

High-temperature creep response of a commercial grade siliconized silicon carbide

HUA-TAY LIN, SHIRLEY WATERS, KRISTIN BREDER

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6068

E-mail: linh@ornl.gov

Creep studies conducted in four-point flexure of a commercial siliconized silicon carbide (Si-SiC, designated as Norton NT230) have been carried out at temperatures of 1300, 1370, and 1410 °C in air under selected stress levels. The Si-SiC material investigated contained ~90% α -SiC, 8% discontinuous free Si, and 2% porosity. In general, the Si-SiC material exhibited very low creep rates (2 to $10 \times 10^{-10} \text{ s}^{-1}$) at temperatures ≤ 1370 °C under applied stress levels of up to 300 MPa. At 1410 °C, the melting point of Si, the Si-SiC material still showed relative low creep rates (~ 0.8 to $3 \times 10^{-9} \text{ s}^{-1}$) at stresses below a threshold value of ~ 190 MPa. At stresses > 190 MPa the Si-SiC material exhibited high creep rates plus a high stress exponent ($n = 17$) as a result of slow crack growth assisted process that initiated within Si-rich regions. The Si-SiC material, tested at temperature ≤ 1370 °C and below the threshold of 190 MPa at 1410 °C, exhibited a stress exponent of one, suggestive of diffusional creep processes. Scanning electron microscopy observations showed very limited creep cavitation at free Si pockets, suggesting the discontinuous Si phase played no or little role in controlling the creep response of the Si-SiC material when it was tested in the creep-controlled regime. © 1999 Kluwer Academic Publishers

1. Introduction

Siliconized silicon carbide (Si-SiC) exhibits high thermal conductivity, good thermal shock resistance, and good retention of mechanical properties at elevated temperatures. As a result, this material has been considered as one of the candidates for a ceramic heat exchanger application in the US Department of Energy, Combustion 2000 and Clean Coal Programs [1, 2]. Therefore, the intended application environments will involve not only high temperature, but contain coal ash derived oxides and alkali vapors. It is anticipated that the application environments would cause severe degradation in material properties and thus limit its long-term mechanical reliability. Degradation of material components due to the corrosive environments can be enhanced by the presence of mechanical stresses. Therefore, an understanding of the material response subjected to fatigue and/or creep loading conditions is needed prior to component applications.

A recent dynamic fatigue study was conducted by Breder [3] on a commercially available Si-SiC (Norton NT230) at temperatures of 1100 and 1400 °C in air at stressing rates ranging from 1 to 0.0001 MPa/s. The results showed that no slow crack growth (SCG) was detected at 1100 °C, whereas at 1400 °C SCG occurred within Si-rich regions. On the other hand, several researchers [4–11] have reported creep studies on various grades of commercially available Si-SiC materials. The free Si content in the SiC materials that

were investigated ranged from 10 to 36 vol %. Previous results showed that the creep rates of Si-SiC materials increased with increasing Si content, applied stress, and test temperature [4–9]. For instance, at low Si content (< 15 vol %) the Si-SiC materials exhibited stress exponents of ~ 1 at elevated temperatures in air. The creep mechanism was, in general, attributed to diffusional creep controlled processes [10, 11]. As for the materials with high Si content (30 to 37 vol %) the creep deformation and rupture at temperatures between 1100 and 1300 °C in air was dictated by the cavitation occurring at Si/SiC interfaces and within the Si pockets. Creep cavities grow, coalesce, and eventually form a dominant macro crack, resulting in final rupture of the materials. The high creep rates and high stress exponents observed at stresses above the so-called threshold stress level were found to be associated with the enhanced creep cavitation and crack formation [4, 8, 9]. The threshold stress was defined, in previous studies, as the stress at which a transition in the slope of the creep rate versus stress curves occurred.

As a part of material property evaluation efforts for the Combustion 2000 and Clean Coal Programs, this study was carried out to evaluate the flexural creep behavior of a commercial Si-SiC (designated as Norton NT230) at temperatures of 1300, 1370, and 1410 °C in air. The creep damage and controlling processes as a function test temperature and applied flexural stress level were then determined.

