Letters

On relation between strength and microstructure of pyrolytic SiC

As silicon carbide (SiC) has good mechanical properties and high resistance to neutron irradiation damage at high temperature [1], the material has been utilized in nuclear applications. SiC prepared by pyrolysis is used as the coating layer of fuel particles for HTGR and GCFR, while tubes of self-bonded SiC have been prepared as fuel cladding for CO_2 Gas-Cooled Reactors [2, 3]. For these applications the mechanical properties of the material under severe conditions, i.e. out-of-pile at high temperature or in-pile, have been studied, and the failure stress and Young's modulus of the SiC layers removed from fuel particles were measured by several methods [4–6]. Gulden [7] studied the strength and fracture mode of pyrolytic SiC plates in the temperature range of 25 to 1400° C. The effect of neutron irradiation on both strength and Young's modulus of pyrolytic SiC was negligible up to a neutron flux of $2.8 \times 10^{21}\,n\,cm^{-2}$ at 1030° C [8]. Grain-boundary self-diffusion coefficients in hot-pressed SiC were studied by measuring stress and strain-rate in the temperature range of 1900 to 2200° C [9], and the effect of porosity on the Young's and shear moduli of hot-pressed SiC was also studied [10]. There are several reports concerning the strength of self-bonded SiC [2, 3, 11-13].

In spite of such work, however, the relation between the mechanical strength and microstructure has not been reported. In the present experiments, therefore, the relation between the strength and the microstructures of pyrolytic SiC produced by isothermal annealing, was studied.

SiC was deposited on a graphite substrate (150 mm × 200 mm × 10 mm) by pyrolysis at 1200° C of $SiCl_4$ and hydrocarbon carried with H_2. By X-ray diffraction, the material was found to be composed mainly of β-SiC with a small amount of α-SiC. Free Si could not be detected, but the atomic fraction, C/Si, was obtained by chemical analysis as 0.99.

For the strength measurements, SiC chips (7 mm × 1.2 mm × 0.2 mm) were obtained by cutting off the material from the substrate and polishing on a rotating diamond wheel to uniform thickness. Dimensions of the samples were measured both by a micrometer and a cathetometer. The samples were annealed in a graphite resistance furnace, under Ar gas flow, for times up to 1256h at 1600° C. The variations of the crystallite size and density of the sample produced by annealing are shown in Table I.

TABLE I Properties of the pyrolytic SiC

Annealing time (h)	Number of samples	Crystallite size (Å)	Density (mean) ($g\,cm^{-3}$)
As-deposited	3	200	3.19
50	5	380	3.18
264	3	470	3.18
696	3	490	3.17
1246	4	500	3.17

Measurement of the strength was made by the three-point bending method at room temperature, and fracture strength (σ_b) and Young's modulus (E) were calculated by the following equations;

$$\sigma_b = \frac{3Wl}{2bh^2} \tag{1}$$

$$E = \frac{Wl^3}{48Iv_{\max}}, \tag{2}$$

where W is the fracture load, l the span length of the knife-edges for bending, b and h the width and thickness of the sample, respectively, $v_{\max}$

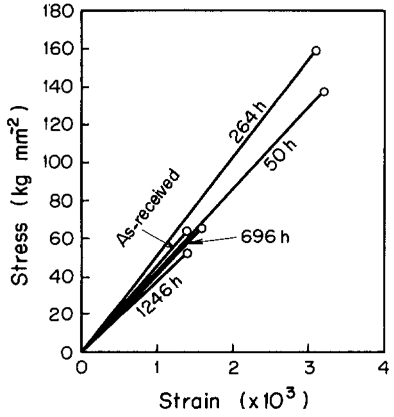

Figure 1 Typical stress–strain curves of SiC sample.

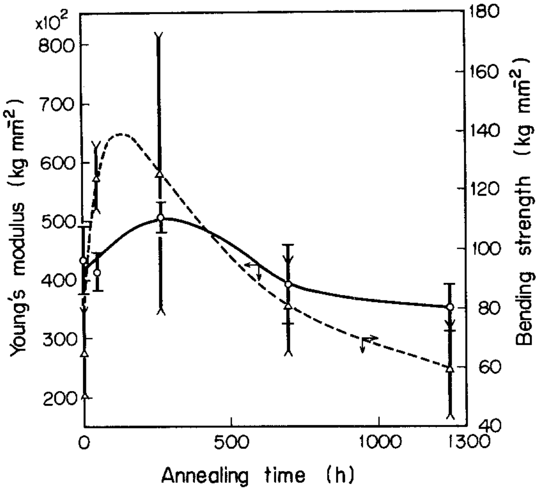

Figure 2 Variations of bending strength and Young's modulus of SiC sample.

the maximum displacement of the sample to fracture, and I the moment of inertia of the area. After the test, the fractured surface of the sample was observed by scanning electron microscopy, and the surface, polished and etched by a two stage method [14], was also observed with a Nomarsky lens.

