High-Temperature Mechanical Property Improvements of SiC Ceramics by NITE Process

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Dense SiC ceramics fabricated by NITE process (NITE-SiC), using SiC nano-powder, were subjected to exposure tests from 1000 to 1800°C in an argon-oxygen gas mixture with an oxygen partial pressure of 0.1 Pa. The thermal stability of NITE-SiC was examined through mass change, 3-point bending test, XRD analysis and TEM/SEM observation. The NITE-SiC presented excellent bending strength (above 800 MPa) up to ~1800°C while the conventional liquid-phase sintered SiC ceramics (LPS-SiC), using SiC sub-micron powder, indicated severe degradation at 1300°C due to volatilization and softening of amorphous grain boundary phase. The in situ 3-point bending test at 1300°C was carried out to evaluate in-service fracture behavior, where excellent improvements in bending strength, elastic modulus and fracture behavior were confirmed, compared with the conventional LPS-SiC. These are interpreted by the modification with reduction and crystallization of grain boundary phase (Y₂Al₃O₁₂). The decomposition of Y₂Al₃O₁₂ was caused by the reactions with CO gas on the surface of NITE-SiC exposed at 1800°C, but the severe degradation was not identified in strength.

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1. Introduction

Silicon carbide (SiC) is a prevalent ceramic material for many applications in harsh environmental conditions due to its resistance against high-temperature, aggressive chemicals and abrasion. SiC is difficult to densify without additives because of covalent nature of Si–C bonding and low self-diffusion coefficient.¹Solid-state sintered SiC (SSS-SiC), with addition to boron and carbon becomes a routine process to obtain dense SiC ceramics. However, these materials were characterized by a coarse microstructure and strength values lower than about 500 MPa due to reduced flaw tolerance caused by the low fracture toughness.¹–³ Liquid-phase sintered SiC (LPS-SiC) has the potential to become a commercially attractive material, which can be densified at low temperature and have high fracture toughness, compared with SSS-SiC. Al₂O₃–Y₂O₃ and AlN–Y₂O₃ were extensively employed as processing additives.⁴–⁸ Recently, a process has been developed which produces nearly-full dense matrix SiC at the “lower” sintering temperature (above 1800°C) while protecting SiC fibers and interphase after induced processing conditions. This process is named the “nano”-slurry, incorporating SiC nano-sized powder with oxide additives, infiltrated eutectic phase (NITE) process.⁹ Because of excellent mechanical properties, extreme gas tightness and lower fabrication cost, NITE-SiC/SiC composites are considered as promising structure materials for advanced nuclear gas-cooling systems.¹⁰–¹² However, small amount of oxide remnants is a remaining issue because LPS-ceramics are strongly affected by the intergranular residue of additional oxide additives, which is (partly) amorphous glassy phase. This amorphous glass softens and vaporizes at elevated temperatures, thus dramatically decreasing the strength as well as the oxidation and creep resistance.¹³–¹⁶ It was well known that under low oxygen partial pressure and at elevated temperatures, SiC is oxidized in the active-oxidation regime, causing the generation of gaseous products and serious mass loss. Consequently, active oxidation leads to severe degradation of the strength of SiC ceramics.¹⁷,¹⁸ For the present work, dense SiC ceramics by NITE process using SiC nanopowder and LPS process using conventional SiC submicron powder with Al₂O₃–Y₂O₃–SiO₂ additive systems, were exposed from 1000 to 1800°C under Ar–O₂ mixtures in low oxygen partial pressure (O₂ partial pressure: P_O₂ = 0.1 Pa). The thermal stability of NITE-SiC and LPS-SiC in the active oxidation region was investigated by focusing on the changes in strength and microstructural evolution that resulted from the environmental exposure. The in-situ 3-point bending test at 1300°C was carried out to evaluate in-service fracture behavior.

2. Experimental Procedure

Ultra-fine (average particle size: 30 nm) beta-SiC powder was used as a starting material, with oxide additives to Al₂O₃ (Sumitomo Chemical Industries Ltd., Japan), Y₂O₃ (Kojundo Chemical Industries Ltd., Japan) and SiO₂ (Kojundo Chemical Industries Ltd., Japan). Al₂O₃–Y₂O₃–SiO₂ system offers the formation of liquid-phase at lower temperature compared with other sintering additives, which enhances matrix densification of inside fiber bundles. Dense SiC ceramics were fabricated by NITE and LPS process in our laboratory. Processing details for the NITE-SiC have been reported elsewhere.¹⁹ We have shown that it is difficult to obtain dense SiC ceramics and SiC/SiC composites using SiC submicron-powder at “low” temperature (below 1800°C).²⁰ As shown in Table 1, the amount of additives and sintering temperature in LPS-SiC need to be increased in order to
Table 1 Difference between NITE and LPS process in the fabrication conditions.

