

Effect of Increased Oxygen Content due to Intensive Milling on Phase and Microstructural Development of Silicon Nitride

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ABSTRACT

Compacts of a mixture of fine α -Si₃N₄ powders, 6% Y₂O₃ and 1% Al₂O₃ were attrition milled and, then, nitrogen gas-pressure sintered in order to understand the effect of milling time on phase and microstructural development in silicon nitride ceramics. The sintered surface and the interior showed different behaviors in phase and microstructural developments. Increased oxygen content with increased milling time of powder mixture leads to the formation of Si₂N₂O phase at temperatures as low as 1550 °C. Si₂N₂O is stable in the interior of the samples but unstable in the surface region of the specimen sintered at higher temperature. This results in a duplex structure where the interior consists of Si₂N₂O grains dispersed in β -Si₃N₄ matrix and a surface which contains only β -Si₃N₄. The alpha to beta phase transformation and the microstructural development are shown to be influenced by the formation and decomposition of the Si₂N₂O.

Key words : Si₃N₄, Attrition milling, Increased oxygen content, Si₂N₂O, Duplex structure

1. Introduction

Silicon nitride, with its potential for obtaining high strength and toughness, has been intensively studied as a candidate for structural applications. In general, care must be taken in processing the silicon nitride powder to form the final products because the powder characteristics (e.g., particle size, oxygen and carbon content) as well as the processing variables (e.g., forming techniques, binder content, sintering conditions) all affect the final microstructure and, therefore, the resultant properties.¹⁻⁸⁾ The oxygen uptake during processing can be influenced by the solvent,⁹⁾ milling time and sintering atmosphere. The milling time can generate large changes in the oxygen content due to a combination of particle size reduction and reaction with oxygen in the milling environment. When the oxygen content increases, the phase assemblage after sintering will change and, therefore, the densification response and properties will vary.

Submicron sized α -Si₃N₄ particles can result in a fine grained matrix after sintering possibly due to the 2-D nucleation and growth mechanisms proposed recently.^{10,11)} This also suggests that fine α -Si₃N₄ starting particles are essential to provide the bimodal microstructure,¹²⁾ which can enhance the strength and fracture toughness simulta-

neously.^{13,14)} But in reducing the particle size of α -Si₃N₄, an increase in oxygen content is inevitable. Above a critical oxygen content, silicon nitride will be in equilibrium with Si₂N₂O (and Y₂Si₂O₇ when Y is present).¹⁵⁾ Since silicon oxynitride has better oxidation resistance than silicon nitride, efforts were made to examine the response of Si₂N₂O/ β -Si₃N₄ composites.¹⁶⁻¹⁷⁾ Recently, Wang and Emoto et al.^{18,19)} also reported that it was possible to incorporate elongated silicon oxynitride grains dispersed in a silicon nitride matrix to obtain a toughening effect. On the other hand, Woetting et al.³⁾ reported that the formation of silicon oxynitride in silicon nitride matrix was detrimental to both densification and mechanical properties.

In the present study, the effect of increased oxygen content due to milling on the phase and microstructural development of silicon nitride was examined. Special attention was paid to the differences between the interior and the near surface regions of samples resulting from formation and decomposition of Si₂N₂O phase.

2. Experimental Procedure

Powder mixtures of α -silicon nitride (E-10, Ube Industries Ltd., Tokyo, Japan) with 6 wt% Y₂O₃ (Fine, H. C. Starck Co., Berlin, Germany) and 1 wt% Al₂O₃ (AKP-30, Sumitomo Chemical Co., Osaka, Japan) were attrition milled for 3 and 24 h (hereafter referred to as AM 3 and AM 24, respectively) using 3 mm diameter silicon nitride balls and isopropyl

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alcohol in order to manipulate the particle size and the oxygen content. The resultant slurries were dried on a hot plate while stirring, and the dried powder mixtures were sieved to -100 + 150 mesh. Fifteen-millimeter diameter pellets were uniaxially pressed at 35 MPa and, then, cold-isostatically pressed at 350 MPa. The pressed pellets were calcined at 600°C for 10 h in air. The weight loss after calcination was 0.9%, comparable to thermal gravimetric analysis results. The green density after calcination was 1.80 g/cm³ (55% TD). The pellets were placed in a graphite crucible with a silicon nitride powder bed, and this assembly was placed again in a larger graphite crucible with a silicon nitride powder bed. The graphite crucibles have lids, one side of which is notched to allow easy gas transfer. Sintering was performed in a gas-pressure sintering furnace (Thermal Technology Inc., Model No. 612, U.S.A.) at selected temperature in the range of 1450 to 1850 °C under 1 to 2 MPa N₂ over pressure with heating and cooling rates of 15 °C/min. A hold time of 0.5 h was employed for the investigation of phase development at temperatures between 1450 to 1750 °C and a 6 h hold at 1850 °C was used to study microstructural development.

