# Crack healing in liquid-phase-pressureless-sintered silicon carbide–aluminum nitride composites

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## Abstract

Crack healing in liquid-phase-pressureless-sintered SiC–AlN composites was investigated by introducing cracks into specimens and subsequently heat-treating the specimens. It was observed that cracks were healed and the strength was recovered. Cracks were filled with silica or mullite produced by the oxidation of the composites. It was shown that the healing temperature could be fixed in the range 1100–1300 °C and that large cracks up to about 300 μm could be healed completely. Our results imply that a simple oxidation heat-treatment can improve the reliability of silicon carbide–aluminum nitride components.
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*Keywords:* SiC; AlN; Crack healing; Mechanical properties

## 1. Introduction

Several studies reported that cracks can be healed by means of a heat-treatment with a beneficial effect on the flexural strength of ceramics.[1–6] Gupta[1] reported that cracks in alumina were healed by a mechanism similar to that of densification during sintering. Choi and Tikare[2] reported that cracks in silicon nitride were healed by being filled with an oxidation product. In silicon carbide cracks were filled by amorphous silica[3] and Korous et al.[4] reported that the cracks in silicon carbide, once healed, surprisingly became even stronger than the original silicon carbide. Furthermore, the crack-healing ability of monolithic silicon carbide makes it possible to reduce machining costs because most of the surface flaws could be healed using a pre-oxidation technique.[5] Reaction-bonded silicon carbide showed the same mechanism of monolithic SiC with the possibility to recover as much as 60% of the strength of as-machined specimens without cracks.[6]

Crack-healing behaviour of silicon carbide–aluminum nitride (SiC–AlN) composites, one of the best candidate for high tem-perature applications among SiC-based materials, has not been characterized up to now. These materials present high flexural strength and oxidation resistance up to 1500 °C[7–8] and the study of the crack-healing ability consequently represents an important issue to be investigated in order to assess the reliability of SiC–AlN components. Therefore, in this paper the crack-healing ability of pressureless-sintered SiC–AlN ceramics is studied and compared with crack-healing behaviour of sintered silicon carbide reported by other authors.

## 2. Experimental procedure

SiC–AlN composites has been prepared by means of pressureless sintering using yttria (Y$_2$O$_3$) as sintering aid. A batch of powder composed by 48 wt% SiC–48 wt% AlN–4 wt% Y$_2$O$_3$ was wet-mixed in ethanol for 12 h using SiC grinding balls. After drying and sieving, the powder was compacted by die pressing at 67 MPa and subsequently pressed at 150 MPa by CIP.

Sintering was performed in a graphite element furnace in flowing nitrogen at 1 atm with green bodies put inside a graphite crucible without protective powder bed. Sintering was performed at 1950 °C, while an annealing step was conducted at 2050 °C. Thermal cycle was characterised by heating and
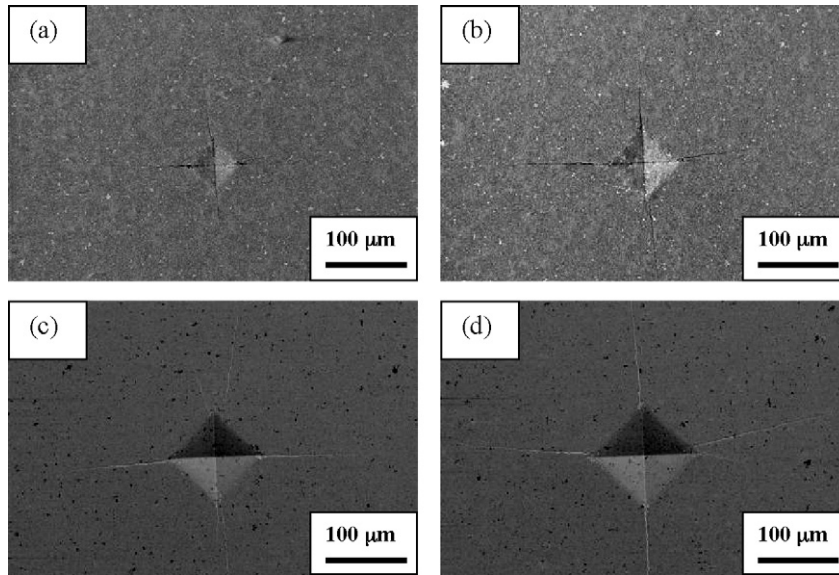
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Fig. 1. SEM images of the Vickers indentations obtained with a load of (a) 49 N, (b) 98 N, (c) 147 N and (d) 196 N.

cooling rate of 20–30 °C/min and by dwell time of 0.5 h at the sintering temperature.

