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R-curve behavior of layered silicon carbide ceramics with surface fine microstructure

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By adjusting the $\alpha:\beta$ SiC phase ratios in the individual starting powders, a layered SiC consisting of surface and inner layers with distinctively different microstructures are produced by hot-pressing and subsequent annealing. The surface layer consisted of relatively fine, equiaxed α-SiC grains, designed for high strength, while the inner layer consisted of elongated α-SiC grains, designed for high toughness. By virtue of the common SiC phase and the same sintering aids (Al_2O_3-Y_2O_3), the interlayer interfaces are chemically compatible and strongly bonded. R-curve behavior of the layered SiC was measured and compared with the related monolithic materials. The layered SiC showed better damage tolerance than monolithic materials and stronger R-curve behavior than surface layer. This superior performance of layered SiC ceramics was attributed to the contribution of both high strength of the surface layer for small flaws and high toughness of the inner layer for larger flaws.

1. Introduction

The development of reliable ceramics for structural applications has been approached from at least two different directions. One common approach is to develop stronger materials through better processing and microstructural refinements [1–3]. These techniques typically improve strength to an approximately equal extent throughout the range of starting flaw sizes, but still leave a low toughness. Another approach is to activate an R-curve inducing toughening mechanism such as crack bridging [4–6]. It is well recognized that the toughness of silicon carbide ceramics can be profoundly increased by suitably tailoring the microstructure, e.g., by growing large elongated grains [7–10] and/or by manipulating the grain boundary phase [11], in order to enhance bridging and deflection. Although the increased toughness imparts the beneficial property of damage tolerance [6, 12], the toughness increase is generally limited to the long-crack region. These improvements are often achieved at the expense of strength. Recently, multilayer cramics have been fabricated to attack the above problems [13–17]. By placing a thin layer of high-strength material on the surface of a high-toughness body, the toughness and damage tolerance of the whole body have been maintained with minimal loss in bending strength [13–17].

In this study, α-SiC and α-SiC seeded β-SiC were used for the surface and inner layers, respectively. The strength with controlled flaw and R-curve behavior of the layered silicon carbide ceramics were investigated and compared with those of surface and inner monolithic materials.

2. Experimental procedure

Commercially available β-SiC (Ultrafine grade, Ibiden Co., Nagoya, Japan), α-SiC (A-1 grade, Showa Denco, Tokyo, Japan), Y_2O_3 (Fine grade, H. C. Starck, Berlin, Germany), and Al_2O_3 (grade AKP-30, Sumitomo Chemicals, Osaka, Japan) were used as starting powders. The α-SiC powder was used for fabricating surface layer and also added to act as seeds for grain growth and phase transformation in inner layer. To prepare a powder composition for surface layer, 83.8 wt% α-SiC, 9.2 wt% Y_2O_3 and 7.0 wt% Al_2O_3 were ball milled in ethanol with SiC grinding balls for 24 h. To prepare a powder composition for inner layer, 1 wt% α-SiC, 82.8 wt% β-SiC, 9.2 wt% Y_2O_3, and 7.0 wt% Al_2O_3

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were ball milled in ethanol with SiC grinding balls for 24 h. The milled slurry was dried and sieved through a 60 mesh screen. Individual batches were loaded alternatively in graphite mold for surface and inner layers of the three-layered materials. Approximately 2.1 g of the powder from the surface-layer-batch was placed in a cylindrical mold (30 mm diameter) and was pressed under a pressure of 5 MPa. After removing the die punch, 5.2 g of powder from the inner-layer-batch was laid down and pressed under the same pressure. Finally, 2.1 g of the powder from the surface-layer-batch was poured over the compact in the mold cavity and was pressed again under the same pressure. Two monolithic materials from separate batches also were prepared as references (designated as surface layer and inner layer). The three-layer compact and two monolithic forms were hot-pressed separately at 1800°C for 2 h under a pressure of 25 MPa in an argon atmosphere. The hot-pressed materials were subsequently annealed at 1900°C for 5 h under an atmospheric pressure of Ar to enhance grain growth.

