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Crack-healing behavior of CVD grown silicon carbide

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CVD grown silicon carbide is ideal performance material for silicon wafer processing. It outperforms conventional forms of silicon carbide, as well as other ceramics, quartz, and metals. The combination of excellent thermal, electrical, and chemical properties makes this material well-suited to applications for RTP, epi, etch, implant, and across various industries where a high performance material requires. CVD SiC ceramics are brittle and sensitive to flaws. As a result, the structural integrity of ceramic component may be seriously affected. Crack- healing ability of CVD SiC ceramics is a very useful technology for higher structural integrity and for reducing the machining and non-destructive inspection costs. This study focuses on CVD SiC ceramic performance and its crack-healing behaviors were investigated as a function of crack-healing temperature, time, size, and temperature dependence of the resultant bending strength. Three-point bending specimens were made and a semi-elliptical crack was introduced on the specimen by a Vickers indenter. Pre-cracked specimens were healed at various temperature conditions. The main conclusions were: (1) CVD grown SiC has cubic β, structure, it offers isotropic characteristics. (2) Optimized crack-healing condition is; temperature: 1500 °C, 1 hr in air. (3) The bending strength is increased as testing temperature increased, means the material can be safely used up to a temperature of 1500 °C with a good retention of thermal and mechanical properties.

Key words: Crack-healing, Silicon carbide, CVD, Mechanical properties.

Introducton

Silicon Carbide material has been developed into a high quality technical grade ceramic with very good mechanical properties; high hardness, high elastic modules, and good thermal properties; low thermal expansion, excellent thermal shock resistance, and superior chemical inertness. Silicon carbide is formed in several ways, reaction bonding, sintering, and CVD. Each forming method greatly affects the end microstructure. Reaction bonded SiC is made by infiltrating compacts made of mixtures of SiC and carbon with liquid silicon. The silicon reacts with the carbon forming more SiC which bonds the initial SiC particles. Sintered SiC is produced from pure SiC powder with non-oxide sintering aids. Conventional ceramic forming processes are used and the material is sintered in an inert atmosphere at temperatures up to 2000 °C or higher. Chemical vapor deposition (CVD) silicon carbide that is superior to any silicon carbide. The table 1 shows the comparison of each forming method. The material can also be made an electrical conductor and has applications in resistance heating and electronic components for semiconductor process equipment.

The demand is for the highest structural integrity, CVD grown silicon carbide is ideal performance material for silicon wafer processing. It outperforms conventional forms of silicon carbide, as well as other ceramics, quartz, and metals. To grow high density and polycrystalline silicon carbide, CVD process is applied as accumulated thin solid film from the gaseous phase by a chemical reaction. The grown CVD SiC has a beta phase 3C polycrystalline structure. A critical crack diameter of CVD SiC is about 20-50 μm, the strength is reduced to about 50% by this crack, thus it is almost impossible to detect nondestructive inspection of the crack with high reliability. Crack- healing ability of CVD SiC ceramics is a very useful technology for higher structural integrity and for reducing the machining and non-destructive inspection costs. It is well known that

Table 1. Silicon Carbide Property by forming method.

	CVD SiC	Hot pressed SiC	Reaction bonded SiC	Sintered SiC
Purity	99.999%+	97-99.9%+	99%+	99
Density (g/cm^3)	3.21	3.15-3.20	3.00-3.15	3.15
Porosity	negligible	< 1%	< 1%	1-2%
Thermal Conductivity (W/m.K)	250-300	100-180	100-150	100-140
Flexural Strength (Mpa)	590	440	150	350
Elastic Modulus (10^6 psi)	65	65	65	60

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sintered SiC exhibits a very interesting crack-healing ability [1-6]. However, bulk grown SiC by CVD has not been discussed about the crack healing behavior as a function of crack-healing temperature, time and crack size. The CVD SiC and sintered SiC were compared side by side in terms of crack healing behavior. If a CVD SiC were able to exhibit high crack-healing ability similar to the silicon nitride [7], mullite [8] and alumina [9] with very high crack-healing ability, it would be very desirable for structural integrity.