The sintered material was cut into test specimens measuring 3 mm × 4 mm × 20 mm. These specimens were subjected to three-points bending with a span of 16 mm. Semi-elliptical surface cracks of 60–560 μm in surface length were introduced at the center of the tensile surface of the specimens by means of

Vickers indentations. The ratio of depth ($a$) to half surface length ($c$) of the crack (aspect ratio) was $a/c = 0.9$.

The pre-cracked specimens were heat-treated for 1 h at temperature between 900 and 1300 °C in air. The specimens were furnace-cooled to room temperature. After crack-healing process, monotonic bending tests were carried out at room temperature. For a comparison, bending tests for smooth specimens
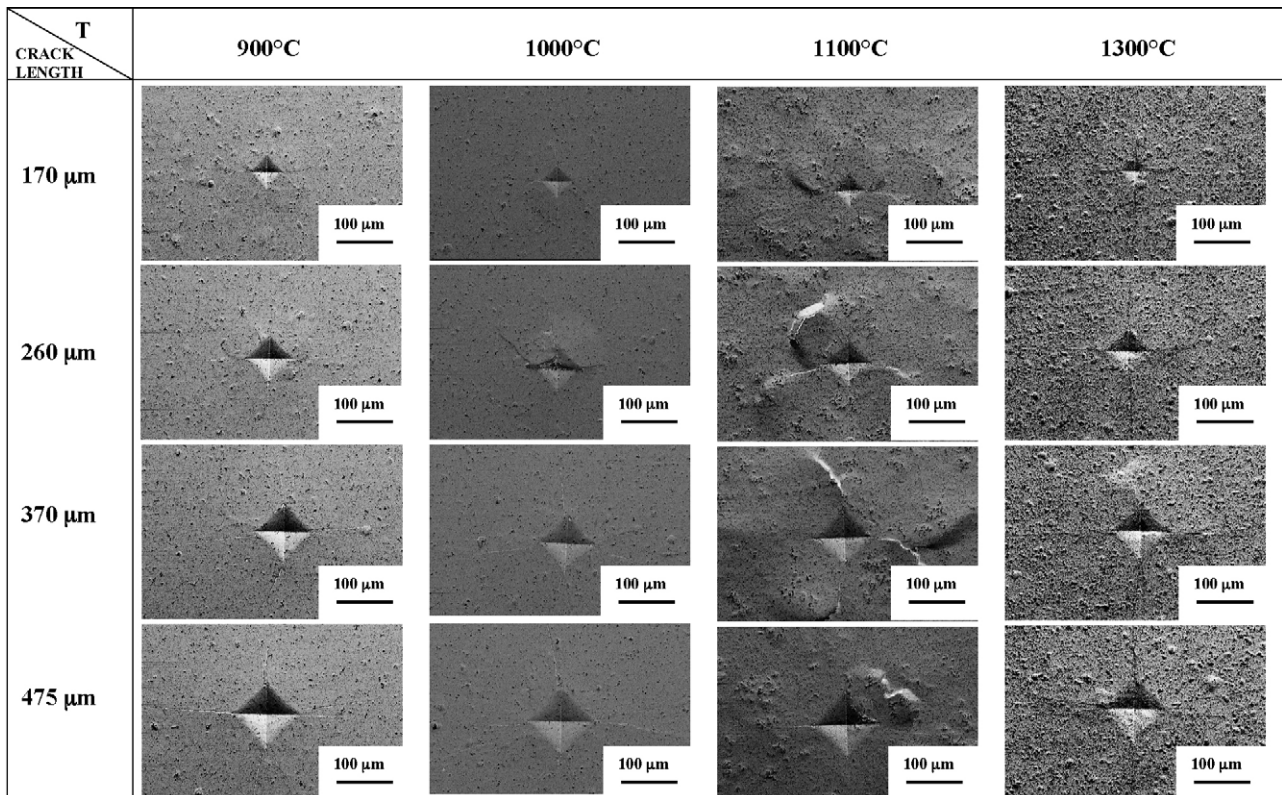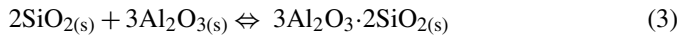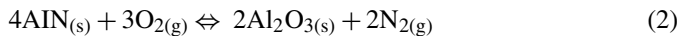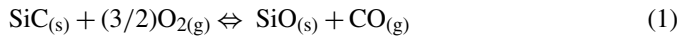


