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**Mechanical Properties of Microwave Sintered Si$_3$N$_4$-based Ceramics**

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**Abstract:** The mechanical properties and microstructure formation processes in Si$_3$N$_4$+3% Al$_2$O$_3$+5% Y$_2$O$_3$(Yb$_2$O$_3$) ceramic compacts sintered under microwave heating (MWH) and under traditional heating (TH) were investigated. The initial ceramic materials were powder blends of silicon nitride with oxides. The mean powder particle sizes were 0.5-1.0 μm. The content of α-phase in the Si$_3$N$_4$ powder was more than 95%. The samples were sintered at 1800°C in nitrogen at normal pressure, the heating rate in all experiments was 60°C/min. The Vickers hardness (HV), fracture toughness (K$_{IC}$) and bending strength (σb) were determined. The microstructures of fracture surfaces of samples were studied by SEM. Quantitative microstructure analysis was carried out. It was shown that the values of HV and K$_{IC}$ of ceramic samples sintered under MWH at 1800°C rose steadily with the sintering time. This caused an increase in density, which reached maximum as fast as after 30 min of the MWH sintering; the mass loss at that time amounted to 3-4 %. The porosity of sintered samples with an addition of yttria was less than 1 %, that of ytterbia was greater, 2.4 %. For similar values of relative density, the hardness and fracture toughness of ceramic samples produced under MWH were higher as compared with those of samples sintered under TH. The microstructure of samples had the form of elongated grains in a matrix of polyhedral grains of the β-Si$_3$N$_4$ phase. Measurements showed the mean size of grains in samples produced by MWH to be greater that in samples produced by TH. A larger number of elongated grains were formed. It was concluded that for sintering under MWH of Si$_3$N$_4$-based ceramics the growth of elongated β-Si$_3$N$_4$ grains and formation of a "reinforced" microstructure were promoted and thereby improved the mechanical properties of such ceramics.

**Keywords:** Silicon nitride; Microwave sintering; Mechanical properties.

**Резюме:** Исучены механические свойства и процессы формирования микроструктуры в керамике на основе нитрида кремния при спекании в условиях микроволнового (30 ГГц) (ЦВЧН) и традиционного (TH) нагревания. Исходными материалами были смеси порошков нитрида кремния и оксидов алюминия и иттрия (иттербия). Средний размер частиц порошков был 0.5-1 мкм. Содержание α-фазы в порошке нитрида было более 95 %. Образцы спекали при температуре 1800°C в среде азота нормального давления.

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Были определены: твердость по Виккерсу, коэффициент вязкости разрушения, прочность на изгиб. По изломам изучена микроструктура образцов, использован компьютерный анализ микроструктуры. Показано, что твердость и вязкость разрушения образцов, спеченных при СВЧ, возрастают по мере увеличения времени спекания. Это вызвано увеличением плотности образцов, которая достигает максимума через 30 мин выдержки, при этом потеря массы составила 3-4 %.

Минимальная пористость образцов с добавкой оксида иттрия была менее 1 %, а с добавкой оксида иттербия — 2,4 %. При близких значениях относительной плотности величины твердости и коэффициента вязкости разрушения для СВЧ спеченных образцов были выше по сравнению с образцами, спеченными в условиях ТН. Микроструктура образцов, спеченных при СВЧ, представляла удлиненные зерна β-Si₃N₄ фазы расположенные в матрице поликристаллических зерен β-Si₃N₄. Измерения показали, что средний размер зерен в образцах, спеченных при СВЧ, меньше по сравнению с размерами зерен в образцах, спеченных при ТН. Делается заключение, что СВЧ способствует при спекании росту удлиненных зерен β-фазы в керамике на основе нитрида кремния и формированию "самоупрочненной" микроструктуры, в результате чего повышаются ее механические свойства.

Ключевые слова: Нитрид кремния; микроволновое спекание; механические свойства.