Experimental

CVD is controlled by two basic process; mass transfer, and surface reaction [10]. These two processes can be broken down into a sequence of five steps. The reactant gas molecules or precursors, diluted in a carrier gas, are introduced into the reaction chamber, where: (1) The gases diffuse through a boundary layer to the surface, (2) the reactants adsorb to the surface, (3) a chemical reaction takes place, resulting in deposition, (4) the adsorbed species are desorbed, and (5) the by-products of the reaction are diffused out [11]. Hydrogen is used as a carrier gas of the precursor, methyltrichlorosilane (MTS) which contains silicon and carbon participates in the CVD reaction. The schematic of chemical vapor systems is shown in Fig. 1, which is used in the bulk growth of SiC. The temperature uniformity at the hot zone is very important to increase the yield and productivity of the SiC CVD products because the deposition rate usually follows the Arrhenius equation. The phases and morphologies deposited on the substrate are also dependent on the temperature and the gas flow near the substrates [12]. Phase analysis is executed by using XRD peak for both CVD and Sintered SiC in Fig. 2, CVD grown SiC has a beta phase polycrystalline structure and sintered SiC has alpha phase that used alpha phase powder. In an inert environment, SiC

$$Si(CH_3)Cl_{3(g)} \rightarrow SiC_{(s)} + 3HCl_{(g)}$$

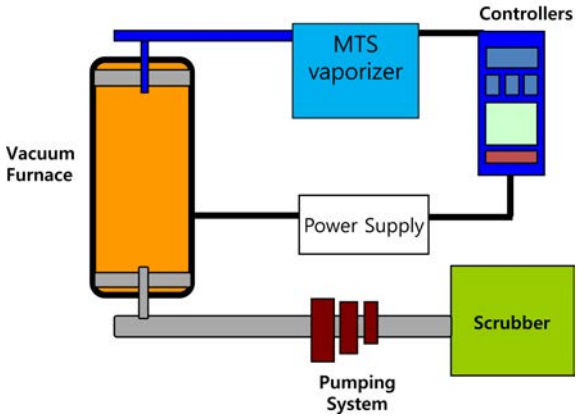


Fig. 1. Schematic of chemical vapor systems for SiC growth.

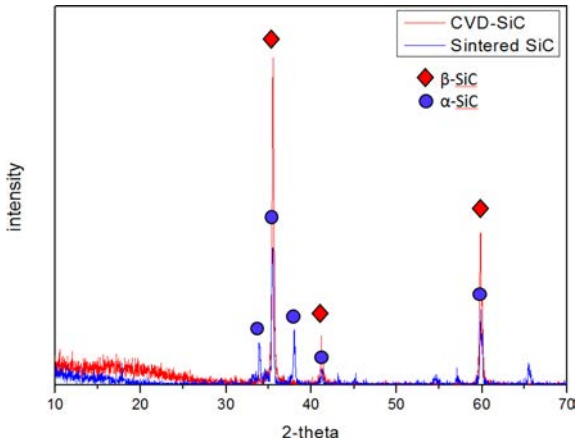
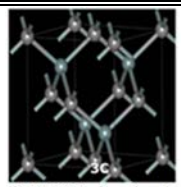


Fig. 2. Phase analysis by using XRD Peak of CVD & Sintered SiC.

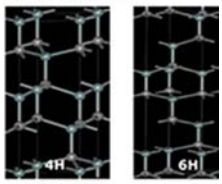
material can be used up to a temperature of 1700 ºC without phase change. Above 1800 ºC there is an onset of phase change from cubic β-phase to hexagonal β-phase in Table 2. To analyze the particle direction and size, XRD, Ramen, and EBSD (electron back-scattered

Table 2. Silicon Carbide Structure.

