Fabrication and characterizations of high density Si$_3$N$_4$ - ZrO$_2$ ceramics

Kamol TRAIPANYA$^{1,7}$, Thanakorn WASANAPIARNPONG$^{1,2}$, and Charusporn MONGKOLKACHIT$^3$

1 Department of Materials Science, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand
2 Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University Research Building, Pathumwan, Bangkok 10330, Thailand
3 National Metal and Materials Technology Center, National Science and Technology Development Agency, Khlong Luang, Pathumthani 12120, Thailand

*Corresponding author e-mail: traipanya@hotmail.com

Abstract

Silicon nitride and zirconia were mixed with SiO$_2$, MgO, Y$_2$O$_3$ as sintering additives and pressureless sintered at 1650°C in N$_2$ atmosphere for 2 h. The XRD results showed α-Si$_3$N$_4$ was partially transformed to β-Si$_3$N$_4$ with 3:3:5 weight ratio of SiO$_2$: MgO : Y$_2$O$_3$. However, at 5 wt% of ZrO$_2$ addition promoted phase transformation of α-Si$_3$N$_4$ to β-Si$_3$N$_4$ while 35 wt% of ZrO$_2$ completely transformed to β-Si$_3$N$_4$ phase. Si$_3$N$_4$ has a lower density than ZrO$_2$, bulk density of samples increases in correlation with the amount of ZrO$_2$. Because there was no difference in hardness and flexural strength between sintered Si$_3$N$_4$ samples with hardness of 13.41 GPa and 648.13 MPa along with increasing ZrO$_2$ variation up to 55 wt%. Furthermore, with 75 wt% ZrO$_2$, the hardness was reduced to 10.57 GPa and the flexural strength decreased to 208.16 MPa. SEM images of Si$_3$N$_4$ samples demonstrated the dense microstructure and 5 wt% ZrO$_2$ showed homogeneous ZrO$_2$ distributed among the Si$_3$N$_4$ grains. As a result, the hexagonal rod-like form of β-Si$_3$N$_4$ is clearly visible in 75 wt% ZrO$_2$. Therefore, Si$_3$N$_4$ with ZrO$_2$ can be sintered with the homogeneous microstructure of the α-Si$_3$N$_4$ to β-Si$_3$N$_4$ transformation and tolerable mechanical properties vary with ZrO$_2$ content.

1. Introduction

Silicon nitride (Si$_3$N$_4$) and zirconia (ZrO$_2$) ceramics have been highly accepted for use in structural applications due to their high fracture toughness, hardness, strength, chemical inertness, high temperature stability, wear resistance, low coefficient of friction, and biocompatibility. Currently, Si$_3$N$_4$ ceramics are one of the most used groups of high thermal application and processing, especially nozzles, valves, cutting tools, turbochargers, heater sheaths, abrasive material, and metallurgical casting and machining in general [1,2]. However, sintered silicon nitride by conventional sintering had failed due to primarily problem of the low interatomic diffusion ability and the high temperature dissociation of Si$_3$N$_4$, which resulted in microstructural coarsening [3]. Nowadays, it is well known that Si$_3$N$_4$ was manufactured using the nitridation mechanism from packed of silicon powder or sintered with various additives in high nitrogen pressure. Accordingly, several sintering aids such as yttria, magnesia, and alumina must be added to reduce the sintering temperature via the liquid-phase mechanism. During sintering, the smaller powders of alpha phase begin to dissolve with the liquid phase and recrystallize into a beta phase with a hexagonal needle shape and grain growth with traces. Due to the fact that the process of transformation from α-Si$_3$N$_4$ to β-Si$_3$N$_4$ is irreversible mechanism. Then, there have been no reports on sintered material mechanical properties testing between alpha phase and beta phase for comparative purposes. A glassy phase exists between the grain boundaries, resulting in a higher density [4]. Moreover, the high nitrogen pressure atmosphere is required to prevent the mass loss of Si$_3$N$_4$. Mitomo et al., in 1977, discovered the Si$_3$N$_4$ with 90% density was obtained by using packing powder with 1 MPa of nitrogen pressure. Subsequently, Giachello et al. demonstrated that high nitrogen pressure could be avoided by using compacted Si$_3$N$_4$ powder containing MgO as a sintering additive embedded in Si$_3$N$_4$ powder [5]. In 2006, Wasanapiarnpong et al. found that the Si$_3$N$_4$ ceramics powder with SiO$_2$:MgO:Y$_2$O$_3$ as sintering additive were successfully sintered with high degree of alpha to beta phase transformation at 1600°C to 1750°C in 1 atm of N$_2$ atmosphere without packing powder [6].

