Journal of Ceramic Processing Research. Vol. 15, No. 6, pp. 451~456 (2014)

J O U R N A L O F
Ceramic Processing Research

Characteristics of corrosion and strength of crack-healed sic ceramics

Seok Hwan Ahn[a], Jin Ryang Hwang[b] and Ki Woo Nam[c]*

[a]*Dept. of Mechatronics, Jungwon University, Goesan-gun, Chungbuk, 367-805, South Korea*
[b]*MR Interdisciplinary Program of Mechanical Engineering, Graduate School, Pukyong National University, Busan, South Korea*
[c]*Dept. of Materials Science and Engineering, Pukyong National University, 365 Sinseonro, Nam-gu, Busan, 608-739, South Korea*

The crack-healing behavior and corrosion resistance of SiC ceramics were investigated. Heat treatment was carried out from 1173 K to 1573 K. The corrosion test of SiC was carried out in acid solution and alkaline solution under KSL1607. Results showed that heat treatment in air could significantly increase the strength. 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 had one hour at an atmospheric level of 1373 K. In the two kinds of solution, the cracks of cracked specimen were dimmed with increasing time, and the surface of the crack healed specimen showed increased black and white spots. The strength of the corroded cracked specimen was similar to that of the cracked specimen. The strength of the corroded crack healed specimen decreased 47 and 75% over that of the crack healed specimen in acid and alkaline solution, respectively. Therefore, the corrosion of SiC ceramics is faster in alkaline solution, than in acid solution.

Key words: Crack-healing, Corrosion, Strength of corroded specimen, Alkaline solution, Acid solution.

Introduction

Silicon carbide (SiC) ceramics find extensive application in several fields of engineering as materials for advanced energy systems, such as high performance combustion systems, fuel-flexible gasification systems, fuel cell/turbine hybrid systems, nuclear fusion reactors and high temperature gas-cooled fission reactors [1-3]. Many studies have been reported in the field of general industry and the nuclear industry, because Silicon carbide composite shows excellent performance as a structural material [4]. It has also been reported that the cracks formed by machining were healed completely [5]. In particular, some results suggest that the cracks in silicon carbide, once healed, surprisingly become even stronger than the original silicon carbide [6]. They conclude from the crack length that it was an important factor of crack-healing by an oxidation product in silicon carbide. From this perspective, researchers are actively doing research into the self-healing ability of structural ceramics, which has a leading role in the world [7]. Structural ceramics with self crack healing ability have superior mechanical properties over the base material [8-11]. Silicon carbide ceramics are being considered in order to apply a blanket to fusion processes [12, 13], as metal can't be applied, because of the strong corrosive effects of plasma. So, there are a few studies on the corrosion resistance and chemical resistance of ceramics [14, 15]. However, study on the corrosion resistance of crack healed specimens is nowhere to be found.

In this paper, three types of SiC specimens, smooth specimen, cracked specimen and crack healed specimen were prepared. We identified the crack-healing condition for optimum strength, and evaluated the corrosion characteristics in acid solution and alkaline solution.

Materials and Test Methods

Commercially available SiC (Ultrafine grade, Ibiden Co., Japan), Al_2O_3 (AKP-700, Sumitomo Chemical Co. Ltd., Japan), Y_2O_3 (CI Chemical Co., Japan), Y_2O_3 (CI Chemical Co., Japan), and SiO_2 (CI Chemical Co., Japan and Prepoll Co., Korea) were used as the starting materials. The mean particle sizes of the SiC, Al_2O_3 and Y_2O_3 powders were 0.27 m, 0.1 m and 31 nm, respectively. The mixtures were milled in isopropanol for 24 hours using Si3N4 ball (φ5). The mixtures were placed in a 363 K furnace to extract solvent, and to make a dry powder mixture. The dry powder was then passed through a 106 m sieve. The mixtures were subsequently hot-pressed in N_2 gas for one hour via hot-pressing, conducted under 35 MPa at 2053 K.

The hot-pressed materials were also machined to produce bar specimens ($3 \times 4 \times 18$ mm that were polished and beveled, to reduce the likelihood of edge-initiated failures. The specimens (span length: 16 mm) were made of JIS standards. For strength testing, a Vickers indentation was made in the center of the polished face of the bar specimen at a load of 29.4 N in air. This loading introduced a semicircular crack (2c) of 125 m in diameter.

*Corresponding author:
Tel : +82-51-629-6358
Fax: +82-51-629-6353
E-mail: namkw@pknu.ac.kr

The condition of crack-healing has a large effect on fracture strength. The crack-healing time in air was one hour, at various temperatures ranging from 1173 K to 1573 K. Cooling was spontaneous in the furnace. The crack-healed specimens were subsequently tested in three-point bending at a crosshead speed of 0.5 mm/min, using a fixture with a span of 16 mm.