Садржај: Проучавана су механичка својства и процеси формирања микроструктуре у Si₃N₄+3% Al₂O₃+5% Y₂O₃(Yb₂O₃) керамичким узорцима синтетиран им коришћењем микроталасног загревања (МТЗ) и традиционалним загревањем (ТЗ). Почетни керамички материјали биле су мешавине прахова силицијум-нитрида и оксида. Средња вредност величине честича била је 0,5-1 μм. Садржај α-фазе у праху Si₃N₄ био је виши од 95 %. Узорци су синтетиране на 1800°C у азоту под нормалним притиском, брзина загревања за све експерименте била је 60°C/min. Одређени су твердноћа по Виккерсу (HV), отпорност на разарање (KIC) и отпорност на савижање (σf). Микроструктура на преломним површинама узорака проучаване су помоћу СЕМ-а. Извршена је квантитативна микроструктурна анализа. Показано је да су се вредности HV и KIC керамичких узорака синтетираних помоћу МТЗ на 1800°C стално повећавале са временом синтетирана. Ово је довело до повећања густине која је достигла максимум већ након 30 мин МТЗ синтетирана; губитак масе у том тренутку био је 3-4 %. Порозност синтетираних узорака са додатком иттријум-оксида била је мања од 1 %, док је за иттријум-оксид износила 2,4 %. За сличне вредности релативне густине, чврстоћа и отпорност на разарање керамичких узорака произведен је коришћењем МТЗ већа у поређењу са узорцима синтетираним коришћењем ТЗ. Микроструктура узорака имала је форму издужених зрна у матрици полиедарских зrna фазе β-Si₃N₄. Мерења су показала да је средња величина зrna у узорцима произведен им коришћењем МТЗ већа од оних у узорцима произведен коришћењем ТЗ. Формирани већи број издужених зrna. Закључено је да је синтетирано керамику на бази Si₃N₄ синтетираном МТЗ дошло до раста издужених β-Si₃N₄ зrna и формирања "ојачане" микроструктуре, чиме су побољшана механичка својства ове керамике.

Кључне речи: Силицијум-нитрид; микроталасно синтетиране; механичка својства.
Introduction

Silicon nitride ceramics offer high mechanical and thermal properties over a broad temperature range, which, together with such a characteristic as a low thermal expansion coefficient, promotes their application as structural materials. However, brittleness of Si$_3$N$_4$-based materials substantially restricts fields of their application. One of the ways for overcoming this drawback is production of “self-reinforced” nitride ceramics with a controlled bimodal microstructure consisting of elongated β-Si$_3$N$_4$ grains with retention of a fine-grained matrix of polyhedral grains, as well as β-Si$_3$N$_4$ ones. Such materials feature a substantially higher resistance to crack propagation [1-3].

Sintering of pure silicon nitride powders is difficult because of a strong covalent bond between silicon and nitrogen atoms. Therefore, Si$_3$N$_4$-based ceramics are produced by the liquid-phase sintering process, for which oxides, in particular, of yttrium and rare-earth metals, forming a liquid phase at relatively moderate temperatures, are added to the silicon nitride powder. During sintering of such powders, along with densification an α-β-Si$_3$N$_4$ phase transformation occurs. To form a bimodal microstructure, a certain relation between the rates of the phase transformation and growth of elongated β-Si$_3$N$_4$ grains, on one hand, and the rate of densification on the other hand, is needed. With a rapid increase in density the growth of elongated β-Si$_3$N$_4$ grains is slowed down.

In recent years sintering of ceramic materials under microwave heating (MWH) has been investigated. A characteristic feature of sintering of both oxide and non-oxide ceramic materials in microwave frequency (millimetre-band) electromagnetic fields is a decrease in the densification temperature as compared with that of sintering using traditional furnace heating (TH). Moreover, under MWH in contrast to TH, the densification rate often exceeds the recrystallization and grain growth rates, with the result that sintered ceramics retain a fine-grained microstructure. In such cases, higher mechanical properties of the ceramic material are expected.

Experimental results evidence a specific impact of a MW electromagnetic field on all the main stages of the process of liquid phase sintering of silicon nitride with oxide additions, namely: rate of densification; rate of α-β-Si$_3$N$_4$-phase transformation and evolution of the pore size distribution [4-5]. Undoubtedly, under MWH the processes of formation of the structure of Si$_3$N$_4$-based materials change as well, which should affect their mechanical properties.

The objective of this work was to study mechanical properties and microstructures of ceramic materials produced by sintering under MWH from silicon nitride with additions of alumina, yttria or ytterbia.

Experimental

Si$_3$N$_4$-ceramics with additions of alumina, yttria or ytterbia were liquid phase sintered under MWH and TH. The starting ceramic materials were powder blends of silicon nitride with oxides: 3 % Al$_2$O$_3$ and 5 % Y$_2$O$_3$ (Yb$_2$O$_3$). The average powder particle sizes were 0.5-1.0 μm. All samples were obtained by double-action compaction in a steel mould. Their starting relative density was about 50 %. The samples were heated to 1800°C at the rate of 60°/min under MWH or TH in nitrogen at normal pressure. Microwave sintering was done using the 30 GHz gyrotron system for microwave processing of materials [6]. Traditional sintering was carried out in a muffle furnace.
Density was measured by the Archimedes method. The β-Si₃N₄ phase content was determined by the XRD method [7]. Hardness (HV) was determined by a Vickers indenter. The fracture toughness (K̇) was determined by the microindentation method on samples 12 mm in diameter and 4-5 mm in height and was calculated by the formula [8]:

\[ K = \frac{N \cdot a^{0.5} \cdot E^{0.44} \cdot H^{0.6}}{\psi^{0.6}}, \]

where \( E \) is the modulus of elasticity equal to 300 GPa, \( H \) – hardness, \( a \) is a print diagonal indenter, \( N \) and \( \psi \) are coefficients. The bending strength was determined in 3-point bending with a 30 mm span on bars with dimensions of 5x3x35 mm. The bars were sintered under MWH at 1780°C for 30 min. The tensile surface was polished after machining edges. The microstructures of the fracture surface of samples were studied by a scanning electron microscope. Quantitative processing of the microstructure was carried out by a SIAMS computer analyser [9].

**Results and Discussion**

Values of HV and K̇ of Si₃N₄+3% Al₂O₃+5% Y₂O₃(Yb₂O₃) ceramics sintered under MWH at 1800°C rose steadily with the sintering time (Tab. I). This stemmed first of all from an increase in density, which reached maximum as fast as after 30 min of sintering under MWH; the mass loss at that time amounted to 3-4%. The porosity of sintered samples containing yttria was less than 1%. For ceramics with ytterbia the minimal porosity was somewhat greater, 2.4%, but their HV and K̇ values were higher.

**Tab. I** Properties of Si₃N₄+3% Al₂O₃+5% Y₂O₃(Yb₂O₃) ceramic samples sintered at 1800°C.

<table>
<thead>
<tr>
<th>Oxide additions</th>
<th>H</th>
<th>t, min</th>
<th>D, g/cm³</th>
<th>P, %</th>
<th>β-phase content, %</th>
<th>M, GPa (load 2 N)</th>
<th>HV (HV), GPa</th>
<th>FT, (load 150 N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H, N</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Y₂O₃+Al₂O₃</td>
<td>MWH</td>
<td>0</td>
<td>3.13</td>
<td>4.3</td>
<td>100</td>
<td>15.9</td>
<td>11.9</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>MWH</td>
<td>30</td>
<td>3.24</td>
<td>0.9</td>
<td>94</td>
<td>18.2</td>
<td>16.0</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>MWH</td>
<td>60</td>
<td>3.24</td>
<td>0.9</td>
<td>91</td>
<td>19.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>TH</td>
<td>60</td>
<td>3.18</td>
<td>2.9</td>
<td>65</td>
<td>15.9</td>
<td>9.7</td>
<td>9.4</td>
</tr>
<tr>
<td>Yb₂O₃+Al₂O₃</td>
<td>MWH</td>
<td>0</td>
<td>3.11</td>
<td>6.3</td>
<td>100</td>
<td>20.6</td>
<td>13.4</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>MWH</td>
<td>30</td>
<td>3.23</td>
<td>2.7</td>
<td>100</td>
<td>16.3</td>
<td>16.3</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>MWH</td>
<td>60</td>
<td>3.24</td>
<td>2.4</td>
<td>98</td>
<td>22.6</td>
<td>18.2</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td>TH</td>
<td>60</td>
<td>3.11</td>
<td>6.3</td>
<td>76</td>
<td>14.4</td>
<td>9.8</td>
<td>9.6</td>
</tr>
</tbody>
</table>

(H – heating regime; t – time; D – density; P – porosity; M – microhardness; H – hardness; FT – fracture toughness; * [MPa·m²/])

Samples sintered at 1800°C under TH with an addition of Y₂O₃ contained about 3% pores; with an addition of Yb₂O₃, 6.3% pores. Possibly, lower values of HV and K̇ of these samples stemmed from their lower relative density. For similar values of relative density, the hardness of samples with Yb₂O₃ sintered under MWH was 40%, and the fracture toughness, 20% higher than that of samples sintered under TH.
Presented below are characteristics of bars sintered under MWH at 1780°C, whose bending strength was determined. It should be noted that after sintering the bars had numerous small cavities on their surface, which were removed by polishing before tests. The bars were 2.0-2.5 mm high. As seen, the bending strength and $K_{IC}$ of specimens with ytterbia are higher than those of specimens with yttria (Tab. II).

