Production of Al$_2$O$_3$–SiC nano-composites by spark plasma sintering

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ABSTRACT

In this paper, Al$_2$O$_3$–SiC composites were produced by SPS at temperatures of 1600 °C for 10 min under vacuum atmosphere. For preparing samples, Al$_2$O$_3$ with the second phase including micro and nano-sized SiC powder were milled for 5 h. The milled powders were sintered in a SPS machine. After sintering process, phase studies, densification and mechanical properties of Al$_2$O$_3$–SiC composites were examined. Results showed that the specimens containing micro-sized SiC have an important effect on bulk density, hardness and strength. The highest relative density, hardness and strength were 99.7%, 324.6 HV and 2329 MPa, respectively, in Al$_2$O$_3$–20 wt% SiC$_{\text{macro}}$ composite. Due to short time sintering, the growth was limited and grains still remained in nano-meter scale.

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Producción de nano-composites – SiC–Al$_2$O$_3$ por spark plasma sinterizado

RESUMEN

En este trabajo se muestran compuestos de Al$_2$O$_3$–SiC producidos por SPS, en vacío, a 1.600 °C durante 10 min. Para la preparación de muestras, se molieron polvos de Al$_2$O$_3$ durante 5 h con la segunda fase de micro-y-nano polvo de SiC. Posteriormente, estos polvos molidos se sinterizaron mediante SPS. Después del proceso de sinterización, se realizaron estudios de fase, densificación y propiedades mecánicas de los compuestos de Al$_2$O$_3$–SiC obtenidos. Los resultados mostraron que micro-SiC en las muestras tiene un efecto importante en su densidad aparente, dureza y resistencia. La mayor densidad relativa, dureza y resistencia fueron respectivamente del 99.7%, 324.6 HV y 2329 MPa para Al$_2$O$_3$ con un 20% en peso micro-SiC. Debido al corto tiempo de sinterización, el crecimiento los granos fue limitado y se mantuvieron en escala nanométrica.

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Introduction

Thermal and chemical stability, relatively high strength, thermal and electrical insulator alongside the availability and abundance of aluminum oxide, lead to use of this material in engineering applications [1–5]. Despite the mentioned advantages, low fracture toughness of this material lead to limitation of its application. Composites are one of the methods which over come to this limitation. In this technique alumina matrix is reinforced by particles or fibers as secondary phase, which can be metal, polymer or ceramic. Silicon carbide (SiC) as a ceramic material can be one of the option which leads to improvement of alumina matrix [6–10]. Nihara et al. reported that sintering of Al₂O₃–SiC composite was done successfully. They found out that adding a little amount of SiC to alumina matrix can improve mechanical properties of composite significantly in comparison with non-composite materials. They increased strength and fracture toughness from 350 to 1520 MPa and 3.5 to 4.8 MPa/m¹/₂, respectively by adding 5 vol.% SiC [11].

There are different methods of sinter this composite. Non-pressure and hot press sintering are the most common method of sintering for this composite, but new technique which is considerable today is spark plasma sintering (SPS) [6,12–15]. On the base of spark plasma, which is created by a pulsed direct current, SPS leads to quick increasing of mold’s and the powder’s temperature. High heating rate, using pressure and electrical current is the specifications of this technique which distinguish this technique in comparison with other method. In addition to reduction of particle’s coarsening, high heating rate increased condensation through the elimination of surface diffusion mechanism and creating of extra driving force by high temperature gradient. Pressure applying during the heating can increase the driving force of process and facilitate the sintering process. Electrical current can condense the powder in mold by creating of many sparks between particles and creating of plasma environment. Effect of plasma on surface’s cleanness of particles and improvement of sintering process has been reported by researchers [16–21].

Synthesis of Al₂O₃–SiC composite by SPS has been investigated by a few researchers [16,17], but the effect of particle size on the densification, mechanical and wear properties has not been reported until now. So in this paper sintering process and properties of Al₂O₃ matrix reinforced by micro and nano-sized SiC will be examined.