Corrosion experiments were conducted by the acid and alkali corrosion test method of fine ceramics under KS standard KSL1607. The solutions are H_2SO_4 3 mol/L and NaOH 5 mol/L. The crack for the corrosion test was made in the center of the specimen by a load of 24.5 N. Hereinafter, the smooth specimen with crack is called a cracked specimen, and the cracked specimen with crack healing at 1373 K during 1 hour is called a crack healed specimen. The two types of specimen were cleaned by ultrasound, and an immersion test was carried out at room temperature for 400 hours in solution, after drying in constant temperature drier of 383 K.

After testing, the surfaces of all specimens were inspected by optical microscope and Scanning electron microscopy (SEM). The component analysis of surface used was the EDX (Energy dispersed X-ray).

Test Results and Discussion

Bending strength at room temperature

Fig. 1 shows the effect of the crack-healing temperature on bending strength at room temperature. This figure is quoted from the reference [9]. The symbols (□, ▽, and ○) show the bending strength of the smooth specimen, cracked specimen, heat treated smooth specimen and crack healed specimen, respectively. The average strengths of the smooth specimen and crack healed specimen were found to be 674 and 337 MPa, respectively. The strengths of the cracked specimens with a crack dimension of 2c ≒ 125 m were lower than half of the smooth strength.

Each material generally has an optimum crack healing temperature, at which the maximum strength has been obtained. After healing from 1173 K to 1573 K, not only had the cracked specimens recovered to a strength similar to that of the smooth specimens, but in most cases had actually surpassed it. Based on the room temperature strength and smooth heat treated strength, the optimum healing temperature of cracked specimens was found to be 1373 K for all specimens. The crack healed specimen showed very good strength properties as 86%, compared to the smooth specimen strength. The symbol (*) indicates a specimen that fractured outside the crack healed zone, as shown in Fig. 1. It is known that in crack healing, the crack is healed by oxidation by the supply of oxygen. Therefore, if a crack of 125 m was healed at optimum temperature and time, it is considered that the crack was healed completely by oxygen penetration to the crack inside.

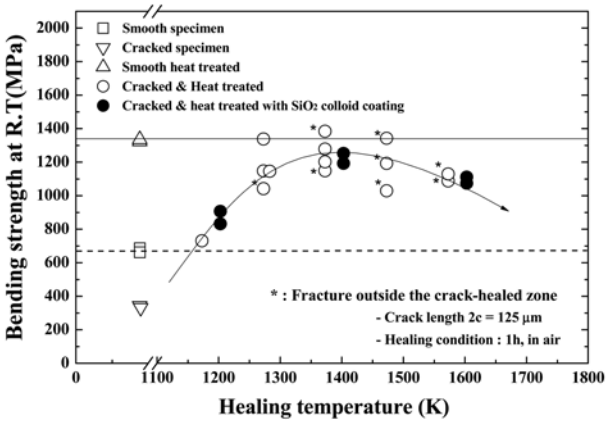

Fig. 1. Effect of healing temperature on the strength of crack-healed specimen.

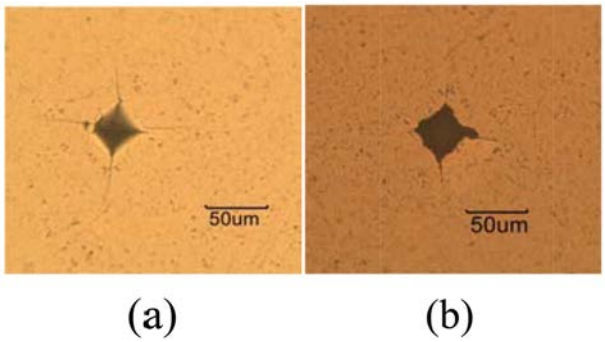

Fig. 2. Appearance of optical microscope. (a) Cracked specimen, (b) Cracked specimen of 400 hour in acid solution.

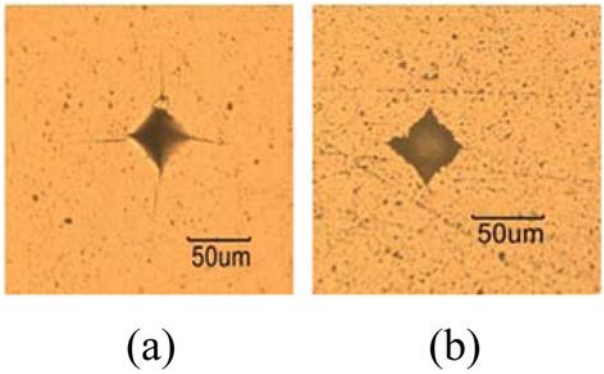

Fig. 3. Appearance of optical microscope. (a) Cracked specimen, (b) Cracked specimen of 400 hour in alkaline solution.

