

## Enhancement of strength of SiC by heat-treatment in air

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An 800 nm-SiC powder (75 vol%) was mixed with a 30 nm-SiC powder (25 vol%) in a 0.3 mol/l Y(NO<sub>3</sub>)<sub>3</sub> solution containing an Al<sub>2</sub>O<sub>3</sub> powder of median size 200 nm at pH 5 to distribute homogeneously the sintering additives (Al<sub>2</sub>O<sub>3</sub> + Y<sup>3+</sup> ion) around the SiC particles. Polyacrylic acid of 1.0 mg/m<sup>2</sup>-SiC surface was added as a dispersant. This suspension was consolidated by casting in a gypsum mold. The green compacts of 43% theoretical density were hot-pressed to a relative density 98.1 ± 2.1% at 1950 °C in an Ar atmosphere. The strength of the dense SiC was in the range from 560 to 1080 MPa (average strength 810 MPa, Weibull modulus 5.9). The as-hot-pressed SiC was heat-treated in air for 24 h at 1100° and 1300 °C. The heat-treatment at 1100 °C improved the strength in the low fracture probability range (< 40%) and narrowed the strength range (700-1250 MPa, average strength 820 MPa). On the other hand, the heat-treatment at 1300 °C shifted greatly the strengths in all the fracture probability range to higher values (750-1180 MPa, average strength 960 MPa). The Weibull modulus was also increased to 8.3. The above results may be related to the decrease of size and shape factor of fracture origins near the SiC surfaces by the formation of SiO<sub>2</sub>. A compressive stress may be also produced on the surface region of the dense SiC which contributes to the increased strength.

**Key words:** Silicon carbide, Sintering additives, Hot-pressing, Oxidation, Fracture strength, Weibull modulus.

### Introduction

Crack healing is an attractive method to repair the damage formed in a brittle ceramic material, because the strength ( $\sigma$ ) of ceramics is dominated by the flaw size ( $a$ ) as predicted by linear fracture mechanics ( $\sigma = K_{IC}/Y\sqrt{a}$ ,  $K_{IC}$ : fracture toughness,  $Y$ : shape factor of flaw). Effective healing has been reported in SiC composites [1-3]. The dispersed SiC particles are oxidized to form SiO<sub>2</sub> layers (SiC + 2O<sub>2</sub> → SiO<sub>2</sub> + CO<sub>2</sub>) on the surface of the composite. This phase change is accompanied by an increase of volume of 118% when 1 mol of SiC (density 3.21 g/cm<sup>3</sup>) is oxidized to 1 mol of amorphous SiO<sub>2</sub> (density 2.2 g/cm<sup>3</sup>) ( $(V_{SiO_2} - V_{SiC})/V_{SiC} = (27.31 \text{ cm}^3 - 12.49 \text{ cm}^3)/12.49 \text{ cm}^3 = 1.18$ ). The resultant compressive stress is induced in the damage zone at a low temperature because of the lower coefficient of thermal expansion for SiO<sub>2</sub> than for SiC. Furthermore, the amorphous SiO<sub>2</sub> formed repairs the damage through the sintering process by viscous deformation. The above two mechanisms cause a decrease of the flaw size and prevent crack propagation at a high temperature. Table 1 summarizes the healing effect of SiC or SiC-containing composites on the mechanical strength [4-9]. It is possible to increase the strength two times of an as-prepared specimen by controlling the healing

conditions. As seen in Table 1, a high strength above 1000 MPa can be achieved by oxidation at 1100°-1300 °C in air. When the strength of the as-prepared specimen becomes higher, the strength after the healing increases more. This paper reports the influence of oxidation in air at 1100°-1300 °C on the Weibull modulus of high strength SiC. This analysis clarifies the relationship between the strengths before and after the oxidation under the same oxidation conditions. In our previous papers [2, 10-15], a liquid phase sintering based on a dissolution-precipitation mechanism was applied to a submicrometre-sized SiC powder with Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> additives to make high strength SiC with 640 MPa by the four-point flexural method. The addition of 30 nm-SiC (25 vol%) to 800 nm-SiC (75 vol%) decreased the grain size and flaw size of the hot-pressed SiC and improved the flexural strength and fracture toughness. The dense SiC with a 2.0 μm average grain size, prepared from the mixed powder system, provided an average four-point flexural strength of 810 MPa, a fracture toughness of 6.0 MPam<sup>1/2</sup> and a Vickers hardness of 18-20 GPa. In this paper, the high strength SiC described above was oxidized at 1100° and 1300 °C for 24 h in air to further increase the strength. The Weibull modulus, fracture toughness and microstructures after the oxidation were compared with those before the oxidation.