Experimental

Al₂O₃ and SiC powders in micro and nano-meter scale with purity 99.8%, 99.5% and 99.9% and mean particle size of 1.5 μm, 10 μm and 50 nm, respectively were used as raw materials. Al₂O₃ powder with two sources of SiC (micro and nano as systems 1 and 2, respectively) powder were milled in a planetary ball mill (as a high energy ball mill) for 5 h in distilled water. Ball to powder ratio was 10 to 1 in all tests. In the following, prepared powders were sintered in a mold with 8 cm in diameter under specific conditions according to Table 1 by SPS
machine. The sintering process was done under high pulsed
direct current (1000–3500 A) in vacuum. A uniaxial pressure of
10 MPa was used during the reaction and increased to 20 MPa
after reaching to the expected temperature and maintained
during holding time. After holding time the uniaxial pressure
decreased to 10 MPa and maintained during cooling.

After sintering process, the samples were polished and cut.
In order to detect of phases in sample’s structure and eval-
uate of properties XRD (Siemens, 30 kV, 25 mA, Cu Kα) was
used. The crystallite size and strain were evaluated through
Scherrer and Williamson–Hall methods applying the follow-
ing equations [18]:

\[
d = \frac{0.9\lambda}{B \cos \theta} \quad \text{Scherrer equation}
\]

\[
B \cos \theta = \frac{0.9\lambda}{d} + 2\eta \sin \theta \quad \text{Williamson–Hall equation}
\]

where \( B, \theta, \lambda, d \) and \( \eta \) are the full width of the peak at half
intensity (rad.), position peak of the pattern (rad.), the wavelength
of X-ray (nm), crystalline size (nm), and mean internal strain,
respectively.

Samples density, open and closed porosity and water
absorption were estimated by Archimedes method [19].
Strength of the samples was measured through three points
test. Five samples with dimension of 3 × 4 × 45 mm were
prepared and average of strength reported [20]. Hardness of
the sample was determined through Vickers method. 5 tests were
done for each sample and average of results were reported [21].
Microstructures of milled and sintered samples were studied
by scanning electron microscope (Cambridge model). Finally,
wear resistance of samples was done in order to determine
the wear properties. In this test composite samples were used
as a pin and alumina was used as the disc. The force on the
pin tip was 15.3 N. The machine was stopped in the distances
of 1000 m and the weight losses of the samples were with the
accuracy of 0.0001 g [22].

**Result and discussion**

Patterns of X-ray diffraction of milled powders are illustrated
in Fig. 1. As it is seen in these patterns, milling has not led
to phase transfer in raw materials, and identified phases are
\( \text{Al}_2\text{O}_3 \) and SiC with 1125-071-01 and 00-002-1048 reference
code, respectively. As it stands, by increasing of SiC phase,
itensity of their peaks has been increased. Crystalline size
(\( d \)) and mean strain (\( \psi \)) of milled powder were measured.
The changes of \( B \cos \theta \) to \( 2\sin \theta \) are seen in Fig. 2. Calculation results
are brought in Table 2, as it is seen in this table crystalline
size of milled powder in all compounds for both phases are
in nano-meter scale. The crystalline sizes of milled powders
(which all of them have been treated in a similar way) have
a range between 36 and 40 nm and 17 and 36 nm for \( \text{Al}_2\text{O}_3 \) and
SiC phases, respectively and no significant difference between
sizes. As it stands, size of phases in the second system is finer
than first system, that can be attributed to two reasons: the
first one is using of SiC with nano scale in the second system
and the next one is the presence of more finer SiC particles in
the second system at equal weight fraction which can operate
as fine balls and facilitate of milling process. These particles
increases milling energy and lead to crush of particles [23].

SEM image form milled samples are presented in Fig. 3. As it
is obvious in this figure, milling lead to decreasing the size
of particles in both systems and the mean particle sizes are
in nanometer scale. The size of particles in the system contain-
ing nano SiC are lower than the system without that.

X-ray pattern of sintered sample is brought in Fig. 4, as it is
seen, there is no change in phases of sintered samples and in
milled sample (Fig. 1), \( \text{Al}_2\text{O}_3 \) and SiC are identified phases. As it
is obvious in Fig. 5, the only considerable point in compar-
ison of this pattern with milled sample pattern is increasing
of peak’s intensity and decreasing of peak’s width in sintered
sample. Increasing of temperature during the sintering can
lead to growth of crystals and reducing of mean lattice strain
[24,25].

