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Crack healing behaviour and high-temperature strength of mullite/SiC composite ceramics

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Abstract

Mechanical properties of sintered mullite/SiC ceramics related to its significant crack healing behavior are discussed in this paper. This investigation was made on four kinds of specimens such as as-received smooth, heat treated smooth, pre-cracked and pre-crack healed. Pre-crack sizes were 100 and 200 μm and they were semi-elliptical in shape. The main conclusions were obtained as follows: (a) mullite/SiC composite ceramic has ability to heal crack, (b) the best healing condition was found to be 1300 °C in air for 1 h, (c) maximum crack size able to be healed is semi-elliptical crack of 200 μm in diameter, (d) crack-healed zone has enough strength up to 1200 °C and most specimens failed outside the crack-healed zone.

Keywords: Composites; Crack healing; Mechanical properties; Mullite/SiC; SiC

1. Introduction

Structural ceramics have excellent heat resistance, corrosion resistance, and wear resistance and may be indispensable materials of the new millennium. However, their machinability is poor and fracture toughness is low; this low reliability has limited their application. It is important to increase the reliability to widen the application area. There are two ways to increase the reliability of ceramics: improve the fracture toughness or confer self-crack-healing ability. Silicon carbide,[1] alumina,[2,3,6] and silicon nitride[4–6] exhibit very interesting crack-healing behavior. However, the maximum size of the crack to be healed, the optimum crack-healing conditions, and the heat resistance of the crack-healed zone have not yet been investigated.

The authors recently clarified the relation between crack healing ability and the chemical composition of silicon nitride.[7] We also reported the maximum size of a crack to be healed, the optimal crack-healing conditions, and the strength characteristics of the crack-healed zone at high temperatures for a Si_3N_4/SiC composite[8–13] and silicon carbide.[14]

We discovered that mullite/SiC exhibited interesting crack-healing behavior.[15,16] We also succeeded in improving the bending strength up to the 900 MPa level by utilizing the crack-healing behaviour and grain-growth suppression effect, which results from the addition of SiC.[17] However, the maximum size of a crack to be healed, the optimal crack-healing conditions, and the strength characteristics of the crack-healed zone at high temperatures have not yet been investigated for mullite/SiC.

The above three aspects are investigated in this study.

2. Materials and test methods

2.1. Material and sintering method

The mullite powder used was KM101 (average particle size = 0.2 μm, Al_2O_3 content = 71.8 wt.%, Kioritz Co. Ltd., Japan) and the SiC powder was ultrafine

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(average particle size = 0.27 μm, Ibiden Co,. Ltd., Japan). The manufacturing processes for the test specimens were as follows. The mullite powder and SiC powder (20 vol.% by volume of mullite powder) were wet blended for 24 h using nylon balls in alcohol. The powder was then dried in a vacuum furnace until all the solvent had evaporated. The resulting powder was hot pressed (35 MPa at 1650 °C) for 4 h in nitrogen gas and produced a sintered material with dimensions of 90×90×5 mm.

2.2. Specimens and experimental method

The bending strength was evaluated by a four-point bending test on 3×4×40 mm specimens in accordance with the JIS Standard,[18] as shown in Fig. 1. The test specimens were surface ground and polished before testing. A pre-crack was introduced into the specimens by the indentation method using a Vickers indenter. The semi-elliptical crack lengths (2*C*) on the surface were about 100 and 200 μm, and the Vickers load was 9.8 or 29.4 N. The shape of the cracks is shown in Fig. 2. The cracks were semi-elliptical with aspect ratios of 0.8–0.9. The specimens were heat treated in air at 1000 °C for 20 h, 1100 °C for 10 h, 1200 °C for 5 h and 1300 °C for 1 h to heal the crack. The heating rate was 10 °C/min and cooling was done spontaneously in the furnace. The bending test was carried out at room temperature (RT), 800, 1000, 1100, 1200 and 1300 °C. The cross-head speed of the test was 0.5 mm/min. The crystal phases of the sintered material and the surface oxides were investigated by the X-ray diffraction method. The X-ray diffraction analysis conditions were cook α radiation (30 kV accelerated voltage and 30 mA electric current) and a detector scanning speed of 0.5°/min. Crack healing at an elevated temperature was observed directly using an ultrahigh-temperature scanning laser microscope (1LM21H-LK1500, Laser Tech Co., Ltd., Japan) which can observe the surface state and measure the surface roughness of a sample at temperature ranging from RT to 1500 °C in the atmosphere as well as in inert gas. This microscope is able to magnify objects up to 10,500 times.

