High-temperature properties of liquid-phase-sintered α-SiC

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Abstract

We have characterized the high-temperature subcritical crack growth and oxidation resistance of a liquid-phase-sintered (LPS) SiC with 20% volume fraction yttrium aluminum garnet (YAG) second phase. Constant stress-rate testing in air in the temperature range 1100–1300°C yielded a crack growth exponent, \(n = 38.9 \pm 9.9\) and an activation energy, \(Q_{scg} = (380 \pm 237)\) kJ mol\(^{-1}\). Oxidation followed parabolic kinetics in the temperature range 1100–1300°C with an activation energy, \(Q_{ox} = (246 \pm 33)\) kJ mol\(^{-1}\). At 1350°C reaction between the growing oxide layer and the YAG second phase produced a low-melting eutectic, resulting in accelerated oxidation. Below 1100°C, oxidation rates were also anomalously high for reasons we do not understand. In the intermediate temperature range, both the oxidation and subcritical crack growth resistance compare favorably with other silicon carbides. Published by Elsevier Science S.A.

Keywords: Silicon carbide; Dynamic fatigue; Constant stress-rate testing; Subcritical crack growth; Oxidation

1. Introduction

There has been growing interest in pressureless liquid-phase sintering (LPS) of SiC, with Al\(_2\)O\(_3\) additions [1] or simultaneous Al\(_2\)O\(_3\) and Y\(_2\)O\(_3\) (or other rare earth oxide) additions [2–5], as it allows sintering at lower temperatures (1850–1900°C) than solid-state sintering (2000–2200°C). Densities in excess of 99% of the theoretical limit can be easily achieved by carefully choosing the composition of the liquid phase and the packing-powder configuration [6,7]. A particularly important aspect of this class of materials is that they can be significantly toughened through careful microstructure design, wherein elongated SiC grain-reinforcements are grown in situ during sintering [8–10]. The elongated nature of the SiC grains and the weakness at the grain boundaries promote crack-wake bridging in these ceramics, resulting in a significant increase in the toughness [8–10]. Liquid-phase-sintered SiC may also be used for elevated-temperature applications. Keppler et al. [11] reported that the strength of LPS SiC fabricated with Y\(_2\)O\(_3\) and A1N begins to drop at 1000°C, but very little other high-temperature mechanical properties data exist. With the exception of work by Liu [12], the oxidation behavior of LPS SiC has not been studied either. The objective of this study was to evaluate and understand the high-temperature mechanical properties and oxidation behavior of a LPS SiC ceramic fabricated in-house.

Preliminary tensile creep experiments revealed that the LPS SiC of this study is highly creep-resistant. For instance, in air at 1300°C and 150 MPa, this LPS SiC crept to less than 0.05% strain in 480 h before failing. Fractography indicated that subcritical crack growth was responsible for the failure. Because of the importance of crack growth in failure, this mechanical properties work focuses on studying the effect of stressing rate on the strength (dynamic fatigue) of this ceramic at high-temperatures.
2. Experimental procedure

2.1. Material

A 99% dense LPS SiC, containing 20% by volume yttrium aluminum garnet (YAG) second phase, was fabricated in our laboratories, using a processing procedure described elsewhere [6–8]. This ceramic contains fine, equiaxed α-SiC grains of average size 1.0 μm; Fig. 2(A) of Ref. [7] shows the microstructure. Characterizing a fine-grained LPS SiC establishes a reference baseline for the high-temperature properties of LPS SiC in general.

