Experimental investigation on the hardness of ultrafine-grained Si₂N₂O–Si₃N₄ composites developed by hot-press sintering technology

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Ultrafine-grained Si₂N₂O–Si₃N₄ composites are fabricated by hot press sintering of amorphous nanosized silicon nitride powders at 1600, 1650, and 1700°C, with nanosized Al₂O₃ and Y₂O₃ as additives. Sintered materials of increasing average grain sizes of 280, 360, and 480 nm were obtained with increasing sintering temperature. The nanoindentation hardness, microhardness and macroscopic Vickers hardness are tested using nanoindentation, microhardness tester, and macroscopic Vickers hardness tester. The hardness is found to decrease with increasing sintering temperature and average grain size. The results of the nanoindentation hardness and microhardness tests obviously reflect the effect of loading. The nanoindentation hardness is related to the ratio of the indentation maximum contact cross-sectional area \(A\) and the average grain cross-sectional area \(S\). As the ratio of \(A\) and \(S\) decreases, the fine-grain strengthening effect becomes less evident. The comparative analysis of nanoindentation hardness and microhardness revealed that the microhardness test is considered more suitable for estimating the hardness of the ultrafine-grained Si₂N₂O–Si₃N₄ composites.

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1. Introduction

Ceramics are used in various technical applications where either specific functional or structural properties are required. Silicon nitride (Si₃N₄) ceramic has received much attention for high-temperature applications in the past decades because of its outstanding properties such as high melting temperature, low density, high elastic modulus and strength, and good resistance to creep, wear, and oxidation.¹–⁴ Silicon oxynitride (Si₂N₂O) ceramic has been recognized as a promising material for high-temperature applications because of its good resistance to oxidation and thermal shock.⁵,⁶ The Si₁₇N₉O phase exhibits the development of elongated grains, which can be used to toughen Si₃N₄ when properly dispersed. Si₂N₂O can optimize the properties of Si₃N₄-based ceramics.⁷–⁹

Si₃N₄–Si₂N₂O ceramics have been investigated by numerous researchers.¹⁰–¹₂ However, the majority of previous studies have focused on the preparation, microstructure, and mechanical properties of grain sizes ranging from 5 to 20 μm.¹³–¹⁵ Although it is an important indicator of material mechanical properties, the research on hardness and the measurement method of Si₃N₄–Si₂N₂O ceramics was little. Further more, most of the research is to use single method, nanoindentation hardness or Vickers hardness, to measure and study the hardness of Si₃N₄–Si₂N₂O composites.¹⁶,¹⁹,²⁰

The purpose of this study is to use different methods studying the hardness of Si₃N₄–Si₂N₂O ceramics, and a suitable method for measuring the hardness of the ultrafine-grained Si₂N₂O–Si₃N₄ composites was found. In this study, ultrafine-grained Si₃N₄–Si₂N₂O in-situ composites were developed by hot press sintering of amorphous nanosized Si₃N₄ original powder at 1600°C, 1650, and 1700°C. Nanoindentation hardness, microhardness and macroscopic Vickers hardness of ultrafine-grained Si₃N₄–Si₂N₂O sintered at different temperature were tested and analyzed.

2. Material preparation

Amorphous nanosized Si₃N₄ powders were used because of their high purity, small particle size, and very narrow particle size distribution. The morphology and physical properties of the powders, with average particle size of 18 nm, are shown in Fig. 1.
and Table 1, respectively. Nanosized Al₂O₃ and Y₂O₃ powders, with a particle size of 20 nm and prepared using polyacrylamide gel method, were used as sintering aids. The powders were homogenized with 5wt% Y₂O₃ and 2wt Al₂O₃ in n-hexane using a Si₃N₄ ball mill. The powder mixtures were hot-pressed at 30 MPa in a nitrogen atmosphere for 30 min at 1600, 1650, and 1700°C. The compacts used were cylindrical discs, 30 mm in diameter and 4 mm in thickness.

The bulk density of the sintered ceramics was measured using the Archimedes method. Besides, the crystallinity and phase composition of the samples were determined by X-ray diffraction (XRD) (D-max-2500) using monochromatic Cu Kα radiation. The microstructure of the grains in the samples was observed using high-resolution transmission electron microscope (TEM; H-800).