Oxygen content for each batch was measured using a hot gas extraction method.^a Specific surface area after milling was determined by BET (ASAP-2010, Micrometrics, Norcross, GA). X-ray diffraction analysis was employed to identify the phases as well as the alpha/beta silicon nitride ratio. In order to investigate the difference in phase assemblage between the sintered surface and the interior, XRD was performed on polished cross sections as well as on sintered surfaces. Gazzara's equation²⁰⁾ was used to calculate the alpha to beta silicon nitride ratio. The microstructure was characterized on the samples mechanically polished to 0.5 mm diamond abrasive and subsequently plasma-etched using a mixture of CF₄ with 5% oxygen for 4 minutes. The samples were then carbon-coated and examined using a field emission gun scanning electron microscope (Hitachi model 4500 S) equipped with an energy dispersive x-ray spectrometer.

3. Results and Discussion

Table 1 lists the specific surface area, the total oxygen contents including and excluding oxygen associated with the sintering additives, and the calculated SiO₂ content as a function of the attrition milling time. The oxygen content after 24 h attrition milling excluding that from the sintering additives is ~2.8 wt% (Table 1), which represents a considerable increase over that of the starting α -Si₃N₄ powder (i.e., ~1.5 wt%).

Oxygen is incorporated in the surface of the α -Si₃N₄ particles and, together with the yttria and alumina, forms a liquid that promotes densification during sintering. Increases in Si content in Y-Al-silicate liquid phase can increase the

Table 1. Powder Characterization of the Systems Investigated

| Milling Time [h] | As received Si ₃ N ₄ powder | 3 h | 24 h |
|--------------------------|---|---------|---------|
| BET [m ² /gr] | 9.8 | 15.1 | 33.4 |
| Oxygen [wt%] | 1.51 | 3.47* | 4.51* |
| Oxygen [wt%] | 1.51 | 1.71** | 2.75** |
| SiO ₂ [wt%] | 2.84 | 3.21*** | 5.17*** |

* : Oxygen content including that from sintering additives

** : Oxygen content excluding that from sintering additives

*** : SiO₂ content calculated from oxygen content excluding that from sintering additives

viscosity of the glass.²¹⁾ As α -Si₃N₄ starts to dissolve in Y-Al-silicate liquid phase, Si and O from the α -Si₃N₄ particle surfaces can be incorporated into an oxynitride glass. The availability of additional oxygen with extended milling can result in a decrease in N/O ratio of the glass, which decreases the glass viscosity, and/or the precipitation of the Si₂N₂O phase within SiO₂ rich oxynitride glass.²²⁾

Since it was reported that the near surface region and the interior can have differences in microstructures and different phase content,²³⁻²⁷⁾ we examined both the cross section and the sintered surface of the specimen. Fig. 1 shows the degree of α to β phase transformation depending on sintering temperature for both the cross section and the sintered surface of AM 3 and AM 24 specimens. It shows that the α to β transformation tends to be slower in the sintered surface than in the cross section of the specimens. Table 2 reveals the differences in the degree of phase transformation and the appearance of Si₂N₂O phase at the cross section and the sintered surface for AM 3 and AM 24 specimens with increasing temperature.

3.1. Interior Regions

First, let us examine the phase development in the AM 3 and AM 24 specimens as determined on polished cross section of the specimen, Fig. 2. AM 3 specimens exhibit phase development similar to that of silicon nitride prepared using the α -Si₃N₄ powder without attrition milling and the sintering additives. Note that the oxygen content increased (by ~0.2 wt%) to ~1.7 wt% after 3 h attrition milling (Table 1). Only the α and β phases are observed for all sintering temperatures. The degree of the α to β phase transformation after sintering at 1650 °C for 0.5 h is about 40% which increases to nearly 100% after 0.5 h at 1750 °C. After the 24 h attrition milling step, the oxygen content of AM 24 specimens increases (by 1.25 wt%) to 2.75 wt%. The AM 24 specimen contains the Si₂N₂O, as well as the α -phase after sintering at 1550 °C, which remains with increase in sintering temperatures. The extent of the α to β phase transformation in AM 24 specimen is about 70% after sintering at 1650 °C which is about 75% higher than that of AM 3 specimen sintered at the same temperature (Fig. 1). This is due, in part, to the particle size reduction resulting from the prolonged attrition milling. With finer α -Si₃N₄