2. Experimental

The ceramic evaluated in the present study is a commercial Si-SiC (designated as NT230), manufactured by Saint-Gobain/Norton Industrial Ceramics Corp., Northboro, MA. This material, developed from the earlier NC430 Si-SiC, was slip-cast and pre-fired prior to the final siliconization step. Details of the processing procedures of Norton NT230 can be found in Ref. [12]. The as-received NT230 Si-SiC material contained ~90 vol% α -SiC, 8 vol% free Si, and some residual porosity (<2 vol%).

Flexural creep tests were conducted in air at temperatures of 1300, 1370, and 1410 °C at outer fiber stress levels ranging from 125 to 300 MPa. The test bars (3 × 4 × 50 mm) were loaded in a fully dense sintered α -SiC four-point flexural fixture with sintered α -SiC loading pins at inner and outer spans of 20 and 40 mm, respectively. The desired stresses were applied to the test specimens through a sintered α -SiC push rod via a dead weight loading system. The creep system was allowed to thermally equilibrate for 30 to 60 min before applying the load. The outer fiber displacement of the bend bars was measured by a high-temperature three-probe extensometer* whose output was continuously recorded. The details of the creep test procedures can be found in Ref. [13]. The outer fiber stress and corresponding deformation strain were calculated based upon the procedures described by Hollenberg *et al.* [14]. It is recognized that when the creep stress exponent is >2, which is generally associated with extensive formation of creep cavities, errors are introduced into the stress calculation. All of the tests were carried out with test times of at least 300 h to ensure a measurable creep strain (thus, creep rate) or until fracture of the specimens.

The microstructures of the specimens before and after creep testing were examined using both optical and scanning electron microscopy (SEM) to characterize the accumulated creep damage as a function of test temperature and applied stress level. Note that all the test specimens were cooled down to room temperature at a cooling rate of ~10 °C/s while under load to preserve the damage accumulated during creep. Quantitative image analysis of the size and number density of pores was performed on polished cross sections of both as-received and crept specimens using an analytical software† and the techniques described in Ref. [15]. Twenty micrographs were analyzed for each sample using a magnification of 500× to obtain statistically significant results for the number density of creep cavities (pores), and average cavity size and size distribution.

3. Results and discussion

Fig. 1 shows the creep rate versus applied stress results for Norton NT230 Si/SiC material at temperatures of 1300, 1370, and 1410 °C under applied stresses ranging from 125 to 300 MPa in air. The results indicated that NT230 exhibited very low creep rates, i.e., ~2 to

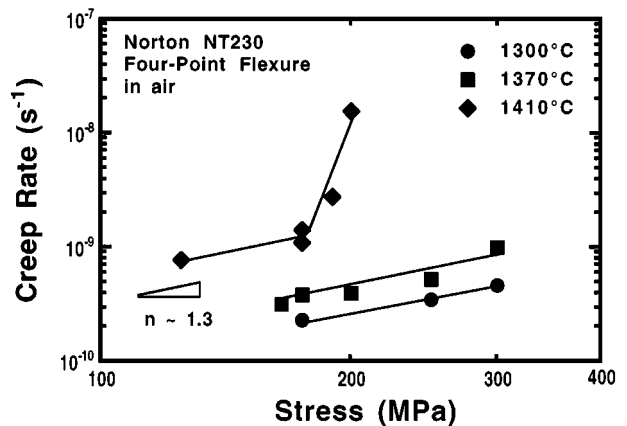


Figure 1 Creep rate versus stress curves of Norton NT230 Si-SiC tested at temperatures of 1300, 1370, and 1410 °C in air.

$10 \times 10^{-10} \text{ s}^{-1}$ at temperatures of 1300 and 1370 °C under the stress range employed in the present study. The results also showed that there was only a minor increase (~ a factor of two) in creep rate from 1300 to 1370 °C (97% of the Si melting point of ~1410 °C). In addition, the slope of creep rate versus applied stress curves at temperatures of 1300 and 1370 °C yielded a stress exponent of one, suggestive of diffusional controlled creep processes. At 1410 °C, the NT230 Si-SiC still exhibited reasonably low creep rates (~0.8 to $3 \times 10^{-9} \text{ s}^{-1}$) with a stress exponent of one at stress levels <190 MPa (Fig. 1). However, at stresses >190 MPa the Si-SiC material exhibited high creep rates plus a very high stress exponent ($n = 17$) as a result of slow crack growth (SCG) assisted process that initiated within Si-rich regions. This was evident by the presence of Si beads on tensile surface regions of fracture surfaces of all specimens tested at 1410 °C and at >190 MPa. The threshold stress, 190 MPa, was similar to the mean flexural strength (176–192 MPa) reported by Breder at 1400 °C [3] for the same batch of NT230 Si-SiC material. Also, note that the creep rates at 1410 °C and at stress <190 MPa (in creep-controlled regime) were eight to ten times higher than those tested at 1370 °C. This substantial increase in creep rates from 1370 to 1410 °C could result from the presence of Si liquid pockets and films that assist the creep deformation processes via diffusion and/or grain boundary sliding.