### Experimental Procedure

#### Raw materials and forming

High strength SiC compacts [10-14] were prepared from

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**Table 1.** Healing conditions and mechanical strengths of SiC-containing composites

| Starting powder                | Additives  | Method   | Healing condition<br>(in air)    | Bending strength (MPa) |                 | Ref.  |   |
|--------------------------------|--|--|----------------------------------|------------------------|-----------------|-------|---|
|                                |  |  |                                  | Before oxidation       | After oxidation |       |   |
| Al <sub>2</sub> O <sub>3</sub> | SiC (15 wt.%)<br>-Y <sub>2</sub> O <sub>3</sub> (2 wt.%)   | HP<br>1600 °C, 1 h<br>35 MPa, N <sub>2</sub>   | 1300 °C<br>1h                    | 590*                   | 900*            | 4     |   |
| Al <sub>2</sub> O <sub>3</sub> | SiC whisker<br>(20 wt.%)   | HP<br>1850 °C, 1 h<br>40 MPa, Ar               | 1300 °C<br>1h                    | 1000*                  | 1150*           | 5     |   |
| Si <sub>3</sub> N <sub>4</sub> | SiC (20 wt.%)<br>-Y <sub>2</sub> O <sub>3</sub> (8 wt.%)   | HP<br>1850 °C, 1 h<br>35 MPa, N <sub>2</sub>   | 1300 °C<br>1h                    | 550*                   | 630*            | 6     |   |
| Mullite                        | SiC (20 vol%)  | HP<br>1650 °C, 4 h<br>35 MPa, N <sub>2</sub>   | 1300 °C<br>1h                    | 340**                  | 520*            | 7     |   |
| α-SiC                          | AlN (5.28 vol%)<br>-Y <sub>2</sub> O <sub>3</sub> (4.72 vol%)  | HP<br>1960 °C, 0.5 h<br>10 MPa, N <sub>2</sub> | 1200 °C<br>12 minutes            | 436 ± 136**            | 1047 ± 202**    | 8     |   |
| α-SiC<br>β-SiC                 | Al <sub>2</sub> O <sub>3</sub> (7.05 wt.%)<br>-Y <sub>2</sub> O <sub>3</sub> (4.08 wt.%)<br>-CaO (1.36 wt.%) | HP<br>1810 °C, 1 h +<br>25 MPa, N <sub>2</sub> | Annealed<br>1910 °C, 4h<br>25MPa | 1100 °C<br>1h          | 721*            | 1034* | 9 |

GPS: Gas pressutr sintering, HP: Hot-pressing, \*3-point bending, \*\*4-point bending

the mixed SiC powders of median size 0.8 μm (SiC: 98.90 mass%, SiO<sub>2</sub>: 0.66 mass%, C: 0.37 mass%, Al: 0.004 mass%, Fe: 0.013 mass%, 13.4 m<sup>2</sup>/g, Yakushima Electric Industry Co. Ltd., Japan, named as SiC A) and median size 30 nm (SiC: 95.26 mass%, SiO<sub>2</sub>: 0.97 mass%, C: 3.76 mass%, 50.4 m<sup>2</sup>/g, Sumitomo Osaka Cement Co. Ltd., Japan, named as SiC B). A high purity Al<sub>2</sub>O<sub>3</sub> powder of median size 0.2 μm (Al<sub>2</sub>O<sub>3</sub> > 99.99 mass%, Sumitomo Chemical Industry Co. Ltd., Japan) and Y(NO<sub>3</sub>)<sub>3</sub> (Purity: 99.9%, Wako Pure Chemical Industries Ltd., Japan) were used as sintering additives. Polyacrylic acid (PAA, average molecular weight 10000, Dai-ichi Kogyo Seiyaku Co. Ltd., Japan) was used as a dispersant of SiC.