Relative density was measured by the Archimedes method. The theoretical density of specimen, 3.375 g/cm^3, was calculated according to the rule of mixtures. X-ray diffraction (XRD) using Cu K_α radiation was performed on ground powders. The hot-pressed and annealed materials were cut, polished, and then etched by a plasma of CF_4 containing 7.8% O_2. The microstructure was observed by scanning electron microscopy (SEM). Specimens for R-curve tests were machined into $2.5 \times 3 \times 25$ mm bars with a surface layer thickness of $\sim$150 μm using an 800 grit diamond wheel. The tensile surface was polished up to 1 μm diamond paste to remove a residual stress due to machining and to produce a finish for optical microscopic observation. Prior to indentation, a thin film of moisture-free silicone oil was spread over the site of indentation to minimize environmental effects. Special care was taken to orient the radial cracks generated from the indentation parallel to the sides of the bar. Three Vickers indentations with load (P) ranging from 1.96 to 294 N were made, 3 mm apart, in the center of the prospective tensile surface of each test piece. A total of 40 indented bars for each of the layered SiC, monolithic surface and inner layers were directly fractured using four-point bending to establish the indentation load-strength relationship. For four-point bending, 10 mm inner and 20 mm outer spans were used. The strength data of specimens that fractured from the indented sites were used for the subsequent R-curve analysis as described by Krause [18].

3. Results and discussion

The characteristics of both the hot-pressed and the annealed materials are summarized in Table I. Relative densities of >99% were achieved by hot-pressing for surface layer, inner layer and layered SiC. However, prolonged annealing at 1900°C resulted in a decrease of the relative density, probably due to the formation of volatile components such as Al_2O, SiO and CO [19]. The microstructure of the hot-pressed and annealed materials are shown in Fig. 1. SiC grains were etched away by the plasma of CF_4, so that the microstructure was delineated by the grain boundary phase. The hot-pressed materials consisted of equiaxed SiC grains for both layers. After subsequent annealing at 1900°C, there was a distinct change in the microstructure between both layers. As shown in Fig. 1a, the layered boundary is sharp and well visible. No processing defects or microstructural inhomogeneities were found at the layered boundaries. As shown in Fig. 1b, the surface layer consisted of mostly fine, equiaxed grains of grain size 1.0–2.5 μm. It is very similar to the microstructure of as-hot-pressed materials except for small increment in grain size. The grain growth through solution-reprecipitation, as evidenced by core/rim structure in Fig. 1b, has been occurred keeping the morphology of SiC grains equiaxed during annealing. In contrast, the inner layer, as shown in Fig. 1c, showed a typical toughened microstructure consisting of elongated α-SiC grains of length 1.5–5.0 μm and diameter 0.5–1.5 μm, owing to the $\beta \rightarrow \alpha$ phase transformation of SiC during annealing [6, 10]. SEM micrographs of each layer shown in Fig. 1b and c included surface traces of radial cracks from a Vickers indentation. As shown in Fig. 1b, the crack in the surface layer is predominantly deflected by equiaxed grains. On the other hand, Fig. 1c for inner layer shows a tortuous crack path with distinct occurrence of crack-wake bridging and deflection by elongated SiC grains. Previous results showed that the elongated grain morphology is beneficial for toughening while the fine, equiaxed morphology for strengthening [20]. Thus, the surface layer with fine, equiaxed microstructure is expected to have higher strength than the inner layer. The toughness of surface layer and inner layer, measured by indentation with a load of 98 N, were 4.2 ± 0.3 and 6.7 ± 0.5 MPa $\cdot$ m$^{1/2}$, respectively. Difference in toughness values of two layers was due to the difference in grain size.