Another purpose of this study was to compare the present creep results of NT230 with those reported previously for other commercial Si-SiC materials, as shown in Fig. 2. Fig. 2a compares the creep results of NT230 tested at 1300 and 1370 °C with two earlier Si-SiC materials evaluated at 1350 °C in air [10, 11]. The comparison with Si-SiC materials indicated that NT230 tested at 1370 °C still exhibited creep rates that were three to ten times lower than both Norton NC430 (~10 vol% free Si) and Coors Si-SiC (~12 vol% free Si) materials tested at 1350 °C. The difference in measured creep rates might result from variations in free Si content and SiC grain size. Note that the reported average grain sizes of Coors Si-SiC and Norton NC430 were 5 to 12 and 2 to 10 μm , respectively [10, 11]. Earlier reports [10, 11] also showed that both NC430 and Coors Si-SiC materials exhibited a stress exponent of

* Applied Test System, Butler, PA.

† Prism Image Analysis software, Analytical Vision, Inc., Raleigh, NC.

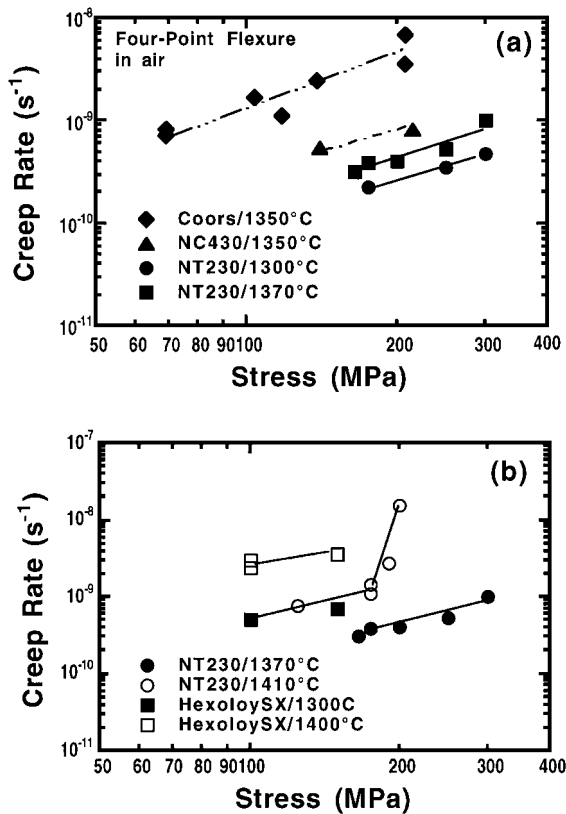


Figure 2 Comparison of creep results between NT230 and (1) earlier commercially available Si-SiC materials tested at 1350°C, and (2) developmental sintered α -SiC tested at 1300 and 1400°C.

one that was attributed to diffusional creep processes. In addition, the creep results of a developmental sintered α -SiC material (designated as Hexoloy SXG1, by Carborundum) tested at 1300° and 1400°C in air [16, 17] were also included in the comparison, as shown in Fig. 2b. Note that this developmental Hexoloy SXG1 α -SiC material was sintered with Y_2O_3 and Al_2O_3 sintering additives (~ 2 wt% in total) [16]. Comparison with sintered α -SiC material again showed that the creep rates of NT230 Si-SiC material were 3–5 times lower than those obtained from this sintered α -SiC material tested in air at temperatures up to 1400°C in air (Fig. 2b). The better creep resistance of NT230 over the sintered α -SiC could result from the lack of amorphous grain boundary phase(s) and/or the larger SiC grains ($4\text{--}6\ \mu\text{m}$ for NT230 vs. $1\text{--}2\ \mu\text{m}$ for Hexoloy SXG1) [16].