Typical stress–strain curves obtained are shown in Fig. 1 which shows negligible plasticity in any sample. The maximum strain is about 0.32% in the samples annealed for 50 and 264h, and about 0.15% in the others. The bending strength and Young's modulus are shown in Fig. 2 as a function of the annealing time. It is seen in this figure that both the strength and Young's modulus increase rapidly with annealing time to maximum values at 264h, which are followed by gradual decrease up to 1246h. The value of the maximum Young's

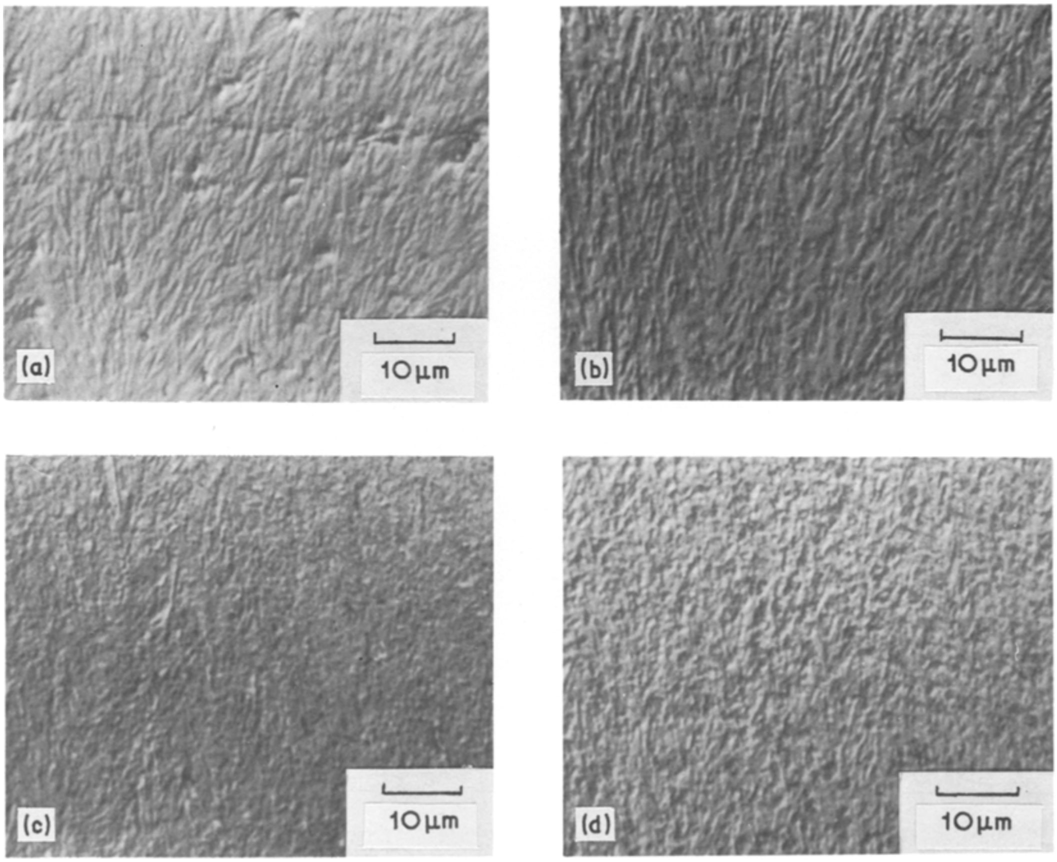

Figure 3 Microstructure of SiC sample annealed at 1600° C. (a) As-deposited; (b) annealed for 50 h; (c) annealed for 264 h; (d) annealed for 1264 h.