The changes of \( B \cos \theta \) to \( 2\sin \theta \) in sintered samples are
shown in Fig. 6. The results of these calculations are brought
in Table 2. As these calculations show, although the crys-
talline sizes are in nanometer scale with the range of 59–66 nm
and 30–52 nm for \( \text{Al}_2\text{O}_3 \) and SiC phases, respectively but sin-
tering leads to growth of crystals and decreasing of mean
lattice strain slightly. Unlike common methods of sintering, which follow extreme growth, sintering though SPS has a little growth, so that the crystals are in nano scale yet. When the sintering (including heating and keeping processes) is completed in a few minutes, the crystals could be small [26].

The changes of sample’s thickness to time for sample which contain different amount of SiC include three zones. At first, the time of less than 35 min, which sample has been heated and has a little expansion. In the following by increasing the temperature, sintering process occurred and samples were contracted quickly during about 5 min and then change of displacement will be constant. As it stands, the sintering process was completed at the end of second zone and samples were dense. According to the changes of sample thickness and temperature versus sintering time plots, beginning temperature of sintering (beginning of second zone) is determined. This information is brought in Table 3. Decrease in thickness of the samples and the starting of second zone is due to the overcoming of contraction of sintering on thermal expansion of the samples.

![Graph](image)

**Fig. 2** – W–H diagram of milled samples for calculation of crystalline sizes and mean strains of phases.

<table>
<thead>
<tr>
<th>Code of sample</th>
<th>Phase</th>
<th>Crystalline size (nm)</th>
<th>Mean strain (%)</th>
<th>Used method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milled samples</td>
<td>5m Al₂O₃</td>
<td>40</td>
<td>1.14</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>35</td>
<td>–</td>
<td>Scherrer</td>
</tr>
<tr>
<td></td>
<td>10m Al₂O₃</td>
<td>45</td>
<td>1.22</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>30</td>
<td>1.43</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>15m Al₂O₃</td>
<td>36</td>
<td>1.13</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>36</td>
<td>1.39</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>20m Al₂O₃</td>
<td>43</td>
<td>1.16</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>29</td>
<td>1.42</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>5n Al₂O₃</td>
<td>42</td>
<td>1.21</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>19</td>
<td>–</td>
<td>Scherrer</td>
</tr>
<tr>
<td></td>
<td>10n Al₂O₃</td>
<td>39</td>
<td>1.20</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>17</td>
<td>1.35</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>5m Al₂O₃</td>
<td>61</td>
<td>0.97</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>52</td>
<td>–</td>
<td>Scherrer</td>
</tr>
<tr>
<td></td>
<td>10m Al₂O₃</td>
<td>63</td>
<td>0.94</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>52</td>
<td>1.10</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>15m Al₂O₃</td>
<td>60</td>
<td>1.03</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>50</td>
<td>1.10</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>20m Al₂O₃</td>
<td>59</td>
<td>0.95</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>52</td>
<td>1.14</td>
<td>W–H</td>
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<tr>
<td></td>
<td>5n Al₂O₃</td>
<td>65</td>
<td>1.01</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>33</td>
<td>–</td>
<td>Scherrer</td>
</tr>
<tr>
<td></td>
<td>10n Al₂O₃</td>
<td>66</td>
<td>1.07</td>
<td>W–H</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>30</td>
<td>1.02</td>
<td>W–H</td>
</tr>
</tbody>
</table>

**Table 2** – Results of calculations of crystalline sizes and mean strain of milled and sintered samples.
As it is seen in Table 3, in the first system by increasing of SiC to 10 wt.%, beginning temperature of sintering has been increased and then decreased. SiC with higher melting point than Al₂O₃, increase the sintering temperature of Al₂O₃. But increasing of SiC which has lower thermal expansion (TEC) coefficient in comparison with Al₂O₃ leads to decreasing of thermal expansion coefficient of composite (melting point and thermal expansion of Al₂O₃ and SiC are 2072 °C and 8.1 × 10⁻⁶/°C and 2730 °C and 4.0 × 10⁻⁶/°C, respectively) [27]. Hence the early expansion has been decreased during the heating and as a result beginning temperature of contraction is decreased too. So, after 10 m sample, decrease of sintering temperature is seen. This treatment is similarly seen in second system too. Only in this system, overcoming of the second phenomenon to first one is quicker than and is happened in less amount of SiC.

