J Mater Sci (2006) 41:4996–5000
DOI 10.1007/s10853-006-0110-z

LETTER

The effect of grain growth on hardness in hot-pressed silicon carbides

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Received: 20 June 2005 / Accepted: 27 January 2006 / Published online: 16 May 2006

Introduction

Silicon carbide (SiC) ceramics are, of course, hard and brittle. Hardness and brittleness are typically inter-related in ionically or covalently bonded ceramics. In applications where resistance to contact-induced cracking is desirable, it may be desirable to compromise hardness to lessen brittleness. A coarser-grained, dense SiC may enable decreased hardness with increased grain size (as represented by a Hall-Petch relation) and greater energy absorption through a more ductile-like (or ''quasi-plastic'') deformation mechanism. Such a ductile-like mechanism is orders of magnitude more effective in absorbing energy than fracture processes are [1]. Grain growth in SiC has been demonstrated [2–5]; however, those efforts involved conventional sintering methods (without pressure assistance) and some residual porosity was always present, and porosity undesirably facilitates cracking, crushing, and fracture processes in ceramics.

Interest existed in the present study to examine if the grain growth of hot-pressed (i.e., fully dense) SiCs could be promoted without significant density loss or introduction of porosity, and, if so, then what effect would that grain size increase have on hardness.

Procedure

Two commercially available hot-pressed SiCs were examined (Cercom, Vista, CA).[1] One grade is designated SiC-SC-1R and has a relatively fine nominal grain size (1.2 μm mean) and the other is SiC-N and has a coarser nominal grain size (~4.1 μm mean). The uncensored characteristic strength (ASTM C1161B-2002 [6]) and Weibull modulus were 763 MPa and 12 for the SiC-SC-1R, and 624 MPa and 15 for the SiC-N (15 specimens tested with each SiC grade). A myriad of mechanical properties for both SiC grades exists in the literature (e.g., [7–12]).

The SiCs were exposed to temperatures in excess of their hot-pressing temperature. One tile ($100 \times 100 \times 4$ mm) of each SiC grade was heated in a graphite resistance heated furnace under 1 atm of argon. The furnace was ramped up at 10 °C/min to a soak temperature of 2,250 °C or 2,500 °C and held there for 5 h. The furnace was then ramped down at 5 °C/min. A type C thermocouple was used to measure the temperature to 1,400 °C. Above 1400 °C a pyrometer was used to measure the temperature. A third high temperature trial was attempted; however, temperature control and measurement were lost when the pyrometer site tube became clogged by the growth of graphite whiskers, so the actual temperature and time at temperature were unknown, although the

Research sponsored by WFO sponsor US Army Tank-Automotive Research, Development and Engineering Center under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

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[1] The use of specific materials in this study in no way implies their official endorsement from the authors or their institutions or that they are necessarily the best material for its purposes.

temperature was believed to have exceeded 2,550 °C. Material characterization from this trial was included although the actual exposure conditions were unknown.

Specimens were prepared for scanning electron microscopy (SEM) and hardness testing. Small slices were sectioned from each of the six exposed tiles as well as from as-received tiles of each SiC grade. The cut surfaces were cast in metallographer's epoxy, polished to a quarter micron finish, and then chemically etched. Other slices were manually fractured to enable the examination of the microstructure on the fractured surfaces. Polished and fractured surfaces were examined with SEM, while energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) were also performed on the former.

Knoop microhardness testing was performed on all eight sets. A Knoop indenter was chosen over the Vickers indenter because it has been shown that better quality indents would result in SiC with this indenter geometry [9, 11] and, therefore, the hardness (H) results would have more legitimacy. To validate the calibration of the microhardness tester (Tukon 2100, Instron, Canton, MA), five 2000-gram (19.6 N) Knoop indents were generated in NIST standard reference material SRM 2830 [13]; their average H was found to be 13.8 GPa (< 1% difference from the certified average value of 13.92 GPa). Knoop hardness of the SiC test samples was measured at 500 (4.9 N), 1,000 (9.8 N), 2,000 (19.6 N), and 5,000 grams (49.1 N), 7 indents per load, using the practices in ASTM C1326 [14].