The XRD curves and phase composition of the materials sintered at different temperatures are shown in Fig. 2 and Table 2, respectively. The sintered material crystallized completely at 1650°C, which indicates the completion of reaction between O₂ and Si₃N₄. Then, the volume percentage of Si₂N₂O decreased gradually, and no SiO₂ was observed. This result confirms that the reaction, Si₃N₄(s) + 1.5 O₂(g) = 3 Si₂N₂O(s) + N₂(g), is reversible, and the reaction, 2 Si₃N₄(s) + 1.5 O₂(g) = 3 SiO₂(s,l) + N₂(g), does not occur. Thus, the Si₂N₂O phase can be synthesized not only by the reaction, Si₃N₄(s) + SiO₂(g) = 2 Si₂N₂O(s), but also by 2 Si₃N₄(s) + 1.5 O₂(g) = 3 SiO₂(s,l) + N₂(g).

Figure 3 shows the high-resolution TEM images of the sintered samples. The sintering results of the samples presented in Table 3 indicate that the relative density, aspect ratio of the grains, and average grain size of the sintered composites increase with the sintering temperature. The average grain size of all sintered samples was found to be less than 500 nm. As can be observed from the TEM images, the Si₂N₂O–Si₃N₄ composite obtained by sintering at 1600°C has uniform equiaxial fine grains with an average grain size of 280 nm. With increase in sintering temperature to 1650°C, several rod-like Si₂N₂O grains start appearing in the sample. With further increase in sintering temperature to 1700°C, a substantial growth of Si₂N₂O grains is observed in the sintered material.

### Table 1. Physical properties of amorphous nanosized Si₃N₄ powders

<table>
<thead>
<tr>
<th>Powder</th>
<th>Silicon nitride (wt%)</th>
<th>Oxygen (wt%)</th>
<th>Grain size (nm)</th>
<th>Specific area (m² g⁻¹)</th>
<th>Real Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
<td>&gt;99</td>
<td>&lt;0.6</td>
<td>18</td>
<td>80</td>
<td>3.44</td>
</tr>
</tbody>
</table>

### Table 2. Phase composition of composites sintered at different temperatures

<table>
<thead>
<tr>
<th>HP temperature (°C)</th>
<th>β-Si₃N₄ (vol%)</th>
<th>Si₂N₂O (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>47</td>
<td>52</td>
</tr>
<tr>
<td>1650</td>
<td>39</td>
<td>60</td>
</tr>
<tr>
<td>1700</td>
<td>46</td>
<td>53</td>
</tr>
</tbody>
</table>

### Table 3. Sintering results at different temperatures

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Relative dense (%)</th>
<th>average grain size (nm)</th>
<th>aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>98.2</td>
<td>280</td>
<td>1.5</td>
</tr>
<tr>
<td>1650</td>
<td>99.1</td>
<td>360</td>
<td>3</td>
</tr>
<tr>
<td>1700</td>
<td>99.3</td>
<td>480</td>
<td>3.5</td>
</tr>
</tbody>
</table>

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the ground specimens using a polishing machine. The nanoindentation experiment was performed using an in-situ nano-mechanical testing system equipped with a Berkovich indenter. During each loading–unloading cycle, the loading and unloading rates were kept constant, maintaining a dwelling time of 5 s at each peak load. The loading curves thus obtained are shown in Fig. 4.

3.2 Microhardness and macroscopic Vickers hardness test

To further examine the relationship among the hardness, grain size, and loading weight of the specimens, the microhardness of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites was also measured using the digital hardness tester HV1000, applying loads of 100, 200, and 300 g. Besides, the macroscopic Vickers hardness of the specimens was measured using macroscopic Vickers hardness tester HV-120 at the load of 30 kg. The images of macroscopic Vickers hardness indentation are shown in Fig. 5. The values of macroscopic Vickers hardness can be calculated by Eq. (1).

\[ H_V = 1.8544 \times 10^{-4} \times \frac{P}{d^2} \] (1)

Where \( P \) is load, \( d \) is indentation diagonal length.

