Dielectric properties of silicon nitride ceramics prepared by low temperature spark plasma sintering technique

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In this study, α-Si3N4 ceramics were successfully prepared using MgO and AlPO4 as the sintering additives and a low temperature spark plasma sintering (SPS) technique. The resultant α-Si3N4 ceramics sintered from 1300 °C to 1500 °C show a fine microstructure within nearly no grain growth and phase transformation. The sintering process is not completed within such a short sintering time [11]. It is assumed that the initial temperature of the α to β transformation is about 1400 °C and the temperature of completion is about 1800 °C. Otherwise, the SPS technique thus provides us with a unique possibility to manipulate the sintering kinetics. The inherent advantages of SPS technique are the reasons why it is selected in this study. AlPO4 is chemically inert, thermally stable (melting point of ~2000 °C), electrically neutral, and highly covalent, which makes AlPO4 an attractive candidate material for high temperature applications [12]. On the other hand, it is also a low temperature binder material which makes it possible for the low temperature sintering of α-Si3N4 ceramic. 

In this research, we explore an effective method to prepare the α-Si3N4 ceramics by using MgO and AlPO4 as the sintering additives and the SPS technique. The effect of a low sintering temperature and AlPO4 content on the dielectric properties of the sintered samples is mainly investigated.

Experimental Procedure

Starting materials

The raw materials used in the present study are as follows: α-Si3N4 rich powder (produced by UBE Industries, Co., Ltd, Japan with an average particle size of ~0.5 μm and α/(α + β) > 93 wt%), light magnesia (MgO) powder (produced by H.C. Starck, Germany, with an average particle size of ~0.2 μm and a purity of 99.9%) and aluminium phosphate (AlPO4) powder (produced by H.C. Starck, Germany, with an average particle size of ~0.5 μm and a

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Introduction

Silicon nitride (Si3N4) ceramic has been studied intensively and used in numerous applications as both a structural and functional material because of its superior properties, such as high-temperature strength, good oxidation resistance and low thermal expansion coefficient [1-4]. Si3N4 has two forms, α and β phases [5]. Previous studies focused mainly on a complete phase transformation from α-Si3N4 to β-Si3N4 and achieving perfect mechanical and thermal properties by using different sintering additives, and were aimed at obtaining fully-dense products [6, 7]. However, better dielectric properties [8] of α-Si3N4 ceramic whose dielectric constant (ε) is 5.6 and dielectric loss (tgδ) is 0.003 at room temperature than β-Si3N4 (ε = 7.9, tgδ = 0.005) should not be ignored because it can be utilized as an electromagnetic wave penetration material [9].

It is known that spark plasma sintering (SPS) is a newly-developed sintering technique [10] which is similar to the conventional hot-press sintering in configuration, where the precursor powders are loaded in a die and a uniaxial pressure is applied during the sintering process. However, instead of using an external heating source, densification is enhanced by the use of a pulsed direct current passing through the electrically-conducted die and the sample. A high sintering speed and possibly low temperature sintering are characteristics of the SPS technique. It is reported that Si3N4 ceramic can be sintered within 15 minute of heating and holding time, but the α to β transformation is not completed within such a short sintering time [11]. It is assumed that the initial temperature of the α to β transformation is about 1400 °C and the temperature of completion is about 1800 °C. Otherwise, the SPS technique thus provides us with a unique possibility to manipulate the sintering kinetics. The inherent advantages of SPS technique are the reasons why it is selected in this study. AlPO4 is chemically inert, thermally stable (melting point of ~2000 °C), electrically neutral, and highly covalent, which makes AlPO4 an attractive candidate material for high temperature applications [12]. On the other hand, it is also a low temperature binder material which makes it possible for the low temperature sintering of α-Si3N4 ceramic.

In this research, we explore an effective method to prepare the α-Si3N4 ceramics by using MgO and AlPO4 as the sintering additives and the SPS technique. The effect of a low sintering temperature and AlPO4 content on the dielectric properties of the sintered samples is mainly investigated.

