**DISTRIBUTION OF SINTERING ADDITIVES VIA SOL-GEL METHOD IN SiC BASED CERAMICS**

M. Balog, L. Hric, J. Křesťan, L. Bača, P. Šajgalík

**Abstract**

The present paper deals with the liquid phase sintering of SiC based ceramics. Sol-gel method has been applied for the introduction of the Y$_2$O$_3$ sintering additive on SiC starting powder. Required yttrium oxide was prepared by decomposition of Y(NO$_3$)$_3$.6H$_2$O during heat treatment. The samples were densified by hot pressing method at 1900°C in the presence of different sintering atmospheres. Nitrogen, argon or carbon monoxide were used as sintering environment. The samples have densities up to 96.5% of theoretical density. In general, sinterability of modified SiC powder depends on the content of sintering additives and furnace atmosphere as well. The effect of sintering additive content and furnace atmosphere on microstructural development was studied in more detail. The macro hardness and indentation fracture toughness were also affected by the sintering process. The changing of microstructure and consequently mechanical properties (macro hardness and fracture toughness) depends on kind of sintering atmosphere used. The most significant increase of macro hardness and indentation fracture toughness was observed for the sample with 2.4 wt.% of sintering additives densified in a nitrogen furnace atmosphere (HV = 23 GPa and $K_Ic = 6.1$ MPa.m$^{1/2}$, respectively).

**Keywords:** SiC, sol-gel, distribution, hardness, fracture toughness, microstructure

**INTRODUCTION**

Polycrystalline silicon carbide is the material usually used in advanced engineering applications. Good mechanical and chemical properties at room and elevated temperatures are the main reason for its practical utilization. On the other hand, wider application of SiC is limited owing to relatively low fracture toughness [1].

Silicon carbide itself is a highly covalent bonded compound. Therefore, it is difficult to densify the SiC based materials without sintering additives. Silicon carbide can be sintered either by solid state or liquid phase sintering. In the case of solid-state sintering, SiC can be densified with the addition of B and C at temperatures around 2100°C [2]. Nowadays, traditional additives used for solid state sintering of SiC were replaced by metal oxides such as Al$_2$O$_3$ and Y$_2$O$_3$, which create liquid phase at temperatures 1850-2000°C [3, 4]. Such an approach results in higher efficiency of the sintering process. Additionally, these materials exhibit higher fracture toughness compared to solid state sintered SiC. The fracture toughness of liquid phase sintered SiC with Y$_2$O$_3$ and Al$_2$O$_3$ additives reached the value of 7 MPa.m$^{1/2}$ [5]. Partial increase of fracture toughness is achieved when SiC phase...
transformation occurs [6, 7]. The main commercially used method for the preparation of starting powder is the conventional homogenization of powders in suspension. On the other hand, distribution of sintering additives by sol-gel was also studied [8]. The sol-gel method allows distributing sintering additives close to the ceramic grains.

In the present study sol-gel method was used for distribution of sintering additives in commercial SiC powder. The samples were doped with a different amount of Y$_2$O$_3$ oxides as sintering additives. The influence of furnace atmosphere on densification is evaluated in details. Hardness and fracture toughness of the sintered ceramic body were measured.

### EXPERIMENTAL

Fine-grain β-SiC powder (Superior Graphite, USA) was mixed with Y(NO$_3$)$_3$.6H$_2$O. The SiC powder was dispersed in yttrium nitrate solution by ultrasonic vibration. The deposition was controlled by the addition of NH$_4$OH. The final mixture was washed. The Y(NO$_3$)$_3$.6H$_2$O is the precursor of yttria oxide and was decomposed during the sintering. Final chemical composition of studied samples calculated after precursor decomposition is listed in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition [wt.%]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SiC</td>
</tr>
<tr>
<td>SC-1</td>
<td>97.6</td>
</tr>
<tr>
<td>SC-2</td>
<td>81</td>
</tr>
</tbody>
</table>

Axially pressed samples, 12 mm in diameter and 10 mm high, were embedded in BN and located into graphite die. Afterwards the samples were hot pressed at 1900°C for 0.5 h under mechanical pressure of 30 MPa in Ar, N$_2$ or CO atmosphere. Densities were measured by Archimedes method in mercury. The theoretical densities were calculated according to the linear rule of mixture. The hot-pressed materials were cut and polished, then etched by CF$_4$ with O$_2$ plasma. The microstructures were observed by scanning electron microscopy (SEM, ZEISS, EVO-40). Hardness and fracture toughness was measured using a LECO Hardness tester by the Vickers method, at a load of 9.81 N and 98.1 N, respectively. Indentation fracture toughness was calculated by Shetty’s formula [9].