Results and discussion

Massive grain growth resulted in both SiC grades as a consequence of exposure to all three temperatures. The initial equiaxed grain structure in both grades changed to an acicular structure (shown in Figs. 1 and 2, respectively) and grain-size changes are summarized in Table 1. The nominal 1.2 μm mean grain size of the fine-grained equiaxed SiC (SiC-SC-1R) increased by ~5× along the *a*-axis and by over an order of magnitude or more along the *c*-axis, while the grain size of the coarser, equiaxed-grained SiC (SiC-N) increased by ~2× along the *a*-axis and by about an order of magnitude along the *c*-axis. Density decreased only by ~0.2-0.4% in the 2250 and 2,500 °C exposed SiC-N but by 6.5% for temperature >2550 °C, and ~1.0–1.6% and 10.1% for respective exposure temperatures for the SiC-SC-1R. SiC-N exposure at 2,250 °C and 2500 °C showed that high density (i.e., minimum porosity) could be sustained. The large decrease in density (or increase in porosity) for both SiCs when exposed to >2550 °C indicates the temperature was above the peritectic temperature for the Si-C binary phase diagram [15] and SiC having a relatively low vapor pressure above

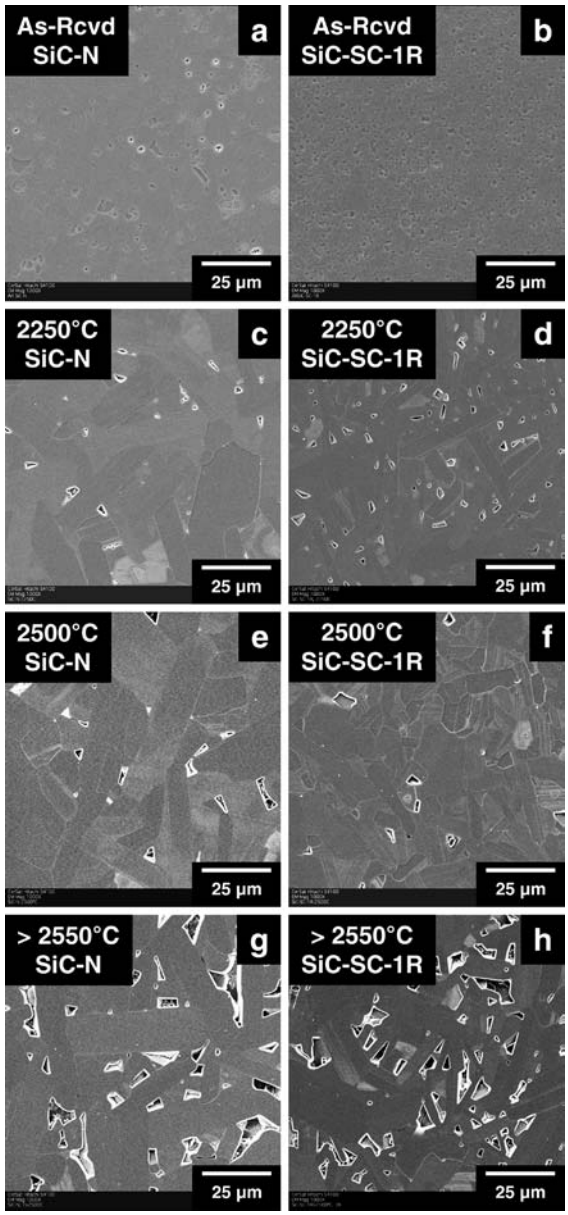

Fig. 1 Polished and chemically etched surfaces of SiC-N and SiC-SC-1R in the as-received state (**a**)–(**b**), after 2,250 °C for 5 h (**c**)–(**d**), after 2,500 °C for 5 h (**e**)–(**f**), and after >2,550 °C for 5 h (**g**)–(**h**). Massive grain growth occurred during exposure at all three temperatures. Porosity increases dramatically during the >2,550 °C exposure

2490 °C [16]. A substantial fraction of intergranular fracture occurred during fracture of both SiCs exposed to 2,250 °C and 2,500 °C; however, transgranular fracture totally dominated during fracture after they were exposed to >2550 °C (see Fig. 2).

The minor amount of oxygen (as identified by EDS in the multigrain junctions) in both as-received SiCs was gone after 2,250 °C and 2,500 °C exposures and a silicide having iron or aluminum or both remained in the multigrain junctions. X-ray diffraction showed that both SiCs were