SiC A and B powders were mixed in the volume ratio of 75 : 25 vol% and dispersed at 30 vol% solid in a 0.3 M-Y(NO<sub>3</sub>)<sub>3</sub> aqueous solution at pH 5.0. PAA of 1.0 mg/m<sup>2</sup>-SiC surface was added to the SiC suspension. The Al<sub>2</sub>O<sub>3</sub> powder was added to the SiC suspension at a volume ratio SiC/Al<sub>2</sub>O<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub> = 1/0.012/0.012. The suspension was consolidated into a rectangular shape with sizes of 17 mm height, 25 mm width and 38 mm length by casting in a gypsum mold at room temperature. The consolidated green compacts were hot-pressed under a pressure of 39 MPa at 1950 °C for 2 h in an Ar flow (FVH-5, Fuji Dempa Kogyo Co. Ltd., Japan). The heating and cooling rates were controlled to be 10 K·minute<sup>-1</sup>. The density of the hot-pressed compact was measured by the Archimedes method using kerosene. The measured bulk density of the hot-pressed SiC was compared with the theoretical density of 3.23 g/cm<sup>3</sup>, which was calculated from the true densities of 3.23 g/cm<sup>3</sup> for SiC A, 3.1 g/cm<sup>3</sup> for SiC B, 3.99 g/cm<sup>3</sup> for Al<sub>2</sub>O<sub>3</sub> and 4.95 g/cm<sup>3</sup> for Y<sub>2</sub>O<sub>3</sub>. The hot-pressed SiC was cut into specimens with sizes of 3 mm height, 4 mm width and 38 mm length. The specimens were polished with

SiC papers Nos. 240, 600, 1200 and 2000 and diamond paste of 6 and 1 μm. The polished SiC were oxidized at 1100° and 1300 °C for 24 h in air.

### Mechanical properties

The flexural strengths of hot-pressed and oxidized SiC were measured at room temperature by the four-point flexural method over spans of 30 mm (lower span) and 10 mm (upper span) at a crosshead speed of 0.5 mm/minute. The fracture toughness was evaluated by the single-edge V-notch beam (SEVNB) method. A thin diamond blade 1 mm thick, where the tip of the V-notch had a curvature radius of 20 μm, was used to introduce a V-notch of a/W = 0.1–0.6 (a: notch length, W: width of the beam). The strengths of the notched specimens were measured by three-point loading over a span of 30 mm at a crosshead speed of 0.5 mm/minute. Equation (1) provides the fracture toughness for the SEVNB method and equation (2) indicates the shape factor (Y) of the crack at S/W = 7.5. S, P, and B in Eqs. (1) and (2) are the span width, applied load and thickness of beam, respectively.

$$K_{IC} = \frac{3PS}{2BW^2} Y \sqrt{a} \quad (1)$$

$$Y = 1.964 - 2.837\lambda + 13.711\lambda^2 - 23.250\lambda^3 + 24.129\lambda^4 \quad \lambda = \frac{a}{W} \quad (2)$$

The concentrations of Si, C and O of the oxidized SiC were measured by an electron probe X-ray microanalyzer (EPMA, JXA-8600S/M, Japan Electron Optics Lab. Co. Ltd., Japan). The phases formed on the surface of oxidized SiC were identified by X-ray diffraction (RINT 2200PCH/KG, Rigaku Co., Japan). The microstructures of SiC were observed by a scanning electron microscope (SM300,

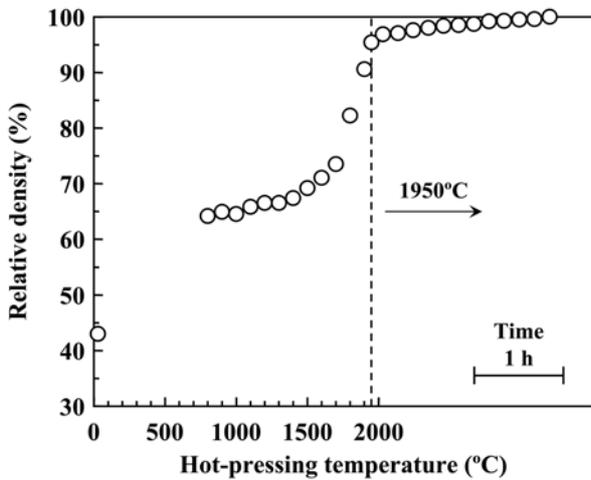


Fig. 1. Densification curve of SiC compacts during the hot-pressing at 1950 °C.

Topcon Technologies Inc., Japan). The Young's modulus (E) was measured from the slope of the stress-strain curve. The fracture energy ( $\gamma$ ) was calculated from the fracture toughness and Young's modulus ( $\gamma = K_{IC}^2/2E$ ).

