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Cracked-healing and the bending strength of Si_3N_4 composite ceramics with SiO_2 additions

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This study analyzed the crack-healing behavior of Si_3N_4 composite ceramics based on variations in the heat-treatment temperature and the amount of colloidal SiO_2 added. Semi-elliptical cracks about 100 μm length were obtained from a Vickers indenter using a load of 24.5 N. The results showed that the use of an optimum amount of added colloidal SiO_2 and the coating of colloidal SiO_2 on the cracks could significantly increase the bending strength. Meanwhile, the heat-treatment temperature has a profound influence on the extent of crack healing and the degree of strength recovery. The optimum heat-treatment temperature is dependent on the amount of added colloidal SiO_2 employed. The crack healing strength was far greater in the case of the cracked specimen when colloidal SiO_2 had been coated on the crack surfaces. When scanned with a microscope probe, the cracks were found to have almost entirely disappeared when heat treated at a temperature of 1,273 K. The bending strength of the SSTS-1 cracked specimen not coated with the colloidal SiO_2 recovered to the same extent as the smooth specimen at the optimum healing temperature of 1,273 K. However, the bending strength of the cracked specimen with the colloidal SiO_2 coating increased by up to 140%. The optimum amount of the added colloidal SiO_2 was found to be 1.3wt.%. Moreover, the bending strength of the crack-healed specimen with the colloidal SiO_2 coating was up to 160% greater than that of the smooth specimen with 0.0 wt.% of the added colloidal SiO_2 coating. Crack closure and the rebonding of the cracks caused by the oxidation of cracked surfaces were thus identified as the dominant healing mechanism of Si_3N_4 composite ceramics.

Key words: Si_3N_4 composite ceramics, SiO_2 colloidal, Additive, Crack-healing, Bending strength.

Introduction

Because of its excellent mechanical properties, abrasion resistance, and thermal performance properties, silicon nitride (Si_3N_4) has been widely used in a variety of applications such as turbo chargers and turbo rotors, diesel engine parts, cutting tools, and bearings. Industrial ceramics that include silicon nitride have crack healing properties [1-6]. The presence of crack-healing properties where structural members designed for industrial applications are concerned results in many advantages. These include an increase in the reliability of the ceramic structure, precision inspections, and a decrease in machining and polishing costs [7]. In this regard, the authors carried out studies on silicon nitride (Si_3N_4), silicon carbide (SiC), and alumina (Al_2O_3), all of which are regarded as having advanced crack-healing properties. That is, a) optimum crack-healing conditions for high temperature strength [8, 9]; b) the maximum length of cracks which can be completely healed [8, 10]; c) the effects of SiO_2 on crack healing [10-12]; d) the effects of the additive Y_2O_3[9, 13]; and e) elastic wave properties of crack-healed materials [14, 15]. Although SiO_2 oxides have long been regarded as contributing to the crack-healing behavior, no studies have to date been formulated regarding the result of the use of SiO_2 as a sintering additive.

This study examined the crack healing and bending strength at room temperature of 0.2 μm Si_3N_4 and 0.27 μm SiC composite ceramics based on the amounts of colloidal SiO_2 added as dispersed nano particulates.

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Materials and Experimental Methods

A powder composed of 0.2 μm Si_3N_4, 0.27 μm SiC and a sintering additive (33 nm Y_2O_3, commercially purchased anatase TiO_2, and 12% colloidal SiO_2) were used for the experiments. The powder was composed of Si_3N_4 80 wt.% and SiC 20 wt.%. Y_2O_3 5 wt.% and TiO_2 3 wt.% were added to the powder as sintering additives. To analyze the crack-healing effects based on the amount of colloidal SiO_2 employed, 0.0 wt.%, 1.3 wt.%, 2.6 wt.%, 5.2 wt.%, 10.4 wt.% of 12% colloidal SiO_2 were separately added as a sintering additive. When sintered, the colloidal SiO_2 added forms SiO_2 oxides at temperatures higher than 500 °C. The batch compositions of specimens are given in Table 1. Fig. 1 shows the sintering flow chart of the composite ceramics. The sintered samples were cut into the 3.0 × 4.0 × 22 mm rectangular

Table 1. Batch composition of specimens (wt.%)

	Si_3N_4	SiC	Y_2O_3	TiO_2	SiO_2 colloidal
SSTS-1					0.0
SSTS-2					1.3
SSTS-3	80	20	5.0	3.0	2.6
SSTS-4					5.2
SSTS-5					10.4