Fig. 2. SEM images of the Vickers indentations after heat-treatments at 900, 1000, 1100 and 1300 °C.

with or without heat-treatment in air at 1300 °C for 1 h were also carried out. These tests were carried out using a universal monotonic testing machine. The cross-head speed for the monotonic bending tests was 0.5 mm/min. Finally, the change in microstructure caused by the heat-treatment was characterized by scanning electron microscopy (SEM) and X-ray microprobe (EDS).

## 3. Results and discussion

Vickers indentations obtained on the surface of the sintered sample with indentation loads of 49, 98, 147 and 196 N are shown in Fig. 1. Cracks lengths were 170, 260, 370 and 475 μm, respectively. Effects on the pre-crack samples of the heat-treatments in the temperature range 900–1300 °C are shown in Fig. 2. The oxidation treatment performed at 900 °C was not able to heal the defects induced by the indentation. The increase of the oxidation temperature led to a gradual healing of the cracks and to a variation of the superficial roughness of the samples. After heat-treatment at 1300 °C the cracks with length ≤370 μm appear completely healed. In this case, crack closure and rebonding of crack surface occurred almost along the entire length of the cracks. The possible mechanism of the crack healing is based on the formation of oxides (α-cristobalite, mullite) on the basis of the following reactions:

$$SiC_{(s)} + (3/2)O_{2(g)} \Leftrightarrow SiO_{(s)} + CO_{(g)} \tag{1}$$

$$4AlN_{(s)} + 3O_{2(g)} \Leftrightarrow 2Al_2O_{3(s)} + 2N_{2(g)} \tag{2}$$

$$2SiO_{2(s)} + 3Al_2O_{3(s)} \Leftrightarrow 3Al_2O_3 \cdot 2SiO_{2(s)} \tag{3}$$

Reactions (1) and (2) are, respectively, the oxidation of silicon carbide (passive oxidation) and aluminum nitride, while reaction (3) leads to the formation of mullite. The XRD spectra reported in Fig. 3 shows that mullite and α-cristobalite were formed after heat-treatment at 1300 °C. Traces of yttrium disilicate (γ-$Y_2Si_2O_7$) were also detected due to the decomposition of the grain boundary phase $Y_{10}Al_2Si_3O_{18}N_4$.[8]

Another confirmation of the mechanism for the crack healing could be extracted by the analysis of the EDS spectra reported in Fig. 4. In fact, it is clearly shown that the oxygen content increases with the temperature of the heat-treatment as a consequence of the increase of the silica-based oxides content. These crystalline phases filled or healed the surface cracks after heat-treatment in air. Analogous mechanism was proposed by Kim et al.[9] in liquid-phase sintered silicon carbide (LPS-SiC) where crack healing also made it possible to recover the strength of different LPS-SiC ceramics treated at different temperature.

In the case of the SiC–AlN composites, results of the bending strength of pre-cracked specimens with or without crack healing as a function of surface length of pre-cracks are reported in Fig. 5. In this graph the open circle and solid circle indicate smooth specimens without or with heat-treatment at 1300 °C for 1 h in air.

