Effect of Cooling Cycle after Sintering on the Thermal Diffusivity of Y_2O_3 Doped Si_3N_4 Ceramics

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Abstract As a result of the studies that have been made for increasing the thermal conductivity of Si_3N_4 , increasing thermal conductivity values have paved the way for the technologic applications such as using the Si_3N_4 in electronic devices as heatsink and substrate. Two important parameters such as density and grain boundary phase that affect the thermal conductivity of the Si_3N_4 ceramics are based on the sintering additives and techniques. Exposure time to gas applied in the sintering and cooling cycle after sintering are the critical factors that affect the intergranular phase crystallization. In this study, the effect of Y_2O_3 doped Si_3N_4 ceramics and different cooling cycle after gas-pressure sintering to the phase crystallization and thermal diffusivity was researched. The samples were subjected to two different cooling cycles after sintering. The thermal diffusivity value of the sample applied by slow cooling cycle is $17.79 \text{ mm}^2/\text{sec}$, the sample applied by rapid cooling cycle is $16.2 \text{ mm}^2/\text{sec}$. As a result of slow cooling cycle, the crystallization has increased but thermal diffusivity has decreased at the rate of $\sim 8.94\%$.

Keywords Thermal Conductivity, Crystallization, Microstructure Characterization

1. Introduction

Si_3N_4 ceramics have high thermal conductivity, electrical resistance, fracture toughness and strength properties [1]. Haggerty and Lightfoot calculated the [2] thermal conductivity of $\beta\text{-}Si_3N_4$ at room temperature as 200-320 W/mK. The recent studies showed that the thermal conductivity of Si_3N_4 has reached to the value of 100-155 W/mK [3-5]. These increasing thermal conductivity values have paved the way of new technologic applications of Si_3N_4 as substrates for heat sinks and integrated circuits in electronic devices.

Due to the strong covalent bonding structure of Si_3N_4 , it has noticed that sintering at high density is difficult via traditional ceramic sintering methods and liquid phase sintering technique that is the alternative production technique was started to be used. Despite the fact that oxide additions during the sintering have generated a liquid phase having low eutectic, a liquid is occurred that could be dissolved without separating the Si_3N_4 . It is more than important in which temperature the liquid phase is occurred, its viscosity and solubility of the Si_3N_4 . For that reason, different additional materials and different compositions have been tried accordingly. It is important that such additions are distributed as uniform and those should pack around Si_3N_4 grains [6, 7].

In order to increase the thermal conductivity of Si_3N_4 ceramics, it is important to increase the density and to decrease the amount of grain boundary phase. These parameters are based on the sintering additions and sintering techniques. Y_2O_3 is a suitable oxide additive to enhance the thermal conductivity of $\beta\text{-}Si_3N_4$ ceramics [8]. When sintering additions are on the grain boundaries, it is the reason for decreasing the thermal conductivity. High N_2 pressure that is one of the sintering methods prevents the decomposition at Si_3N_4 and thus, it allows increasing at high temperatures. When sintering temperature is increased, occurrence of big rod like grains is provided in thin matrix structure. As a result of this, the thermal conductivity is increased [5]. In Si_3N_4 ceramics produced by GPS, by taking into the consideration of exposing to the nitrogen gas, it was found that the phases among the current grains have changed. Additionally, the cooling cycle after sintering has important effect in the occurrence of intergranular phases [9]. Type, amount, and distribution of grain boundary phases in microstructure effect thermal conductivity [10-15].

The aim of this study was to investigate the effects of different cooling cycles applied in gas pressure sintering on crystallization and thermal diffusivity at Y_2O_3 added Si_3N_4 .

2. Material and Method

2.1. Starting Si_3N_4 Powder and Preparing the Compositions

By grinding starting Silzot Si_3N_4 powder for 6 hours, grain size was (Table 1). As sintering addition, MgO , Y_2O_3 and SiO_2 powders were used.