	3C	4H	6H
Crystal Structure	Cubic	Hexagonal	Hexagonal
Lattice Constant(A)	4.3596	3.0730 10.053	3.0730 15.11
Density (g/cm^3)	3.21	3.21	3.21
Bandgap (eV)	2.36	3.23	3.05
T.C. (W/cm · K)	3.6	3.7	4.9



β-SiC (3C) forming below 1,700℃
Cubic Structure



α-SiC (6H) forming over 1
Hexagonal Structure

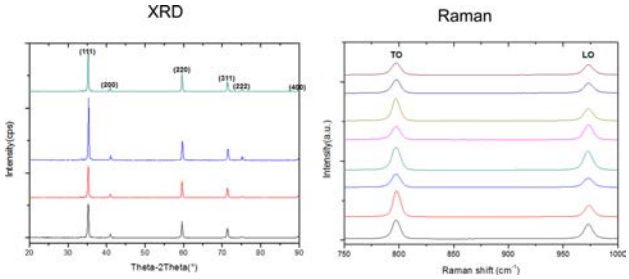


Fig. 3. Structure Analysis of CVD SiC: XRD, Raman.

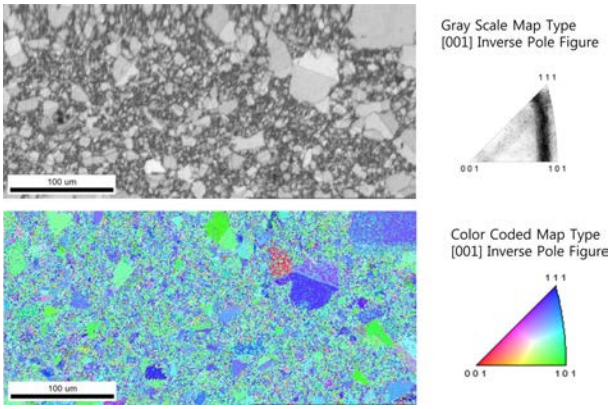


Fig. 4. Structure Analysis of CVD SiC: EBSD (Electron Back-Scattered Diffraction).

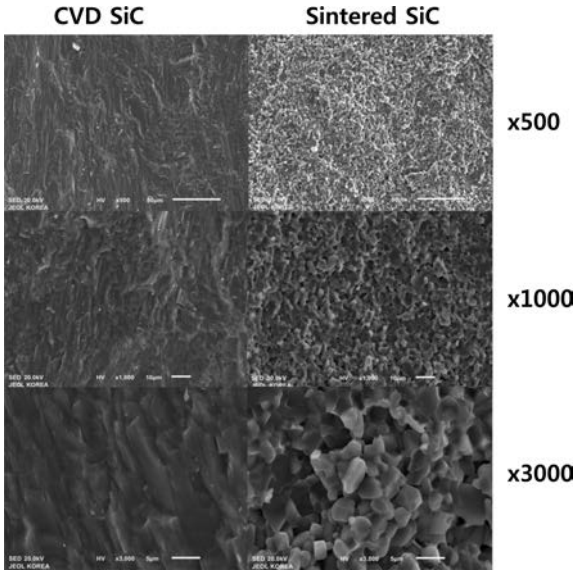


Fig. 5. SEM images of Fractured Surface in CVD & Sintered SiC.

diffraction) is taken in Fig. 3 and Fig. 4. The grown CVD SiC has 3C polycrystalline with mainly (111) direction and mixtures of (222), (101), (110). The particle and crystalline size has a big variations depends on the directions. SEM images of fractured surface in CVD and Sintered SiC has shown big differences in Fig. 5, which decide the mechanical strength and crack healing behavior. CVD grown structure has dense and columnar jointing such as spectacular volcanic rock formation, on the other hand, Sintered structure could