Fracture strength vs indentation load for surface layer, inner layer and layered SiC ceramics are shown in Fig. 2. The strengths from natural flaws of each materials were arbitrarily plotted at $P = 1$ N. The natural strength values for surface layer (511.6 ± 18.8 MPa) was higher than that for inner layer (347.9 ± 19.0 MPa), owing to the finer microstructure, and the value of layered SiC (410.6 ± 17.4 MPa) was between those of both monolithic layers. The indented strengths for layered SiC were slightly higher than those of inner layers in the range of indented load tested. The bending strength for

TABLE I Characteristics of hot-pressed and annealed materials

	Hot-pressed material			Annealed material		
		Crystalline phase			Crystalline phase	
Material	Relative density(%)	Major	Trace	Relative density(%)	Major	Trace
Surface layer	99.6	6H	YAG*	97.7	6H	4H, YAG
Inner layer	99.3	3C	YAG	97.6	4H, 6H	YAG
Layered body†	99.2	—	—	97.5	—	—

*$Y_3Al_5O_{12}$ (yttrium aluminium garnet).
†The thickness of the surface layer is $\sim$150 μm.

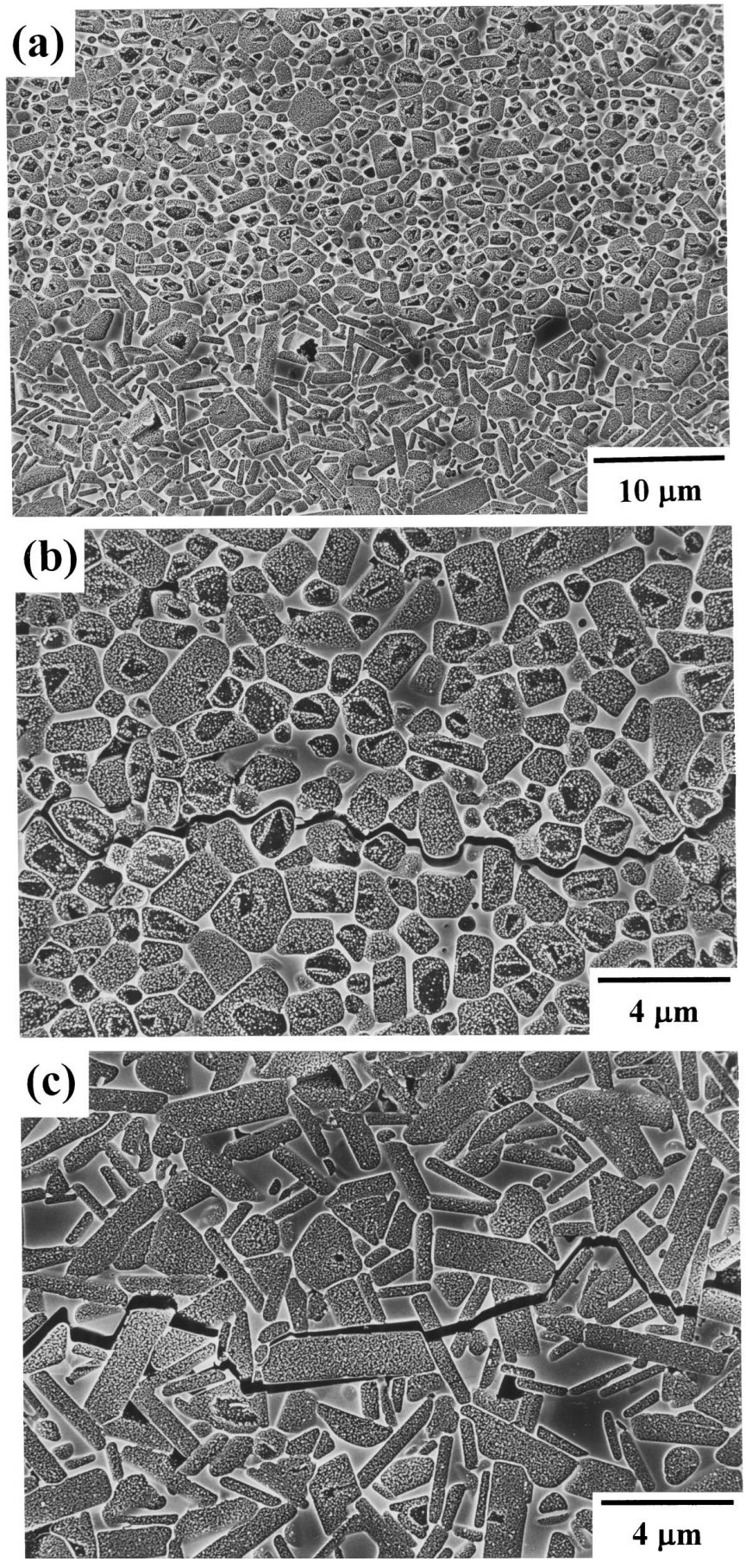

Figure 1 SEM micrographs of crack paths induced by a Vickers indentation in (a) layered SiC, (b) surface layer and (c) inner layer.

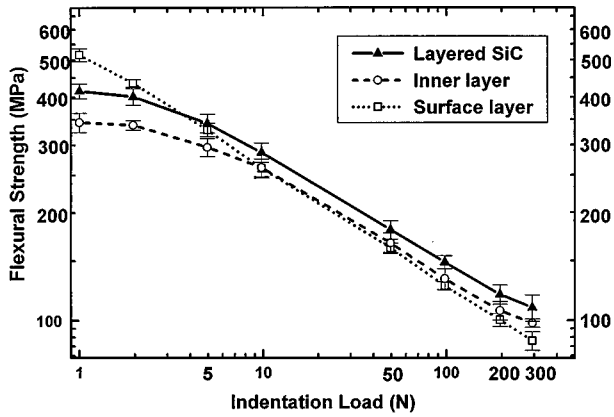

Figure 2 Plots of strength versus indentation load for layered SiC, surface layer and inner layer.

the surface layer declined from natural strength with increasing the indentation load, with a slope close to $-1/3$ in logarithmic coordinates. In contrast, the bending strength for the inner layer and layered SiC deviated significantly from the aforementioned $P^{-1/3}$ dependence: instead, showed a slower declination from the natural strength with increasing the