### Results and Discussion

#### Phases and microstructures of hot-pressed SiC

Fig. 1 shows the relative density of the SiC during hot-pressing. The green density (43.0%) of the SiC with  $Al_2O_3$ - $Y_2O_3$  additives increased to 99.7-100% of the theoretical density after the hot-pressing at 1950 °C for 2 h. The increased density at a low temperature below 1000 °C is due to the shrinking of the green compacts by the applied pressure. The eutectic temperature of the sintering additives at a given composition of the  $SiO_2$ - $Al_2O_3$ - $Y_2O_3$  system is about 1400 °C [16]. The densification of SiC compacts started above 1500 °C by liquid phase sintering. Fig. 2 shows the X-ray diffraction patterns of SiC compacts hot-pressed at 1950 °C. The as-hot-pressed SiC consisted of 6H-, 33R- and 3C-type SiC. The 6H- and 33R-SiC phases were contained in the starting 800 nm SiC. The 3C-SiC was included in the starting 30 nm SiC. No crystalline  $Al_2O_3$  or  $Y_2O_3$  was identified in the diffraction patterns. After the oxidation in air at 1100° (d) and 1300 °C (e), cristobalite was formed on the surfaces of SiC. The surface structures of oxidized SiC are shown in Fig. 3. After the oxidation at 1100° and 1300 °C,  $SiO_2$  layers 0.4 and 1.4  $\mu m$  thick were formed on the SiC surfaces, respectively.

Fig. 4 shows the elemental distribution of Si, C and O atoms of SiC oxidized at 1300 °C as a function of distance from the surface. The relatively high concentration of O atoms at the surface represents the formation of  $SiO_2$ . The low concentration of O atoms inside the polished SiC reflects the existence of oxide additives ( $Al_2O_3$ - $Y_2O_3$  sintering additives). Higher concentrations of Si and C were measured inside of the SiC compact.

In our previous paper [3], the oxidation rate of sintered SiC fibers with a stoichiometric SiC composition was

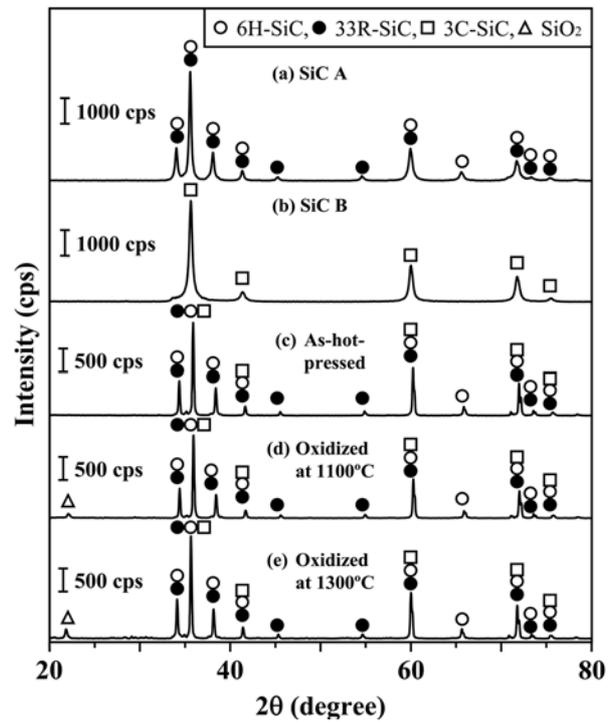


Fig. 2. X-ray diffraction patterns of starting SiC powder A (a), starting SiC B powder (b), as-hot-pressed SiC (c), SiC oxidized at 1100 °C (d) and SiC oxidized at 1300 °C (e).