Following creep tests, detailed microstructure characterizations by both optical microscopy and SEM analyses were carried out to understand the creep damage evolution as a function of test temperature and applied stress. Fig. 3 shows the SEM micrographs of pores (creep cavities) for specimens in the as-received condition and after creep testing in air for 300 h at 1300 and 1370°C under an applied stress of 300 MPa and at 1410°C/175 MPa. Note that all the SEM micrographs of crept specimens were taken from the tensile surface regions. The histogram plots of pore size analyses for specimens shown in Fig. 3 are shown in Fig. 4. SEM

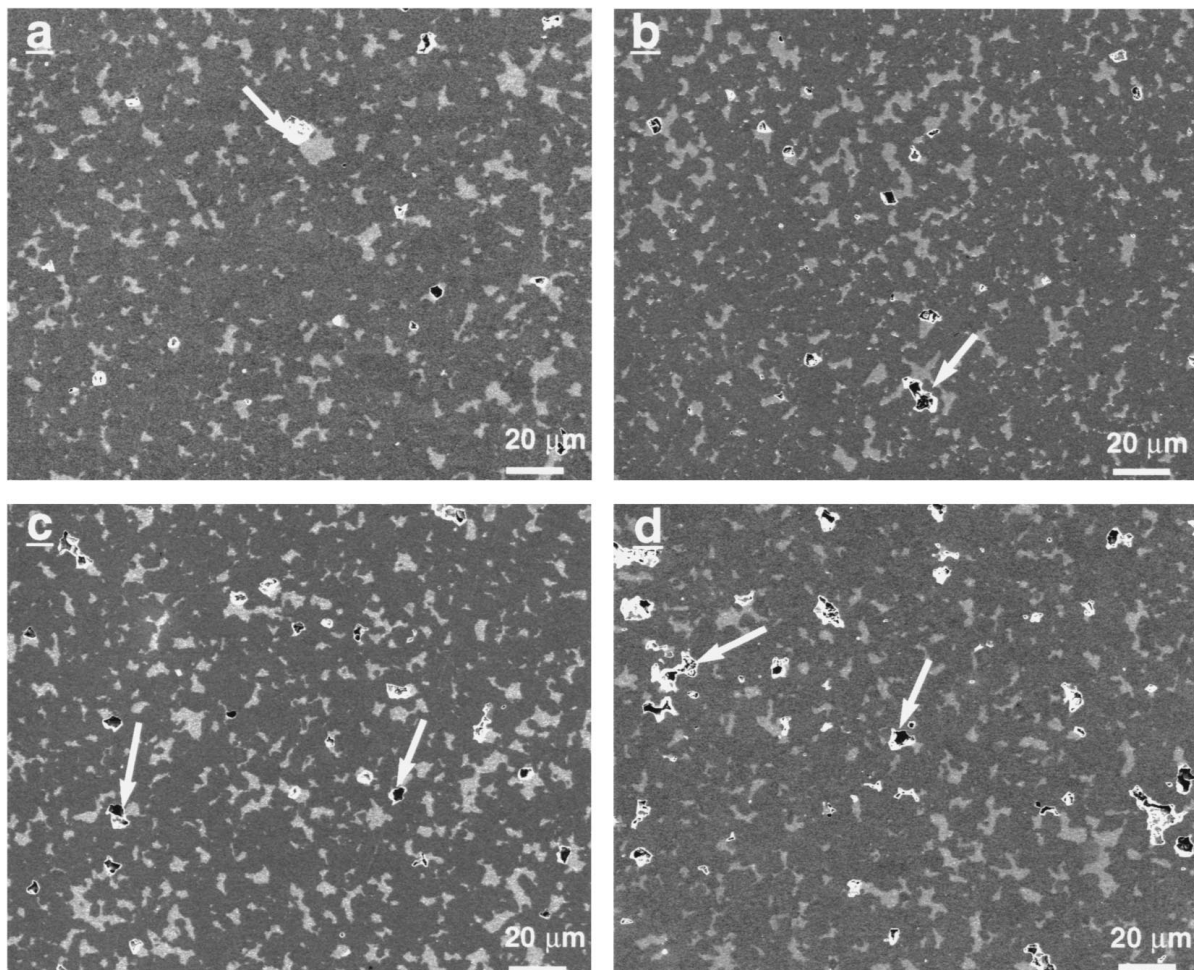


Figure 3 Scanning electron micrographs showing the pore (creep cavities) features in (a) as-received condition and after (b) 1300°C, (c) 1370°C, and (d) 1410°C creep test. Light gray phase is the free Si and arrows indicate the pores.

