



## 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  $\text{N}_2$  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  $\text{N}_2$  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  $\text{N}_2$  atmosphere. While high  $\text{N}_2$  concentration was useful for the formation of the pure  $\beta\text{-Si}_3\text{N}_4$  ceramics, low  $\text{N}_2$  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  $\text{O}_2$  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.

$\text{Si}_3\text{N}_4$  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  $\text{ZrO}_2$  [18],  $\text{Al}_2\text{O}_3$  [19] and  $\text{Y}_2\text{O}_3$  [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  $\text{Li}_2\text{O}$ , 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 ( $P_{\text{O}_2}$ ) and nitrogen partial pressure ( $P_{\text{N}_2}$ ) 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  $\text{Li}_2\text{O}$  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  $\text{Si}_3\text{N}_4$  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  $\text{Si}_3\text{N}_4$  powder was oxidized at 1000 °C for 2 h. As starting materials, the pre-oxidized  $\text{Si}_3\text{N}_4$  powders and sintering additives (2 wt.%  $\text{Li}_2\text{CO}_3$ , 99% purity, Xilong Scientific Co., Ltd. China) were mixed and milled with  $\text{Si}_3\text{N}_4$  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  $\text{N}_2$  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 $\alpha$  radiation), and the fractured surface of specimens was coated with Pt for SEM (FESEM; JEOL JSM-6700F, Japan) observation.

## III. Results and discussions

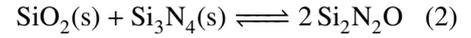
Figure 1 shows XRD patterns of the prepared samples. It can be seen that XRD pattern of the centre of the samples under  $\text{N}_2$  atmosphere contains only sharp peaks of  $\text{Si}_2\text{N}_2\text{O}$ , while the surface XRD pattern for the same samples mainly consists of  $\text{Si}_3\text{N}_4$  peaks. On the contrary, in the samples obtained under air atmosphere XRD patterns showed that the obtained composites mainly consisted of  $\text{Si}_3\text{N}_4$  and minor amounts of  $\text{SiO}_2$ .

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

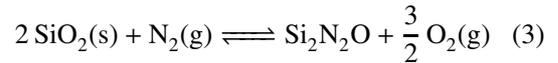
via presence of liquid phase whereby the liquid phase is generally provided by the intentionally added  $\text{Li}_2\text{O}$  and facilitates  $\text{Si}_3\text{N}_4$  decomposition [23,24]. Possible material balances for formation and decomposition of  $\text{Si}_2\text{N}_2\text{O}$  were considered and as the first approximation thermodynamics was used to calculate the standard Gibbs free energy at the time of the reaction equilibrium:

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

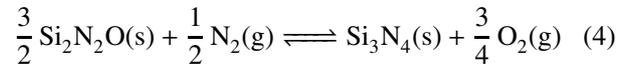
According to this:



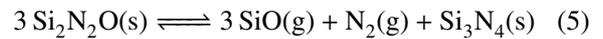
$$\Delta G_T^\circ(1) = 182.159 - 20.79T$$



$$\Delta G_T^\circ(2) = 903210 - 119.45T$$



$$\Delta G_T^\circ(3) = 631905 - 39.58T$$



$$\Delta G_T^\circ(4) = 1710359 - 676.02T$$

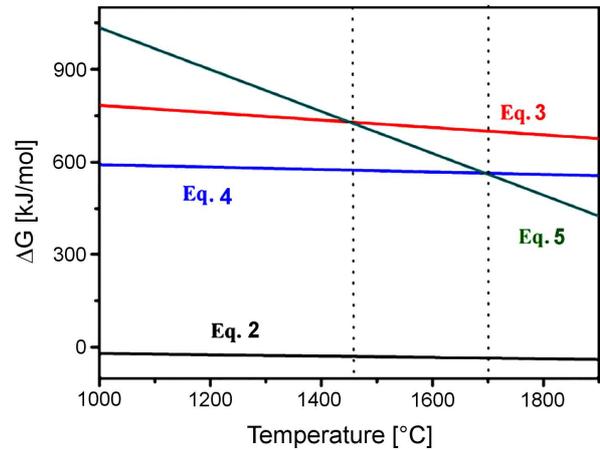


Figure 2. Variation of Gibbs free energy of formation for  $\text{Si}_2\text{N}_2\text{O}$  according to the reactions presented by Eqs. 2-5 from 1000 to 1900 °C

