) centre structure; (c) surface structure

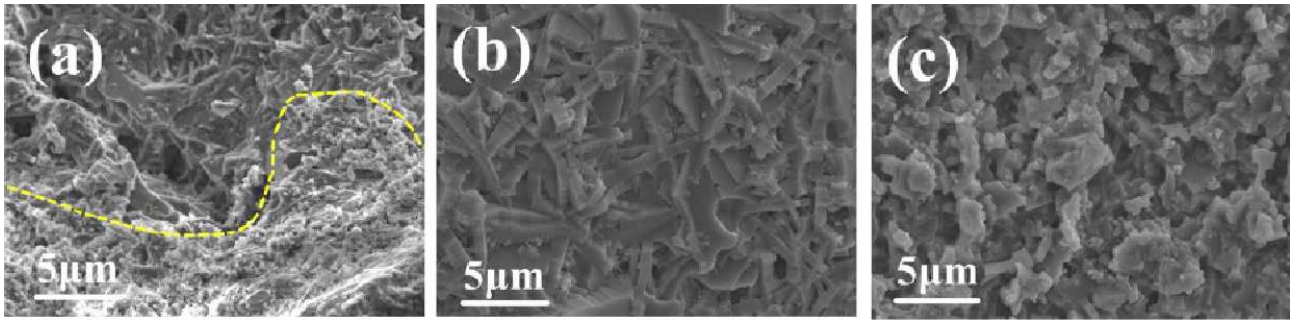


Figure 5. SEM images of the sintered samples in the N_2 atmosphere (a) the gradient structure of the samples; (b) centre Si_2N_2O layer; (c) surface Si_3N_4 layer

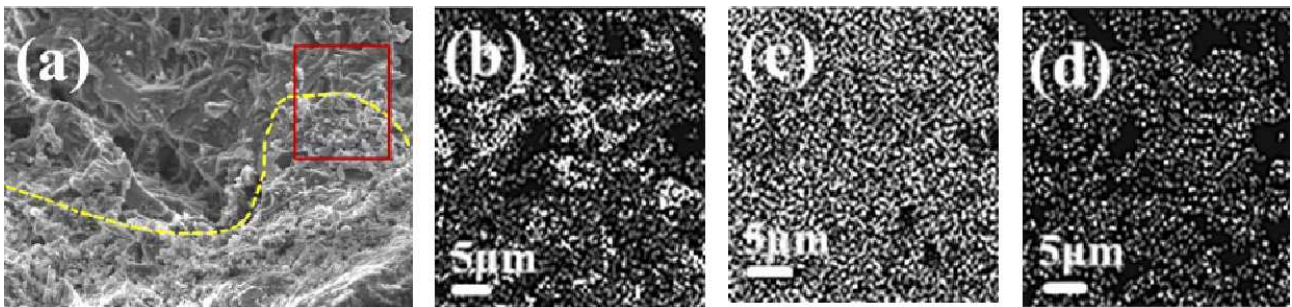


Figure 6. elements maps of the gradient region in the samples sintered under N_2 atmosphere, (a) SEM images of the gradient region, the EDS elements maps of (b) O, (c) Si, (d) N

there is a microstructural gradient from the interior (Fig. 5b) to surface (Fig. 5c), as shown in Fig. 5a. In the inner layer, elongated platelike Si_2N_2O grains and several small pores are observed in the Si_2N_2O ceramics composites, as shown in Fig. 5b; while in the surface layer, broad grain diameter distribution of β - Si_3N_4 can be found, as shown in Fig. 5c. Mitomo *et al.* [25] reported that high N_2 pressure was useful for the prevention of thermal decomposition of Si_2N_2O and bloating of the compact. Lin *et al.* [29] reported that the Si_2N_2O matrix composites could withstand a thermal shock of 1100 °C without strength degradation in N_2 , while only the sample with adequate porosity exhibits high thermal

shock resistance in air. In this study, the high amount of N_2 could result in the microstructure difference, which promotes decomposition of Si_2N_2O phase in the surface layer as indicated by Eq. 4, facilitate the β - Si_3N_4 grain growth, and lead to the longer and fatter rod-like grains and low porosity.