For the zirconia (ZrO$_2$) has been utilized in various commercial products in the field such as seal, pump and milling media [7]. In the past, pure ZrO$_2$ is difficult to sintering because restriction of phase transformation from tetragonal to monoclinic at 950°C on cooling resulting in 4% of volume expansion. This change in shape of volume transformation can result in catastrophic fracture and structural inconsistency [8]. Presently, stabilized zirconia with many oxides such as Y$_2$O$_3$, MgO, CeO$_2$ etc. could be eliminated effect from phase transformation especially when yttria was added into zirconia has two important effects. It broadens the range of the tetragonal phase field and lowers the temperature at which the tetragonal-monoclinic transformation occurs. From the excellent property about stress induce...
transformation toughening mechanism of zirconia is widely accept
that led zirconia used as reinforcing in ceramic composite. The most
dominant are alumina-zirconia composites, which outperform
conventional alumina in terms of strength, toughness, and wear
resistance. Recently, zirconia-based nanocomposites for biomedical
applications as dental implants, hip joint have been developed with
linking several toughening mechanisms such as tetragonal-monoclinic
transformation, microcracking, and crack deviation due to the
secondary phases. During the past decade Si3N4 and ZrO2 have been
studied in the different sintering atmosphere. However, a recent study
was attempted to develop Si3N4 composite materials utilizing ZrO2
as a reinforcement phase. Although the use of tetragonal zirconia as
a reinforcement phase can effectively improve the fracture toughness
of Si3N4 ceramics, the well-known high-temperature interaction
between the ZrO2 component and the Si3N4 matrix has been frequently
observed during sintering at temperatures above 1600℃, resulting
in the formation of deleterious ZrN or ZrON phases [9].

Therefore, this study focused on various composition
between Si3N4-ZrO2 materials with sintering additives in unique
sintering atmospheres and without packing powder by investigated
on phase, density, hardness, flexural strength and microstructure after
nitrogen gas pressureless sintering.

2. Materials and experimental

The raw materials used were various compositions of high purity
α-Si3N4 powders (SN E-10 grade, Ube Industries Ltd., Tokyo, Japan)
and 3 mol% Y2O3 stabilized ZrO2 powders (Inframat, Advanced
Materials) at 5, 35, 55 and 75 wt% with SiO2 (KE-P30, Nippon
Shokubai Co. Ltd., Osaka, Japan), MgO (MJ-30, Iwatani Corp., Tokyo,
Japan), and Y2O3 (RU, Shin-Etsu Chemical Co. Ltd., Tokyo, Japan)
as sintering additives by weight ratio of SiO2 : MgO : Y2O3 at 3:3:5
was shown in Table 1. Then the starting material powders were mixed
by ball milling in a high-density polyethylene bottle (HDPE) with
Si3N4 ball in 99.9% ethanol for 24 h. The slurry was dried to powder
through a 100-mesh screening sieve.

The powders were uniaxially pressed at 25 MPa and cold isostatic
press at 250 MPa for 5 min. The pellets were sintered at 1650℃ for
2 h in a nitrogen atmosphere of 0.1 MPa. All sintered samples were
polished surface of samples was chemically etched with HF
for 15 s for the microstructure observation using a scanning electron
microscope (JSM 6480LV, JEOL Ltd., Tokyo, Japan).