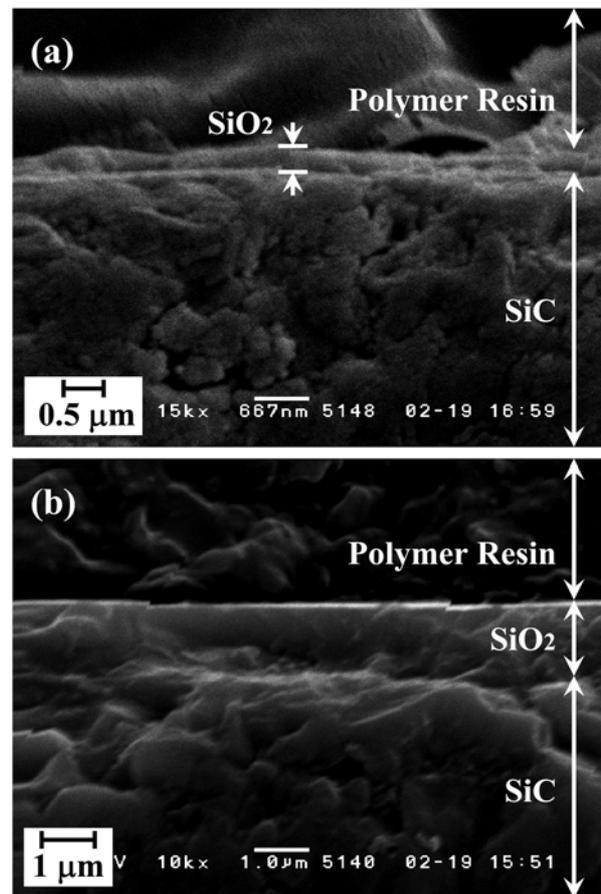


Fig. 3. Cross sections of SiC compacts after the oxidation at 1100 °C (a) and 1300 °C (b).

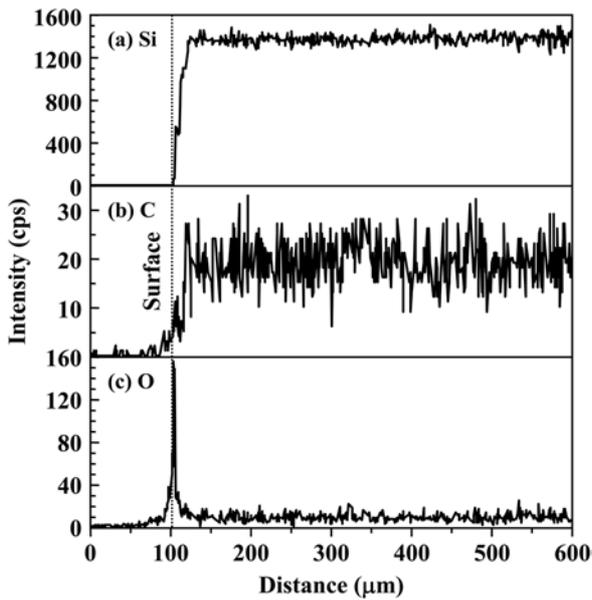


Fig. 4. Elemental distribution of (a) Si, (b) C and (c) O atoms of SiC oxidized at 1300 °C as a function of distance from the surface.

measured in air at 1000°-1200 °C. The oxidation was controlled by a diffusion process of gases through the dense SiO<sub>2</sub> layer formed on the SiC surface. The activation energy for the oxidation of the SiC fibers was 299 kJ/mol and close to that for the diffusion of oxygen atoms in silica glass. The SiO<sub>2</sub> layer formed after the oxidation at 1100 °C for 24 h in this paper was slightly thicker than the SiO<sub>2</sub> layer formed on the SiC fibers (0.2-0.3 μm).

#### Mechanical properties of SiC compacts

Fig. 5 summarizes the mechanical properties of SiC compacts before and after the oxidation. The strength of an as-hot-pressed SiC compact (average, 807 MPa) increased to 959 MPa by oxidation at 1300 °C. The maximum strength was significantly higher and 1080, 1250 and 1180 MPa for the as-hot-pressed SiC, SiC oxidized at 1100 °C and 1300 °C, respectively. On the other hand, the fracture toughness and fracture energy decreased after the oxidation. The Young's modulus increased slightly after the oxidation at 1300 °C. Since the cracks propagated through grain boundaries, the decrease of fracture energy reflects the weakened chemical bond at grain boundaries. The thickness of the SiO<sub>2</sub> layer was very thin as compared with the size of the hot-pressed SiC specimen but the influence on the mechanical properties was significant. This result may be related to the preferred oxidation through grain boundaries. More investigation is needed to understand the above oxidation effect.