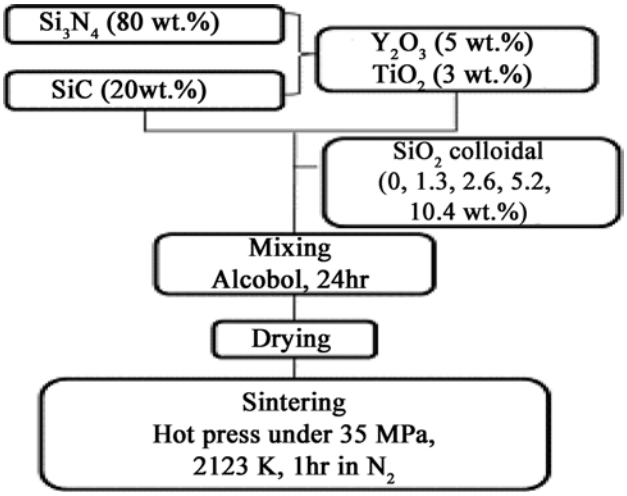

Fig. 1. Sintering flow chart.

specimen bars that were polished to a mirror finish on one face and the edges of specimens were beveled 45° to reduce the likelihood of edge-initiated failures. Fig. 2 shows the geometry of specimen and the three point bending system used for this study.

A semicircular crack was made at the center of the tensile surface of specimens with a Vickers indenter using a load of 24.5 N. By this method, semicircular cracks about 100 μm in diameter (with an aspect ratio of about 0.9) were made. The heat treatment for the optimum crack healing conditions was carried out in an air atmosphere for one hour at temperatures ranging from 773-1,573 K. To analyze the effect of the colloidal SiO_2 on crack healing, heat treatment was conducted after coating the colloidal SiO_2 on the cracked surface under the same conditions. The surface state and surface roughness of the crack-healed specimens were also examined using a SPM (scanning probe microscope). All fracture tests were performed on a three-point loading system with a span of 16 mm and cross head speed of 0.5 mm/minute.

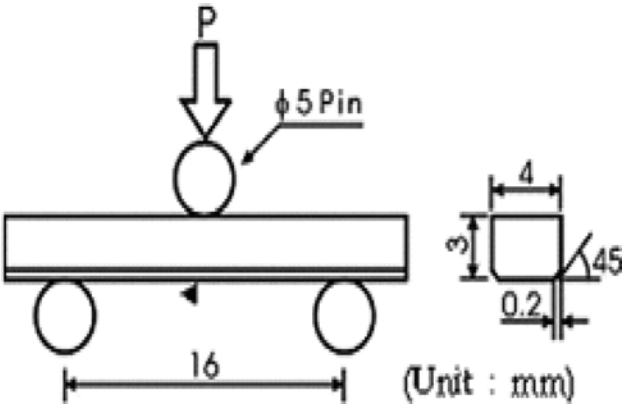

Fig. 2. Dimensions of the specimen and the three-point bending system used for this study.

Results and Discussions

In-Situ Observation of Crack Healing

Fig. 3 shows the state of in-situ crack healing of the SSTS-1 specimen after 1 h at 1,273 K and 1,573 K. (a) show the cracked specimen using a Vickers indenter. (b) and (d) show crack-healed specimens on which the SiO_2 colloidal was not coated, (c) and (e) show crack-healed

