Si₃N₄ and MgSiN₂-based ceramic composites have excellent thermo-physical and mechanical properties, however with limited industrial applications. In this paper the preparation of Si₃N₄/MgSiN₂ composite by gas pressure sintering (GPS) is described and some of the mechanical properties like Vickers hardness and indentation fracture are characterised and compared with hot pressed (HP) samples. The 15.3 GPa hardness and 7.6 MPa·m¹/₂ fracture toughness of GPS composites was slightly lower compared to HP samples (16.5 GPa, 8 MPa·m¹/₂).

**Key words:** ceramic, powder, composites, nitridation, mechanical properties.

**INTRODUCTION**

Silicon nitride based ceramics are intensively studied for more than 40 years as engineering materials due to their excellent mechanical properties [1]. Polycrystalline Si₃N₄ ceramics have a high strength (800 - 1 200 MPa), fracture toughness (6 - 10 MPa·m¹/₂) and good creep resistance. The hardness of β - Si₃N₄ is 14 - 16 GPa, while the hardness of α - Si₃N₄ is higher, 21 GPa [2]. Despite these good mechanical properties there is still a high interest to improve some properties of Si₃N₄ ceramics and especially decrease the price of ceramic products and promote the wider industrial application of this material [3].

Magnesium silicon nitride (MgSiN₂) is intensively studied in the recent years, as an alternative material for the substrates of the integrated circuits owing to its good thermal conductivity and high electrical resistance [4]. MgSiN₂ has high hardness (20 GPa), reasonable strength (280 MPa), and fracture toughness (3 MPa·m¹/₂), which makes it suitable for some engineering applications [5]. In this work Si₃N₄ – MgSiN₂ composites were prepared by two different sintering methods, by gas pressure sintering (GPS) and by hot pressing (HP) and their mechanical properties were evaluated. Although HP is more effective sintering method for the preparation of dense ceramic composites, the shape variety of products is limited. For that reason also GPS method was tested, which allows the sintering of ceramics with complicate shape and is more suitable for industrial applications.

**EXPERIMENTAL METHOD**

MgSiN₂ powder is not available on the market, for that reason it was prepared in lab from the mixture of Mg₂Si (99 %, Kojundo Chem. Lab., Japan), a - Si₃N₄ (grade SN-E10, Ube Industries Ltd., Japan) and Si (99.9 %, Kojundo Chem. Lab., Japan). The composition of starting powder mixture was calculated according to the following equation:

\[ y \cdot Mg_2Si + (1 - 3 \cdot x - y) Si + x \cdot Si_3N_4 + (1 - 2 \cdot x) N_2 = MgSiN_2 \]  

Where \( y = 0.5 \) and \( x = 0.06 \). This starting powder mixture is depicted as MSN – s1. The details of MgSiN₂ powder preparation, i.e. temperature and gas regime are described elsewhere [6]. The same a - Si₃N₄ powder (SN-E10, Ube) was used also for the matrix of composites, Yb₂O₃ and Lu₂O₃ (both from Treibacher AG, Austria) were used as sintering additives. The compositions of starting powders for the preparation of Si₃N₄ – MgSiN₂ composites are listed in Table 1. The number in the sample name shows the MgSiN₂ content, i.e. SMN – 20 sample is composed of 20 % MgSiN₂ and 80 % Si₃N₄.

It was shown that Yb₂O₃ and Lu₂O₃ as sintering additives improves the room and high-temperature properties of Si₃N₄ and MgSiN₂ ceramics [7-9]. Itatani et al. reported that the addition of 1 mol.% Yb₂O₃ sintering aid is sufficient for the densification of Si₃N₄ – MgSiN₂ composites by hot pressing at 1 600 °C [10].

**Table 1** Composition of starting powders for the preparation of Si₃N₄ – MgSiN₂ composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si₃N₄ / wt.%</th>
<th>MSN-s1 / wt.%</th>
<th>Yb₂O₃ / wt.%</th>
<th>Lu₂O₃ / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMN – 5</td>
<td>78.78</td>
<td>3.22</td>
<td>8.96</td>
<td>9.04</td>
</tr>
<tr>
<td>SMN – 10</td>
<td>75.62</td>
<td>6.1</td>
<td>9.1</td>
<td>9.19</td>
</tr>
<tr>
<td>SMN – 20</td>
<td>69.02</td>
<td>12.09</td>
<td>9.4</td>
<td>9.49</td>
</tr>
<tr>
<td>SMN – 30</td>
<td>62.07</td>
<td>18.41</td>
<td>9.72</td>
<td>9.81</td>
</tr>
<tr>
<td>SMN – 40</td>
<td>54.72</td>
<td>25.09</td>
<td>10.05</td>
<td>10.15</td>
</tr>
<tr>
<td>SMN – 50</td>
<td>46.94</td>
<td>32.15</td>
<td>10.4</td>
<td>10.51</td>
</tr>
<tr>
<td>SMN – 80</td>
<td>20.59</td>
<td>56.09</td>
<td>11.6</td>
<td>11.72</td>
</tr>
</tbody>
</table>
The samples were nitrided at 1 390 °C (below the melting point of Si) for 4 hours under 0.107 MPa nitrogen atmosphere. After nitridation the samples were further densified either by hot-pressing or GPS. Samples were hot pressed at 1 600 °C for 1 hour under 30 MPa pressure in nitrogen atmosphere (0.1 MPa). The temperature and gas regime applied during GPS is listed in Table 2.