Variations of the standard Gibbs free energy values ( $\Delta G_T^\circ$ ) 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  $\text{SiO}_2$  in the raw materials should be nitrated into  $\text{Si}_2\text{N}_2\text{O}$  with higher  $\text{N}_2$  pressure. As it is known, it is difficult for  $\text{Si}_3\text{N}_4$  to react with  $\text{SiO}_2$  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  $\text{N}_2$  pressure or choosing suitable powder bed ( $\text{Si}_3\text{N}_4$  bed). Considering the  $\Delta G_T^\circ$  of

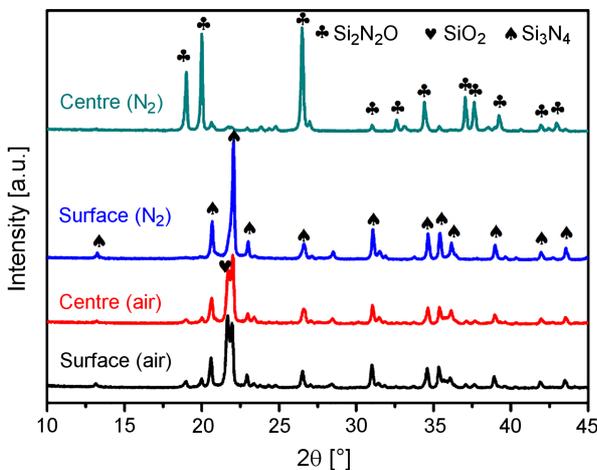
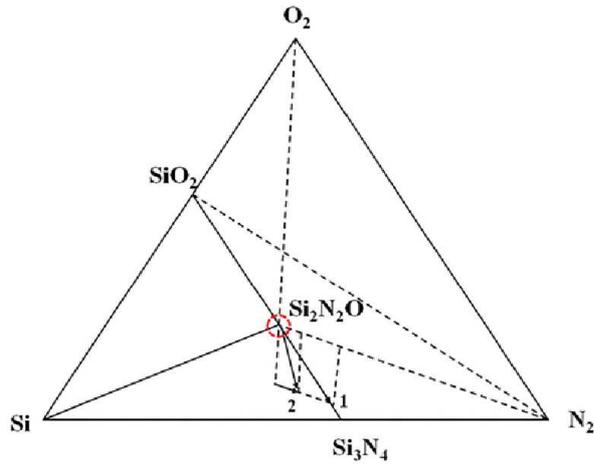


Figure 1. XRD patterns of  $\text{Si}_2\text{N}_2\text{O}$  matrix composites sintered under different atmosphere for 2 h



**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  $\text{N}_2$  pressure: 1) at equilibrium, 2) when the pressure of  $\text{N}_2$  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 ( $P_{\text{N}_2}$ ) is high and it changes to active nitride process when  $P_{\text{N}_2}$  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  $\text{N}_2$  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  $\text{N}_2$  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.

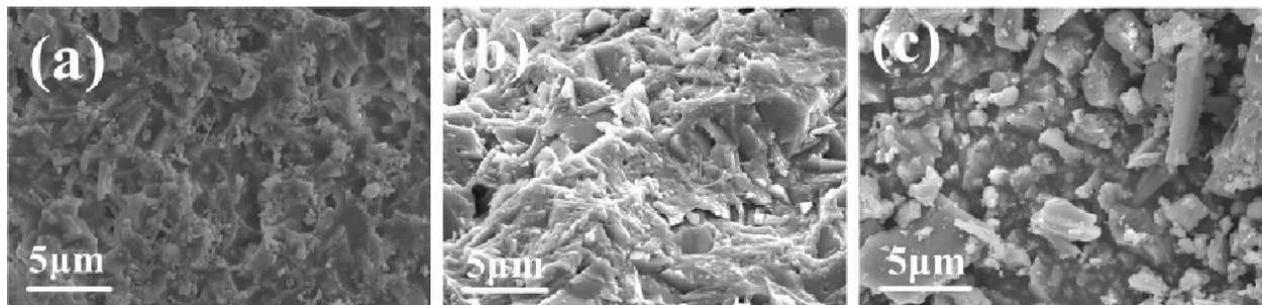
Ternary phase diagram of the Si-N-O system at  $T < 1827\text{ }^{\circ}\text{C}$  is shown in Fig. 3. We found that the  $\text{N}_2$  and  $\text{O}_2$  partial pressures have a very important effect on the final