<table>
<thead>
<tr>
<th>SiC powder size</th>
<th>Amount of additives</th>
<th>Fabrication temperature</th>
<th>Relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td>NITE-SiC</td>
<td>12 mass%</td>
<td>1800°C</td>
<td>96.8%</td>
</tr>
<tr>
<td>LPS-SiC</td>
<td>12 mass%</td>
<td>1800°C</td>
<td>82.3%</td>
</tr>
<tr>
<td>LPS-SiC</td>
<td>24 mass%</td>
<td>1820°C</td>
<td>97.1%</td>
</tr>
</tbody>
</table>

LPS-SiC: as the same fabrication conditions as NITE-SiC.

avoid the effect of porosity on the strength. The straight bar type specimens with mirror polishing on the all surfaces and chamfered corners were prepared for both the exposure test and the in-situ 3-point bending test. The specimens are \(1 \times 25 \times 7 \text{mm}^3\) in dimension. Specimens were placed in a carbon crucible and then exposed from 1000 to 1800°C for 1 h in Ar–O\(_2\) gas mixture with an oxygen partial pressure of \(P_{O_2} = 0.1 \text{Pa (10}^{-7}\text{ atm)\). Twenty specimens were exposed for each temperature. The furnace containing specimens was cooled by room-temperature. All specimens were carefully weighted before and after the exposure test to obtain mass change. The crystal phase of both surface and interior part was determined by X-ray diffractometry (XRD). The 3-point bending test was investigated to evaluate mechanical properties of exposed all specimens in INSTRON 8861S test machine with the crosshead speed of 0.5 mm/min and the span of 18 mm at room-temperature. Microstructural evolution after exposure was observed by JEOL JSM-6700F field emission scanning electron microscopy (FE-SEM) with energy dispersion X-ray spectrometry (EDS) and JEOL JEM-2010 transmission electron microscopy (TEM).

The in-situ 3-point bending test was performed using three specimens after stacking time of 1 h at 1300°C under the same atmosphere. The temperature was increased at the rate of 20°C/min to test temperature for both tests.

3. Results and Discussions

3.1 Bending strength and fracture behavior

Figure 1 shows the bending strength of NITE- and LPS-SiC after exposure. The NITE-SiC presented excellent bending strength up to \(\sim 1800°C\) (above 800 MPa). The highest bending strength (above 1 GPa) was achieved at 1300°C. This is supposed to be because porosity was decreased and grain boundary phase was crystallized through exposure. Although the bending strength decreased above 1400°C, its degradation is gradual. On the other hand, the conventional LPS-SiC indicated severe degradation at 1300°C due to volatilization and softening of amorphous grain boundary phase. This severe degradation of LPS-SiC at 1300°C is well correspond to the result reported by Sciti et al.\(^{21}\)

Figure 2 shows the bending strain-stress curve before, in situ and after exposure of 1300°C. Excellent improvements in bending strength, elastic modulus and fracture behavior were confirmed, compared with conventional LPS-SiC. Improvement in the high temperature strength resulting from the crystallization of a grain boundary phase was reported by Si\(_3\)N\(_4\) with Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\) additions.\(^{22}\)

Therefore, these results could be interpreted by the grain boundary phase modification with reduction and crystallization of grain boundary (Y\(_3\)Al\(_5\)O\(_12\)).

![Fig. 1 Bending strength of NITE- and LPS-SiC as the function of exposure temperature.](image1)

![Fig. 2 Stress/strain curve of NITE- and LPS-SiC from bending test before, in situ and after exposure of 1300°C.](image2)

![Fig. 3 Residual mass of NITE- and LPS-SiC as the function of exposure temperature.](image3)
3.2 Mass Change

Figure 3 shows the relationship between the residual mass, \(100 \times (1 - \Delta W/W_0)\), and exposed temperature. Here, \(W_0\) is the initial mass of NITE- and LPS-SiC and \(\Delta W\) is the mass change determined from the difference of the NITE- and LPS-SiC before and after the exposure test. The mass loss of NITE-SiC was very small (below 1%) up to 1600°C. On the other hand, that of LPS-SiC exhibited severe degradation at 1300°C (about 3%). Because of little mass loss of NITE-SiC, this severe mass loss of LPS-SiC was difficult to explain with only the result of active oxidation of the SiC crystallities as the following reaction:

\[
\text{SiC (s) + O}_2 \rightarrow \text{SiO (g) + CO (g)}
\]  

The mass loss indicated that SiC decomposition by active oxidation occurred concurrently with the vaporization of the amorphous grain boundary phase which was comprised mainly of the additives. At 1800°C, NITE-SiC exhibited a marked mass loss (about 6%), but the value was smaller than that of LPS-SiC (above 10%). Therefore, large amount of the additives must have caused the poor crystallization of grain boundary phase, resulting in the promotion of the vaporization of the amorphous grain boundary phase and the decomposition of SiC at high-temperature.

