Microstructures and Fracture Characteristic of Si₃N₄–O’SiAlON Composites using Waste-Si-Sludge

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Si₃N₄–O’SiAlON composites using waste-Si-sludge was fabricated by gas-pressure-sintering (GPS) process at 1950°C for 3.5 h. The percent nitridation of waste Si compacts showed a lower value than that of using commercial Si powders caused by the high contents of oxygen in the waste Si particles. Some amounts of Si₂N₂O and Y₂Si₂O₇ phases were also detected in the reaction-bonded Si₃N₄ (RBSN) although main components were α-Si₃N₄, β-Si₃N₄ and residual Si phases. In the post-sintered body by GPS, no residual Si, α-Si₃N₄, β-Si₃N₄ and Y₂Si₂O₇ phases were detected except the β-Si₃N₄ and O’SiAlON. The grain growth of rod-like Si₃N₄ grains was inhibited by the dispersion of fine O’SiAlON phases. The fracture toughness and strength of Si₃N₄–O’SiAlON composites were 5.6 MPa m¹/² and 456 MPa, respectively.

Keywords: gas-pressure-sintering, microstructure, waste-silicon, reaction-bonded Si₃N₄, silicon nitride, fracture

1. Introduction

Reaction-bonded Si₃N₄ (RBSN) which has some advantages such as low price of raw Si powders, easy control of dimensions and low cost of production, has been actively developed since the removal of residual Si and pores has been made possible by post-sintering process such as gas-pressure-sintering (GPS) process.¹,²

The large amounts of waste-Si-sludge have been produced from the cutting process of single crystal Si ingots to make the Si wafer. In the waste-Si-sludge, some amounts of organic agent which was used for the improvement of cutting ability are contained as well as a lot of Si particles. The waste-Si powders obtained by filtering of waste-Si-sludge can be used as a raw material for RBSN ceramics. In our previous works on the nitridation process, it was confirmed that the nitridation rate of Si compact using waste Si powders was lower than that of using commercial Si powders due to the existence of large amount of SiO₂.³ However, the nitridation rate was improved by the addition of 1 mass%Fe or 30 mass%SiC powders and/or the removal of the SiO₂ layer on the Si powders by HF treatment.³ Until now, most of waste-Si-sludge produced in semiconductor industry was thrown away into landfills except some recycling for making low grade of refractory materials. It is a typical example of the loss of natural resources and environmental pollution, nevertheless, there was no detail reports on the fabrication and microstructure characterization of RBSN and GPSed-RBSN using waste Si-sludge. Thus, our basic research is focused on the possibility of using waste-Si-powders for the GPSed-RBSN ceramics. In this work, RBSN and GPSed-RBSN bodies were fabricated by direct nitridation process using waste-Si-powders. The relation between microstructures and fracture characteristic of RBSN and GPSed-RBSN bodies was investigated using by SEM and TEM.

2. Experimental Procedure

From the waste-Si-sludge, the Si powders were obtained by vacuum filtering and sieving process. The chemical compositions of waste-Si and commercial-Si-powders were analyzed by ICP (HITACHI P-5200), and oxygen and carbon were analyzed by nitrogen/oxygen detector (LECO/TC-436) and carbon/sulfur detector (LECO/CS-444LS), respectively. The waste-Si-powders and sintering additives (5 mass%Y₂O₃ and 2 mass%Al₂O₃) were thoroughly mixed in ethanol using a planetary ball mill and Si₃N₄ balls as milling media. The mixtures were dried on a hot plate while stirring. The powder mixture was pressed into pellets and cold-isostatic pressed at 250 MPa. The pellets, 40 mm in diameter were nitrided in flowing N₂–10%H₂ gas mixture at 1410°C for 20 h. The post-sintering was carried out at 1950°C for 3.5 h under 1050 psi N₂ gas-pressure. The bending strength was measured by 3-point bending method using specimens measuring 3 × 4 × 30 mm³. The fracture toughness (Kıc) was calculated by indentation method with a load of 294N.⁵ The residual Si phases were identified by optical microscope (OM). The XRD was used to examine crystal phases of the RBSN over a wide scale. The detailed internal microstructures and grain boundaries of GPSed-RBSN were examined using TEM (JEOL-2010) and HRTEM (JEOL-4000EX) techniques.

3. Results and Discussion

Figure 1(a) is a SEM image showing waste-Si powders obtained from waste-Si-sludge. From the analysis of particle size, the size range was from 0.1 to 10 μm and the average size (d₅₀) was 7 μm with irregular shape.³¹ Figures 1(b) and (c) show TEM images of waste-Si-powders with about 7 and 2 μm in size, respectively. As shown in Fig. 1(b), most of Si powders with large size contained a few of cracks as indicated with arrowheads. The inserted electron diffraction pattern (in Fig. 1(b)) seen with sharp spots was taken from the direction of [110]Si₃N₄ zone axis. However, in the fine Si particle as showed in Fig. 1(c), the large amounts of microcracks and...
Fig. 1  SEM (a) and TEM micrographs (b, c) of waste-Si-powders.