The changes of relative density of sintered samples for the two systems are presented in Table 3. As it is obvious, in system 1, addition of different amount of SiC to Al₂O₃ matrix leads to completing of sintering and achievement to samples with nearly full density. Lower sintering temperature, short temperature and holding times have prepare it possible to produce nano-composite of SiC-Al₂O₃ to near theoretical density with little crystal growth [28]. To attainment full density by common sintering technique, higher temperature and soaking time is needed. Shi et al. succeeded to sinter Al₂O₃–SiC composite with relative density of 100% via hot press technique at temperature over 1700 °C. They reported sintering by hot press led to abnormal growth in some samples [29].

Against, presence of nano-sized SiC in system 2 could not obtain a sample with high density. A great difference between particle size of matrix and the reinforcement phase in the
second system decreased packing and leads to decrease of final density. There is evidence when a SiC as fine component are added to the Al$_2$O$_3$ particles, it adhere to the large particles strongly and delay the penetration of fine components to the mixtures [30]. Wide distribution of particles in system 2 confirms this point (Fig. 3b). Furthermore, as it is obvious in Table 3, by increasing the weight percent of SiC, density is decreased. This could be due to the poor sintering property of SiC at examined temperatures in this paper. Similar result was reported by other researchers [29,31,32].

Fig. 7 shows the SEM images for the microstructure of the sintered compacts. There are two different phases in both systems, i.e., dark and light phase. As it is seen from Fig. 4 and as it was discussed earlier, XRD pattern implied that there was no reaction between the raw materials. So Al$_2$O$_3$ and SiC are only phases in sintered samples. According to these images,
SiC with lower mass absorption coefficient than Al₂O₃ as light and dark phases, respectively were dispersed in the matrix [33,34]. As it was calculated porosity by Archimedes method, porosity can be seen in microstructural images of samples. The amount and sizes of porosity in system 2 is higher than system 1.

Flexural strength and hardness of sintered samples are illustrated in Fig. 8. As it stands, in system 1 with a density close to each other, the flexural strength of samples increased by increasing the amount of SiC particles up to 10% and after that adding more SiC could not increase the flexural strength. When the weight percent of SiC was more than 10, a suitable distribution of this phase cannot be seen [32,35]. Existence of hard SiC particles with a fine structure could be improve the mechanical properties [36]. Furthermore, due to residual stress from the mismatch of TEC between SiC and Al₂O₃, matrix is under the compressive stress during cooling. So, existence of SiC in the matrix of Al₂O₃ increases the strength [37]. Adding hard SiC as reinforcement phase to the Al₂O₃ matrix could increase the hardness numbers significantly (hardness of SiC and Al₂O₃ are 1175 HV and 2800 HV) [27]. Since in system 2 achievements to samples with full density were not happening, flexural strength and hardness were weaker than specimens of first system. The porosity effects on the mechanical properties of ceramic materials meaningfully [29].

Loss of weight in the sample after wear resistance is seen in Fig. 9. Due to high hardness in sample which contain hard SiC, wear resistance of them are increased. During dry sliding, the SiC particles do not easily come out in the debris because of their reasonably good bonding with the matrix. By decreasing the particle size, bonding takes place better and the wear resistance increases. Furthermore, the formation of oxide layer on the wear surface of the composite reduced wear resistance. These oxides consist of very fine with sizes of about 10–100 nm.

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**Fig. 7** – Microstructure of sintered samples (a) 10m sample and (b) 10n sample.

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**Fig. 8** – The changes of flexural strength and hardness of sintered samples.
which have been compacted onto the composite’s surface, preexisting surface oxide layers, or compressed coarse wear debris [38]. Because of lower density of samples in the second system, wear properties of these samples are lower than the first system.

**Conclusion**

Al$_2$O$_3$–SiC composites were prepared successfully by SPS with relative density of 100%. The composites with denser structure have higher flexural strength. 293.1 MPa and 2329 HV of the highest hardness and flexural strength were obtained from the samples reinforced by 10 and 20 wt.% SiC, respectively. By increasing the amount of SiC, flexural strength was improved first and then decreases because of a bad distribution of seconded phase in the matrix. Due to lower density in samples containing nano-sized SiC, mechanical properties were weaker than specimens of the first system.

**References**


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