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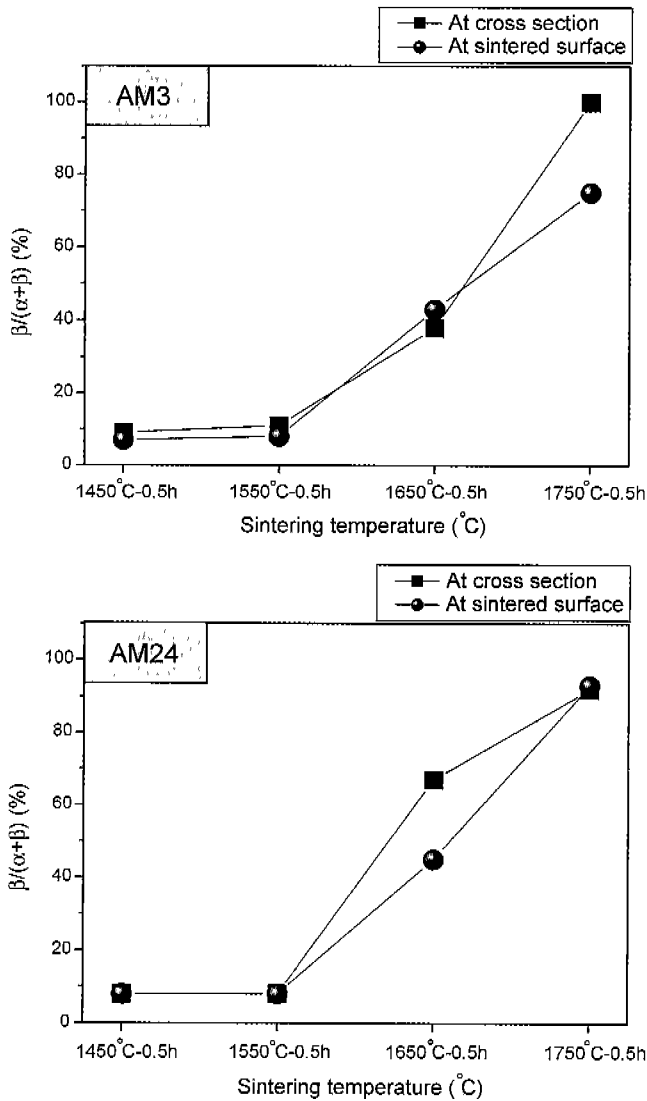


Fig. 1. Degree of α to β transformation depending on temperature for both the sintered surface and the cross-section of AM 3 and AM 24 specimens.

particle, the dissolution-precipitation of Si_3N_4 occurs faster. After sintering at 1750°C , the beta content of the AM 24 specimen is 92%, slightly less than that for the AM 3 sample for the same conditions. If precipitation of $\text{Si}_2\text{N}_2\text{O}$ continues to occur with increasing temperature, this can decrease the amount of liquid and slow down the phase transformation. In addition, $\alpha\text{-Si}_3\text{N}_4$ was reported to act as a seed for the formation of $\text{Si}_2\text{N}_2\text{O}$ ²⁸⁾ and can be trapped inside the $\text{Si}_2\text{N}_2\text{O}$ grains. This would also have a little impact on the retention of the alpha phase in the AM 24 specimen.