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purity of 99.9%). Table 1 lists the main compositions of the α-Si₃N₄ raw powder.

| Table 1. Phase and elemental composition of Si₃N₄ raw material, wt.%.
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>material</td>
</tr>
<tr>
<td>Si₃N₄</td>
</tr>
</tbody>
</table>

Materials preparation

According to Table 2, the powder precursors in various ratios were ball milled in ethanol for 10 h in a nylon jar, using sintered Si₃N₄ grinding balls. After the powder mixtures were dried, they were passed through a 100 mesh sieve to eliminate large agglomerates, then loaded in a graphite die with an inner diameter of 32 mm and pre-pressed to some extent and sintered using a SPS system (model-1050, Sumitomo Coal Mining Co. Ltd., Tokyo). The sintering temperature was 1300-1500 °C, which was measured by an optical pyrometer focused on the surface of the graphite die. An average heating rate of 100 K·min⁻¹ was applied and the holding time for each sample was 5 minute. A uniaxial pressure of 30 MPa and a nitrogen (N₂) atmosphere were applied from the start to the end of the sintering cycle. The samples were cooled naturally within the furnace.

Characterization

After sintering, the bulk density of the sintered products was determined by the Archimedes’ immersion method using distilled water. The relative density was calculated directly in this way. The phase compositions were analyzed by X-ray diffraction (XRD) using a Rigaku-D/Max-III A diffractometer. Cu radiation was used and operated at 35 kV and 30 mA. The microstructure of the fractured surfaces was observed by scanning electron microscopy (SEM). The dielectric constant and dielectric loss of bulk samples was tested at a frequency of 10 GHz.

Results and Discussion

Sintering behavior

The porosity of A1-A4 as a function of sintering temperature and the sintering additives content is illustrated in Fig. 1. It can be seen from Fig. 1 that the porosity shows a sharp variation against the sintering temperature from 1300 °C to 1400 °C when the AlPO₄ content is 6 wt.% (A3) and 16 wt.% (A4), while this phenomenon happens from 1400 °C to 1500 °C for samples A1 and A2. Samples with the porosity from 2% to 35% are acquired. Thus, we can conclude that when the AlPO₄ content or the sintering temperature reaches certain values, this material can be fully-dense sintered. Moreover, nearly the same porosity of the sintered samples can be obtained by adjusting the AlPO₄ content and sintering temperature. For example, the porosity of A3 sintered at 1400 °C is less than 3%, and the sintering temperature for A1 and A2 with the same porosity is 1500 °C and 1450 °C, respectively. This indicates that Si₃N₄ ceramics can be sintered at a lower temperature with an increase in the AlPO₄ content.

Microstructure and phase analysis

The X-ray diffraction patterns of A4 at different sintering temperatures are shown in Fig. 2. It is obvious that the crystal phases of A4 are α-Si₃N₄, β-Si₃N₄, MgSiO₃, AlPO₄. The existence of α-Si₃N₄, β-Si₃N₄ is understood because the raw material of the α-Si₃N₄ powder includes α-Si₃N₄ and a little of β-Si₃N₄. The product identified as MgSiO₃ illustrates one of the sintering mechanisms that MgO can react with SiO₂ presenting on the surface of the silicon.

<table>
<thead>
<tr>
<th>Table 2. The composition ratio (wt.%) of raw powders of every sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
</tr>
<tr>
<td>A1</td>
</tr>
<tr>
<td>A2</td>
</tr>
<tr>
<td>A3</td>
</tr>
<tr>
<td>A4</td>
</tr>
</tbody>
</table>

Fig. 1. The porosity of the sintered samples as a function of sintering temperature and the content of sintering additives.

Fig. 2. The XRD patterns of A4 at different sintering temperatures: (a) 1350 °C; (b) 1500 °C.
Different contents of AlPO$_4$ composite is finished at 1300°C to 1500°C according to the different contents of AlPO$_4$, which was the other sintering mechanism.