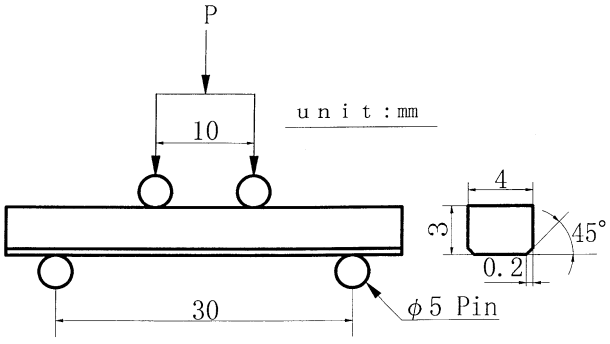

Fig. 1. Specimen dimension and loading system.

3. Results and discussion

3.1. Crack-healing behavior

Fig. 3 shows the experimental data of the crack-healing behavior of the mullite/SiC composite ceramics as a result of the bending test carried out at room temperature. The ○ symbols in the figure represent the as-received specimens that did not receive the heat treatment; the bending strength was about 340 MPa. The △ symbols indicate the bending strength of the as-cracked specimens with a surface crack length of about 100 μm.

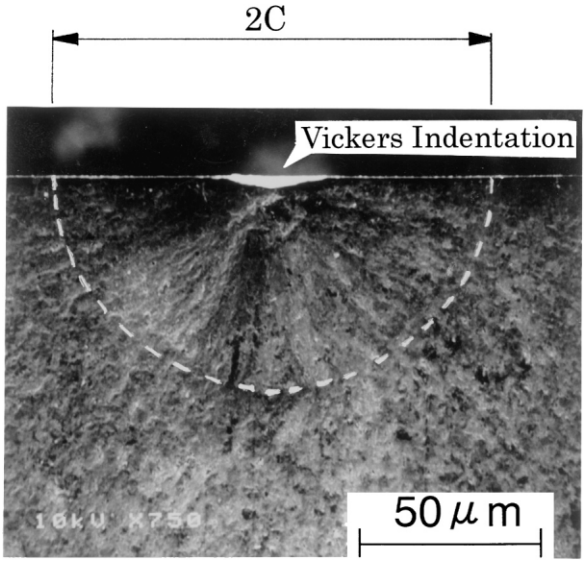

Fig. 2. A SEM photograph of a pre-crack.

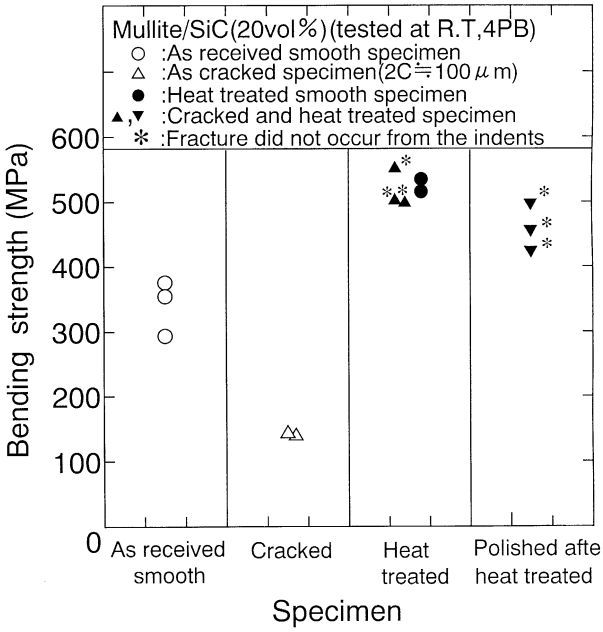

Fig. 3. The effect of heat treatment on the room-temperature bending strength of a mullite/SiC composite.