3.2. Surface Layers

Phase transformation at the sintered surface for AM 3 specimens is comparable to that at the interior until 1650°C (Fig. 1). At higher temperature such as 1750°C , the degree of phase transformation at the sintered surface is 75% while

Table 2. Phase Transformation with Increasing Temperatures and Appearance of $\text{Si}_2\text{N}_2\text{O}$ Phase for AM 3 and AM 24 Specimens

| Sintering Condition | AM 3 | | AM 24 | |
|------------------------------------|----------------------------|---------------------------------|----------------------------|---------------------------------|
| | $\beta/(\alpha+\beta)$, % | $\text{Si}_2\text{N}_2\text{O}$ | $\beta/(\alpha+\beta)$, % | $\text{Si}_2\text{N}_2\text{O}$ |
| At cross section | | | | |
| $1450^\circ\text{C} - 0.5\text{h}$ | 9 | N | 8 | N |
| $1550^\circ\text{C} - 0.5\text{h}$ | 11 | N | 8 | Y |
| $1650^\circ\text{C} - 0.5\text{h}$ | 38 | N | 67 | Y |
| $1750^\circ\text{C} - 0.5\text{h}$ | 100 | N | 92 | Y |
| At sintered surface | | | | |
| $1450^\circ\text{C} - 0.5\text{h}$ | 7 | N | 8 | N |
| $1550^\circ\text{C} - 0.5\text{h}$ | 8 | N | 8 | Y |
| $1650^\circ\text{C} - 0.5\text{h}$ | 43 | N | 45 | N |
| $1750^\circ\text{C} - 0.5\text{h}$ | 75 | N | 93 | N |

N : No $\text{Si}_2\text{N}_2\text{O}$ detected
 Y : $\text{Si}_2\text{N}_2\text{O}$ present

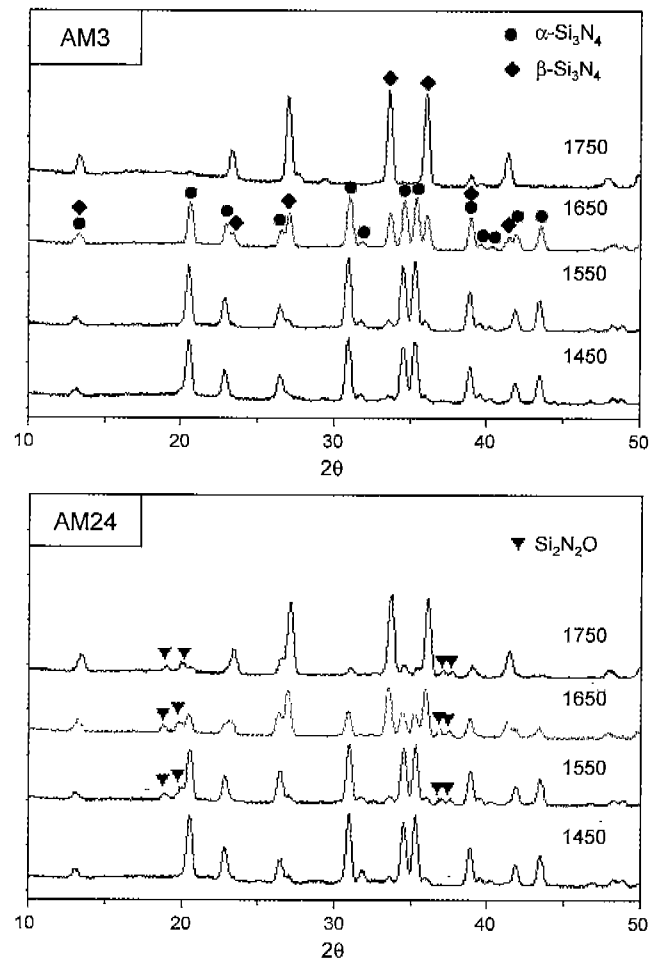


Fig. 2. XRD patterns from the cross-section of AM 3 and AM 24 specimens as a function of sintering temperature.

that at the interior is 100%. The remarkable slower transformation at the sintered surface for AM 3 specimens sin-

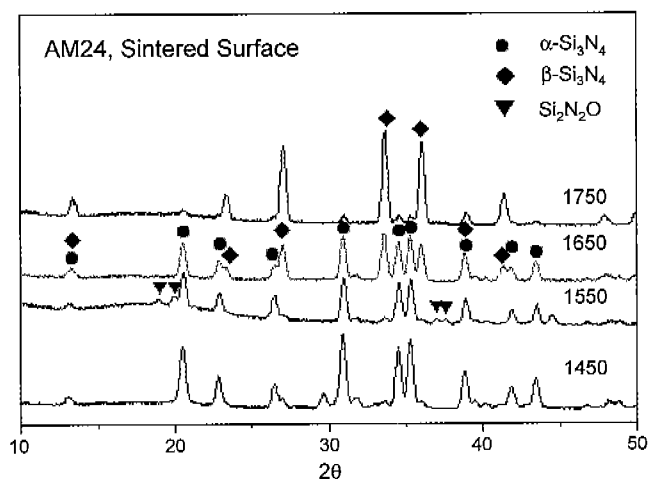
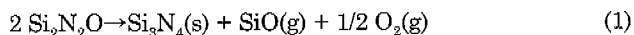