Table 1  Chemical composition of (wt%) of commercial and waste Si powders.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial Si</td>
<td>&lt;0.0002</td>
<td>0.064</td>
<td>0.088</td>
<td>0.0143</td>
<td>0.142</td>
<td>0.185</td>
</tr>
<tr>
<td>Waste Si</td>
<td>0.0015</td>
<td>0.039</td>
<td>0.012</td>
<td>0.0073</td>
<td>0.942</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Table 1 shows the chemical composition of waste-Si-powders as well as the commercial-Si-powders. In the waste-Si-powders, high contents of carbon and oxygen were detected which are compared with that of commercial-Si-powders. It is considered that the main reason for showing the high contents of carbon and oxygen in the waste-Si-powders is respectively caused by the residual organic agent and formation of SiO₂ film on the surfaces of fine Si particles. In general, the specific surface areas of waste Si particles are increased as increasing the number of microcracks. Furthermore, the SiO₂ films on the fine Si particles can be easily formed due to the reaction with cooling water during the cutting process of Si wafers. However, the impurity contents of Cu, Fe, Al and Ca elements in the waste-Si-powders showed lower values than that of commercial-Si-powders. These impurities in the waste-Si-powders were caused by the wear loss of the shank part of the diamond wheel, during the cutting process of Si ingots.

Figure 2(a) shows an OM image of RBSN body nitrided at 1410°C. Many residual pores less than 2.5 μm in size are observed with dark contrast while the residual Si particles are seen with white contrasts as indicated with arrowheads. The
percent nitridation of RBSN body nitried at 1410°C showed a low value with 62% which was compared with that of using commercial Si powders (99.5% at 1400°C). The reason for showing with low percent of nitridation is caused by the existence of large amounts of oxygen content that was covered with SiO2 on the waste-Si-powders, i.e., at the initial stage of nitridation of Si compact, the SiO2 film on the waste-Si-powders must be decomposed firstly. Of cause, the percent nitridation value of RBSN bodies using waste-Si-sludge were also increased as increasing the nitridation temperature and then no residual Si particles were observed in the sample nitried at 1470°C by OM and XRD. From the TEM images of RBSN body in the Figs. 2(b) and (c), it is confirmed that the grain size was about less than 0.3 µm and many fine pores were observed with white contrasts, which were similar to those of RBSN bodies using commercial-Si-powders. Some grains contained stacking fault were Si2N2O phase (indicated with arrows) that was observed in the XRD pattern in Fig. 3(a).

Figures 3(a) and (b) show XRD patterns of the RBSN body nitried at 1410°C and GPSed-RBSN body at 1950°C for 3.5 h, respectively. In the RBSN body, the α-Si3N4 and β-Si3N4 peaks are detected with high intensity as well as residual Si as observed in Fig. 2. From the XRD profiles, the percent phase ratio of β/α is 45.2%. In particular, it is noticed that the comparatively strong Si2N2O and weak Y2Si2O7 peaks are detected in the RBSN bodies. However, they are not detected in the RBSN body using commercial-Si-powders. When the large amounts of oxygen are contained in the Si3N4 body during the high-temperature processing, the Si2N2O and Y2Si2O7 phases are coexisted in the phase relation of Si3N4-SiO2-Al2O3 systems. On the other hand, in the GPSed-RBSN body of Fig. 3(b), α-Si3N4 peaks are not detected due to the α/β phase transformation during the GPS processing. Also, instead of Si2N2O and Y2Si2O7 phases, the O'-SiAlON phases are strongly detected in the GPSed-RBSN body. Although it is difficult to identify between Si2N2O and O'-SiAlON phase, it is considered that the Si3N4 phases are changed into O'-SiAlON phase as increasing the sintering temperature that caused by solution of Al component in the liquid phase.

Figure 4(a) is a TEM image showing the GPSed-RBSN body. Many Si3N4 grains are observed with various shapes caused by random distribution of rod-like Si3N4 grains in the GPSed-RBSN body. The average diameter of rod-like Si3N4 grains is about 1.5 µm that is smaller than that of using commercial-Si-powders. Furthermore, the aspect ratio of rod-like Si3N4 grains shows low value. A few of dislocations accompanying strong strain field contrasts are observed in the Si3N4 grains as indicated with arrowheads. Some fine particles were also observed with spherical shape as indicated with arrowheads at Si3N4 grain boundaries and triple regions. Electron diffraction patterns of Figs. 4(b), (c) and (d) were taken from O'SiAlON (marked P), triple-point (marked Q) and Si3N4 (marked R) regions in Fig. 4(a), respectively. Figures 4(e) and (f) are EDS profiles taken from the marked ‘P’ (fine spherical shape region) and ‘Q’ regions (triple region) in Fig. 4(a), respectively. These EDS profiles indicate that the ‘P’ and ‘Q’ regions are constructed with Si–Al–O–N and Y–Si–Al–O–N components. From the analysis of electron diffraction patterns as well as EDS profiles, they are confirmed with O'-SiAlON phase (detected in XRD pattern of Fig. 3(b)) and Y–Si–Al–O–N amorphous phase. An important observation is that the aspect ratio of rod-like Si3N4 grain is smaller than that of using commercial Si powder. It is considered that the main reason for showing with low aspect ratio of Si3N4 grains is caused by the existence of O'-SiAlON particles in the GPSed-RBSN bodies, in which they inhibit the growth of Si3N4 grains with large size.