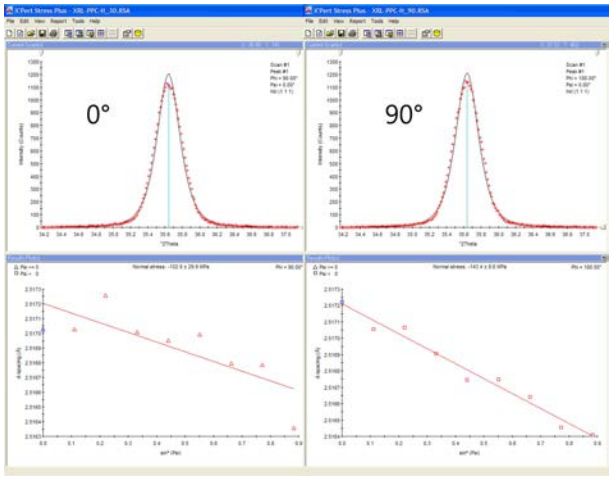


Fig. 6. Residual stress measurement by HR XRD.

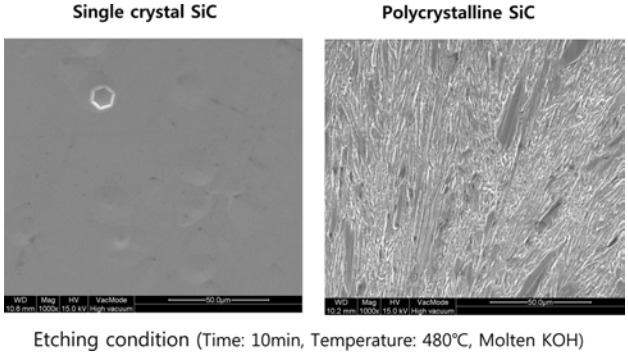


Fig. 7. Single crystal and Polycrystalline Structure by Etching.

find granule shape jointing and less dense with pore contained. The d value in Bragg's law ($n \cdot \lambda = 2d \cdot \sin\theta$) is decreasing in Fig. 6, which means CVD grown SiC structure implied tensile force. The residual stress also could be a factor because it needs to release to improve mechanical strength and crack healing behavior. To compare apparently the poly and single structure, both SiC specimens etch with KOH acid, 10 min, at temperature 480. The solution is typically used to find the single crystal structure defect such as micro pipe, crystal mismatch and structure dislocation. In Fig. 7, the single SiC shows clean and smooth, however, the poly SiC disclose columnar jointing structure which are shown previously in Fig. 5.

Results and Discussion

Pre-crack generation & bending strength

A semi-elliptical surface crack was made at the center of the tensile surface of the test specimen using a Vickers indenter at a load of 4.9-490N. A micrograph of crack profile observed by scanning electron microscopy (SEM) is shown in Fig. 8 [13]. By this method, semi-elliptical cracks of 25-350ìm in surface crack length were made as shown in the standard surface crack used for evaluating the basic crack-healing behavior. The specimens used in this paper were made according to 3

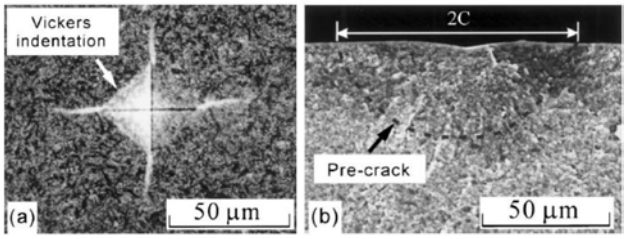


Fig. 8. SEM micrographs of (a) indentation crack and (b) fracture surface.

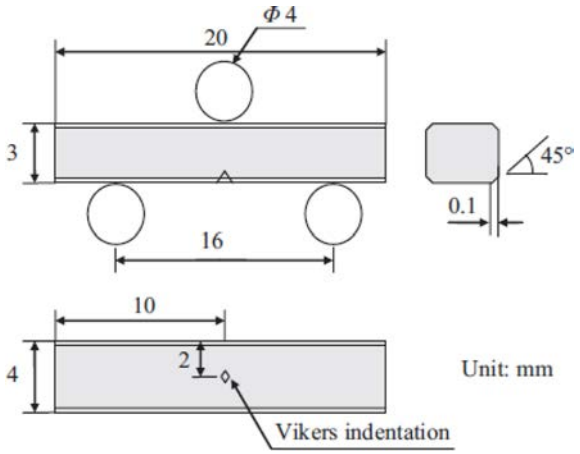


Fig. 9. Three point bending specimens and test.