indentation load, which is indicative of flaw-tolerant behavior. Initially, strength of surface layer was higher than those of inner layer and layered SiC. However, after 4.9 N indentation, surface layer loses about 35% of its initial strength, while layered SiC loses about 15% of its natural strength and becomes a stronger material than surface layer for an equivalent indentation load. This result indicates that the layered SiC possesses better damage tolerance than surface layer.

For the R-curve analysis, linear regression was used to obtain the best fit for the data from the both layers and layered SiC. It showed that slopes of surface layer, inner layer, and layered SiC were 0.302, 0.268, and 0.276, respectively. Because the slopes of all materials were less than 1/3, the rising R-curve behavior was evident for the materials [18]. R-curve behavior was estimated from the indentation-strength data (Fig. 2) by assuming that the fracture resistance was related to the crack length by a power-law relation, as suggested by Krause [18]. The estimated R-curves for three types of SiC are shown in Fig. 3. The layered SiC and inner layer have higher fracture resistance than surface layer in the measured crack size range between 10 and 900 μm as expected from the strength-indentation results (Fig. 2). Superior performance of layered SiC ceramics could be attributed to the contribution of both the high strength of the surface layer for small flaws and the high toughness of the inner layer for larger flaws. Further progress in layered SiC ceramics might be crucially dependent on the development of processing route for obtaining large difference in grain size, i.e., microstructure, between surface and inner layers.