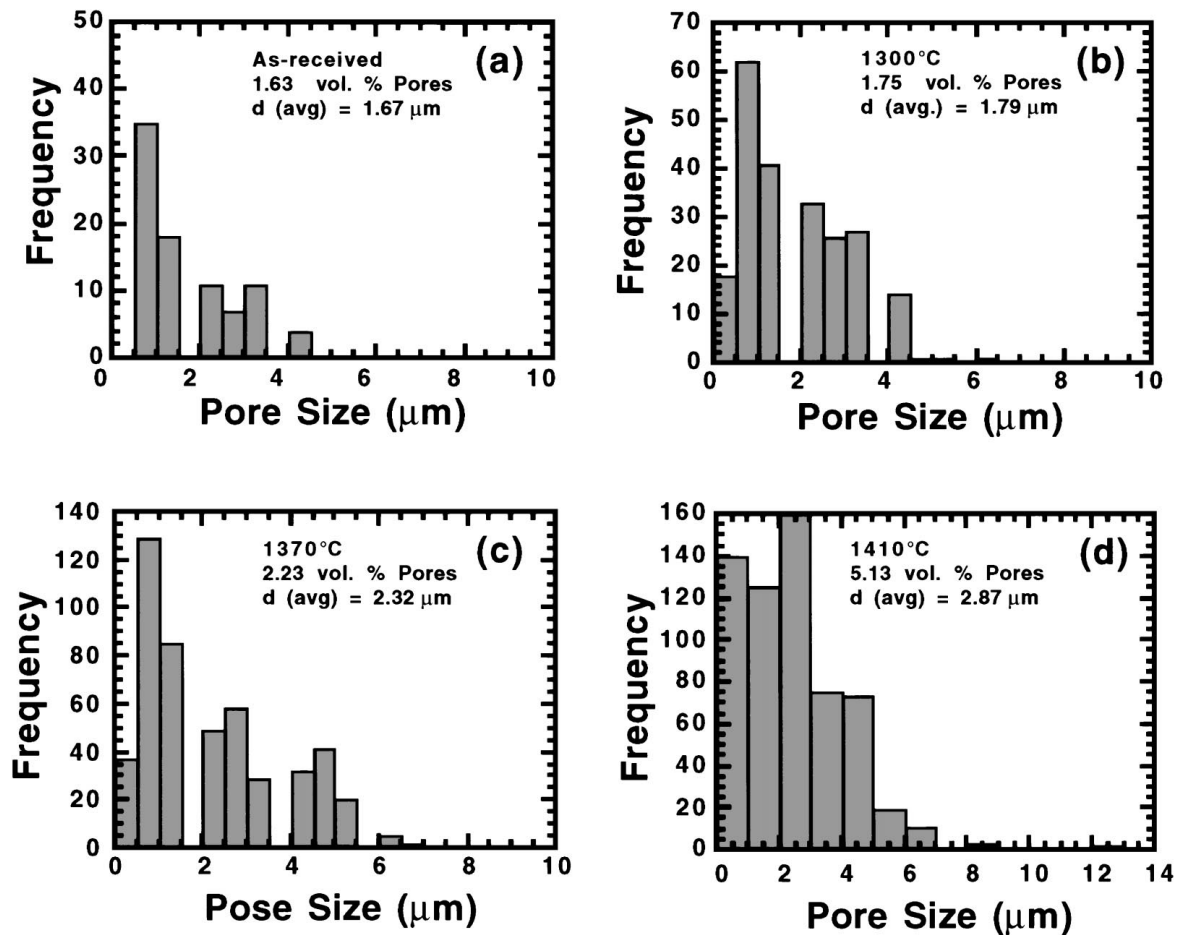


Figure 4 Histogram plots of frequency versus pore (cavity) size for specimens in (a) as-received condition, and after (b) 1300 °C, (c) 1370 °C, and (d) 1410 °C creep test.