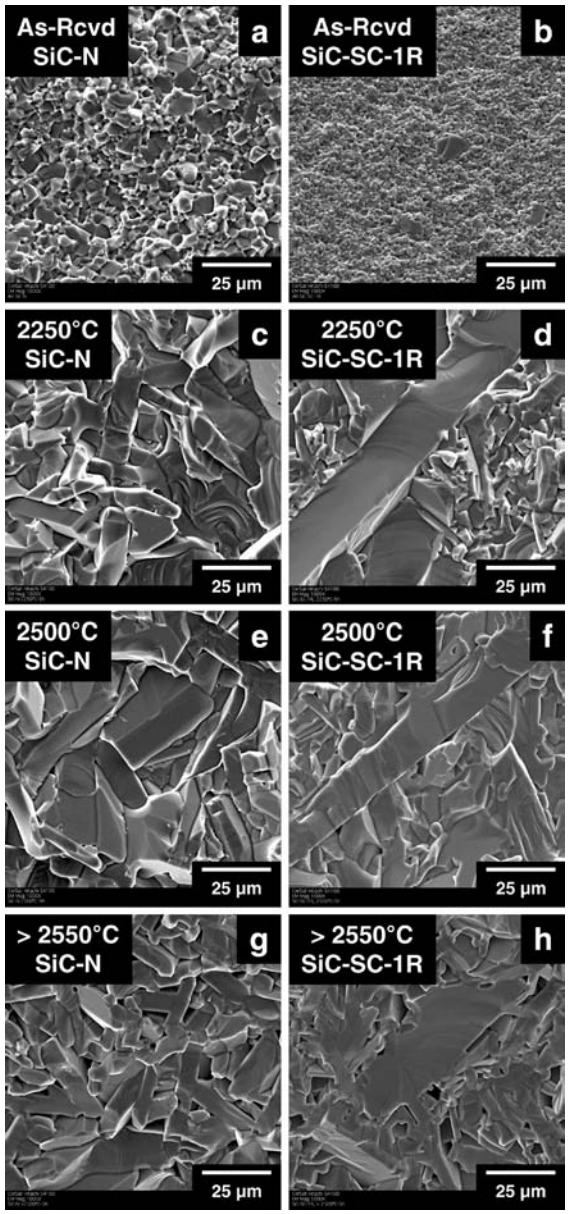

Fig. 2 Microstructures on fracture surfaces of SiC-N and SiC-SC-1R in the as-received state (**a**)–(**b**), after 2,250 °C for 5 h (**c**)–(**d**), after 2,500 °C for 5 h (**e**)–(**f**), and after >2,550 °C for 5 h (**g**)–(**h**). Porosity is evident in the >2,550 °C surfaces of both SiC grades

comprised of 6H and 15R polymorphs in their as-received state, and that the 4H, 6H, and 15R polymorphs were present after all high temperature exposures with 4H being the most dominant. The presence of those polymorphs is consistent with the observations of Sacks et al. [3] and Tanaka et al. [5]. The silicides that were present in the exposed SiCs had a low concentration that rendered them undetectable by the XRD.

The Knoop hardness of the test samples decreased as a consequence of the high temperature exposures (and associated increases in grain size and changes in microstructure), and these H changes are plotted in Fig. 3. Hardness decreased by ~25 and ~15% in the SiC-SC-1R and SiC-N, respectively, after they had been subjected to 2,250 °C or 2500 °C exposure. Those decreases are attributed to the large increases in grain size and greater ductile-like response in the SiCs as illustrated in the comparison of the as-received and 2500 °C SiC Knoop indents shown in Fig. 4 and the easier activation of shear-induced cleavage within the indented coarsened grains. Porosity increases may have been influential too in the H decreases but its role was likely minor as described below. Rice, Wu, and Borchelt [17] argued that H exhibits a minimum with increase in grain size because local cracking around the indent reaches a maximum effect when the indent and grain size are similar; in our case, the greater ease of local cracking is believed to be linked to the greater ease of initiating shear-induced cleavage with the larger SiC grains.

Table 1 Grain size (*a*-axis) and density changes

SiC Grade	Condition	Density (g/cm^3)	Grain size (μm)
SiC-SC-1R	As-received	3.190 (100%) ± 0.005	1.2 ± 0.6
	2,250 °C Treatment	3.157 (99.0%) ± 0.014	4.7 ± 1.6
	2,500 °C Treatment	3.140 (98.4%) ± 0.017	6.5 ± 1.6
	>2,500°C Treatment	2.867 (89.9%)	6.9 ± 4.1
SiC-N	As-received	3.195 (100%) ± 0.010	4.1 ± 1.6
	2,250 °C Treatment	3.182 (99.6%) ± 0.022	9.3 ± 3.6
	2,500 °C Treatment	3.189 (99.8%) ± 0.017	10.1 ± 3.1
	>2,500 °C Treatment	2.988 (93.5%)	8.5 ± 2.8

± Values are standard deviations. Percentages are densities relative to the as-received density

Hardness decreased by ~50 and 40%, respectively, after they had been subjected to a temperature in excess of 2,550 °C. These large decreases are attributed to the combination of the high volume fraction of introduced porosity and large grains that exists in the SiC grades as a consequence of the highest exposure temperature. Although the Knoop hardness decreased with increasing grain size in both SiC grades, the magnitude of the ISE was essentially consistent irrespective of the exposure temperature.