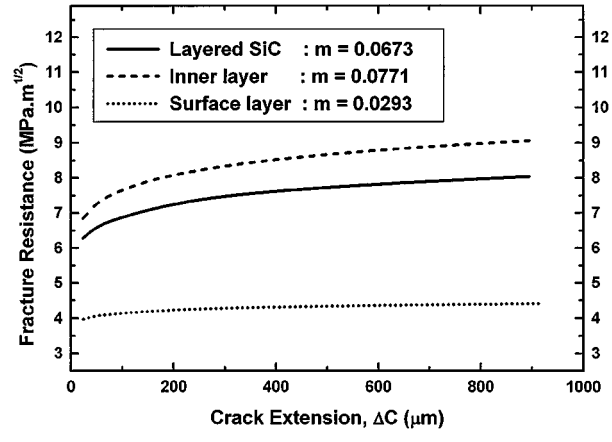

Figure 3 Estimated R-curves for layered SiC, surface layer, and inner layer.

4. Summary

Layered SiC ceramics, consisted of inner layer with an *in situ*-toughened microstructure and surface layer with an equiaxed microstructure, has been fabricated through hot-pressing and subsequent annealing route. R-curves for layered SiC ceramics were determined by the indentation-strength method and compared with the related monolithic materials. The layered SiC ceramics showed better flaw tolerance than monolithic materials and stronger R-curve behavior than the surface layer. Superior performance of layered SiC ceramics was attributed to the contribution of both high strength of the surface layer for small flaws and high toughness of the inner layer for larger flaws.

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References

1. F. F. LANGE, *J. Amer. Ceram. Soc.* **66** (1983) 396.
2. S. K. LEE, Y. C. KIM and C. H. KIM, *J. Mater. Sci.* **29** (1994) 5321.
3. G. D. ZHAN, M. MITOMO and Y.-W. KIM, *J. Amer. Ceram. Soc.* **82** (1999) 2924.
4. C. W. LI and J. YAMANIS, *Ceram. Eng. Sci. Proc.* **10** (1988) 632.
5. S. R. CHOI and J. A. SALEM, *J. Amer. Ceram. Soc.* **77** (1994) 1042.
6. N. P. PADTURE and B. R. LAWN, *ibid.* **77** (1994) 2518.
7. N. P. PADTURE, *ibid.* **77** (1994) 519.
8. Y.-W. KIM, M. MITOMO and H. HIROTSURU, *ibid.* **78** (1995) 3145.
9. C. J. GILBERT, J. J. CAO, L. C. DE JONGHE and R. O. RITCHIE, *ibid.* **80** (1997) 2253.
10. M. A. MULLA and V. D. KRSTIC, *Acta Metall. Mater.* **42** (1994) 303.
11. J. Y. KIM, Y. W. KIM, M. MITOMO, G. D. ZHAN and J. G. LEE, *J. Amer. Ceram. Soc.* **82** (1999) 441.
12. C. J. GILBERT, J. J. CAO, W. J. MOBERL CHAN, L. C. DE JONGHE and R. O. RITCHIE, *Acta Mater.* **44** (1996) 3199.
13. N. P. PADTURE, D. C. PENDER, S. WUTTIPHN and B. R. LAWN, *J. Amer. Ceram. Soc.* **78** (1995) 3160.
14. C. J. RUSSO, M. P. HARMER, H. M. CHAN and G. A. MILLER, *ibid.* **75** (1992) 3396.
15. P. SAJALIK, Z. LENCES and J. DUSZA, *J. Mater. Sci.* **31** (1996) 4837.

16. T. OHJI, Y. SHIGEGAKI, T. MIYAJIMA and S. KANZAKI, *J. Amer. Ceram. Soc.* **80** (1997) 991.
17. L. AN, H.-C. HA and H. M. CHAN, *ibid.* **81** (1998) 3321.
18. R. F. KRAUSE, *ibid.* **71** (1988) 338.
19. Y.-W. KIM, H. TANAKA, M. MITOMO and S. OTANI, *J. Ceram. Soc. Japan.* **103** (1995) 257.
20. Y.-W. KIM, M. MITOMO, H. EMOTO and J. G. LEE, *J. Amer. Ceram. Soc.* **81** (1998) 3136.

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