### RESULTS

Densities of the investigated samples are summarized in Table 2. The hot-pressed samples have density in the range of 86.9-96.5% theoretical densities. In the case of the samples with a lower addition of sintering additives, a strong influence of sintering atmosphere on obtained density is evident. Densities increase in this order of used gases: N$_2$ > CO > Ar due to the different interaction of the atmospheres with the samples. Especially, interaction with the grain boundary melt was expected. In the case of nitrogen environment the oxynitride grain boundary phase could be produced [10]. Such modified glass could result in increased density. Generally, the densification of SiC with oxide additives is accompanied by high weight losses. The main contributors to weight loss is SiO$_2$ (present in SiC starting powder as an impurity), due to the reactions with SiC or with free carbon, producing gaseous species like SiO and CO, respectively. Therefore, the densification in the CO sintering atmosphere can hinder the grain boundary phase decomposition. No
influence of sintering atmosphere on densification was observed in the second batch of the samples because of the high content of grain boundary phase.

Relatively high densities of a few sintered SiC samples indicate that the investigated processing is suitable for liquid phase sintering of SiC. However, further optimization of heat treatment schedule is necessary.

Tab.2. Sample densities after thermal treatment.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Density [g.cm(^{-3})]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>SC-1</td>
<td>3.22</td>
</tr>
<tr>
<td>SC-2</td>
<td>3.45</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Absolute / Relative</th>
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<tbody>
<tr>
<td></td>
<td>Atmosphere</td>
</tr>
<tr>
<td></td>
<td>Ar</td>
</tr>
<tr>
<td>SC-1</td>
<td>2.80 / 86.9</td>
</tr>
<tr>
<td>SC-2</td>
<td>3.31 / 95.9</td>
</tr>
</tbody>
</table>

Characteristic microstructures of sintered SiC samples are shown in Fig.1. Significant change of the microstructure was observed as a consequence of the different furnace atmosphere. It is known that nitrogen atmosphere hinders phase transformation and grain growth of SiC, while an argon atmosphere appears to enhance phase transformation from \(\beta\rightarrow\alpha\)-SiC [11]. The CO atmosphere retards decomposition of grain boundary phase. Such effect results in microstructure with a higher amount of grain boundary phase. A finer microstructure was observed in the sample SC-1N\(_2\) due to the presence of modified grain boundary oxynitride phase. Such grain boundaries with higher viscosity change the diffusivity of SiC [12]. Consequently the grain growth was inhibited effectively.

![Fig.1. Characteristic microstructure of the samples.](image)

Dependence of mechanical properties on sintering atmosphere and content of sintering additives are shown in Fig.2 and Fig.3, respectively. The samples SC-1 sintered in Ar and CO atmospheres had very poor mechanical properties, therefore they are not presented there.
The furnace atmosphere causes different microstructural development and consequently a different effect of used atmosphere on hardness (Fig.2) and fracture toughness (Fig.3) was observed. Interestingly the sample SC-1N₂ with low content of sintering additives (only 2.4 wt.%) has higher hardness and fractures toughness compared to the other compositions due to microstructure with finer grains and strong grain boundaries. In the case of samples with a higher addition of sintering additives the finer microstructure results in higher hardness. In this case, the fracture toughness depends on the grain boundary chemistry. The sample SC-2Ar where decomposition of grain boundaries was expected, has higher $K_{IC}$ compared to the SC-2N₂ with the modified grain boundaries. The sample with the stabilized grain boundaries composition SC-2CO has lower fracture toughness.

It could be concluded that the reduction of sintering additives content could be a suitable approach for preparation of SiC based ceramics with good mechanical properties. The lower content of sintering additives introduced by sol-gel method can result in creep resistance improvement. Additionally, the process of ceramics preparation would be cheaper compared with the conventionally used higher content of sintering additives.

On the other hand, influence of various rare-earth oxides on liquid phase sintering of SiC was studied [13, 14]. The rare-earth oxides might be as effective as Y₂O₃ in
densification of SiC. Although, the chemical and physical properties of rare-earth oxides are similar, the difference in cationic field strength of individual rare-earth might result in different grain boundary phase properties and microstructure [15]. Therefore the sol-gel method used in the present study can be modified by creation of incorporated rare earth oxides. Such approach to grain boundary variation could result in effective properties modification.

CONCLUSIONS

The effect of sintering additives deliberately added via sol-gel method on densifying SiC was investigated in the present work. Silicon carbide was sintered in presence of the liquid phase generated from Y₂O₃ and silica (impurity of SiC). Required yttrium oxide was prepared by the decomposition of Y(NO₃)₃.6H₂O during heat treatment. Hot-pressing technique was used for densification. The samples have densities in a range of 86.9-96.5% depending on sintering processing. Different kind of sintering atmospheres have different effects on microstructure and mechanical properties. The most significant increasing of hardness and fracture toughness was observed for sample SC-1N₂ with 2.4 wt.% of sintering additives (23 GPa and 6.1 MPa.m¹/², respectively) sintered in nitrogen atmosphere. Therefore it seems that the sol-gel method is a suitable route for distribution of sintering additives into SiC-based ceramics.

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REFERENCES