Figure 5 shows a HRTEM image (a) and enlarged images (b, c) which was taken from the marked ‘P’ and ‘Q’ regions in Fig. 5(a), respectively. As indicated with arrowheads in Fig. 5(a), most of grain junctions in the GPSed-RBSN body were existed with amorphous phase. Also, most of Si3N4/SiAlON interfaces are covered with a morphous phase with about 1–3 nm in thickness as shown in Fig. 5(b). Figure 5(c) shows a low angle Si3N4 grain boundary in which contains local thin amorphous. The reason for showing with periodic dark contrast (marked with arrowheads) is caused by the existence of edge dislocations by lattice mismatching of both Si3N4 grains.

The material properties of GPSed-RBSN bodies are listed in Table 2. The values of fracture strength and fracture toughness of GPSed-body were 466 MPa and 5.7 MPa-m1/2, respectively. Although these values are not so high compared with that of GPSed-RBSN using commercial Si powders, it seems to improve their mechanical properties by the de-
development of microstructure with high aspect ratio of Si₃N₄ grains.

Figure 6 are SEM and TEM images of GPSed-RBSN body showing a fracture surface and a crack propagation made by 3-point bending and micro-indentation techniques, respectively. In Fig. 6(a), although some local regions were seen with rough surface due to the intergranular fracture, the main fracture mode was transgranular fracture showing with flat surface morphology. In Fig. 6(b), a crack propagated straightly into an O’-SiAlON (marked with arrowheads), an amorphous phase (dark region) and a rod-like Si₃N₄ grain (marked with ‘R’) as indicated with arrows. When a crack propagated into GPSed-body, the crack seems to propagate easily into rod-like Si₃N₄ grains without absorption of crack propagation energy since a few of dislocations were contained in most of rod-like Si₃N₄ grains as showed in Fig. 4(a). Furthermore, since the diameters of rod-like Si₃N₄ grains were comparatively small, the crack deflection and crack bridging mechanisms that were frequently observed in the GPSed-RBSN body using commercial-Si-powders are not applied in the GPSed-RBSN body using waste-Si-powders. Thus, it should be mentioned that the key to improve the mechanical properties of GPSed-RBSN body using waste-Si-powders is how we can make the reduction of oxygen contents in the waste-Si-powders for RBSN. The O’-SiAlON particles that inhibited the development of large-rod-like Si₃N₄ grains with high aspect ratio must be removed by carbothermal reduction treatment which can made to decrease the oxygen content or by compositional change of sintering additives such as using a sintering additives without Al₂O₃.

4. Conclusions

From the study on the microstructure and fracture characteristic of RBSN and GPSed-RBSN using waste-Si-sludge, which were respectively nitrided at 1410°C and post-sintered at 1950°C for 3.5 h, the following results were obtained. Many cracks and large amounts of oxygen were detected in the waste Si particles. The percent nitridation of Si compact using waste-Si-powders showed low value with 62% caused by the existences of large amounts of oxygen. After post-sintering by GPS, the sintered body was fully nitrided and became with high relative density as well as change into Si₃N₄--O’SiAlON composite. A lot of fine O’-SiAlON particles with spherical shape were observed intergranularly, and they inhibited the grain growth of rod-like Si₃N₄ grains. The fracture toughness and strength of Si₃N₄--O’SiAlON composite showed 5.6 MPa·m¹/² and 456 MPa, respectively. No remarkable fracture toughening mechanisms were observed in the Si₃N₄--O’SiAlON composite caused by the existence of O’-SiAlON phase, and the fracture mode was mixed type with intergranular and transgranular fracture.

Table 2 Material properties of GPSed Si₃N₄ bodies at 1950°C for 3.5 hours.

<table>
<thead>
<tr>
<th>Relative density (%)</th>
<th>Fracture strength (MPa)</th>
<th>Fracture toughness (MPa/m²)</th>
<th>Hardness (Hv)</th>
</tr>
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<tbody>
<tr>
<td>99.8</td>
<td>466</td>
<td>5.7</td>
<td>1553</td>
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</table>

Fig. 4 TEM image (a) and electron diffraction patterns (b, c, d) taken from the marked ‘P’, ‘Q’ and ‘R’ regions. EDS profiles (e, f) were taken from the marked ‘P’ and ‘Q’ regions in Fig. 4(a), respectively.
**Acknowledgments**

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**REFERENCES**