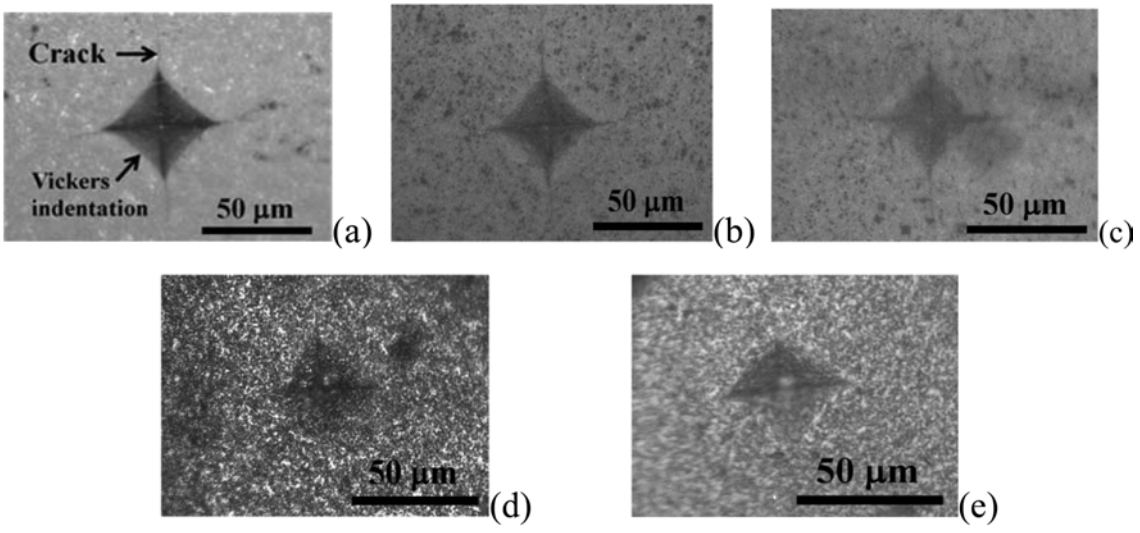

Fig. 3. crack healing for 1 h in air without/with colloidal SiO_2 coating (SSTS-1 specimen), (a) as-cracked (crack length : 100 μm), (b) without colloidal SiO_2 coating at 1,273 K, (c) with colloidal SiO_2 coating at 1,273 K (d) without colloidal SiO_2 coating at 1,573 K, (e) with colloidal SiO_2 coating at 1, 573 K.

specimens on which the colloidal SiO_2 was coated. The in-situ observations revealed that at a temperature of 1,273 K (b) and (c) exhibited clearer crack-healing properties than (d) and (e) did at a temperature of 1,573 K. Meanwhile, (c) and (e), on which the colloidal SiO_2 was coated, exhibited more advanced crack-healing properties. The specimens on which the crack was healed at 1,573 K superficially showed a higher degree of crack healing than did those healed at 1,273 K. However, the specimens showed the highest crack-healing strength at 1,273 K as shown in later.

In order to analyze the cause of these results, the crack-healed surface and surface roughness of the specimens observed in-situ were examined using a SPM. The results are shown in Fig. 4. In Fig. 4(a), to which the colloidal SiO_2 was not coated and heat treatment was conducted at 1,273 K, and Fig. 4(b), to which the colloidal SiO_2 was coated and the heat treatment was conducted at 1,273 K, cracks were healed completely. Nevertheless, we can see that the surface of Fig. 4(a) is a slightly rougher than the surface of Fig. 4(b). Meanwhile, Fig. 4(c) and Fig. 4(d), both of which involved heat treatment being conducted at 1,573 K, exhibited a tendency that was similar to Fig. 4(a) and Fig. 4(b), where the heat treatment was carried out at 1,273 K. However, certain cracks are still visible in the cases of Fig. 4(c) and Fig. 4(d) and their surfaces are rougher than was the case with Fig. 4(a) and Fig. 4(b). These differences can be regarded as the causes of the decrease in crack-healing strength. We were thus able to determine the materials in which oxides cause an increase in crack-healing strength using electro probe microanalysis EPMA [8, 12]. The crack healing reactions of Si_3N_4 composite ceramics are as follows [16, 17]:

$$Si_3N_4 + 3O_2 + SiO_2 \rightarrow 4SiO_2 + 2N_2 \quad (1)$$

$$SiC + SiO_2 + 2O_2 \rightarrow 2SiO_2 + CO_2(CO) \quad (2)$$

$$2SiC + 2Y_2O_3 + 2TiO_2 + SiO_2 + 4O_2 \rightarrow Y_2Si_2O_7 + Y_2Ti_2O_7 + SiO_2 + 2CO_2 \quad (3)$$

Here, $Y_2Si_2O_7$ and $Y_2Ti_2O_7$ are crystalline phases. The anatase type TiO_2 becomes a rutile-type crystal phase at higher than 500 °C. The SiO_2 has two phases; a glassy and a crystalline phase. The amount of crystallized SiO_2 is dependent on the crack-healing temperature. Therefore, it can be concluded that ceramics containing Si recovered their bending strength by means of the glassy phase SiO_2. And, based on the above facts, that the cracks in Fig. 4(c) and (d), which were crack-healed at high temperature, were caused by the vaporization of glassy SiO_2[8].