4. Results and discussion

For all the three analyses presented respectively in Figs. 6–8, a total of five test points were selected for each measurement, with the final hardness value being the average of the results measured at the five test points. The average values of the nanoindentation hardness, microhardness, and macroscopic Vickers hardness of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites sintered at different temperatures are listed in Table 4. As is seen, the hardness values decrease with increase in sintering temperature and average grain size, which is in accordance with the Hall–Petch relationship. The observed decrease in nanoindentation hardness and microhardness with increase in loading weight obviously reflects the effect of loading.

The macroscopic Vickers hardness value is almost 15% larger than the average values of microhardness for each material sintered at the same temperature. The observed mismatch in the hardness values could be attributed to the fact that the microhardness is directly detected from the testing equipment, whereas the macroscopic Vickers hardness is calculated from the indentation diagonal length with a certain level of error. Hence, microhardness is considered more accurate than macroscopic Vickers hardness, especially for testing high hardness materials.

The nanoindentation hardness and microhardness can be calculated by using the Eqs. (2) and (3), respectively.

\[ H_N = \frac{P_{\text{max}}}{A} \] (2)

\[ H_M = \frac{P_{\text{max}}}{A_r} \] (3)

Where \( A \) is the real-time contact area and \( A_r \) is the residual contact area. The value of \( A \) is larger than \( A_r \), when large elastic deformation occurs in the testing process. Therefore, in general, the value of microhardness is typically larger than the nanoindentation hardness value. This explains the observed mismatch in the hardness values of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites prepared in this study.

Furthermore, the results of composition and relative density show very minimal difference among the different ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites obtained at various sintering temperatures. The difference in the hardness values can be attributed to the variations in grain size, indenter size, loading weight, and dislocation density of the samples. In principle, the movement of dislocations inside the grains plays a major role in material deformation, especially when the grain size and indentation size are different. However, the effects of grain boundary sliding and deformation on the hardness value of the samples are more pronounced with decrease in the grain size or increase in the indentation size.\(^{16,17}\) At room temperature, the values of hardness and strength at the grain boundaries are higher than those in the interior of the grain. Therefore, the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composite sintered at 1600°C exhibits higher hardness at room temperature.

In addition, comparing the nanoindentation hardness values of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites determined at the same loading weight, it could be realized that the grain boundary
sliding and deformation play an important role, contributing to a higher value of hardness, especially when the difference in grain size and indentation size is larger. Assuming that all grains contact cross-sectional of Si$_2$N$_2$O–Si$_3$N$_4$ composites are circle, Tables 5–7 show the ratio of the indentation maximum contact cross-sectional area $A$ and the average grain cross-sectional area $S$ at the loading weight of 5000, 6000 and 7000 µN respectively. The larger is the ratio of $A$ and $S$, the higher is the number of grains that get in contact with the indenter. Consequently, fine-grain strengthening effect becomes more evident. The ratio of $A$ and $S$, and the nanoindentation hardness tend to decrease with increase in the grain size. Furthermore, the greater is the decrease in the ratio of $A$ and $S$, the greater is the decrease in the nanoindentation hardness value.

The nanoindentation testing of the specimens lead to large elastic deformation, while the microhardness testing induced obvious plastic deformation. According to Eqs. (1) and (2), the values of nanoindentation hardness are more accurate, whereas the values of microhardness are slightly larger than the true hardness. However, the nanoindentation hardness value does not truly reflect the fine-grain strengthening effect, especially when the ratio of $A$ and $S$ is small. Thus, microhardness test is considered more suitable for determining the hardness of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites.
5. Conclusions

(1) The ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites are fabricated by hot press sintering of amorphous nanosized Si$_3$N$_4$ powders with nanosized Al$_2$O$_3$ and Y$_2$O$_3$ as additives. The average grain size is less than 500 nm. Average grain size increases with increasing sintering temperature.

(2) The hardness values of the composites were found to decrease with increase in sintering temperature and average grain size. The results of the nanoindentation hardness and microhardness tests obviously reflect the effect of loading.

(3) In case of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites, the ratio of the indentation maximum contact cross-sectional area $A$ and average grain cross-sectional area $S$ is small, and hence the nanoindentation hardness value cannot truly reflect the fine-grain strengthening effect. Thus, the microhardness test is considered more suitable for estimating the hardness of the ultrafine-grained Si$_2$N$_2$O–Si$_3$N$_4$ composites.

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References