Fig. 3. XRD patterns from the sintered surface of the AM 24 specimens sintered at the temperatures indicated.

tered at 1750°C seems to be due to the volatilization of oxygen in the form of SiO or O₂ gases.^{25,27,29} Wada et al. reported similar results²⁷ and argued that the oxygen loss from the liquid phase in the surface region of the specimen in contact with graphite container was the major reason of slower transformation. A decrease in the oxygen would increase the N to O ratio in the liquid and, thus, increase the liquid phase viscosity. The result would be a decrease in the diffusion rates through the liquid and be accompanied by slower phase transformation rates.

Next, we consider the phase evolution in the sintered surface of AM 24 specimens, Figure 3. The specimen sintered at 1550°C reveals the formation of Si₂N₂O, which is also detected in the interior regions. However, unlike results from studies of the cross sections, the Si₂N₂O phase disappears from surfaces at sintering temperatures > 1650°C, which seems to be due to the atmosphere generated by the graphite furnace. Assuming that the nitrogen gas contains 0.1% oxygen impurity, oxygen pressure in equilibrium with graphite and carbon monoxide gas at 1727°C is calculated to be 1.8×10^{-17} bar.³⁰ Based on the data reported by Neidhardt et al.,²⁹ oxygen pressure in equilibrium with silicon nitride and silicon oxynitride is calculated to be as low as 2.5×10^{-14} bar under 10 bar nitrogen pressure at 1727°C. Therefore, the loss of Si₂N₂O in the near surface region can be related to the reduction potential in the sintering atmosphere associated with the graphite heating element, and Si₂N₂O would decompose by the following reaction;



This will lead to loss of oxygen in the form of volatile SiO or oxygen mainly from the surface region. At the same time, the degree of the transformation to β-Si₃N₄ in the cross section of AM 24 specimens at 1650°C is about 70% while that on the surface is about 45% (Fig. 1).

The reduction in the α to β transformation noted here for AM 24 specimen is more likely explained by the observed increase in the decomposition of Si₂N₂O in the surface region. Once α-Si₃N₄ starts to dissolve in SiO₂ rich Y-Al silicate glass, SiO₂ rich oxynitride glass will form to give rise to the precipitation of Si₂N₂O, which can reduce the amount of glass as well as the amounts of Si, O, and N in Y-Si-Al-O-N glass composition. At higher temperature such as 1650°C Si₂N₂O preferentially in the surface region of the specimen will decompose due to the reduction potential of graphite furnace system. Decomposition of Si₂N₂O during sintering will give rise to a oxygen loss in the form of SiO or O₂ gases as well as to an increase in Si₃N₄, as seen in reaction 1 above. Assuming that the decomposition product, Si₃N₄, is very fine and reactive, it will rapidly dissolve in the glass, which gives rise to the increase in Si and N contents in Y-Si-Al-O-N glass, which will result in the increase in N/O ratio of the glass. This will result in the increase in viscosity of the oxynitride glass, which will reduce the diffusion rate through the glass and slow down the alpha to beta Si₃N₄ transformation. At higher temperature such as 1750°C the tendency will be less significant possibly due to the complete dissolution of fresh silicon nitride particles.

In order to assess the microstructural difference between the surface region and the interior, AM 24 specimen sintered at 1850°C for 6 h was examined by SEM (Fig. 4). The cross section exhibits a 300 μm thick skin layer (Fig. 4a). The detailed surface region microstructure (Fig. 4b) exhibits a very dense microstructure in which large elongated grains are uniformly dispersed in a fine grain matrix. The detailed microstructure of the specimen interior (Fig. 4c) shows some unusual morphologies in the form of irregular shaped needle clusters dispersed in otherwise typical Si₃N₄ microstructure. The literature on the morphology of Si₂N₂O phase indicates that Si₂N₂O formed in silicon nitrides containing Y₂O₃-Al₂O₃ additive system exhibits very irregular shapes while that from Y₂O₃-MgO additive system in uniform needle shapes.^{18,19,28} Keeping in mind that this specimen contains Si₂N₂O phase as well as β-Si₃N₄, these irregular shaped and clustered needles appeared to be the Si₂N₂O phase. This was confirmed by EDS analysis of irregular-shaped grains (e.g., arrowed in Fig. 4c), which exhibit a large oxygen peak, in addition to the Si and N peaks, and no Y and Al, (Fig. 5).