Fig. 6 shows the fracture probability for the SiC before and after the oxidation at 1100 °C. The as-hot-pressed SiC specimen provided a Weibull modulus of 5.8 and an average strength of 812 MPa. Most of the observed flaws in the as-hot-pressed SiC were coarsened SiC grains and in the size range from 20 to 70 μm [13]. After the oxidation, the strength for lower fracture probability (<40%)

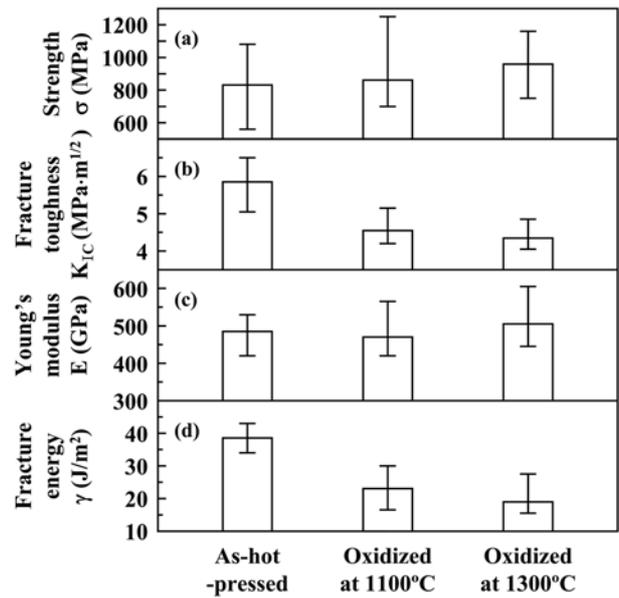


Fig. 5. Mechanical properties of SiC compacts before and after the oxidation at 1100 °C and 1300 °C.

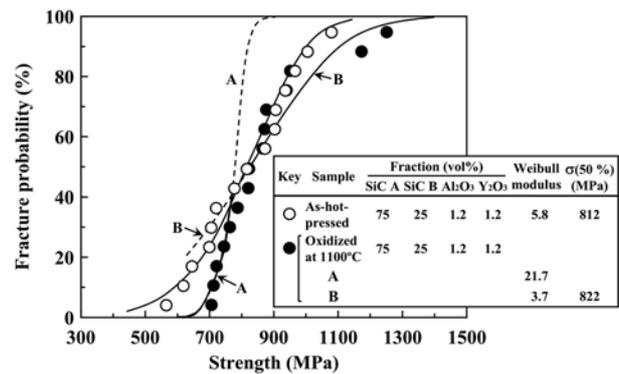


Fig. 6. Fracture probability for the SiC compacts before and after the oxidation at 1100 °C.

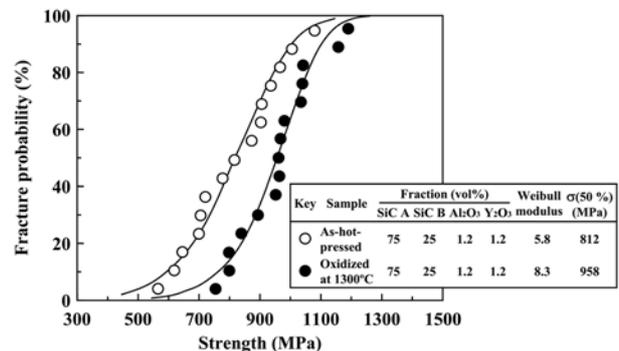


Fig. 7. Fracture probability for the SiC compacts before and after the oxidation at 1300 °C.

was shifted to a higher value. However, no change of the strength was measured for the intermediate fracture probability (40% < F < 80%). In the higher fracture probability range (F > 90%) the strength increased again and reached 1170-1250 MPa. This observation is discussed latter. Fig. 7 shows the influence of oxidation