observations and pore analyses indicated that there were very small (1.1 to 1.5 fold) increases in both the number densities and sizes of pores for specimens tested at 1300 and 1370 °C at an applied stress of 300 MPa as compared with those of the as-received materials. The minimal increases in pore number density and size were consistent with the measured low creep rates at 1300 and 1370 °C (Fig. 1) under the stress levels employed in the present study. The specimens tested at 1410 °C/175 MPa, however, exhibited a ≥ 3 -fold increase in the number density of pores but with a small (~ 1.7 fold) increase in average pore size (from 1.7 to 2.9 μm). The increases in number density and size of pores contribute to higher creep strains (and thus creep rates) at 1410 °C.

In general, the dominant creep controlling processes in Si-SiC materials are governed by the deformation of free Si phase, grain boundary sliding or diffusional processes along the SiC grains. In the present study the free Si pockets in Norton NT230 material are discontinuous (Fig. 3a) and the measured creep rates (Fig. 1) are very low, it is, thus, anticipated that the free Si pockets play no or little role in governing the creep deformation process when tested in creep regime and at temperatures ≤ 1370 °C. In this case, creep processes would then be controlled by the deformation of large contact area between two SiC grains and SiC multigrain junctions via grain boundary sliding (GBS) and/or diffusional processes (as evidenced by the stress exponent of ~ 1),

similar to the creep behavior of dense polycrystalline α -SiC materials [18, 19]. However, as temperature increased to 1410 °C the Si present in multigrain junctions and SiC grain boundaries becomes liquid-like and could promote the GBS and/or diffusional creep processes, resulting in an increase in number of creep cavities (as shown in Figs 3d and 4d) and, thus creep rates (Fig. 1). The enhanced creep cavitation at 1410 °C is further supported by SEM observations on fracture surfaces of specimens tested at 1410 °C/175 MPa for 300 h in air and regenerated at room temperature (Fig. 5). The fracture surfaces exhibited features of (1) spherical creep cavities within free Si pockets at multigrain junctions and (2) residual Si film on SiC grain facets, which were not observed in specimens tested at ≤ 1370 °C. The greater tendency of cavity formation in Si at 1410 °C is due to the low surface tension ($\gamma \sim 0.73$ N/m) of liquid Si [20]. Consequently, it only requires an applied tensile stress ($\sigma = 2\gamma/r$) > 15 MPa to form a cavity with 0.1 μm diameter in Si. Note the applied flexural stress levels in present study ranged from 100 to 300 MPa. Therefore, it would be easy to nucleate creep cavities at 1410 °C, especially in free Si pockets. However, the large contact area of SiC grain boundaries may limit the cavity growth rate via GBS and/or diffusional processes and, therefore, the size of pores (creep cavities) still remained relatively small under the test times employed in the creep regime (≤ 190 MPa) at 1410 °C.