Cracking decreased the bending strength to about 140 MPa. The blackened symbols ● and ▲ illustrate the bending strength of the heat-treated smooth specimens and the cracked and heat-treated specimens. The heat treatment was performed in air at a temperature of 1300 °C for 1 h. The bending strength of the as-received specimens and as-cracked specimens ($2C = 100$ μm) increased significantly after the heat treatment to about 520 MPa. Both exhibited a bending strength greater than that of the as-received smooth specimens.

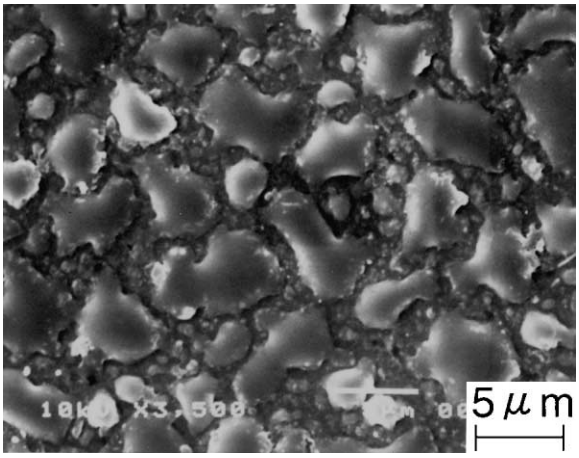

Fig. 4. A SEM photograph of the surface of a specimen heat treated at 1300 °C for 1 h in air.

Fig. 4 shows the surface conditions of the heat-treated specimens. As shown in the figure, marks like water droplets could be seen on the surface of the specimens. These deposits were removed by polishing the surface longitudinally using No. 1000 and 2000 abrasive paper. The bending strengths of these polished specimens are indicated in Fig. 3 by inverted solid triangles. The bending strength decreased to 460MPa after polishing, which is somewhat less than the unpolished heat-treated specimens but considerably higher than the as-cracked (△) specimens. The ∗ marks in Fig. 3 indicate specimens on which the fracture occurred from outside the Vickers indent. All cracked and heat-treated specimens failed from outside of the pre-crack zone.

The pre-crack zone was observed directly with a laser microscope during the heat treatment process to investigate the strength recovery. The result is shown in Fig. 5. The crack was obvious at 1000 °C [see Fig. 5(a)], and no changes were observed. However, the crack could not be clearly distinguished 10 min after it reached 1300 °C, as shown in Fig. 5(c). The crack could barely be observed after 1 h at 1300 °C because the surface was covered with some newly created phases [Fig. 5(d)]. We used the X-ray diffraction method to investigate the composition of these materials. The