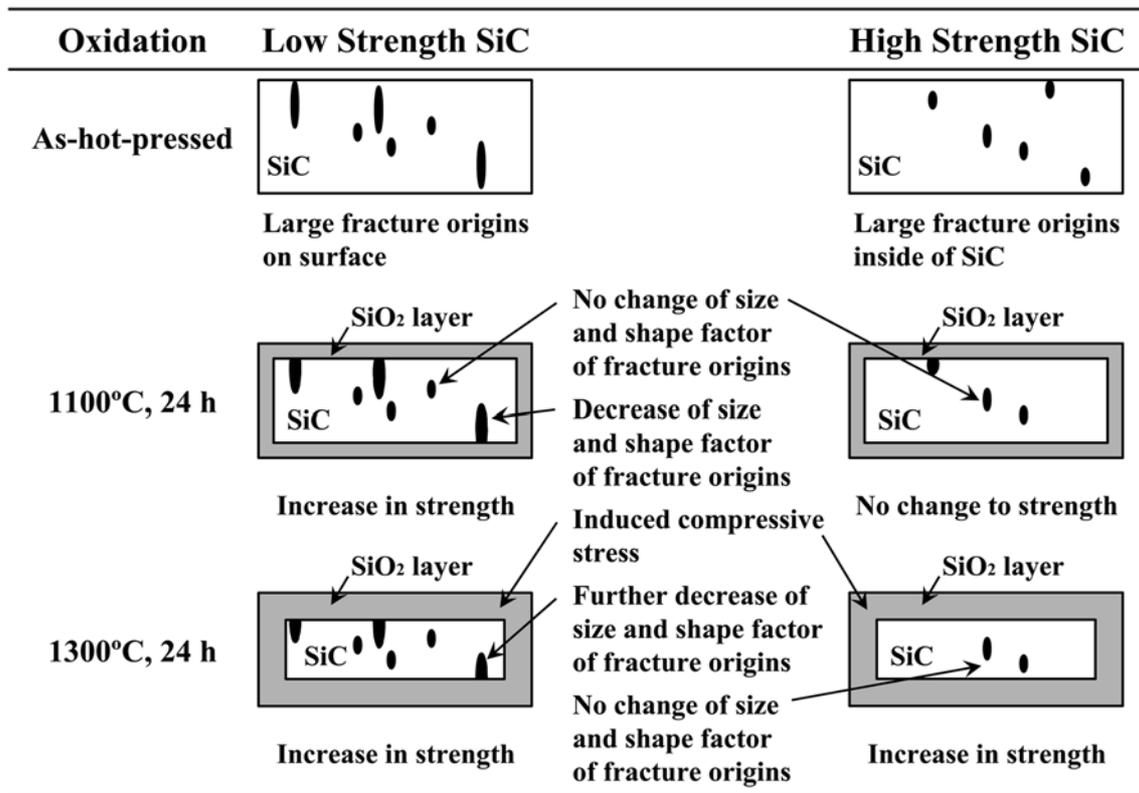


Fig. 8. Scheme explaining the oxidation effect on the size and shape of fracture origins of SiC.

at 1300 °C on the fracture probability of SiC. In the wide fracture probability range, the strength of SiC increased to higher values by the oxidation. The average strength increased to 960 MPa. The Weibull modulus was also improved to 8.3 after the oxidation.

Fig. 8 shows the scheme of the oxidation effect on the size and shape of fracture origins of SiC. In this model, fracture origins are present on the surface for low strength SiC and inside for high strength SiC, respectively. After the oxidation at 1100 °C, the size and shape factor of the fracture origins located on the surface decrease and the resultant strength increases. Since the sizes of the observed flaws were significantly larger than the thickness of the SiO<sub>2</sub> layer, the oxidation effect is interpreted as increasing the radius of curvature of flaws (a decrease of the shape factor of flaws). On the other hand, no influence is given to the fracture origins located inside of the SiC, leading to no change of strength. After the oxidation at 1300 °C, the strength of SiC with fracture origins on its surface is increased by a further decrease of the crack size and shape factor. In addition, the induced compressive stress on the surface region contributes to the increased strength. The increased strength at a high fracture probability in Fig. 7 may be also related to the compressive stress induced on the surface region.

### Conclusions

A bimodal powder system of 75vol% 800 nm SiC-

25 vol% 30 nm SiC with Al<sub>2</sub>O<sub>3</sub> (1.2 vol%) and Y<sub>2</sub>O<sub>3</sub> (1.2 vol%) was hot-pressed at 1950 °C for 2 h in an Ar atmosphere and then oxidized at 1100° or 1300 °C for 24 h in air. An 0.4 μm thick SiO<sub>2</sub> layer was formed on the SiC surface after an 1100 °C oxidation. Little influence of the oxidation was measured on the average strength (822 MPa) but the fracture toughness decreased (4.4 MPa·m<sup>1/2</sup>). The strength of SiC in the low fracture probability range (< 40%) was shifted to higher values by the oxidation. The thickness of the SiO<sub>2</sub> layer increased to 1.4 μm after the oxidation at 1300 °C. After this oxidation, the strengths in all the fracture probability range were increased and the average strength reached 960 MPa. The maximum strength was 1180 MPa and the Weibull modulus was also increased to 8.3. No change of fracture toughness was observed between the SiC compacts oxidized at 1100° and 1300 °C.

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