2.2. Constant stress-rate testing

Four-point bend specimens (2 × 1.5 × 25 mm) were machined in-house according to the procedure outlined in the ASTM standard for high-temperature flexural strength [13]. Because of the low Weibull modulus of the as-fabricated material, the specimens were indented using a Knoop diamond pyramid at a load of 98 N. This indentation flaw was oriented perpendicular to the long axis of the specimen. To facilitate the examination of the pre-cracks, the indentation was offset 0.5° from vertical, following the indentation procedure (Section A3.3) for the surface crack in flexure (SCF) method of the ASTM provisional standard for fracture toughness of advanced ceramics [14]. After indenting, the surface residual stress from the indent was eliminated by removing a layer of 4.5 times the depth of the indentation hardness impression by polishing. Strength results in constant stress-rate tests were reproducible only when the indented face was the one that originally faced the interior of the billet. Even with this approach, a number of specimens did not fail from the indentation, and were not included in the analysis.

Constant stress-rate testing of indented specimens in the range 1100–1300°C employed a hot-pressed SiC fixture with 20 mm outer and 10 mm inner spans [15]. Loading rates were 0.01, 1.0, and 1000 MPa s\(^{-1}\). Tests in air employed an electromechanical testing machine (Instron Model 8562, Canton, MA, USA)\(^2\) with SiC push rods in a MoSi\(_2\) element furnace. Tests in nitrogen employed a screw-driven testing machine (Instron Model TT, Canton, MA, USA) with the specimen in a sealed MoSi\(_2\) element box furnace. All specimens were heated to temperature at 600°C h\(^{-1}\) under a 10 N (approximately 33 MPa) preload, soaked for 1 h, and then tested. Specimens tested at 1300°C were soaked for only 10 min. The fracture surfaces were examined with a stereo optical microscope (Leica Wild M10, Heerbrugg Switzerland).

2.3. Oxidation

Specimens for oxidation rate studies were nominally 3 × 4 × 10 mm, although some were slightly wider and shorter. During oxidation in still, room air in a MoSi\(_2\) element box furnace, the specimens rested on a sintered SiC plate. At intervals, they were removed from the furnace, weighed to ±0.0001 g, and returned for further oxidation. Some cross-sections of oxidized specimens were examined using a scanning electron microscope (ESEM2020, Phillips Electron Optics, The Netherlands).

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*Fig. 1. Strength a function of stressing rate for LPS SiC specimens with 98 N Knoop indentations. Error bars represent the estimated uncertainty of the mean strength. The symbols for the 1 MPa s\(^{-1}\) stressing rate have been displaced slightly for clarity. The solid lines are the fit of the natural log of Eq. (2) with parameters \(n = (38.9 ± 9.9), Q_{scg} = (380 ± 237) \text{kJ mol}^{-1}\), and log \(D_0(n + 1) = (5.11 ± 0.45)\) where \(D_0\) has units to give strengths in MPa when stressing rates are in MPa s\(^{-1}\).*

<table>
<thead>
<tr>
<th>(T) (°C)</th>
<th>(\dot{\sigma}) (MPa s(^{-1}))</th>
<th>Strengths, (\sigma_f) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room</td>
<td>80</td>
<td>334, 312, 219</td>
</tr>
<tr>
<td>1100</td>
<td>1</td>
<td>391, 387, 354, 353</td>
</tr>
<tr>
<td>1200</td>
<td>1000</td>
<td>465, 462, 438, 404</td>
</tr>
<tr>
<td>1200</td>
<td>0.1</td>
<td>388, 366, 358, 293</td>
</tr>
<tr>
<td>1200</td>
<td>0.1</td>
<td>382, 381, 358, 357</td>
</tr>
<tr>
<td>1300</td>
<td>1</td>
<td>359, 351, 326, 296</td>
</tr>
</tbody>
</table>

Tests conducted in nitrogen

| 1200 | 0.1 | 356, 339, 322, 296 |

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*The use of commercial designations or company names is for identification only and does not indicate endorsement by the National Institute of Standards and Technology.*
Fig. 2. Specific mass gain as a function of oxidation time. Note that the data for 1000°C lie above much of the higher temperature data. Data for 1350°C lie off-scale. Solid lines are the fits of Eq. (3) to the data.