3. Results and discussion

3.1 Phases composition

Table 1. Starting materials with various composition.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SN</th>
<th>5Zr</th>
<th>35Zr</th>
<th>55Zr</th>
<th>75Zr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si3N4</td>
<td>89</td>
<td>84</td>
<td>54</td>
<td>34</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>SiO2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Y2O3</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>ZrO2</td>
<td>5</td>
<td>5</td>
<td>35</td>
<td>55</td>
<td>75</td>
<td>100</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Figure 1. XRD patterns of Si3N4 (SN), 5 wt% ZrO2 (5Zr), 35 wt% ZrO2 (35Zr),
55 wt% ZrO2 (55Zr), 75 wt% ZrO2 (75Zr), ZrO2 (Zr) samples sintering at
1650℃ for 2 h.
3.2 Density and Water Absorption

For the bulk density and relative density in Table 2, it shows the changes in the bulk density, and relative density of the Si₃N₄-ZrO₂ composite ceramic samples SN, 5Zr, 35Zr, 55Zr, 75Zr, and Zr, respectively. With an increase in the ZrO₂ content of the raw material, it can be seen that the bulk density of the samples increased relatively. The Si₃N₄(SN) samples have a density of about 3.18 g cm⁻³ and the 5Zr samples have 3.28 g cm⁻³ where the bulk density increases related to the amount of ZrO₂ due to the density of ZrO₂ being higher than that of the Si₃N₄ materials. Furthermore, 75Zr samples have a density of 6.05 g cm⁻³ close to normal sintered ZrO₂ that shows no effect of the ambient pressure N₂ for ZrO₂ and the XRD results demonstrated α-ZrO₂ without any ZrN formation. The bulk density of sintered samples was contrasted with relative density since the α-Si₃N₄ hexagonal rod-like grains is remain uniform with light area of the ZrO₂ grain in their microstructure. The SN sample with SiO₂, MgO, and Y₂O₃ as sintering additive and Zr sample, the microstructure becomes homogeneous, dense, and low porosity correlate with high relative density and good mechanical properties.

3.3 Mechanical Properties

Figure 2 shows the mechanical properties between Vickers hardness and flexural strength of all sintered samples as a role of ZrO₂ content. The hardness decreased with increasing amount of ZrO₂. The inappreciably decrease in porosity of the samples may be related to the slightly dropped in hardness. A similar pattern emerged in the results of the flexural strength test. The SN samples exhibited higher hardness value when compared with a higher ZrO₂ content. It can be seen that the hardness value of samples with 5 wt% to 75 wt% of ZrO₂ decreases from 13.34 GPa to 10.57 GPa with increasing of the zirconia. It is widely known that the intrinsic property of the material has a significant impact on the hardness of dense multiphase ceramics because the hardness of Si₃N₄ is mostly higher than the hardness of ZrO₂. According to reports, the hardness values of ceramics made of TZZ, α-Si₃N₄, and β-Si₃N₄ are respectively between 11 GPa and 13 GPa, 23 GPa, and 20 GPa [12,13].

Additionally, we should be considered how α-Si₃N₄ transform to β-Si₃N₄ during sintering because the significant partial portion of alpha phase dissolve by SiO₂-MgO-Y₂O₃ liquid phase system and change to the beta phase was mainly referred by the phase transformation for the sample containing higher amounts of stabilized ZrO₂. As a result, the accelerated modification of alpha to beta may also subsidize to the recognized hardening decreasing in Si₃N₄-ZrO₂ ceramics [14]. The coincidental trend of the flexural strengths with hardness has shown a high value of 648.13 MPa for the SN sample particularly results from the achievement of a 98.43% relative density and a slightly decrease to 622.73 MPa for 5Zr by increasing the amount of ZrO₂. With regard, the increment of porosity results in the low flexural strength falling from 541.97 MPa for 35Zr, 474.21 for 55Zr, and 208.16 MPa for 75Zr respectively. Although the porosity of the Zr sample is not different from that of another sample but high strength because its exhibits a monolithic ZrO₂.