The open triangles indicate the pre-cracked specimens and it is clearly shown that, as the surface length of the pre-crack increased, the bending strength decreased.
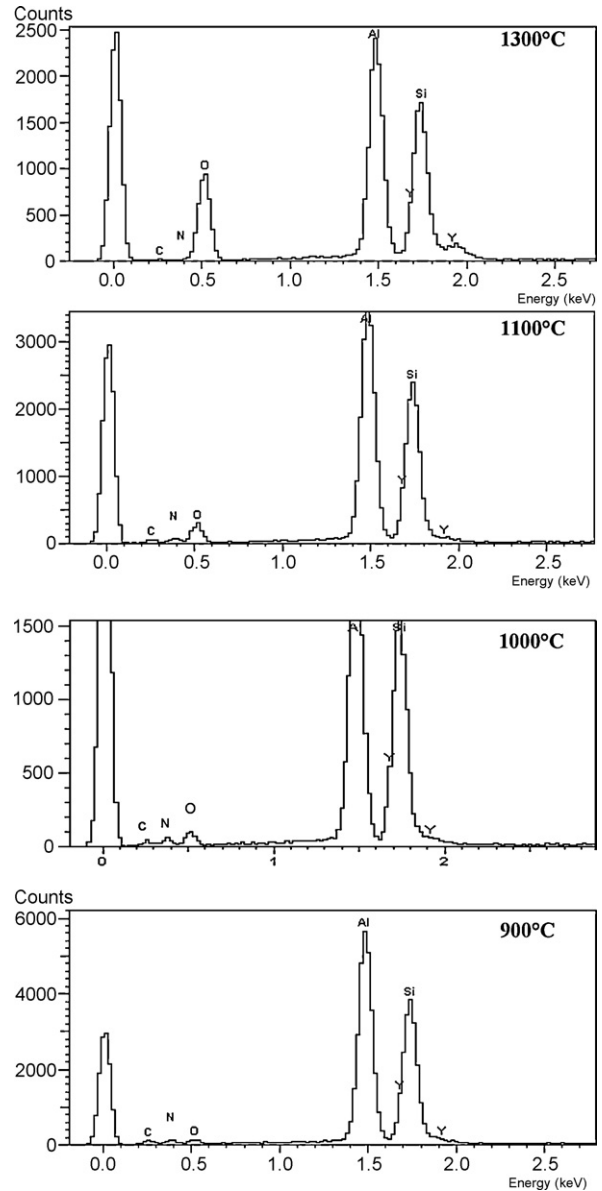


Fig. 3. XRD patterns of the as-sintered and healed (1300 °C, 1 h) SiC–AlN specimens.

The solid triangles indicate the bending strength of crack-healed specimens. The specimens subjected to crack healing at 1300 °C showed an increase of the bending strength. The experimental results indicated that large cracks up to about 300 μm could be completely healed at 1300 °C. In fact, the cracks of this length are completely closed at this temperature (Fig. 2) and the increased strength was due to a substantial increase in the bonding force acting across the crack surfaces as a consequence of the formation of the oxidation products. This result represents a substantial improvement of the crack-healing behaviour of silicon carbide-based materials since a previous study of solid-state sintered SiC demonstrated that the complete recovery of strength at room temperature was possible with a crack size of only 200 μm.[4] Furthermore, the dashed line reported in Fig. 5 demonstrates that the bending strength values obtained with the
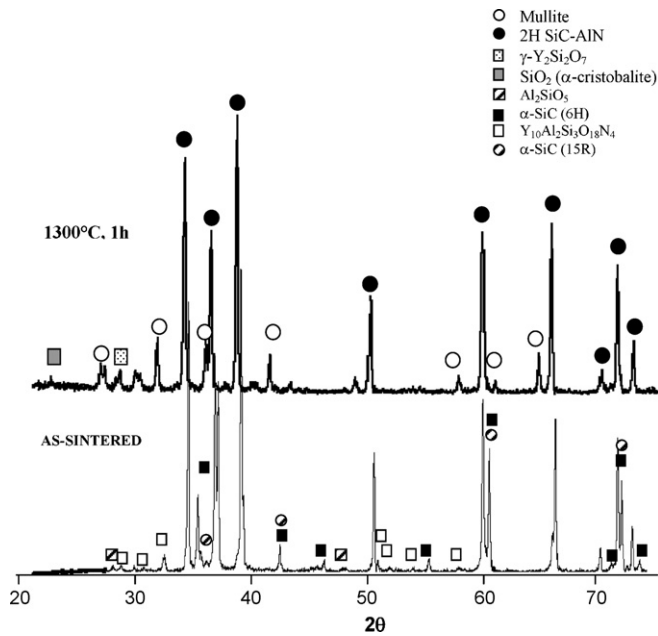
Fig. 4. EDS spectra acquired on the surface of SiC–AlN ceramics after heat-treatments in the temperature range 900–1300 °C.



Fig. 6. Effects of healing temperature on the bending strength of crack-healed specimens with a pre-crack length of 100 μm (healing condition: 1 h in air).

pre-cracked samples obey to the Griffith model:

$$\sigma_B = \frac{K_{IC}}{F\sqrt{\pi a}} \qquad (4)$$

where $\sigma_B$ is the bending strength, $K_{IC}$ is the fracture toughness (3.5 MPa m$^{0.5}$ determined by indentation fracture method), $F$ is the geometry factor (0.69 for semi-elliptical surface crack with aspect ratio $a/c = 0.9$)[10] and $a$ is the half length of the surface crack.