Work flow diagram that summarizes production and characterization activities is given in Figure 1. At the rate of 1:3 powder-alcohol in volume, isopropyl alcohol and at the weight of 1:1.5-5 powder: ball have added to powder blend at the amount of 40 gr that has been prepared in certain compositions and in the planetary ball mill

(Fritsch-Pulverisette5), they were mixed for 1.5 hour at 300rpm. The mud was dried in rotary evaporator (Heidolph 4001) (turning speed 30rpm and water temperature is 55°C). The mixtures that became powder by drying were sifted (by the sieve with $300\mu\text{m}$) and made prepared to be shaped accordingly [16].

Table 1. Properties of Si_3N_4 powders

Code	Grain size (μm)	Producing Company	Production Method
S	2.55	SKW-Trostberg, AG, Germany	Direct Nitridation
S6	1.11	It was achieved after grinding Silzot powder for 6 hours.

Figure 1. Flow diagram of experimental procedure

2.2. Shaping and Sintering

Powders were pre-shaped by uniaxial hand press (Alpha trademarked) at 25 MPa pressure. Afterwards, by cold isostatic press (CIP-Stansted Fluid Power trademarked FPG2568/2569), 300 MPa pressure was applied to the samples. Sintering process was performed for 2 hours under 5 bar nitrogen gas pressure (GPS) at 1775°C in the furnace of KCE-FPW 100/150-2200-25. The sintering process was shown schematically in Figure 2. The heating speed in temperature rise steps was kept at $10^\circ\text{C}/\text{min}$. Sintering process was performed in two steps. In the first step, it was attempted to have fully closed pore in nitrogen pressure (3 bar) to prevent the decomposition of Si_3N_4 , in the second step, by increasing the nitrogen gas pressure (5 bar), it was attempted to have high condensation. Speed cooling system was applied by $70^\circ\text{C}/\text{min}$ speed, slow cooling cycle was applied between 1775 - 1700°C at $10^\circ\text{C}/\text{min}$, 1700 - 1400°C at $5^\circ\text{C}/\text{min}$ and 1400°C -RT at $70^\circ\text{C}/\text{min}$ in three steps. In order to decrease formation of nitrogen phases in rich, relatively short GPS cycle was applied.

Figure 2. Schematic representation of the sintering process

2.3. Characterization

2.3.1. Measurement of Grain Size and Distribution

The grain size of starting Si_3N_4 powders and distribution of the grain size were determined by the laser particle size analyzer (Malvern Mastersizer 2000).

2.3.2. Phase Analysis

In order to define the phases contained in the raw powder and sintering samples, by using the radiation of X-rays diffractometer (Rigaku Rint 2000) and by using radiation of $\text{CuK}\alpha$ ($\lambda=1.54056 \text{ \AA}$), XRD analysis was made. Approximate rates of the α and β - Si_3N_4 phases were calculated by using peak intensities obtained from the bases of (102)-(210) and (101)-(210) respectively for α - Si_3N_4 and β - Si_3N_4 and calculated by means of equality (1) [17].

$$I_{\beta}/(I_{\alpha}+I_{\beta}) = 1/(1+K[(1/W_{\beta})-1]) \quad (1)$$

In the equality, I_{α} and I_{β} index are respectively peak intensity values of α and β - Si_3N_4 phases. W_{β} , β - Si_3N_4 is weight fraction, K is proportionality constant and this constant is respectively 0,518 and 0,544 for β (101)- α (102) and β (210)- α (210) diffractions.

2.3.3. Density Measurement

Density measurement was made by the principle of Archimedes (ASTM-C373). The samples were boiled for 2.5 hours in the pure water to remove the air in the pores after weighting their dry weights (W_1) and after cooling their suspended weights (W_2) and their weights at liquid leaked (W_3) were measured. According to the Equality, their bulk densities were calculated accordingly.

$$\text{Bulk Density} = W_1/(W_3-W_2) \quad (2)$$

2.3.4. Microstructure Characterization

Grain size and grain type investigations of starting Si_3N_4

powders were made by SEM (Zeiss Supra 50 VP) in secondary electron image mode (SE). The microstructure image of the sintering samples was received by using back scattered electron (BSE) detector. Before microstructure characterization, by cutting the samples (Struers-LaboPress3), the polishing process of the sample surface was performed by automatic polishing device (Struers-TegraPol25).