Effect of Crack Healing Temperatures on Bending Strength

Fig. 5 shows the bending strength of the smooth specimens (■ , □), cracked specimens (● , ○), and heat-treated smooth specimens (▲ , △) of the SSTS-1 and SSTS-2 batches. The black and white symbols respectively indicate the SSTS-1 and SSTS-2 batches. The average bending strength of the smooth specimens was found to be 595 MPa (■) and 935 MPa (□). As such, the SSTS-2 specimen to which 1.3 wt.% of the colloidal SiO_2 had been added exhibited a higher bending

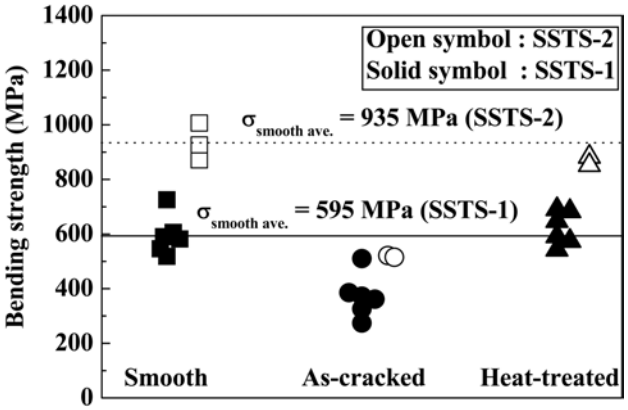

Fig. 5. Bending strength of smooth and as-cracked specimens for SSTS-1 and SSTS-2 batches.

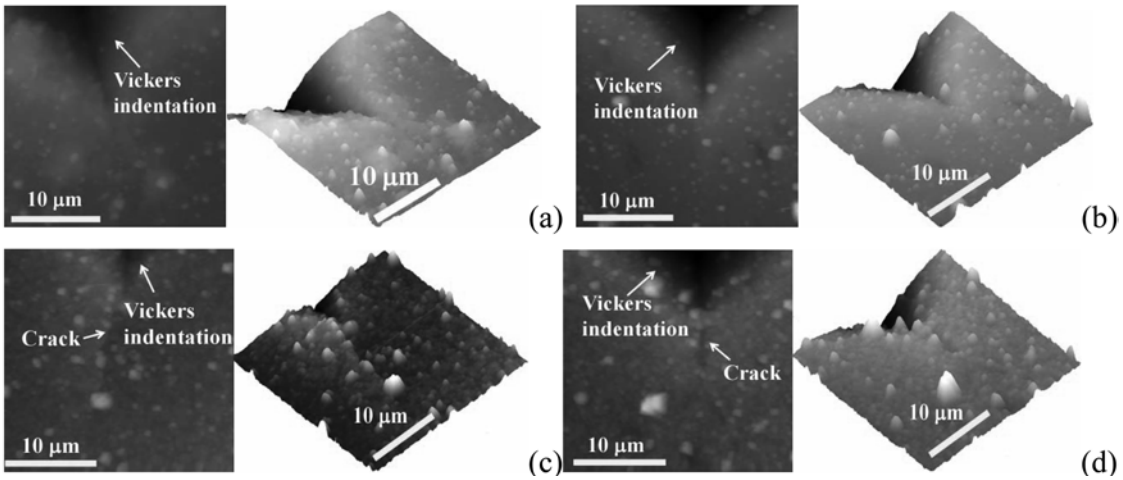

Fig. 4. crack healing appearance and surface roughness by SPM (SSTS-1 specimen), (a) without colloidal SiO_2 coating at 1,273 K, (b) with colloidal SiO_2 coating at 1,273 K, (c) without colloidal SiO_2 coating at 1,573 K, (d) with colloidal SiO_2 coating at 1, 573 K.

strength. Furthermore, both smooth specimens heat-treated for one hour at 1,573 K exhibited a bending strength that was similar to that of the smooth specimen. However, the cracked specimen showed a bending strength that was approximately 60% (371 MPa) (■) and 55%(518 MPa) (□) of that of the smooth specimens. From this figure, the conclusion was reached that the cracked specimens showed a lower bending strength than the smooth ones.

Si_3N_4 composite ceramics have self crack-healing properties by the SiO_2 oxides caused by the heat treatment. Therefore, we examined the effects of the colloidal SiO_2 coating on the bending properties of the SSTS-1 crack-healed specimens, and show the relationship with the crack-healing temperature in Fig. 6. In this figure, the black (●) and white (○) symbols refer to the absence or presence of the colloidal SiO_2 coatings on the cracked surfaces. The dotted line indicates the average bending strength of the SSTS-1 smooth specimen. The crack-healed specimen, on which the colloidal SiO_2 was not coated, showed the highest bending strength at 1,273 K. This was in line with the bending strength of the smooth specimen. This represents a phenomenon unlike those reported in other studies, where Si_3N_4 composite ceramics were found to exhibit their peak bending strength after heat treatment at 1,573 K [18]. The reaching of an optimum strength at a lower crack-healing temperature was made possible by the use of the sintering additive TiO_2 [11].