Fig. 6 shows the effect of healing temperature on the bending strength of the crack-healed specimens at room temperature.

The average bending strength of heat-treated smooth specimen (solid circles) is about 750 MPa. The fracture strength $\sigma_B$ of the pre-cracked specimens with $2c = 100$ μm (open triangles) is 270 MPa, which is a 36% reduction from $\sigma_B$ of the heat-treated smooth specimens. The solid triangles indicate the $\sigma_B$ of crack-healed specimens. The average values of $\sigma_B$ for the specimen crack healed at 1100 and 1300 °C are 682 and 637 MPa, respectively. These bending strengths are close to that of the heat-treated smooth specimens (750 MPa). Thus, the surface cracks with $2c = 100$ μm can be healed at 1100 or 1300 °C for 1 h in air. However, the value of $\sigma_B$ for the specimens crack healed below 1000 °C is lower than that of the heat-treated smooth specimens.

## 4. Conclusion

The crack-healing behaviour of pressureless-sintered SiC–AlN composite was characterised. This material with surface cracks ≤300 μm recovered its strength fully at room temperature by thermal treatment in air at temperature higher than 1100 °C. Crack closure and rebonding of crack walls due to oxidation of cracked surfaces is suggested as a dominant healing mechanism in SiC–AlN ceramics. Mullite and α-cristobalite are the main oxidation products and their content increase with the temperature of the heat-treatment.
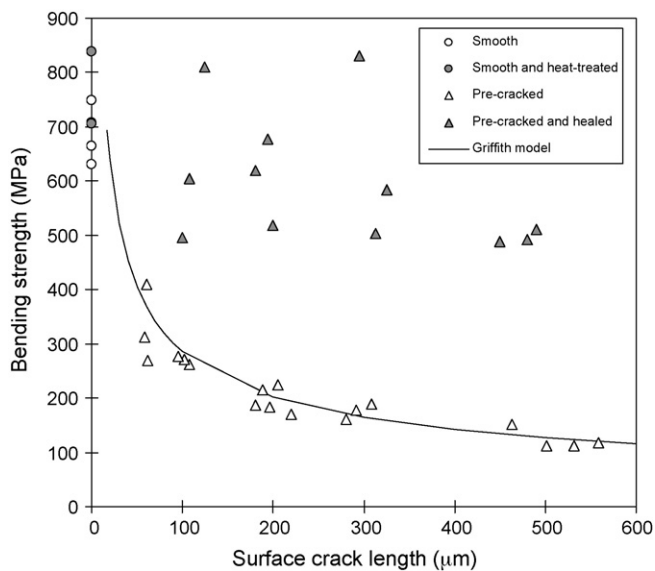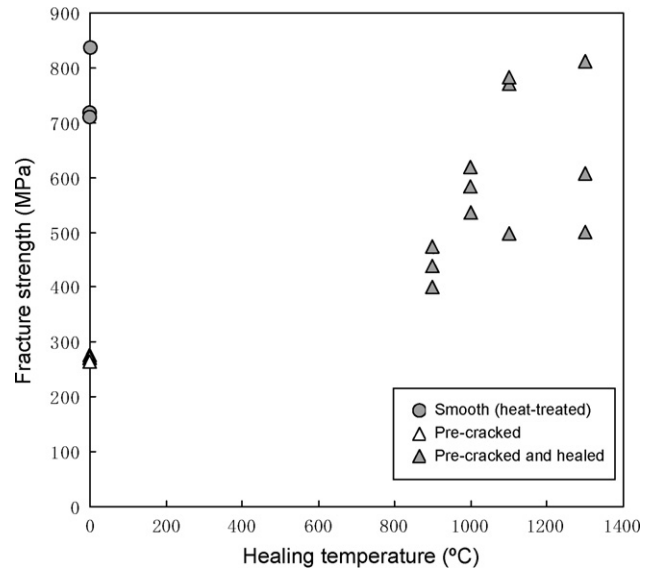


Fig. 5. Bending strength of pre-cracked specimens with or without crack healing as a function of surface length of pre-cracks (healing condition: 1300 °C, 1 h in air).

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