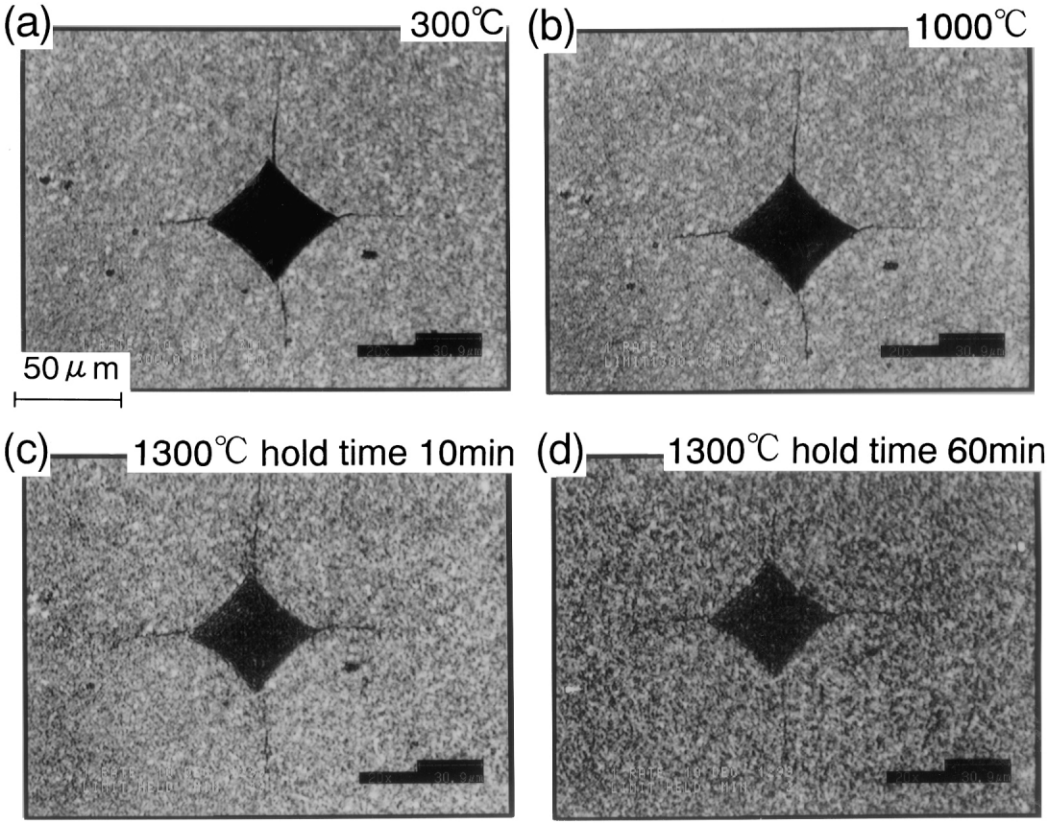

Fig. 5. Observation of the crack-healing process using a laser microscope.

X-ray patterns are shown in Fig. 6. Fig. 6(a) and (b) shows the results for the as-received and heat treated specimens. A comparison of Fig. 6(a) and (b) indicates that only mullite and SiC were detected, and no differences can be observed in the figures. In addition, no other crystalline phase was observed. This fact suggests that the new phases are non-crystalline phases and contribute to healing the pre-crack. Figs. 3–6 lead us to conclude that the strength improvement results in healing of the pre-crack and a surface crack due to the pre-oxidation process.

3.2. Effect of healing condition on bending strength

We investigated the effect of the crack-healing conditions on the bending strength. The test result is shown in Fig. 7. The bending strength of the cracked and heat-treated specimens was not dependent on the crack-healing conditions in this experimental range, and all cracked and heat-treated specimens exhibited higher bending strength than that of the as-received specimens. Two reasons were considered for this. One is the residual stress due to mismatching of the thermal expansion