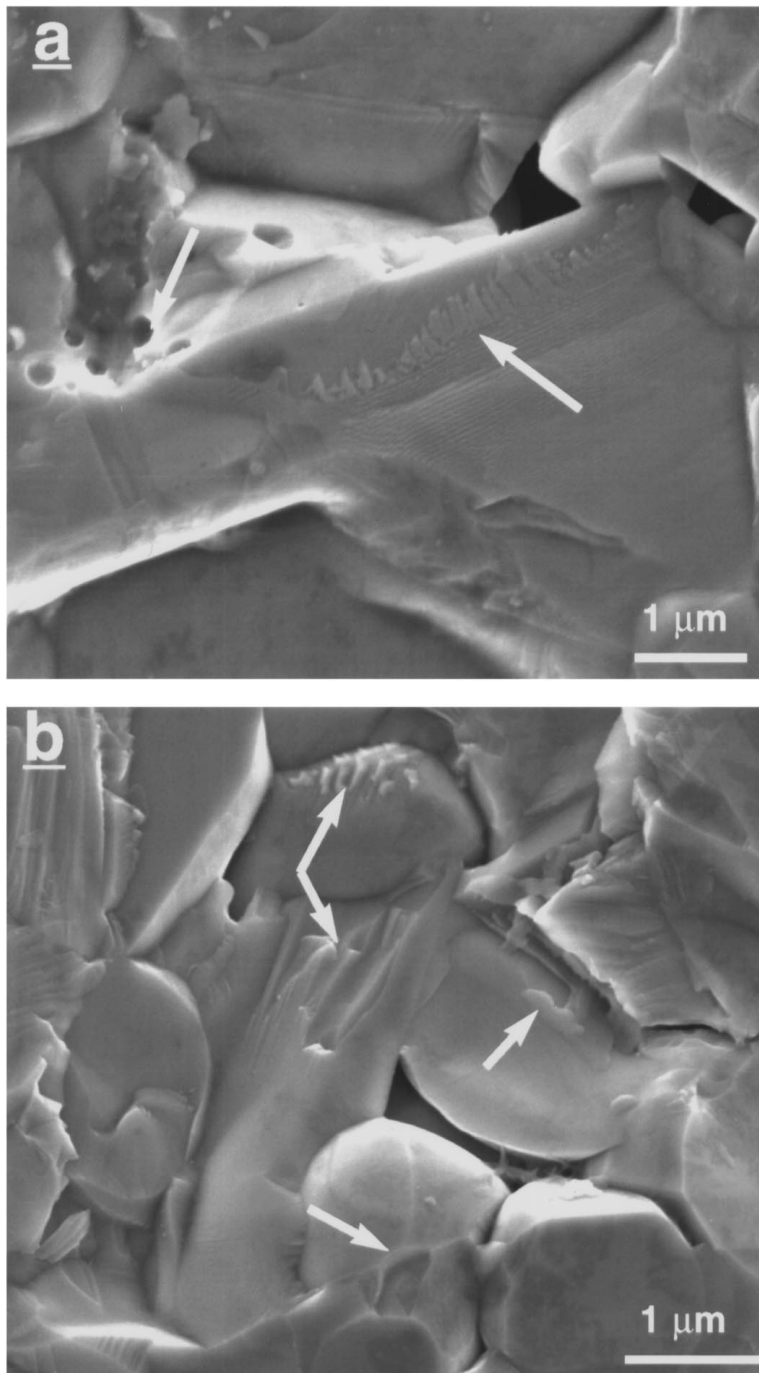


Figure 5 Scanning electron micrographs showing fracture surface features of specimen after testing at 1410 °C/175 MPa in air. (a) Creep cavities formed at triple-point Si pocket, as indicated by arrow, and (b) Si films on the SiC grain facets, as indicated by arrows.

4. Summary

The creep response of a commercial siliconized silicon carbide (Si-SiC, designated as Norton NT230) was evaluated in four-point flexure at temperatures between 1300 and 1410 °C in air. The results indicated that the Si-SiC material exhibited low creep rates of 2 to $10 \times 10^{-10} \text{ s}^{-1}$ at temperatures ≤ 1370 °C under stress levels employed. At 1410 °C, melting point of Si, the Si-SiC material still exhibited relatively low creep rates (~ 0.8 to $3 \times 10^{-9} \text{ s}^{-1}$) at stresses below a threshold value of ~ 190 MPa, which was about equal to the average flexural strength at this temperature. At stress level ≤ 190 MPa the Si-SiC material exhibited high creep rates plus a high stress exponent ($n = 17$)

as a result of slow crack growth assisted process that initiated within Si-rich regions as evidenced by the presence of Si beads on fracture surfaces. The Si-SiC material, tested at temperatures ≤ 1370 °C and below the threshold (~ 190 MPa) at 1410 °C, exhibited a stress exponent of one, indicative of diffusional creep processes.

Scanning electron microscopy observations and pore analyses revealed very limited creep cavitation at free Si, which suggested that the Si played no or a little role in controlling the creep response of NT230 material when it was tested in the creep-controlled regime at temperatures < 1410 °C. At 1410 °C, the creep processes, diffusion and/or GBS, were promoted due to the

presence of liquid Si film, resulting in higher number density of creep cavities and thus creep rates. Finally, comparisons of creep results between NT230 and other commercial Si-SiC materials indicated that NT230 exhibited superior creep resistance at temperatures up to 1410 °C in air. A follow-up tensile creep study will be then carried out to generate a database for engineering design purpose.