Porosity increases may have contributed to the measured decreases in H but probably not significantly in reference to the literature. Rice [18] provided a comprehensive overview of H dependence on porosity (P) for a variety of ceramics in which $H \sim e^{-bP}$ with the constant b ranging between ~2 and 7. If the values in Table 1 are used with this expression, then an observed ~15% decrease in H for the SiC-N and a 25% decrease in H for the SiC-SC-1R treated at 2,250 °C and 2,500 °C would result in $b \sim 40$ and $b \sim 20$–30, respectively (i.e., b-values that are 3–6x larger than reported for any other ceramic). If porosity increase is instead considered in this expression, then the

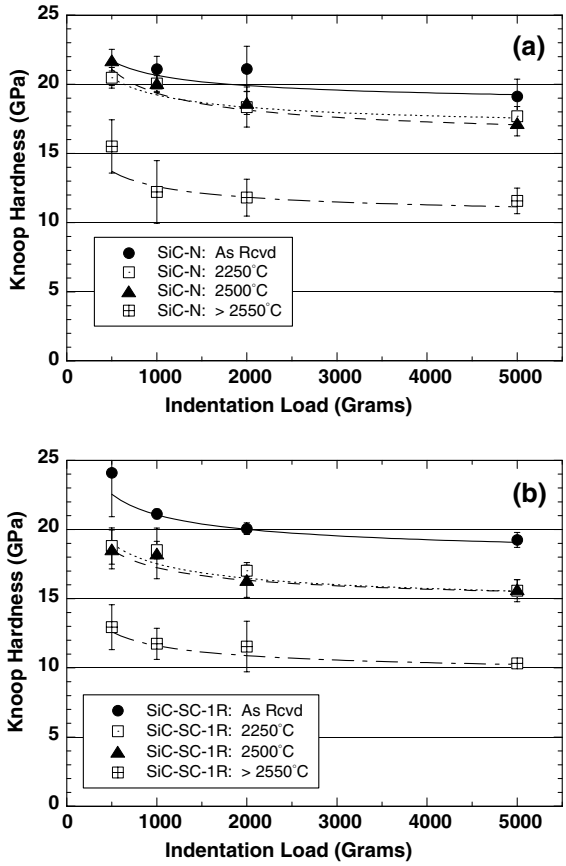

Fig. 3 Average Knoop hardness as a function of indentation load and exposure condition for (**a**) SiC-N and (**b**) SiC-SC-1R. Compared to the as-received state, the average hardness of SiC–N decreased by ~15% when exposed to 2,250 °C and 2500 °C whereas the decrease was ~25% for SiC-SC-1R at for those exposure temperatures. Average hardness decreased by ~40 and ~50% when SiC–N and SiC-SC-1R, respectively, were subjected to >2,550 °C. Indentation size effect is evident in all conditions. Shown bars represent standard deviations

measured increases for $b \sim 7$ would predict H decreases of ~2–3% for the SiC-N and 7–11% for the SiC-SC-1R (i.e., predicted H decreases much less than what was measured).

Summary

Two hot-pressed SiCs (~1 or ~4 μm nominal grain size in each) were heat treated in argon at 2,250 °C, 2,500 °C, and >2550 °C. Massive grain growth and an equiaxed-to-acicular grain structure change resulted in both SiCs at all three temperatures. The *c*-axis grain size of the fine-grained SiC increased by more than an order of magnitude while that for the coarser-grained SiC increased by about one order of magnitude. A substantial fraction of intergranular fracture occurred during fracture of both SiCs exposed to 2,250 °C and 2,500 °C; however, transgranular fracture totally dominated during fracture after they were exposed