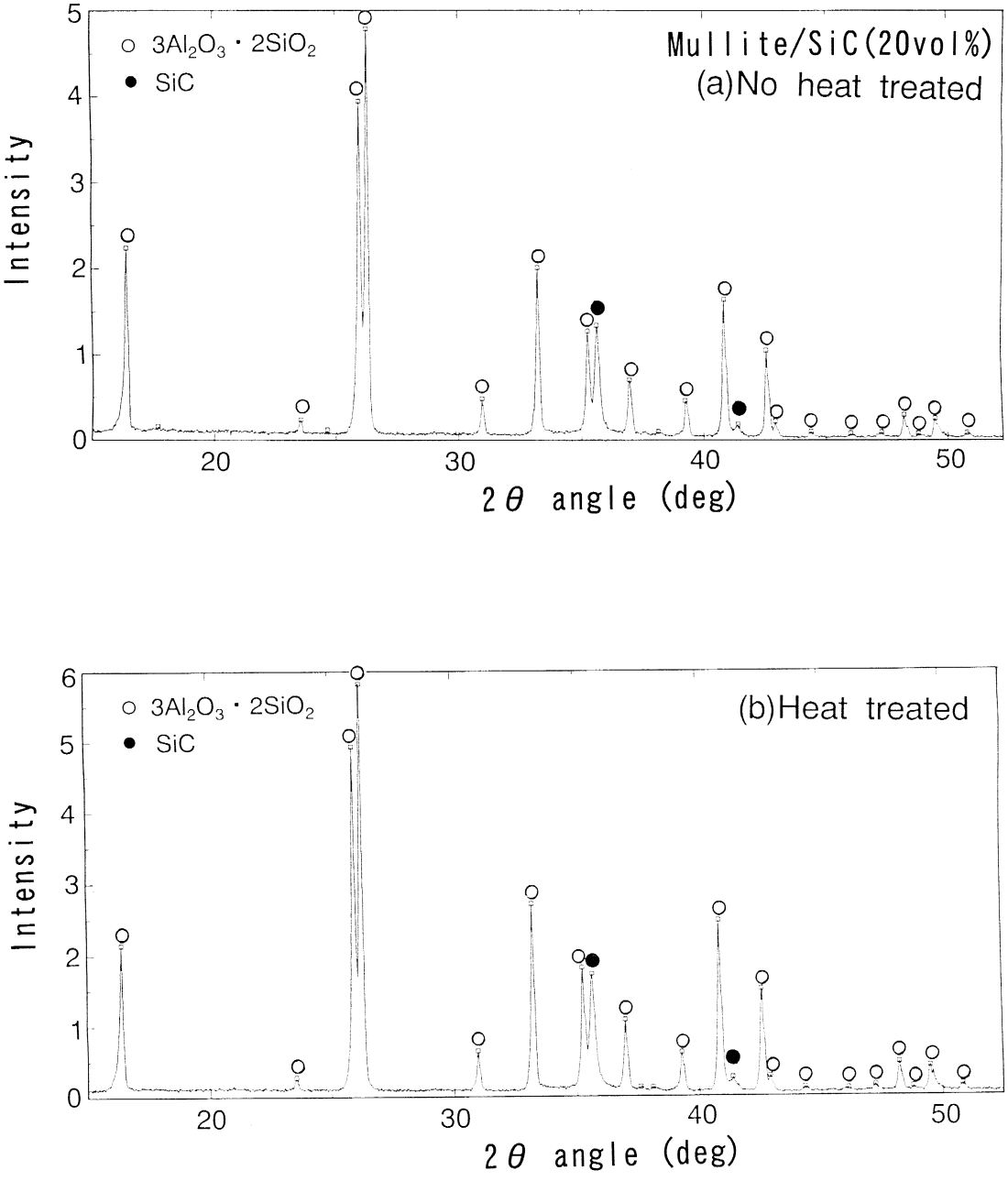

Fig. 6. X-ray diffraction patterns of (a) a no-heat-treatment specimen and (b) a heat-treated specimen.

coefficient and the elastic modulus between the matrix and the surface oxides that were created during the heat treatment in air. As mentioned in Section 3.1 (see Fig. 3), the strength of the specimen with the surface oxides removed was greater than that of the as-received specimen, and therefore, this is not a valid explanation. The other reason considered is healing of both the pre-crack and other cracks that could be created on the specimen surface during machining. This material has a low fracture toughness of about 2.8 MPa$\sqrt{m}$. Therefore, it is easy to create a crack during machining, and it appears that the cracks affect the strength of the as-received specimen. Based on this fact, we considered that the increase in strength is a result of healing of the cracks that were created by machining.

The bending strength shows the highest value, at about 520 MPa, when a pre-cracked specimen has been heat-treated at 1300 °C for 1 h in air. Therefore, that condition was applied in this study as the standard crack-healing condition of this material.

3.3. Maximum crack size to be healed under the standard crack-healing conditions

It is important to determine the maximum size of a crack that can be healed perfectly. The maximum crack size was investigated using specimens with a surface pre-crack that was introduced by a Vickers indenter. The test result is shown in Fig. 8. The bending strength of the as-received specimen was about 340 MPa. The strength was increased by heat-treating and showed a value of 520 MPa. It appeared that this improvement in strength was caused by healing a crack on the specimen surface that was introduced in machining. The bending strength of the as-cracked specimens was 140 and 100 MPa for 100 and 200 μm crack diameters. The strength was increased by heat-treating and showed values of 520 and 420 MPa. The strength was higher than that of the as-received smooth specimen in both cases. However, the strength was as low as 100 MPa for the 200 μm diameter specimen, compared with that of heat-treated smooth specimen. In this case, all three specimens failed from the Vickers indentation. The indentation size was about 60 μm, and this was sufficient to decrease the strength of the heat-treated pre-cracked specimen. These results indicate that this material has the ability to heal surface semi-elliptical cracks 200 μm in diameter.