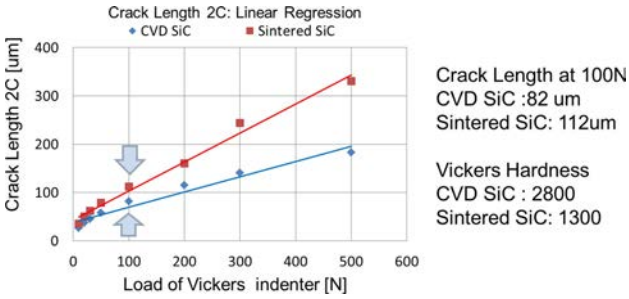


Fig. 10. Indicative dimensions of the crack caused by application of different load during Vickers indentation.

point bending method that is shown in Fig. 9.

CVD SiC material has higher Vickers hardness than sintered SiC, each shown 2800 and 1300. The crack length has linearity according to load of Vickers indenter. The crack length at 100N, CVD has 82 μm and sintered has 112 μm in Fig. 10. The bending strength as received has difference between CVD and sintered, 505 Mpa and 354 Mpa each. Also, as cracked have difference, 255 Mpa and 206 Mpa in Fig. 11. The sintered has higher strength drop and higher standard deviation among the samples, which means CVD SiC is denser and less pore contributing higher mechanical structure property. The CVD SiC has good linearity in terms of crack size up to 180 μm and bending strength down to 185 Mpa in Fig. 12. The bending strength has a tendency to increase as test temperature going up in Fig. 13, which means CVD SiC material flexibility or cracking curing by the test temperature.

Average (unit:Mpa)	CVD SiC	Sintered SiC
as received	505	354
as cracked	255	206
Standard Deviation	7.37	21.75
Strength Drop	51%	58%

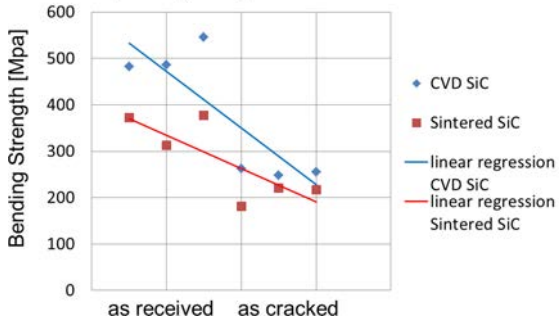
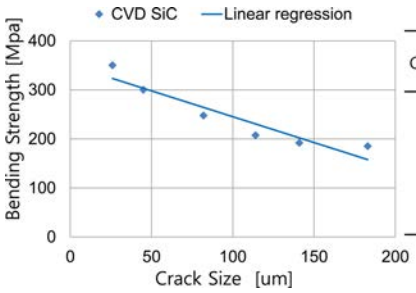
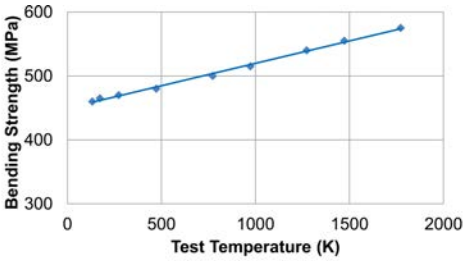


Fig. 11. Bending strength of as received and as cracked specimens between CVD SiC and Sintered SiC.



CVD SiC	
Crack size (um)	Bending Strength (Mpa)
0	505
26	350
45	300
82	248
114	207
141	192
183	185

Fig. 12. CVD SiC Bending strength as of cracked size.