4. Discussion

4.1. Subcritical crack growth resistance

The resistance to subcritical crack growth in structural ceramics at elevated-temperature is typically evaluated by one of three techniques. Double torsion tests have the advantage that the growing crack is large and easy to follow, but suffer from the disadvantage that the growth of large cracks may not represent the growth of the type of small flaws responsible for failure in service. Constant stress tests (so-called static fatigue or stress rupture) probe the small flaws that are ultimately responsible for failure under service conditions, and have the advantage that they can indicate the propensity for failure from other time-dependent mechanisms besides SCG. Difficulties in interpreting the data if high-temperature exposure generates new flaws and the long testing times are disadvantages. Constant stress-rate testing (dynamic fatigue) allows more numerous tests and mitigates the contribution of purely time-dependent exposure effects.

Regardless of the test technique, traditionally one assumes that the crack velocity, \( v \), of flaws follows a power law function of the applied stress intensity, \( K \) [17,18]:

\[
v = v_0 \exp\left(-\frac{Q_{scg}}{RT}\right)\left(K/K_0\right)^n
\]  

(1)

For extension under constant loading rate, \( \dot{\varepsilon} \), the failure stress, \( \sigma_f \), has the form [19]:

\[
\sigma_f = D_0 \exp\left(\frac{Q_{scg}}{RT}\right)\dot{\varepsilon}^{n+1}
\]  

(2)

where \( D_0 \) is a constant term. Large values of the exponent, \( n \), indicate good resistance to SCG.

Fig. 1 shows the bilinear regression of the natural logarithm of Eq. (2) to the data. This method is the one recommended in ASTM Standard 1368 [20] for determination of subcritical crack growth parameters in structural ceramics at room temperature, although that standard does not employ indented specimens, and folds the activation energy term, \( Q_{scg} \), into the constant, \( D_0 \).

The uncertainty in the crack growth exponent, \( n(38.9 \pm 9.9) \), comes from the uncertainty in the slope of the log \( \sigma_f - \log \dot{\varepsilon} \) curve, and arises primarily from the anomalously high mean strength at 1200°C at the lowest loading rate. It is possible that flaw blunting by oxidation during the loading may have caused this increase. The tests in the inert environment, where no such blunting should have occurred, have a much lower strength, \((325 \pm 11) \) vs. \((369 \pm 7) \) MPa, than those
tested in air, and lie along the global fit. Specimens in these low stressing rate tests were at temperature for nearly 2 h before failure (1 h soak at no load, plus 1 h to reach the failure load), in contrast to only 1 h total for the specimens at the middle loading rate and 10 min at the highest loading rate.

Fig. 3 and Table 2 compare the data for constant stress-rate tests of this study with those for other silicon carbides densified with oxide additives. None of the materials show a great propensity toward subcritical crack extension: the exponents, \( n \), are all near 20 or greater. The yttria-alumina sintered SiC \([21]\) (designated Hexoloy SX-G1), had a substantially smaller mass fraction of additives (0.02) than the LPS SiC of this study (0.26). Evans et al. \([22]\) and Minford et al. \([23]\) agree well on the properties for \( \text{Al}_2\text{O}_3 \) hot-pressed SiC (Norton NC-203). Interestingly, Choi et al. \([24]\) reported the absence of subcritical crack growth \((n = 108)\) at 1200°C in the same vintage material, but found \( n = 28 \pm 6 \) at 1300°C. The SiC of Braue et al. may have a slightly better resistance to SCG than NC-203; one difference is that it was HIP-ed with much less \( \text{Al}_2\text{O}_3 \).

### 4.2. Oxidation

Typically, oxidation of SiC ceramics, whether sintered or single-crystal, is assumed to be limited by the rate of oxygen transport across the growing silica scale \([25–27]\). Diffusion-limited reactions such as this give rise to parabolic oxidation kinetics:

\[
\Delta m^2 = k_p t,
\]

where \( \Delta m \) is the specific mass gain (mass gain per unit area) during time, \( t \).