3.4. Effect of the testing temperature on the bending strength of a pre-cracked, healed specimen

Fig. 9 shows the effect of the testing temperature on the bending strength. The bending strength of the as-received smooth specimens (○) was independent of the testing temperature in experiments ranging from room temperature to 1300 °C. The bending strength decreased slightly for the cracked and heat-treated specimen (▲) with increases in the testing temperature up to 1200 °C. The strength decreased dramatically at 1300 °C to 290 MPa. This value is approximately the same as that of the as-received smooth specimen as well as the heat-treated one. In contrast, the strength behaviour of the heat-treated smooth specimen (●) was similar to that of the cracked and heat-treated specimen in this experimental range. The bending strength of the as-cracked specimen (△) was 140 MPa at RT and decreased slightly at 800 °C. However, the strength increased above that temperature with increases in the test temperature and

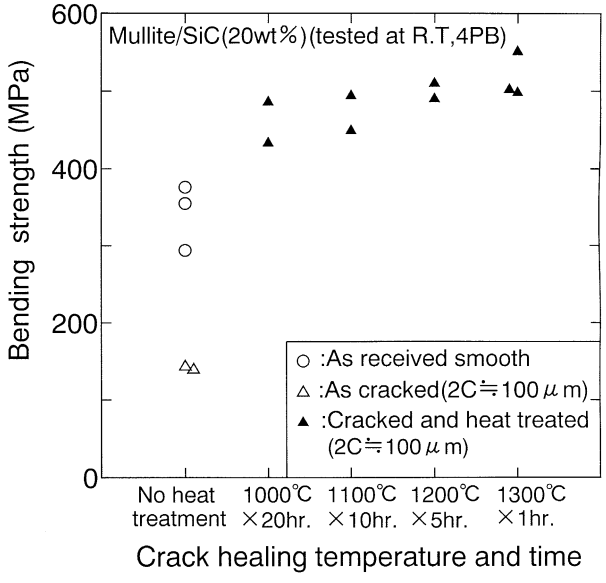

Fig. 7. The effect of the heat treatment conditions on the room-temperature bending strength of a mullite/SiC composite with a pre-crack.

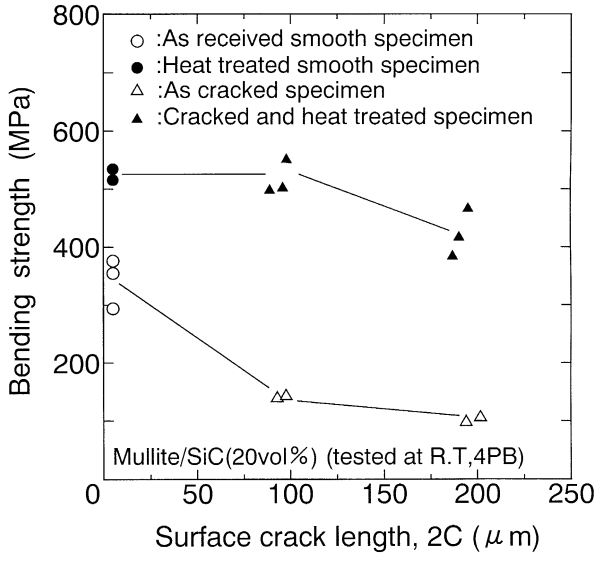

Fig. 8. Effect of the pre-crack size on the room-temperature bending strength of a cracked and heat-treated specimen.

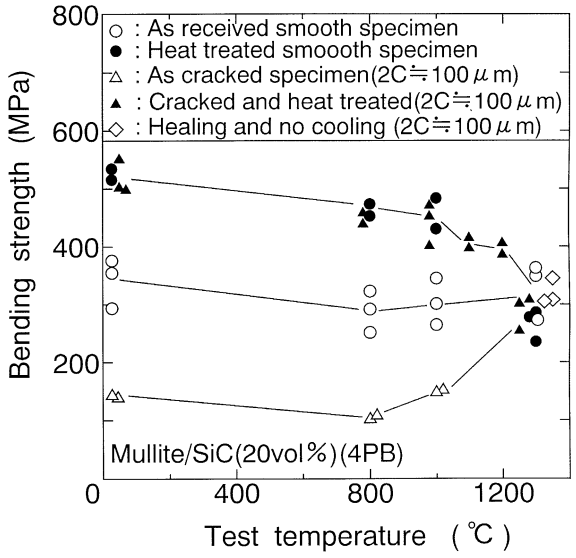

Fig. 9. Effect of the testing temperatures on the room-temperature bending strength of a heat-treated specimen.