Temperature (K)	133	173	273	473	773	973	1273	1473	1773
4-pt Bending Strength(Mpa)	460	465	470	480	500	515	540	555	575

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Fig. 13. Temperature dependency on the Bending Strength of CVD SiC.

Healing conditions and results

Cracks occur by the usual machining process (grinding, polish, etc.), lowering the reliability. In order to prevent this, precise polishing is required in the final stage, which is time-consuming, and there are also problems with fabrication efficiency and fabrication cost. Crack sizes of about 10 ~ 30 μm in depth affect the reliability. The non-destructive inspection technology for detecting cracks of 10 ~ 30 μm is underdeveloped. Therefore, the reliability of major parts is low. There is a possibility that a crack will occur in the components while they are being used at higher temperatures, by whatever cause. When a crack occurs, the reliability is

Table 3. Crack healing behavior between CVD SiC and Sintered SiC.

Average value (unit:Mpa)	CVD SiC	Sintered SiC
as received	505	354
as cracked	255	206
crack healed at 1100 ºC	562	416
crack healed at 1300 ºC	941	470
crack healed at 1500 ºC	1180	596
recovery at 1100 ºC	111%	118%
recovery at 1300 ºC	186%	133%
recovery at 1500 ºC	234%	168%

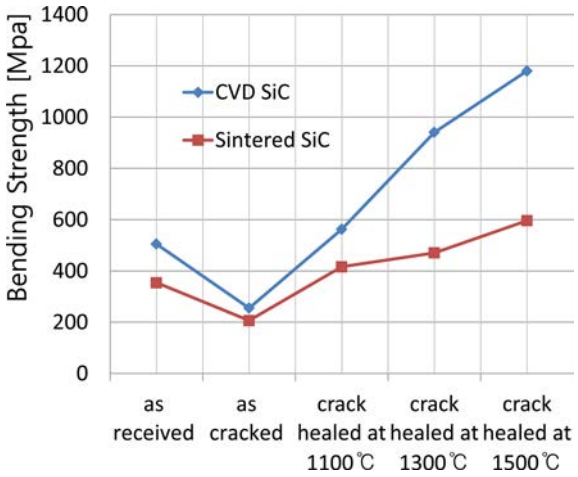

Fig. 14. Crack healing behavior between CVD SiC and Sintered SiC.

greatly lowered.

There are several ways of resolving crack problem in industrial world. First, improving the fracture toughness of the material by means as microstructure control, second, conduct a nondestructive inspection before use and detect and repair any dangerous cracks found, third, conduct a proof test to prevent use of a low reliability member. The most effective and less cost way is inducing a self-crack-healing ability, so that all dangers cracks can be healed.

The cracking healing behavior measured by the bending strength by mainly applying temperature and it holding time. It is not detectable the healing effect lower than 1100 ºC, but bending strenth remarkably improved as healing temperature increase. The 1100 ºC is a kind of threshhold temperature of crack healing in SiC material. The crack healing at 1100 ºC looks similiar between CVD and Sintered material, recovery rate 111% and 118% each in Table 3. Because crack is healed but recovered only as received, even healing time increase up to 5-10x does not much impact healing behavior. However, both bending strength dramatically changes at 1300 ºC and 1500 ºC in Fig. 14. The recovery rate shows different between CVD and Sintered, 186% at 1300 ºC and 234% at 1500 ºC in CVD, and 133% at 1300 ºC and 168% at 1500 ºC in Sintered. The CVD shows good crack healing behavior

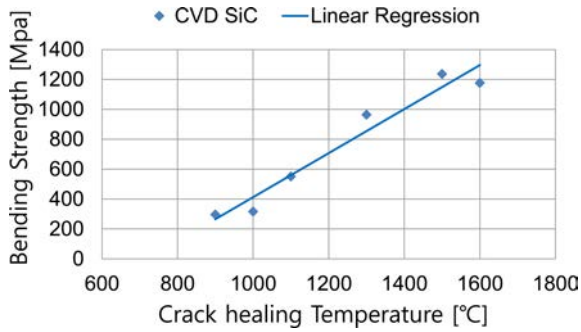

Fig. 15. Temperature dependency of Crack healing strength.