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  $\text{N}_2$  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  $\text{N}_2$  pressure,  $\text{Si}_3\text{N}_4(\text{s})$  phase was observed due to the decomposition of  $\text{Si}_2\text{N}_2\text{O}$ .  $\text{Si}_3\text{N}_4$  could be formed when  $\text{N}_2$  partial pressure is above the  $1.4 \times 10^{-2}$  Pa and oxygen partial pressure is below the  $2.5 \times 10^{-30}$  Pa.

The  $P_{\text{O}_2}$  in the centre position of the sintered body could not be measured. Therefore, we do not know whether  $P_{\text{O}_2}$  was higher than  $2.5 \times 10^{-30}$  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  $\text{Li}_2\text{CO}_3$  which decreases the melting temperature by forming a Li-Si melt [28]. It enhances the dissolution of  $\text{Si}_3\text{N}_4$ , 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  $P_{\text{O}_2}$  was too low to precipitate  $\text{SiO}_2(\text{s,l})$  in the flowing nitrogen gas atmosphere, which can react with  $\text{Si}_3\text{N}_4$  and  $\text{N}_2$ . 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  $\text{Si}_3\text{N}_4$  phase was detected. Therefore, it is not difficult to understand that the mixed phase includes  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  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  $\text{N}_2$  atmosphere.

The gradient structure of the prepared samples under the  $\text{N}_2$  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

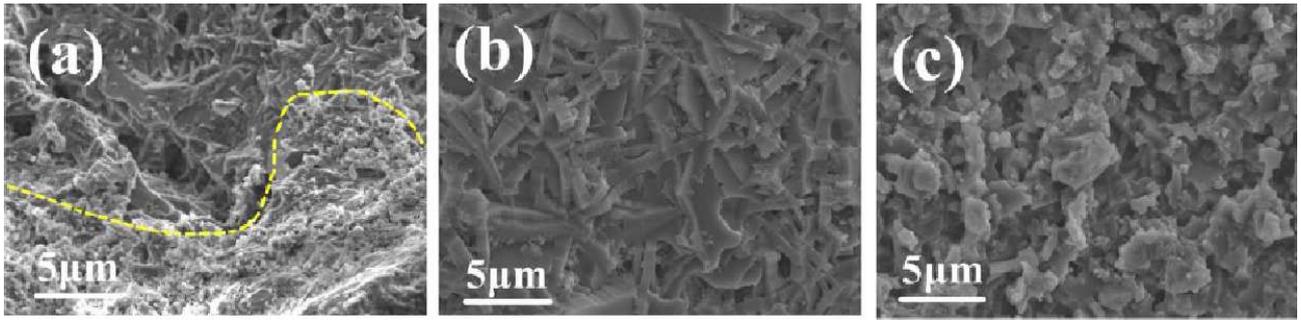


Figure 5. SEM images of the sintered samples in the  $N_2$  atmosphere (a) the gradient structure of the samples; (b) centre  $Si_2N_2O$  layer; (c) surface  $Si_3N_4$  layer