The SEM images of the sintered samples at different sintering temperatures are shown in Fig. 3. From the SEM images of the fracture surfaces of A4 sintered at 1400°C and 1500°C, it is worth noting that nearly no β-Si$_3$N$_4$ is observed and the grain size is about 0.5 µm which maintains the characteristic of the raw Si$_3$N$_4$ materials, indicating there is no obvious grain growth in the SPS process. Porosity in this situation is mainly caused by partially-sintered Si$_3$N$_4$ particles and a non-compact structure is observed. On the other hand, it is seen that the AlPO$_4$ binder phase performs a good binding property with Si$_3$N$_4$ grains, indicating a good adhesion between the grains and, thus, overall good sintering behavior and promising mechanical properties.

**Dielectric properties**

The dielectric constant and dielectric loss of the sintered samples as a function of porosity and sintering temperature are listed in Table 3. It is clearly observed that the highest dielectric constant is 7.4 and the lowest is below 5.0 when the porosity varies from 2% to 30%. Obviously, the dielectric constant is almost decreased with an increase of the porosity, which is in good agreement with the following formula:

$$\log\varepsilon_p = (1-p)\log\varepsilon_0$$  \hspace{1cm} (1)

where $p$ is the porosity of the sample, $\varepsilon_p$ is the dielectric constant when the porosity is $p$ and $\varepsilon_0$ is the dielectric constant when the porosity rate is 0.

On the other hand, it can be seen that the dielectric loss is less than $10 \times 10^{-3}$ for each sample regardless of the porosity and sintering temperature, and it increases with a decrease of the porosity as shown in Table 3.

The effect of AlPO$_4$ content on both the dielectric constant and dielectric loss is compared. We can conclude that increasing the AlPO$_4$ content greatly reduces both the dielectric constant and dielectric loss due to the low dielectric constant ($\varepsilon_0 = 6.0$) and dielectric loss (The existence of a high AlPO$_4$ content not only affects the sintering behavior of α-Si$_3$N$_4$ at a lower temperature but also greatly restrains the transmission of ion and ionic polarization because of the fact that AlPO$_4$ itself embodies excellent adhesive action at elevated temperature) of AlPO$_4$.

**Conclusions**

The effect of sintering additives based on MgO and AlPO$_4$ on the sintering and dielectric properties of α-Si$_3$N$_4$ matrix ceramics has been examined using the spark plasma sintering (SPS) technique. The results obtained are as follows:

1) The main crystal phase of all samples is α-Si$_3$N$_4$, realized by controlling the sintering temperature and the sintering additive content.

2) The sintering mechanism of α-Si$_3$N$_4$ matrix ceramics by adding MgO and AlPO$_4$ could be attributed to both a reaction between MgO and SiO$_2$ present on the powders which promotes the mixed powders adherence and the solid state sintering of AlPO$_4$.

3) The dielectric constant is in the range of 4.5-7.4, the dielectric loss is less than $10 \times 10^{-3}$, and decreases with an increase of the porosity. The existence of a high content of AlPO$_4$ greatly restrains the transmission of ion and ionic polarization because of the fact that AlPO$_4$ itself embodies excellent adhesive action at high temperature.

**Table 3. Dielectric properties of the sintered samples as a function of the porosity and sintering temperature**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temperature (°C)</th>
<th>Porosity (%)</th>
<th>Dielectric constant</th>
<th>Dielectric loss ($\times 10^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>1450</td>
<td>11.2 ± 0.1</td>
<td>5.4 ± 0.1</td>
<td>3.5 ± 0.5</td>
</tr>
<tr>
<td>A2</td>
<td>1450</td>
<td>5.1 ± 0.3</td>
<td>7.0 ± 0.1</td>
<td>6.2 ± 0.7</td>
</tr>
<tr>
<td>A3</td>
<td>1450</td>
<td>3.0 ± 0.2</td>
<td>7.0 ± 0.3</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td>A4</td>
<td>1450</td>
<td>2.7 ± 0.3</td>
<td>7.0 ± 0.1</td>
<td>5.3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>2.1 ± 0.1</td>
<td>7.0 ± 0.1</td>
<td>6.2 ± 0.5</td>
</tr>
</tbody>
</table>

**References**

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