Fig. 2 shows the non-linear least-squares fit of Eq. (3) for the six oxidation conditions. Note that the nature of the fit constrains the lines to pass through the origin. The data at the highest and lowest temperatures deviate strongly from the behavior of the intermediate temperatures, Fig. 4. The oxidation process has an activation

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### Table 2

A comparison of results from constant stress-rate tests on various silicon carbides densified with oxide additives

<table>
<thead>
<tr>
<th>Reference</th>
<th>Additive</th>
<th>( Q_{scg} ) KJ mol(^{-1} )</th>
<th>( n )</th>
<th>( \log_{10} D_0(n+1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>YAG</td>
<td>380 \pm 237</td>
<td>38.9 \pm 9.9</td>
<td>5.11 \pm 0.45</td>
</tr>
<tr>
<td>Chia et al. ([21])</td>
<td>YAG (Hexoloy SX-G1)</td>
<td>1130 \pm 605</td>
<td>28.7 \pm 14.4</td>
<td>3.07 \pm 0.67</td>
</tr>
<tr>
<td>Evans et al. ([22])</td>
<td>( \text{Al}_2\text{O}_3 ) (NC-203)</td>
<td>689 \pm 91</td>
<td>17.9 \pm 2.0</td>
<td>3.09 \pm 0.21</td>
</tr>
<tr>
<td>Minford et al. ([23])</td>
<td>( \text{Al}_2\text{O}_3 ) (NC-203)</td>
<td>806 \pm 231</td>
<td>19.6 \pm 5.4</td>
<td>2.75 \pm 0.35</td>
</tr>
<tr>
<td>Braue et al. ([31])</td>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>445 \pm 45</td>
<td>32.5 \pm 2.4</td>
<td>4.73 \pm 0.09</td>
</tr>
</tbody>
</table>
energy, $Q_{ox} = (246 \pm 33) \text{ kJ mol}^{-1}$, when data for the highest and lowest temperatures are excluded.

We do not understand the origin of the low-temperature increase in oxidation rate. It is possible that the oxide that forms is not sufficiently deformable to prevent cracking and thus allows ingress of oxygen to the SiC surface. If this is the case, the measured parabolic rate constant is not valid because transport across the growing oxide layer no longer controls the oxidation rate.

At 1350°C, it is likely that the dramatic increase in oxidation rate comes from the reaction between the silica scale formed and the YAG second phase. Bondar' [28] reported that the eutectic in the $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ system is at 1345°C. Presumably, silica forming by oxidation of silicon carbide reacts with the YAG to form a low viscosity liquid phase, which allows fast transport of oxygen. There was substantial evidence for such a process in the 1350°C oxidation experiments. Fig. 5 shows that the near-surface of the LPS SiC is depleted in the second phase. The existence of this eutectic probably limits the applicability of YAG-sintered SiC to temperatures much below the 1345°C eutectic temperature.

Fig. 4 shows that, in the intermediate temperature range, the oxidation kinetics of this LPS SiC compare favorably with other silicon carbides, despite its much greater fraction of additives. For comparison, Fig. 4 shows data from a SiC hot-pressed with $\text{Al}_2\text{O}_3$ (Norton NC-203) [29]; the same grade and vintage of material appears in Fig. 3. There are also data from two silicon carbides sintered with boron [29,30] and a high-purity, chemically vapor deposited SiC [27]. All of these show activation energies comparable to the LPS SiC of this study. Only one material, another LPS SiC [12], sintered with 20% mass fraction YAG, has a very much larger activation energy ($880 \pm 158 \text{ kJ mol}^{-1}$), which is calculated from directly from the weight-gain data of Fig. 4 of Ref. [12].

5. Summary

The resistance to subcritical crack growth at elevated-temperatures of this LPS $\alpha$-SiC compares favorably with other silicon carbides densified with oxide additives. The oxidation resistance at intermediate temperatures compares favorably with other silicon carbides, but possible reaction by YAG with silica may limit the upper-use temperature to less than 1345°C.

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References