5. Acknowledgements

The authors thank Drs. P. F. Becher, M. K. Ferber, and A. A. Wereszczak for reviewing the manuscript. Research sponsored by the US Department of Energy, Office of Transportation Technologies, Propulsion Automotive Materials Program and Office of Fossil Energy, Pittsburgh Energy Technology Center, Advanced Combustion Technology Program, DOE/FE 35 35 00 0, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

References

1. D. J. SEERY, J. J. SANGIOVANNI, F. L. ROBSON and W. M. PROCIA, "Combustion 2000: Burning Coal in the Twenty-First Century," in Proc. of the Ninth Annual Coal Preparation, Utilization and Environmental Control Contractors Conference (Pittsburgh, PA, DOE, 1993) pp. 356–363.
2. J. SHENKER, "Development of a High-Performance Coal-Fired Power Generating System with a Pyrolysis Gas and Char-Fired High Temperature Furnace," in Proc. of the Ninth Annual Coal Preparation, Utilization and Environmental Control Contractors Conference (Pittsburgh, PA, DOE, 1993) pp. 349–355.
3. K. BREDER, *J. Amer. Ceram. Soc.* **78**(10) (1995) 2673–2679.
4. S. M. WIEDERHORN, D. E. ROBERTS, T.-J. CHUANG and L. CHUCK, *ibid.* **71**(7) (1988) 602–608.
5. D. F. CARROLL and R. E. TRESSLER, *ibid.* **71**(6) (1988) 472–477.
6. T.-J. CHUANG and S. M. WIEDERHORN, *ibid.* **71**(7) (1988) 595–601.
7. D. F. CARROLL and R. E. TRESSLER, *ibid.* **72**(1) (1989) 49–53.
8. B. J. HOCKEY and S. M. WIEDERHORN, *ibid.* **75**(1) (1992) 1822–1830.
9. B. A. FIELDS and S. M. WIEDERHORN, *ibid.* **79**(4) (1996) 977–986.
10. D. C. LARSEN and J. W. ADAMS, Property screening and evaluation of ceramic turbine materials, Semiannual Interim Technical Report No. 12, Contract F33615-79-C-5100, May 1982.
11. D. C. LARSEN and J. W. ADAMS, Property screening and evaluation of ceramic turbine materials, AFWAL-TR-83-4141, Final Technical Report, April 1983.
12. B. J. MCENTIRE, R. R. HENGST, W. T. COLLINS, A. P. TAGLIALAVORE, R. L. YECKLEY, E. BRIGHT and M. G. BINGHAM, "Ceramic Component Processing Development for Advanced Gas-Turbine Engines," presented at the International Gas Turbine and Aeroengine Congress and Exposition, Orlando, FL, June 1991, published in the Transaction of the ASME.
13. H. T. LIN and P. F. BECHER, *J. Amer. Ceram. Soc.* **73**(5) (1990) 1378–1381.
14. G. W. HOLLENBERG, G. R. TERWILLIGER and R. S. GORDON, *ibid.* **54**(4) (1971) 196–199.
15. J. C. RUSS, "The Image Processing Handbook," 2nd ed. (CRC Press, Ann Arbor, MI 1994).
16. K. Y. CHIA and S. K. LAU, *Ceram. Eng. Sci. Proc.* **12**(9/10) (1991) 1845–1861.
17. H. T. LIN and P. F. BECHER, "Fracture Behavior of Toughened Ceramics," in Ceramic Technology for Advanced Heat Engines Project Semiannual Progress Report for October 1990 through March 1991, ORNL/TM-11859 (Oak Ridge National Laboratory, Oak Ridge, TN, 1991) pp. 313–318.
18. J. E. LANE, C. H. CARTER, JR. and R. F. DAVIS, *J. Amer. Ceram. Soc.* **71**(4) (1988) 281–295.
19. R. D. NIXON and R. F. DAVIS, *ibid.* **75**(7) (1992) 1786–1795.
20. A. W. ADAMSON, "Physical Chemistry of Surfaces," 4th ed. (John Wiley and Sons, New York, 1982).

Received 13 November 1998
and accepted 15 March 1999