The gradient structure of the samples sintered under the N_2 atmosphere was also examined by EDS. The SEM images of the gradient region are given in Fig. 6a, and the EDS elements maps of O, Si and N are presented in Figs. 6b, 6c and 6d, respectively. The EDS elements point scan of the outer layer and the inner layer are presented in Figs. 7a and 7b, respectively. There is

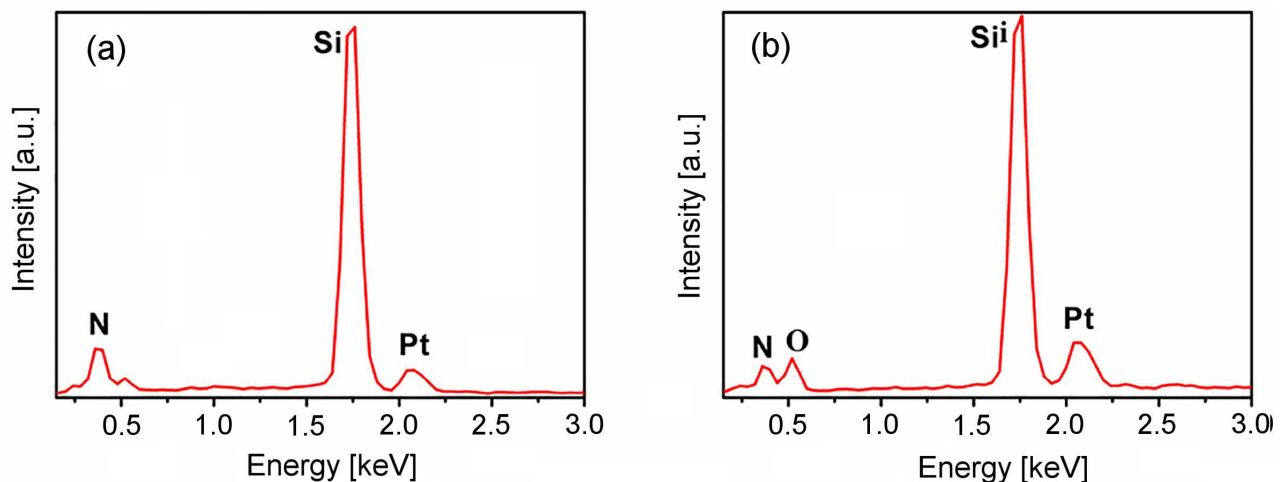


Figure 7. EDS elements point scan of the gradient region in the samples sintered under N_2 atmosphere, (a) the outer layer; (b) the inner layer

an obvious difference in the content of oxygen and nitrogen, but not silicon, in these two regions. This indicates that the composition of these two regions was influenced strongly by the atmosphere during the sintering process. The result is also consistent with the XRD results and this indicates that the influence of air atmosphere on microstructure is not so distinct as that of N₂ atmosphere.

IV. Conclusions

Si₂N₂O matrix composites were fabricated by solid/gas reaction under the air or N₂ atmosphere. The N₂ and O₂ partial pressures have very important effect on the final phase composition of the system. A gradient structure of Si₂N₂O matrix composites was obtained under the N₂ atmosphere. The outer layer is composed of the pure β-Si₃N₄ and the main crystalline phase of the inner layer is Si₂N₂O. When the partial pressures of gases are $P_{O_2} = 2.5 \times 10^{-30}$ Pa and $P_{N_2} = 1.4 \times 10^{-2}$ Pa, the composites are single phase Si₂N₂O. On the other hand, under the air atmosphere, the structure of Si₃N₄/SiO₂ composites is homogeneous without the gradient structure appearing. Also, its composition is influenced by the O₂ concentration changes.

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