2.3.5. Thermal Diffusivity Measurement

Thermal diffusivity measurement was performed by using laser-flash device (Netzsch LFA-457) [18]. The measures were made from the room temperature up to 1000 °C. Each point down in the thermal diffusivity graphics are the average thermal diffusivity values. The failure gap in the measures is $\pm 0.1\%$. Before measurement, each surface of the sample was covered by the carbon. Carbon was used to increase the absorption in the front surface and to increase the emission in the back surface. The measures were made by using the nitrogen gas in the flow rate of 100 mbar/sec. Cape-Lehman model was used to keep the radial thermal loss. In the working principle of the device; Laser energy increases the temperature of the sample and rising temperature occurred in the back surface of the sample is recorded by the InSb (indium-antimony) detector. Current software in the device has analyzed the data to be achieved. First of all, by calculating according to Equality 3, start-up thermal diffusivity value is defined.

$$\alpha = (1,37.th^2)/(\pi^2.t_{1/2}) \quad (3)$$

In the equality, α is thermal diffusivity, th is the thickness of the sample, $t_{1/2}$ is heat transfer half time. Thermal conductivity is stated by the formula shown in Equality 4:

$$k = \alpha \rho c_p \quad (4)$$

In this formula, α is thermal diffusivity [mm^2/sec], ρ ;

density [gr/cm^3], C_p ; heat capacity in the fix pressure [$\text{J}/\text{g}\cdot\text{K}$]. C_p value of Si_3N_4 ceramics is taken as $0.7 \text{ J}/\text{g}\cdot\text{K}$ for each sample by taking into the consideration of previous studies [19].

3. Results and Discussions

3.1. Characterization of the Starting Powders

In order to produce Si_3N_4 based ceramic having high thermal conductivity, it is more than important to know

about the properties of the starting powders. XRD analysis result of Si_3N_4 powder is given in Figure 3. In the Silzot powder, there are 10% β phase and 90% α phase.

The grain size of the starting powders is an important parameter that affects sintering. Using fine-grained powder facilitates sintering. For this reason, it is vital to mill the powders in certain dimensions. The distribution graphic of grain size of unmilled and milled for 6 hours silzot Si_3N_4 powders is in Figure 4, by using the results of the Figure 4, important d_{10} , d_{50} and d_{90} values are given in Table 2.

Figure 3. XRD pattern of starting Silzot Si_3N_4 powder

Figure 4. Distribution graphics of grain size of (a) unmilled, (b) milled for 6 hours Silzot Si_3N_4 powders

Table 2. The distribution of grain size of unmilled and milled for 6 hours Silzot Si_3N_4 powders

Starting powder	Milling time (hour)	d_{50} (μm)	d_{10} (μm)	d_{90} (μm)
Silzot	-	2.55	1.00	5.72
	6	1.11	0.51	11.92

Average grain size of unground Silzot powder is $2.55\mu\text{m}$ and it has narrow grain size distribution. Average grain size of Si_3N_4 powder milled for 6 hours is $1.11\mu\text{m}$ and it has wide grain size distribution. By the milling process, powder grain size has almost decreased in half.

After starting Si_3N_4 powder size figure (prismatic or coaxial), solubility of the powders affects sintering. In order to have information about Si_3N_4 powders morphology, secondary electron SEM images are given in Figure 5-6. Silzot powder has composed of angular powders (Figure 5) and after milling, grain size of the powder was reduced (Figure 6).

Figure 5. Secondary Electron SEM images of Silzot powder (10 KX) **Figure 6.** Secondary electron SEM images of Silzot powder grinded for 6 hours (S6); (10 KX)

3.2. Results of Density and Phase Analysis

XRD patterns of the samples applied by rapid and slow cooling cycle after sintering is given in Figure 7; density and phase analysis results are also given in Table 3.