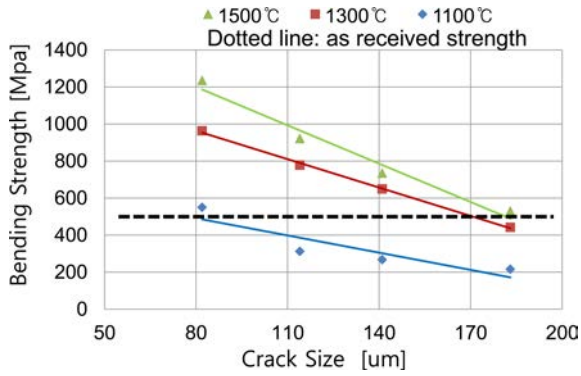

Fig. 16. Crack size dependency of Crack healing strength.

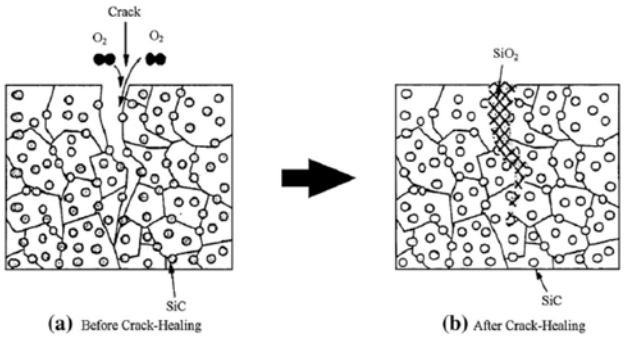

Fig. 17. Crack healing mechanism.

over Sintered material. The temperature dependency has good linearity for 3 hours crack healing at each temperature in Fig. 15, which means controllable and reproducible. The crack size also a factor of healing behavior. As increase of crack size, healing strength is getting less. Healable crack size is up to 170 μm, temperature should over 1300 ºC in Fig. 16. In an industrial process, it is detectable over 100 μm with visual inspection. Optimized crack-healing condition is 1500 ºC, 1 hr in air.

Crack healing mechanism and observation

The crack healing of ceramics developed by the authors is caused by the following oxidation reaction of SiC [14-16].

$$SiC + 2O_2 = SiO_2 + CO_2\ (CO) + 943\ kJ \quad (1)$$

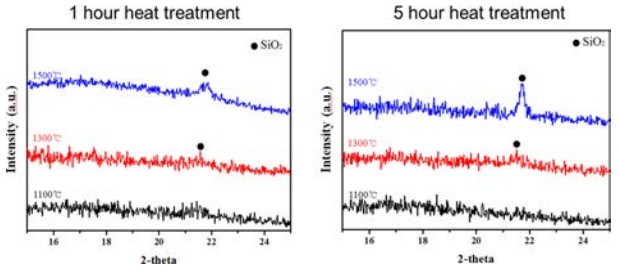

Fig. 18. X-ray diffraction from crack healed sample surface.

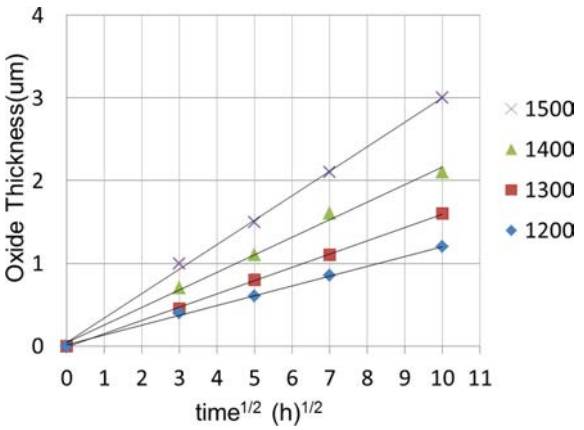

Fig. 19. Oxidation kinetics of CVD SiC in 1 atm oxygen.