3.3 Microstructural evolution

TEM images of the interior part of NITE-SiC before and after exposure of 1300 and 1800°C are shown in Fig. 4. The significant growth of SiC grain was observed with the increasing exposed temperature. As shown in Fig. 5, the eroded surface of NITE-SiC was observed only after exposure of 1800°C. According to EDS results shown in Fig. 6, only Al content on its surface significantly decreased at 1800°C. It can be concluded that the loss of Al is related to the decomposition of the crystallized \(\text{Y}_3\text{Al}_5\text{O}_{12}\) (YAG) as grain boundary phase because sharp XRD analysis of the surface (shown in Fig. 7) identified that YAG peaks on its surface disappeared and produced a diffraction of pattern which matched well with \(\text{Y}_4\text{Al}_2\text{O}_9\) (YAM) only after exposure of 1800°C. YAG undergoes the decomposition
reaction while losing aluminum-containing gaseous species into the atmosphere.\textsuperscript{21,23,24} Equations (2) to (5) represent the possibility for such a decomposition reaction of YAG.

\[
\begin{align*}
4\text{Y}_3\text{Al}_5\text{O}_{12}(s) + 7\text{CO}(g) &\rightarrow 3\text{Y}_4\text{Al}_2\text{O}_9(s) + 14\text{AlO}(g) + 7\text{CO}_2(g) \quad (2) \\
4\text{Y}_3\text{Al}_5\text{O}_{12}(s) + 14\text{CO}(g) &\rightarrow 3\text{Y}_4\text{Al}_2\text{O}_9(s) + 7\text{Al}_2\text{O}(g) + 14\text{CO}_2(g) \quad (3) \\
4\text{Y}_3\text{Al}_5\text{O}_{12}(s) + \text{CO}(g) + 4\text{O}_2(g) &\rightarrow 3\text{Y}_4\text{Al}_2\text{O}_9(s) + 14\text{AlO}_2(g) + \text{CO}_2(g) \quad (4) \\
4\text{Y}_3\text{Al}_5\text{O}_{12}(s) + 28\text{CO}(g) &\rightarrow 3\text{Y}_4\text{Al}_2\text{O}_9(s) + 7\text{Al}_2\text{OC}(g) + 21\text{CO}_2(g) \quad (5)
\end{align*}
\]

The presence of CO gas is essential to initiate the reactions. At 1800°C, CO gas is sufficiently produced by active oxidation which SiC undergoes, as shown in equation (1). Math et al. reported that the loss of Al (solid solution in YAG) due to carbothermal reduction results in the decomposition of YAG to other yttrium aluminates richer in yttria, such as YSi (O, C), Y\textsubscript{2}O\textsubscript{3}, Y\textsubscript{4}Al\textsubscript{2}O\textsubscript{9} (YAM) and YAlO\textsubscript{3} (YAP) at exposure of 1650°C in vacuum with CO gas by EPMA analysis.\textsuperscript{23} Although main gaseous species (AlO, Al\textsubscript{2}O, AlO\textsubscript{2} and AlOC\textsubscript{2}) were difficult to be identified, it was cleared that severe mass loss of NITE-SiC exposed at 1800°C was caused though this decomposition of YAG accompanying generation generous products. Porous structure by this decomposition reaction of YAG in CO gas was about 15 um from the surface, and interior microstructure was dense and not eroded. This leads to the prevention of the severe degradation in strength after exposure at 1800°C.

4. Conclusion

The thermal stability of dense SiC ceramics by NITE process and LPS-SiC in the active oxidation region was evaluated by high-temperature mechanical properties and microstructural evolution. The results are as fellows:

(1) The NITE-SiC presented excellent bending strength (above 800 MPa) up to \(1800°C\) while the LPS-SiC indicated severe degradation at \(1300°C\) due to volatilization and softening of intergranular amorphous phase.

(2) The in-situ 3-point bending test at \(1300°C\) was carried out to evaluate in-service fracture behavior, where excellent improvements in bending strength, elastic modulus and bending fracture behavior were confirmed, compared with conventional LPS-SiC.

(3) The mass loss of NITE-SiC after exposure was very small (below 1%) up to \(1600°C\). Exposed at \(1800°C\), surface of NITE-SiC showed concentrated erosion.
caused by the active oxidation reaction accompanying generation generous products as well as heavy mass loss. These indicated aluminum-containing species evolved because of the decomposition of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG).

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