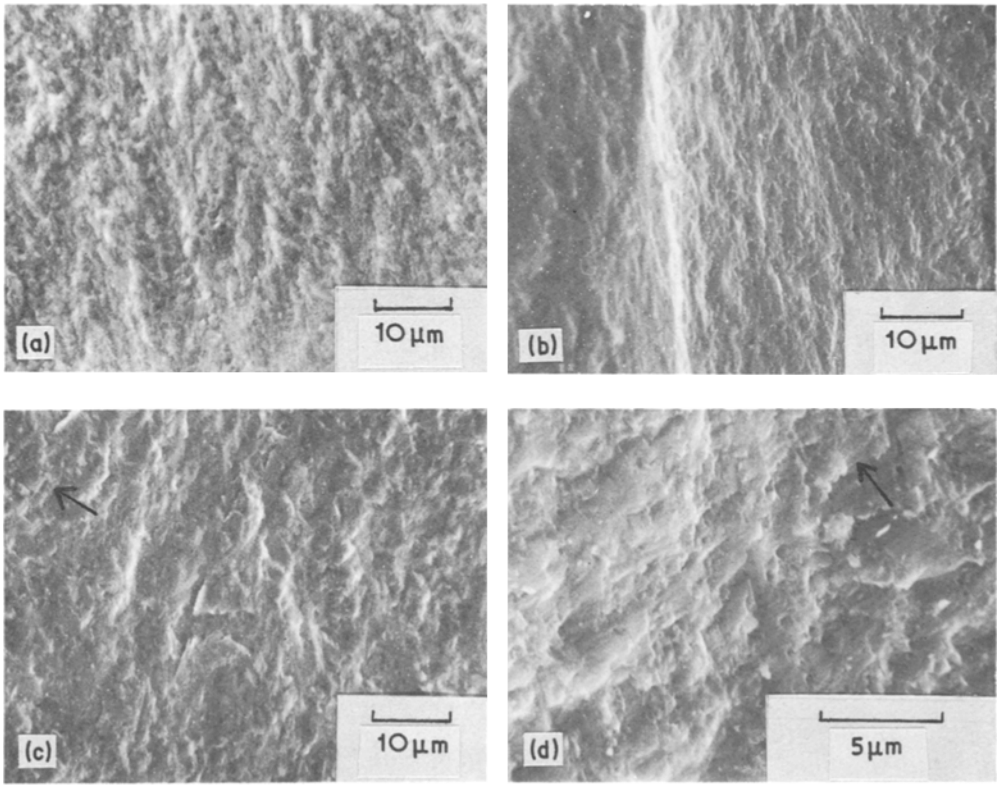

Figure 4 Fractographs of SiC sample annealed at 1600° C; arrows indicate fine cleavage steps. (a) As-deposited; (b) annealed for 50 h; (c) annealed for 264 h; (d) annealed for 1264 h.

modulus is 1.2 times larger than that of the initial value while the value of the maximum bending strength is about 2 times larger. It has not been previously reported that the room temperature strength of pyrolytic SiC changes with annealing time, although the bending strength and Young's modulus of pyrolytic SiC was reported to increase with temperature beyond about 1000°C [7].

The microstructures and fracture surfaces of the various samples are shown in Figs. 3 and 4, respectively. As seen in Fig. 3, the as-deposited SiC shows a fine dendritic structure along the deposition direction. After 50h annealing, however, the structure is partially recrystallized to form new large crystallites and at 264h the dendritic structure becomes faint, although it does not completely disappear. With increase in annealing time beyond 264h, no further change in the structure was observed. The nature of the dendritic structure is explained in detail by Walker [8]. It is noticeable that appearance of the fracture surfaces shown in Fig. 4 is similar to the microstructures in Fig. 3. In the fracture surfaces after 264 and 1246h anneals, however, very fine cleavage steps are also observed, as shown by arrows in the figure. These seem to indicate that fracture occurs intergranularly in the as-deposited and 50h annealed SiC, but that with increase of the annealing time, transgranular fracture also occurs, although the intergranular remains the dominant mode. It is reported [7] that in fine-crystallite low-density SiC ($< 1\,\mu$m in crystallite size), transgranular fracture takes place at room temperature, while intergranular fracture occurs at 1400°C, while the present results indicate that intergranular fracture can occur at room temperature.

The result that the strength and Young's modulus become maximum, and the dendritic structure become faint, after 264h annealing, indicate evidently that a change of the microstructure influences the strength and Young's modulus. Although it is reported [15] that annealing can produce transformation from β to α type, the increase of α-SiC is hardly observed at 1246h by X-ray diffraction analysis. It is thus considered that growth of new crystallites in the dendritic structure may prevent propagation of cracks along the dendritic structure and cause an increase of the strength. Efforts were made to see why the strength subsequently decreases with longer anneals. Although an increase of crystallite size has been related to a decrease in the strength of SiC [2, 8], it is not possible to explain the present results on this basis, as the mean crystallite size in Table I increases up to 264h and thereafter the size is nearly constant up to 1246h. The density of the sample decreases gradually with annealing time (Table I), probably due to the vapourization of excess Si. The decrease of the strength and Young's modulus may be caused by porosity created by this vapourization [16]. However, further experiments are necessary to test this concept.

Acknowledgements

The authors express their thanks to Dr S. Nomura, Head of the Division of Nuclear Fuel Research of JAERI, for his interest and encouragement. Thanks are also due to Mr F. Kobayashi and Mr M. Eto, for their aid in the present experiments.

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Received 9 December 1975
and accepted 7 January 1976

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The thermal conductivity of stabilized zirconia

Kingery *et al.* and also Mirkovitch [1, 2] have shown that the thermal conductivity of calcia stabilized zirconia (CSZ) is low and nearly temperature independent, as shown in Fig. 1. This behaviour is not typical of crystalline refractory oxides and resembles the conductivity of a glass [3]. Data for thorium dioxide, which has the same fluorite crystal structure as CSZ is also included in Fig. 1, for purposes of comparison.

CSZ is a defect fluorite material with random substitution of Zr^{4+} ions by Ca^{2+} ions on the cation sub-lattice; charge compensation is effected by an equivalent number of oxygen vacancies on the anion sub-lattice. Both the cation random solid solution and the anion vacancies probably contribute to the phonon scattering process. However, it is suggested that the anion vacancies are more efficient scatterers than the cation solid solution and only the former need be considered in accounting for the thermal conductivity of CSZ.

There is some justification for this assumption in the light of recent work by Schwarz and Walker [4] who observed phonon scattering by lattice vacancies in KCl doped with as little as 200 to 300 ppm of divalent chlorides. Further insight into the