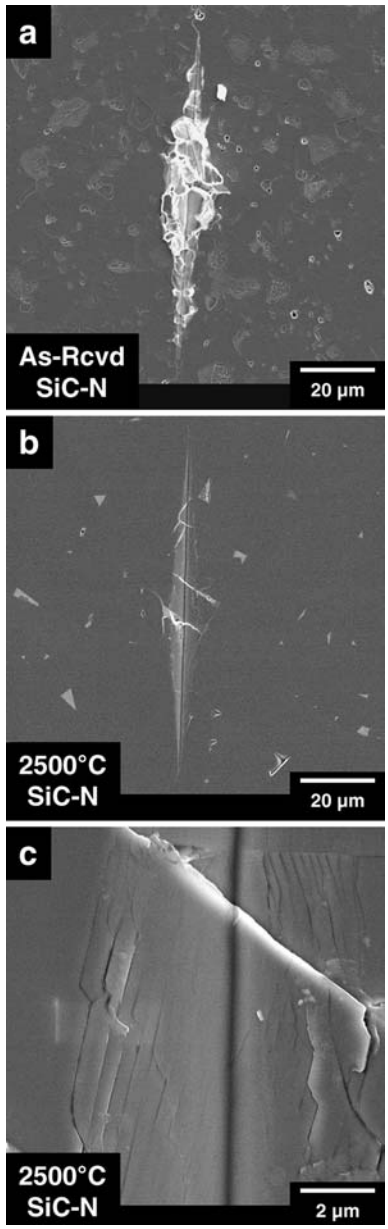

Fig. 4 1000 gram (9.8 N) Knoop indents in (**a**) as-received SiC-N and (**b**) SiC-N exposed to 2,500 °C. Greater amounts of fracture processes occurred with the indentation of the (finer grained) as-received stage than what occurred with the indentation of the exposed (coarser grained) SiC. Shear-induced cleavage (**c**) was prevalent in the indents in the coarsened SiCs

to >2,550 °C. The minor amount of oxygen in both as-received SiCs was gone after 2,250 °C and 2,500 °C exposures and a silicide having iron or aluminum or both remained. The coarser-grained SiC lost little density to 2,500 °C, whereas porosity started to form in the fine-grained SiC at 2,250 °C. Knoop hardness decreased by ~25 and ~15% in the fine- and coarse-grained SiC, respectively, after they had been subjected to 2,250 °C or 2,500 °C exposure, while it decreased by ~50% and 40%, respec-

tively, after they had been subjected to a temperature in excess of 2,550 °C.

Acknowledgments The authors wish to thank ORNL's O. Cavin and S. Waters for their assistance with the XRD and SEM, ORNL's J. Braden for the tile sectioning, ORNL's T. Geer for the metallography, and Cercom's R. Palicka for his helpful comments. Additionally, the authors thank ORNL's P. Becher, M. Ferber, B. Hickey, S. Nunn, USARL's J. Swab, and NIST's G. D. Quinn for their reviews or for their helpful comments and suggestions.

References

1. McColm IJ (1990) Ceramic hardness. Plenum Press, New York, NY
2. Kim Y-W, Mitomo M, Hirotsuru H (1995) J Am Ceramic Soc 78:3145
3. Sacks MD, Scheiffele GW, Staab GA (1996) J Am Ceramic Soc 79:1611
4. Jang C-W, Kim J, Kang S-JL (2002) J Am Ceramic Soc 85:1281
5. Tanaka H, Hirosaki N, Nishimura T (2003) J Am Ceramic Soc 86:2222
6. Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature, ASTM C1161-02c, Vol. 15.01, American Society for Testing and Materials, West Conshohocken, PA, 2003
7. Shih J (1998) Dynamic deformation of silicon carbide, PhD Thesis, University of California, San Diego
8. Wereszczak AA, Caspe RJ, Swab JJ, Kraft RH, Lin H-T. Effect of surface condition on hot-pressed SiC equibiaxial flexure strength, Presented at the 105th Annual Meeting and Exposition of the ACerS, Nashville, TN, 30 Apr. 2003
9. Swab JJ (2004) Hardness and damage associated with pointed indentations in armor ceramics, PhD Thesis, State University of New York at Stony Brook
10. Bakas MP, Greenhut VA, Niesz DE, Quinn GD, McCauley JW, Wereszczak AA, Swab JJ (2004) Int J Appl Ceramic Technol 1:211
11. Swab JJ (2004) Int J Appl Ceramic Technol 1:219
12. Holmquist TJ, Rajendran AM, Templeton DW, Bishnoi KD (1999) A ceramic armor material database, TARDEC Technical Report 13754, January 1999
13. NIST Standard Reference Material for Knoop Hardness of Ceramics, SRM 2830
14. Standard Test Method for Knoop Indentation Hardness of Advanced Ceramics, ASTM C1326, Vol. 15.01, American Society for Testing and Materials, West Conshohocken, PA, 2002
15. Massalski RW, Abbaschian GJ (1986) Binary phase diagrams. ASM, Metals Park, OH, p 882
16. Knippenberg WF (1963) Phillips Res Reports 1:167
17. Rice RW, Wu CC, Borchelt F (1994) J Am Ceramic Soc 77:2539
18. Rice RW (1998) Porosity of ceramics. Marcel Dekker, Inc., New York