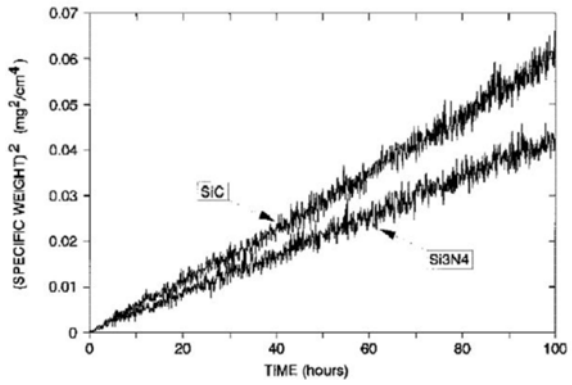

Fig. 20. Oxidation kinetics of CVD SiC and CVD Si_3N_4 determined via thermogravimetric analysis at 1400 °C in dry.

A schematic diagram of the crack healing mechanism is shown in Fig. 17 [17]. To recover completely healing of crack, the bending strength of the crack-healing substance must be equivalent to or higher than that of the matrix. The volume between the crack walls must be completely filled with the products formed by the crack-healing reaction and the crack healing substance must be strongly bonded to a matrix.

There is a glass phase and a crystalline phase in SiO_2. If the crack-healing material was crystal SiO_2, then the crack-healed sample would exhibit high bending strength even at an elevated temperature. However, if the crack-healing material was glassy SiO_2, then the crack-healed sample would exhibit low bending strength at an elevated temperature. A key point of crack-healing technology is how many crystalline phases are deposited in a crack healing substance [1, 18].

Table 4. Oxidation Behavior of Chemically-Vapor-Deposited Silicon Carbide from 1200 °C to 1600 °C.

Average Measured Silica Thickness on Silicon Carbide After 100 h Flowing Oxygen, and Calculated Recession		
Samle temperature (°C)	Silica thickness (μm)	Substrate recession (μm)
1200	1.5	0.7
1300	2.6	1.3
1400	4.0	1.9
1500	5.7	2.8
1550	6.6	3.2

To find the crystal SiO_2 substance, X-ray differaction is used in different crack healing condition. As shown in the healing conditions and resluts, it is clear to have SiO_2 peak at 1300 °C and 1500 °C in Fig. 18 regardless of heat treatment time. By scanning electron microscopy (SEM), the oxide thicknesses were measured at 1 to 8 locations around the fracture surface at chosen time intervals (5, 10, 25, 50, 75, and 100 hrs) in Fig. 19. The oxidation is a fucnction of temperature and time, activation energy for SiC oxidation which is thought to indicate a change in the rate-controlling mechanism, from interstitial permeation of oxygen molecules to network diffusion of oxygen ions [19]. By using thermogravimetric analysis, oxidation kinetics of CVD SiC and CVD Si3N4 determined at 1400 °C in dry was ovserved in Fig. 20. Oxidation protection provided by silica for pure SiC is adequate for long service times under isothermal conditions and 1 atm of dry oxygen at temperatures at or below 1550 °C in Table 4, the 1600 °C exposures resulted in oxide spallation for SiC [20].

Conclusions

CVD SiC ceramics are brittle and sensitive to flaws. As a result, the structural integrity of ceramic component may be seriously affected. Crack-healing ability of CVD SiC ceramics is a very useful technology for higher structural integrity and for reducing the machining and non-destructive inspection costs. The main conclusions were: (1) CVD grown SiC has cubic β, structure, it offers isotropic characteristics. (2) Optimized crack-healing condition is; temperature: 1500 °C, 1 hr in air. (3) The bending strength is increased as testing temperature increased, means the material can be safely used up to a temperature of 1500 °C with a good retention of thermal and mechanical properties.

Acknowlegments

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