When decomposition of the Si₂N₂O is influenced primarily by the sintering atmosphere, a surface layer forms that contains no Si₂N₂O. After sintering at 1650°C, the constituents of the surface region of the specimen are α-Si₃N₄, β-Si₃N₄ and an amorphous phase. The situation is similar to that for silicon nitride prepared from a mixture of the Si₃N₄ powder with sintering additives, but without intensive attrition milling. With increase in temperature, the boundary layer between the surface region in which Si₂N₂O decomposes and the interior would progress into the interior. However, at the same time, the densification

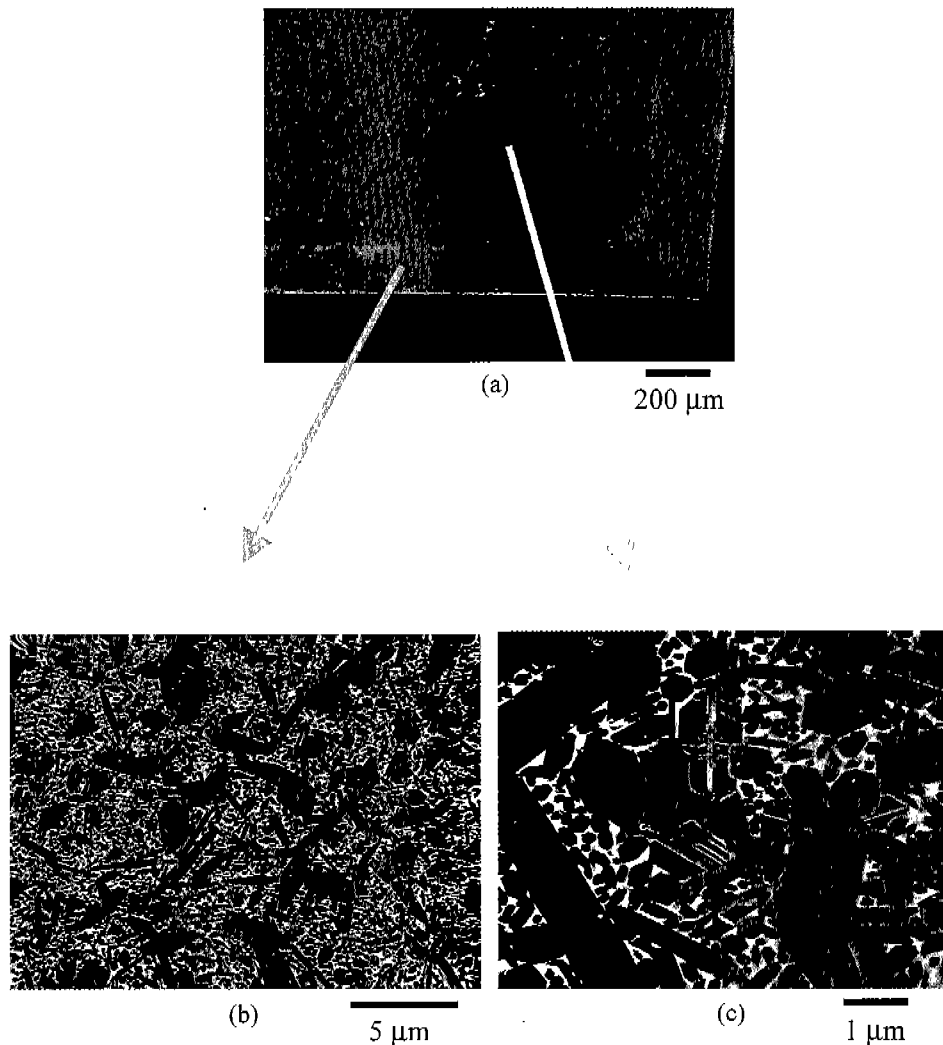


Fig. 4. SEM micrographs for AM-24 specimen sintered at 1850°C for 6 h showing the 300 mm thick surface layer (a), microstructure of the surface layer (b) and details of the microstructure of the interior region showing the different morphologies of $\text{Si}_2\text{N}_2\text{O}$ (arrows indicated).