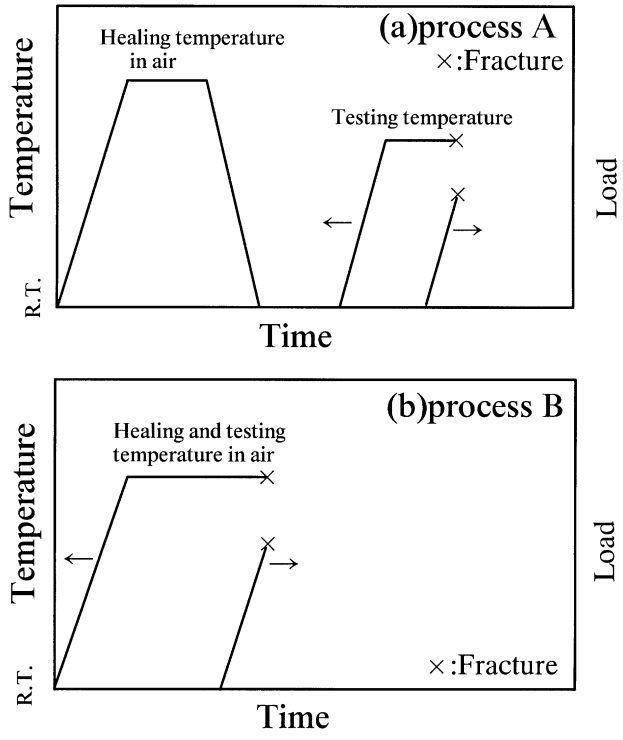

Fig. 10. Schematic illustration of the crack-healing and testing process.

reached about 310 MPa, which is the same as the as-received specimens.

Schematic illustrations of the heat treatment and testing processes are shown in Fig. 10. In process A in Fig. 10(a), the specimen was tested for bending at each temperature after a heat treatment (the crack-healing process). In contrast, the specimen in process B in Fig. 10(b) was tested for bending without any pre-heat treatment. The symbols ▲ and ● in Fig. 9 indicate the test results using process A. The symbols △, ◇, and ○ in Fig. 9 show datum from tests performed using process B. The difference between △ and ◇ is the duration time at the test temperature; the time was 20 and 60 min for △ and ◇. The bending strength of the as-cracked specimen (◇) in Fig. 9 recovered perfectly at 1300 °C with respect to that of the as-received smooth specimen. This result suggests that a surface crack in this material can be healed in service if the necessary conditions are satisfied.

Fig. 9 compares the bending strength of the as-received smooth specimens (○) and the cracked and heat-treated specimens (▲); the strength of the heat-treated specimen was greater than that of the as-received specimen up to 1200 °. However, both specimens had the same strength at 1300 °C. Therefore, the crack healing effect is remarkable up to 1200 °C in this material. The matrix of the mullite does not degrade in strength up to 1300 °C.[2,4] This fact indicates that any degradation above 1200 °C is a result of the crack-healing material being composed of glassy phases that weaken at that temperature.

In contrast, the crack-healing material in a silicon nitride/silicon carbide composite is a crystalline phase, and so the bending strength of the pre-crack healed specimens was equal to that of the matrix up to 1400 °C.[7,8]

4. Conclusions

Crack-healing behaviour and high-temperature strength characteristics were investigated systematically using hot-pressed mullite/SiC composite ceramics. This material exhibits very interesting crack-healing behaviour. The main results of this experiment are described below.

1. The strength of the pre-cracked specimen was recovered by healing the pre-crack using pre-oxidation at an elevated temperature in air.
2. The optimum crack healing condition in this experiment range was 1300 °C for 1 h in air. A semi-elliptical crack 200 μm in diameter could be healed perfectly under this condition.
3. The crack-healed zone had sufficient bending strength compared with that of the matrix up to about 1200 °C.

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