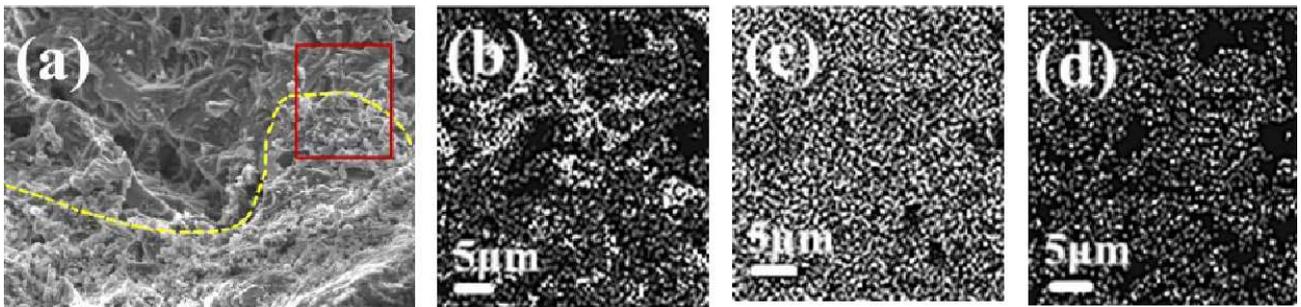


Figure 6. elements maps of the gradient region in the samples sintered under  $N_2$  atmosphere, (a) SEM images of the gradient region, the EDS elements maps of (b) O, (c) Si, (d) N

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  $\beta-Si_3N_4$  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  $1100\text{ }^\circ\text{C}$  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  $\beta-Si_3N_4$  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

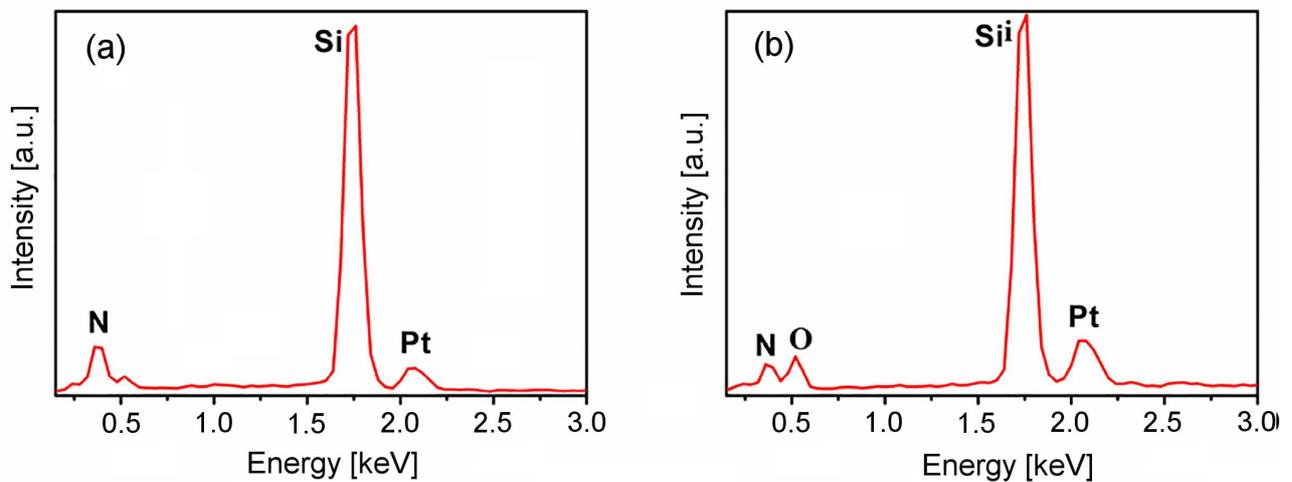


Figure 7. EDS elements point scan of the gradient region in the samples sintered under  $N_2$  atmosphere, (a) the outer layer; (b) the inner layer

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  $N_2$  atmosphere.

#### IV. Conclusions

$Si_2N_2O$  matrix composites were fabricated by solid/gas reaction under the air or  $N_2$  atmosphere. The  $N_2$  and  $O_2$  partial pressures have very important effect on the final phase composition of the system. A gradient structure of  $Si_2N_2O$  matrix composites was obtained under the  $N_2$  atmosphere. The outer layer is composed of the pure  $\beta$ - $Si_3N_4$  and the main crystalline phase of the inner layer is  $Si_2N_2O$ . 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  $Si_2N_2O$ . On the other hand, under the air atmosphere, the structure of  $Si_3N_4/SiO_2$  composites is homogeneous without the gradient structure appearing. Also, its composition is influenced by the  $O_2$  concentration changes.

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