Meanwhile, the crack-healed specimen with the colloidal SiO_2 coating exhibited a higher bending strength, heat treated at 973-1,573 K, than the smooth specimen. That is, the bending strength was greatly recovered at lower temperatures. The specimen with the colloidal SiO_2 coating exhibited a bending strength that was 230% heat treated at 973 K, 140% heat treated at 1,273 K, and 125% heat treated at 1,573 K of that of the specimen without the colloidal SiO_2 coating. The crack-healed specimen with the colloidal SiO_2 coating reached an optimum strength heat treated at 1,273 K. As such, the crack-healing

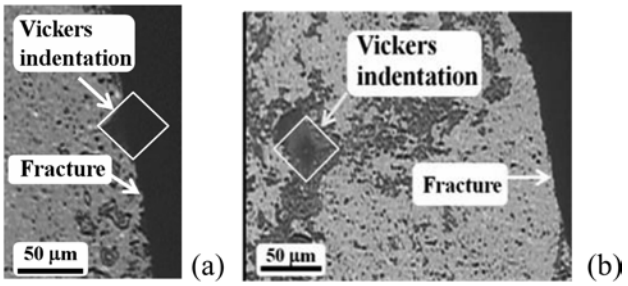

Fig. 7. Fracture patterns from (a) crack-healed zone, (b) outside the crack-healed zone (SSTS-1 specimen).

strength was improved by coating the colloidal SiO_2 on the surface of the cracked parts [11]. The symbol * indicates a fracture which occurred outside the crack-healed zone as shown in Fig. 7(b). Fig. 7(a) indicates a fracture which occurred in the crack-healed zone.

Fig. 8 exhibits the changes in bending strength based on variations in the amount of added colloidal SiO_2 present. Here, the white symbols (○) refer to the bending strength of the smooth specimens, and the black symbols (●) to the bending strength of the crack-healed specimens. In the case of the black symbols, the colloidal SiO_2 was coated on the cracked parts and the specimens were heat treated for an hour in an air atmosphere at 1,273 K. Both the smooth and crack-healed specimens exhibited increases in bending strength in the case of the SSTS-2 batch with 1.3 wt.% of the colloidal SiO_2. However, the bending strength was lower than that of the SSTS-3 batch with 2.6 wt.% of the colloidal SiO_2. While the SSTS-1 crack-healed specimens exhibited a relatively higher increase in bending strength than the smooth specimens, the smooth and crack-healed specimens of the SSTS-2 batch showed similar results in bending strength. The bending strength of SSTS-3, SSTS-4 and SSTS-5 smooth specimens decreased as the amount of the colloidal SiO_2 was increased. But the crack-healed

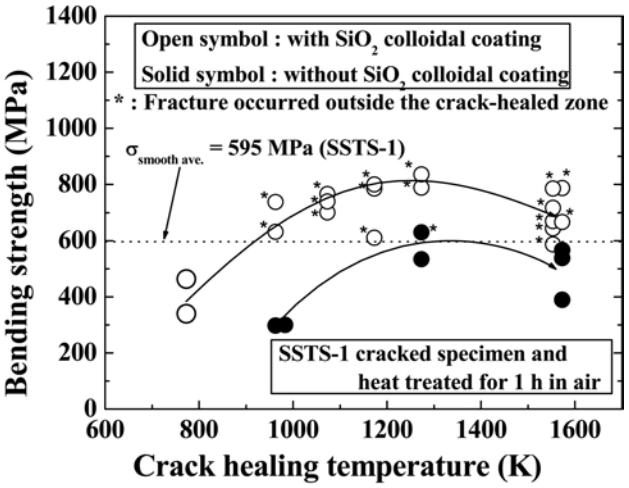

Fig. 6. Relation of bending strength and crack-healing temperature using SSTS-1 cracked specimens without/with a colloidal SiO_2 coating.