**Tab. II Properties of Si$_3$N$_4$+3%Al$_2$O$_3$+5%Y$_2$O$_3$ (Yb$_2$O$_3$) bars sintered at 1780°C.**

<table>
<thead>
<tr>
<th>Rare-earth metal oxide</th>
<th>Porosity, %</th>
<th>Microhardness ($H_V$), GPa (load 2N)</th>
<th>Bending strength ($\sigma_p$), MPa</th>
<th>Fracture toughness, ($K_{IC}$), MPa m$^{1/2}$ (load 150 N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$</td>
<td>4.5</td>
<td>20.0</td>
<td>200-225</td>
<td>8.0</td>
</tr>
<tr>
<td>Yb$_2$O$_3$</td>
<td>5.6</td>
<td>18.7</td>
<td>250-280</td>
<td>8.8</td>
</tr>
</tbody>
</table>

As we showed earlier [3], differences in the course of densification under MWH and under TH arise already in the process of heating of samples to the isothermal holding temperature. This is well shown by comparing the variation of porosity and the content of the $\beta$-Si$_3$N$_4$ phase forming in samples with temperature under MWH and TH without isothermal holding (Fig. 1). Densification of samples under MWH takes place at temperatures below 1500°C, accompanied by a decrease of the porosity of samples by 5 % on average for both ceramic types, whereas under TH a small decrease in porosity occurs only above 1600°C. Also, the $\alpha$- $\beta$-phase transformation under MWH starts already at 1600°C, whereas under TH it begins at a temperature in excess of 1700°C. In samples sintered under MWH the degree of phase transformation at 1800°C reaches 91-100 %, whereas under TH this value is 65 % when Y$_2$O$_3$ is added and 76 % for addition of Yb$_2$O$_3$.

![Fig. 1 Porosity (solid line) and $\beta$-phase content (broken line) via temperature for Si$_3$N$_4$+3%Al$_2$O$_3$+5%Y$_2$O$_3$ (a) and Si$_3$N$_4$+3%Al$_2$O$_3$+5%Yb$_2$O$_3$ (b) under MWH and TH; the heating rate – 60°/min, the time of isothermal holding - 0 min.](image)

Sintering of Si$_3$N$_4$ ceramics with oxide additions proceeds in the presence of a liquid phase. Densification in the first stage of such sintering occurs through rearrangement of particles, and therefore a decrease in the porosity of samples under MWH at a temperature below 1500°C is only possible when a liquid phase appears much earlier than under TH. The densification that begins at relatively moderate temperatures as compared with the
temperature of densification under TH provides subsequently for a higher relative density of sintered samples. A similar regularity was noted for sintering under TH of nitride ceramics to which oxides forming a low-melting liquid phase were added [10-11].

The microstructure of samples had the form of elongated grains in a matrix of polyhedral grains of the β-Si₃N₄ phase (Fig. 2). Size distributions of the following microstructure parameters were determined: the mean size of grains regardless of their form, length of elongated grains (L) and their elongation factor (Fₗ) (the minimum-to-maximum size ratio). Measurements showed the mean size of grains, their form being ignored, in samples produced under MWH to be greater than that in samples produced under TH, 2.3 and 0.8 μm, respectively.

![Fig. 2 SEM micrographs of the fracture surface of Si₃N₄+3%Al₂O₃+5%Yb₂O₃ samples sintered at 1800°C for 60 min under MWH (a) and TH (b).](image)

![Fig. 3 Distributions of length of elongated grains (L) and their elongated factor (Fₗ) for Si₃N₄+3%Al₂O₃+5%Yb₂O₃ samples sintered at 1800°C for 60 min under MWH and TH.](image)
This was due to formation in the first case of a larger number of elongated grains, which also were longer. The mean length of elongated grains was 3.7 and 1.3 µm, respectively. Values of the elongated factor of grains for the two series of samples were close to each other (0.480 and 0.465 for MWH and TH, respectively). However the distribution curve for the samples sintered under MWH is shifted towards lower values, which evidences a greater elongation of elongated grains (Fig. 3). It should be taken into account that the phase transformation at 1800°C in the first case occurs completely and the content of the β-phase is equal to 100 %. In TH-sintered samples the content of the β-phase was 76 %, and the residual porosity was 6.3 %.

The microstructures of samples with yttria sintered under MWH and under TH were different and smaller. Thus, the mean size of grains and the mean length of elongated grains in samples sintered under MWH and TH were 0.6 and 0.8 µm and 1.5 and 1.3 µm, respectively. Apparently it is connected with a smaller degree of phase transformation in these samples, and as a result, is the reason of smaller values of $K_{IC}$ and $HV$ (Tab. 1).

**Conclusion**

Thus, it can be concluded that in sintering of Si₃N₄-based ceramics with the addition of alumina and yttria or ytterbia under MWH a decrease in the initial phase transformation temperature not only speeds up the very transformation, but also promotes growth of elongated β-Si₃N₄ grains and formation of a "self-reinforced" microstructure and thereby improves the mechanical properties of such ceramics.

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