rates of the surface layer and the interior will increase along with the rate of the conversion of α to β - Si_3N_4 . Thus, a very dense surface region will form more rapidly and limit the thickness of the surface layer and the further decomposition of $\text{Si}_2\text{N}_2\text{O}$ grains located within the interior of the specimen. The ceramic will then exhibit an interior consisting of $\text{Si}_2\text{N}_2\text{O}$ grains dispersed in β - Si_3N_4 and a dense surface layer composed of β - Si_3N_4 phase, especially with increases in the oxygen content of the silicon nitride powders.

4. Summary

1. Increased oxygen content leads to the formation of $\text{Si}_2\text{N}_2\text{O}$ at temperature as low as 1550°C. This phase is stable within the sample interior but becomes unstable in the surface region of the specimen at higher temperatures.

2. Increased oxygen content leads to the faster phase

transformation of α to β - Si_3N_4 at intermediate temperatures (e.g., 1650°C). However, the transformation becomes slower at higher temperatures due to the continuous precipitation of $\text{Si}_2\text{N}_2\text{O}$ phase.

3. The slower phase transformation to β - Si_3N_4 noticed in the near surface region for AM 24 specimens at 1650°C, as compared to that in the specimen interior, is due to the decomposition of $\text{Si}_2\text{N}_2\text{O}$ phase in the surface region.

4. The microstructure of the surface region, where $\text{Si}_2\text{N}_2\text{O}$ phase is formed and subsequently decomposes, is similar to that of Si_3N_4 prepared with α - Si_3N_4 with sintering additives which has not been subjected to intensive attrition milling. On the other hand, there are also irregular shaped $\text{Si}_2\text{N}_2\text{O}$ grains as well as fine Si_3N_4 grains within the interior of the specimen. When there is a large amount of oxygen in the starting powder mixture, the interior consists of a mixture of β - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ grains surrounded by a dense surface skin composed only of β - Si_3N_4 .

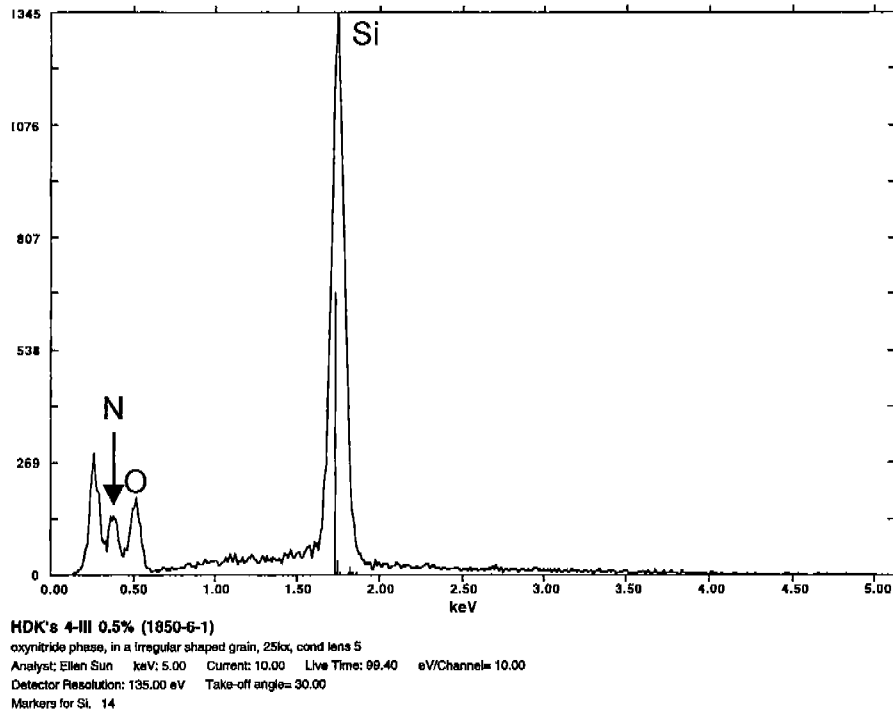


Fig. 5. EDS analysis of an irregular-shaped grain (arrowed in Fig. 4c) revealing the presence of an oxygen peak, in addition to the Si and N peaks.

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