Figure 7. XRD patterns of the samples (P: Pyroxene ($MgYSi_2O_5N$), M: Melilite ($Y_2Si_3O_3N_4$))

Table 3. Density and phase analysis results of the samples (P: Pyroxene ($MgYSi_2O_5N$), M: Melilite ($Y_2Si_3O_3N_4$))

Cooling Cycle	Sintering Condition	Density (g/cm^3)	% O.P.	% W.L.	Secondary Phases
Rapid	1775°C-5b-2s	3.24	0.58	3.20	P, M
Slow		3.21	0.75	4.08	P (high), M

In XRD patterns of the samples (Figure 7) applied by slow cooling cycle, phases of the pyroxene crystalline was observed [20, 21]. In the samples subjected to the slow cooling cycle, the pyroxene crystalline phase peak intensity is high and apparent. Slow cooling cycle increased pyroxene phase crystallization. Density is low and open porosity amount is high (0.75%). The density of the samples applied by rapid cooling cycle is $3.24 g/cm^3$, samples applied by slow cooling cycle is $3.21 g/cm^3$.

3.3. Microstructure and Thermal Diffusivity Results

Microstructure images of the samples are given in Figure 8. The change curves of the thermal diffusivity by temperature are given in Figure 9 and the result of the thermal conductivity is given in Table 4.

Figure 8. Microstructure images of the samples applied by (a) slow and (b) rapid cooling (20 KX)

Figure 9. Changes in thermal diffusivity values of samples as a function of temperature

Table 4. Thermal diffusivity and thermal conductivity results of the samples

Cooling Cycle	Sintering Condition	Density (g/cm ³)	% O.P.	% W.L.	Thermal Diffusivity (mm ² /sec)	Thermal Conductivity (W/mK)
Rapid	1775°C-5b-2s	3.24	0.58	3.20	17.79	40.35
Slow		3.21	0.75	4.08	16.2	36.40

As shown in the microstructure images, there are slightly more pores in the slowly cooled specimens (Figure 8 a). Thermal diffusivity value of the sample applied by slow cooling cycle is 17.79 mm²/sec and sample applied by rapid cooling cycle is 16.2 mm²/sec. When using slow cooling cycle, thermal diffusivity has decreased at the rate of ~ 8.94%. The pore amount in the samples applied by slow cooling cycle is much more. The pore amount and density values affected the results. The results matched up with the literature. The pores decrease the thermal conductivity and when pore is increased, thermal capacity is decreased and additionally, the pore decreases the thermal conductivity by decreasing the grainy size. Pores behave as scattering center. Due to the refractive index difference between pore-body, the thermal conductivity is decreased and effective mean free path is decreased [22].

In the samples applied by slow cooling cycle, the phase of high intensity pyroxene crystalline was observed (Figure 7). On the other hand, dimension and distribution of the secondary phases are different. Crystallization negatively affected the thermal diffusivity in match up with the literature. In the sintering ceramics thermal conductivity, grain boundary film thickness, grain boundary phase and type and amount of the secondary phases affect the thermal conductivity [23]. In the sintering samples, if the secondary phases distribution is not homogenous, a composite based approach could be considered. The thermal conductivity in the composites is based on the phase amount, arrangement and thermal conductivity of each phase. In the multi-phase materials, the heat condition is more than complexed [22].

4. Conclusions

As a result of this study where two different cooling cycles was applied after sintering and the effect of the cooling cycle, intergranular phase occurrence and thermal diffusivity were reviewed;

- Density values of the samples applied by slow cooling cycle are lower.
- The pore amounts in the samples applied by slow cooling cycle are much more.
- When applying slow cooling cycle, the crystallization of the pyroxene phase is increased.
- When applying slow cooling cycle, thermal diffusivity is decrease at the rate of ~ 8.94%.
- The thermal conductivity values of the samples applied by slow cooling cycle are lower.
- Crystallization, pore amount and density effected results. In multi-phase materials, thermal

conductivity is complex and it is also very difficult to interpret.

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