3.4 Microstructure

Figure 3 shows the SEM micrographs of the sintered samples with polished surface. SN sample with SiO₂, MgO, and Y₂O₃ as sintering additive and Zr sample, the microstructure becomes homogeneous, dense, and low porosity correlate with high relative density and good mechanical properties. However, in Figure 3(b), the microstructure of the 5Zr sample is remain uniform with light area of the ZrO₂ grain in their microstructure. According to the results, the grain growth mechanism of the elongated β-Si₃N₄ grains is derived from the phase transformation mechanism and the added ZrO₂ can promote α to β phase transformation [15]. Also, by ZrO₂ addition, complete phase transformation of α to β through liquid phase sintering leads to β-Si₃N₄ hexagonal rod-like grains formation clearly in the 75Zr sample in accordance with XRD results.

Table 2: Bulk density, relative density, apparent porosity, and water absorption of sintered sample at 1650°C for 2 h under 0.1 MPa N₂.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SN</th>
<th>5Zr</th>
<th>35Zr</th>
<th>55Zr</th>
<th>75Zr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>3.18</td>
<td>3.28</td>
<td>3.84</td>
<td>4.31</td>
<td>4.89</td>
<td>6.05</td>
</tr>
<tr>
<td>Theoretical density (g cm⁻³)</td>
<td>3.22</td>
<td>3.30</td>
<td>3.87</td>
<td>4.38</td>
<td>5.03</td>
<td>6.10</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>98.70</td>
<td>99.30</td>
<td>99.15</td>
<td>98.50</td>
<td>97.20</td>
<td>99.18</td>
</tr>
<tr>
<td>Apparent density (g cm⁻³)</td>
<td>3.18</td>
<td>3.28</td>
<td>3.85</td>
<td>4.32</td>
<td>4.90</td>
<td>6.06</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>0.13</td>
<td>0.11</td>
<td>0.26</td>
<td>0.15</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>0.04</td>
<td>0.03</td>
<td>0.07</td>
<td>0.04</td>
<td>0.06</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*3 samples/test

Figure 2. Vickers hardness and flexural strength of sintered Si₃N₄-ZrO₂ ceramics.
4. Conclusions

Silicon nitride and zirconia were mixed with SiO$_2$, MgO, Y$_2$O$_3$ and then pressureless sintering. According to the XRD results, the starting powders of $\alpha$-Si$_3$N$_4$ were partially transformed to $\beta$-Si$_3$N$_4$ with 3:3:5 weight ratio of SiO$_2$ : MgO : Y$_2$O$_3$, respectively. At 5 wt% of ZrO$_2$ was performed phase transformation of $\alpha$-Si$_3$N$_4$ to $\beta$-Si$_3$N$_4$ while 35 wt% of ZrO$_2$ effectively transformed to $\beta$-Si$_3$N$_4$ phase. The bulk density of the samples increases directly with the amount of ZrO$_2$. The hardness and flexural strength between sintered samples with high hardness of 13.41 GPa and 648.13 MPa along with increasing ZrO$_2$ variation up to 55 wt%. But 75 wt% ZrO$_2$, the hardness decreased to 10.57 GPa and the flexural strength reduced to 208.16 MPa. SEM microstructures were presented, which showed a dense and homogeneous ZrO$_2$ dispersion between Si$_3$N$_4$ grains of 5 wt% of ZrO$_2$ corresponding with the hexagonal rod-like of $\beta$-Si$_3$N$_4$ is evidently at 75 wt% ZrO$_2$. From a distinctly sintering atmosphere, Si$_3$N$_4$ and ZrO$_2$ could be sintered together with uniform microstructure and mechanical properties acceptable.

References


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