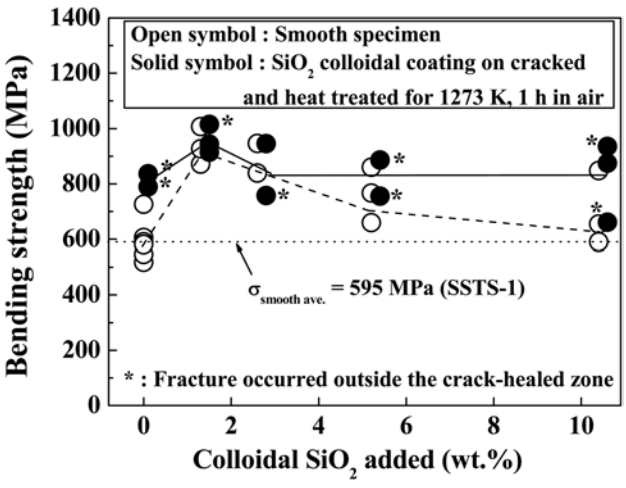

Fig. 8. Bending strength according to the amount of added colloidal SiO_2.

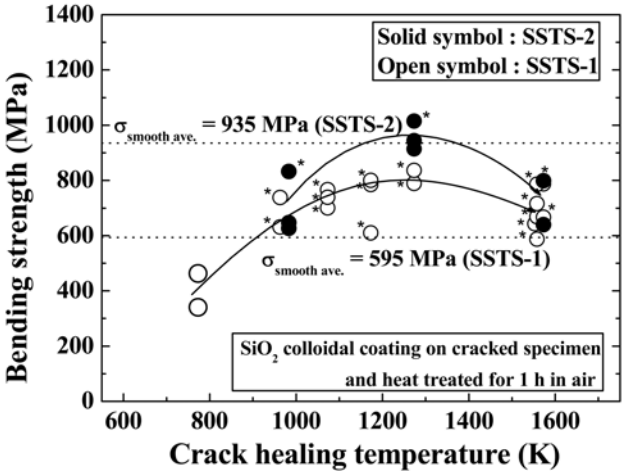

Fig. 9. Relation of bending strength and crack-healing temperature of cracked specimens with colloidal SiO_2 coatings (* Fracture occurred outside the crack-healed zone).

specimens show nearly the same bending strength. It can be concluded that 1.3 wt.% of the colloidal SiO_2, which gives the highest bending strength for smooth and crack-healed specimens, represents the optimum amount.

Fig. 9 shows the relationship between the bending strength and crack-healing temperature in the case of the crack-healed specimens of SSTS-1 and SSTS-2 batches on which the colloidal SiO_2 was coated. The bending strength of the crack-healed specimens of SSTS-1 had increased by a wider margin than that of the SSTS-2 smooth specimens. That is, while the bending strength of the SSTS-1 specimens at 1,273 K increased by 136% (σ_{ave} = 813 MPa), the bending strength of the SSTS-2 specimens exhibited a strength that was similar to that of the smooth specimens (σ_{ave} = 935 MPa). The crack-healed specimens of the SSTS-2 with the colloidal SiO_2 coating exhibited the highest bending strength heat treated at 1,273 K, which amounted to a 160% increase over that of the SSTS-1 smooth specimens.

Conclusions

This study analyzed the effects on the bending strength and crack-healing behavior of Si_3N_4/SiC composite ceramics occasioned by variations in the amount of the colloidal SiO_2 present. As far as the crack-healing behavior was concerned, the bending strengths of smooth, heat-treated smooth, cracked, and crack-healed specimens with different values of the crack-healing temperature were examined. The crack-healing process was examined through in-situ observation.

1) The in-situ observations revealed that the crack healing was more complete at 1,573 K than at 1,273 K. However, when SPM was employed, crack healing was found to be more complete at 1,273 K than at 1,573 K. In terms of the surface of the crack-healed parts, those specimens coated with colloidal SiO_2 were found to be cleaner.

2) The SSTS-1 cracked specimens exhibited the highest bending strength of the crack-healed specimens heat treated at 1,273 K, and this was regardless of whether the colloidal SiO_2 specimens were coated with or not. However, the crack-healed specimens coated with colloidal SiO_2 exhibited a 140% increase in bending strength over the smooth specimens and the crack-healed specimens not coated with colloidal SiO_2.

3)The bending strength of the SSTS-2 specimens was optimized when 1.3 wt.% colloidal SiO_2 was present. The bending strength of the crack-healed specimens coated with colloidal SiO_2 exhibited the highest value heat treated at 1,273 K, recording a 160% increase over the smooth specimens with 0.0 wt.% colloidal SiO_2.

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