### Table 2: Temperature and gas regime applied during GPS of Si₃N₄–MgSiN₂ composites

<table>
<thead>
<tr>
<th>Rate / °C/min</th>
<th>T / °C</th>
<th>Dwell / min</th>
<th>P (N₂) / MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>800</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>15</td>
<td>1 500</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>1 600</td>
<td>120</td>
<td>3.0</td>
</tr>
<tr>
<td>15</td>
<td>1 300</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>END</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The phase composition was investigated using powder X-ray diffraction (PAN analytical, Empyrean, Cu Kα radiation) in the range 2θ = 15° – 80°. The microstructure was observed by scanning electron microscopy (Zeiss EVO40 equipped with EDX analyser, Bruker AXS) on polished and plasma etched (Plasma System-Femto, DienerElectronicGmbH) cross sections of samples. Vickers hardness and fracture toughness were measured using Leco hardness tester (LV-100, Leco Co., USA) by indentation method with a load of 9.8 N and 98 N, respectively. The indentation fracture toughness was calculated according to Shetty equation [11]:

\[
K_{IC} = 0.0889 \left( \frac{H \cdot P}{4l}\right)^{0.5}
\]

Where \( H \) is the hardness, \( P \) the applied load and \( l \) the crack length. It should be mentioned that the indentation method overestimates the values of \( K_{IC} \) compared to notch methods (V-notch, Chevron notch, etc.) [12].

### RESULTS AND DISCUSSION

#### Microstructure

The density measurements and sample cross section analysis showed that the hot-pressed samples reached full density, while the GPS samples containing 5 and 10 % of MgSiN₂ had some residual porosity (3 – 7 %). These results indicate that except of the sintering additives also MgSiN₂ supported the densification of composites.

The microstructure of sample SMN – 40 densified by GPS method is shown in Figure 1 a. The etched elongated and hexagonal shaped particles are β – Si₃N₄, the unmatched grey particles are MgSiN₂, and the white amorphous phase is on the base of sintering additives (Yb₂O₃ and Lu₂O₃) and SiO₂ impurity (always present on the surface of Si₃N₄ powder). With increasing MgSiN₂ content also the size of elongated β – Si₃N₄ increases and the GPS composites with 80 % MgSiN₂ have the coarsest microstructure. During GPS relatively high pressure of nitrogen was applied (3 MPa) and it is known that the higher dissolved nitrogen content in the liquid phase during sintering supports the growth of large β – Si₃N₄ grains [13]. On the contrary, Si₃N₄ composites with 5 and 10 % MgSiN₂ have a fine microstructure with thin elongated whisker-like β – Si₃N₄. These elongated β – Si₃N₄ grains have a positive influence on the fracture resistance of composites.

#### Mechanical properties

Although the GPS conditions were optimised, some of the GPS samples contained residual porosity which has a (negative) influence on the mechanical properties of ceramic composites. Despite the residual porosity the measured Vickers hardness values showed that with increasing MgSiN₂ content (harder phase compared to β – Si₃N₄) the hardness of composites increases. The highest hardness 15.4 GPa was observed for GPS sample SMN – 80 with 80 % MgSiN₂. Contrary to hardness, the fracture toughness of composites decreases with in-
creasing MgSiN₂ content, which has a lower toughness (3.7 MPa·m³/²) compared to β-Si₃N₄ (6–8 MPa·m³/²). The highest indentation fracture toughness 7.3 ± 0.4 MPa·m³/² was obtained for the GPS sample SMN – 5.

The hot pressed samples were fully dense and the highest values of HV and Kic were obtained for the hot-pressed SMN – 30 sample, 16.3 ± 0.3 GPa and 8.0 ± 0.2 MPa·m³/², respectively.

The comparison of obtained HV and Kic values shows that the HP samples have better mechanical properties compared to GPS samples. However, to our best knowledge the reported results for GPS samples are the best obtained for Si₃N₄ – MgSiN₂ composites sintered with this method. The GPS method is more suitable for industrial application compared to hot-pressing, because it allows to sinter much larger number of samples during one sintering run and there are no serious limits to the shape of samples.

The microstructure of hot-pressed Si₃N₄ – MgSiN₂ samples is finer compared to GPS samples. The microstructure of hot-pressed SMN – 40 sample is shown in Figure 1 b and is composed of elongated β – Si₃N₄ grains and equiaxed α – Si₃N₄ and MgSiN₂ grains. The white phase is the amorphous grain boundary phase containing the sintering additives.

CONCLUSION

The densification conditions of Si₃N₄ – MgSiN₂ composites by gas-pressure sintering and hot-pressing were optimised. The HP samples were fully dense and despite the small residual porosity of GPS samples, both composites have a good mechanical properties (HV ~ 15 – 16 GPa, Kic ~ 7 – 8 MPa·m³/²). These properties allow their wider industrial application in engineering, aeronautics, metallurgy, etc.

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REFERENCES


Note: The responsible translator for the English language is Miriam Gabčová, Slovak Republic