Corrosion characteristics

Figs. 2 and 3 are observations of the corrosion of the cracked specimen using an optical microscope. Figs. 2 and 3 were obtained from the acid solution and alkaline solution, respectively. Figs. 2 (a) and 3 (a) show the cracked specimen. Figs. 2 (b) and 3 (b) show the cracked specimen of acid and alkaline solution of 400 hours. The cracks can only dimly be seen in a corrosive environment of 400 hours, regardless of the

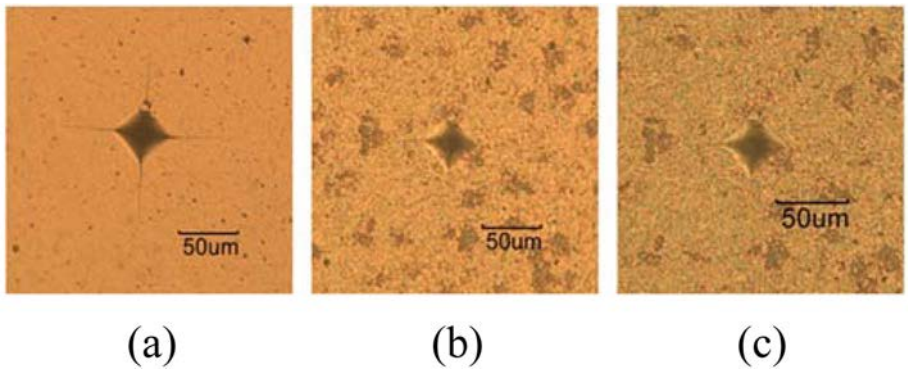

Fig. 4. Appearance of optical microscope. (a) Cracked specimen, (b) Crack-healed specimen, (c) Crack-healed specimen of 400 hour in acid solution.

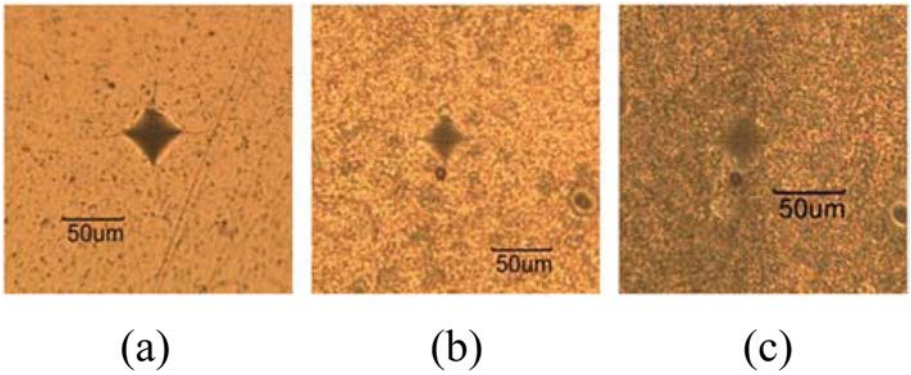

Fig. 5. Appearance of optical microscope. (a) Cracked specimen, (b) Crack-healed specimen, (c) Crack-healed specimen of 400 hour in alkaline solution.

solution. On the other hand, the indentation part was deformed in shape. It is considered that fine cracks were corroded by the disappearance of residual stress in a corrosive environment.

Figs. 4 and 5 observe the corrosion of the crack healed specimen using an optical microscope. Figs. 4 and 5 were obtained from the acid solution and alkaline solution, respectively. Figs. 4(a) and 5(a) show the cracked specimen. Figs. 4(b) and 5(b) show the crack healed specimen. Figs. 4(c) and 5(c) show the crack healed specimen of acid and alkaline solution of 400 hours. The crack healed specimen is completely healed, and cracks could not be observed. The indentation part was slightly smaller. On the other hand, the surface of the crack healed specimen was a little black in a corrosive environment of 400 hours, regardless of the solution. This is influenced by the etching solution.

Figs. 6(a), (b) and Figs. 7(a), (b) observe the corrosion of the cracked specimen of Figs. 2 and 3, respectively, using a SEM. The crack was dimmed with the passage of corrosion time , as in the observation of the microscope. The surface showed increased black and white spots. The indentation parts of (b) and (c) were pitted by corrosion.

Figs. 8(a), (b) and (c) and Figs. 9(a), (b) and (c) observe the corrosion of the crack healed specimen of Figs. 4 and 5, respectively, using a SEM. In the figures, the crack is dimly able to be observed in the crack

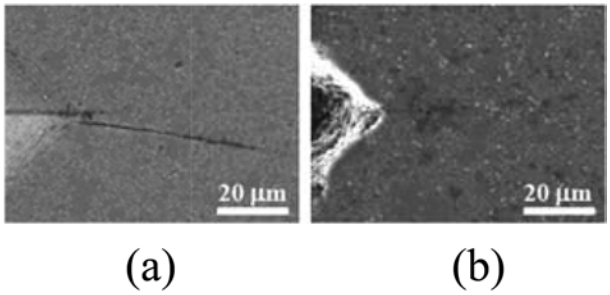

Fig. 6. Appearance of SEM. (a) Cracked specimen, (b) Cracked specimen of 400 hour in acid solution.

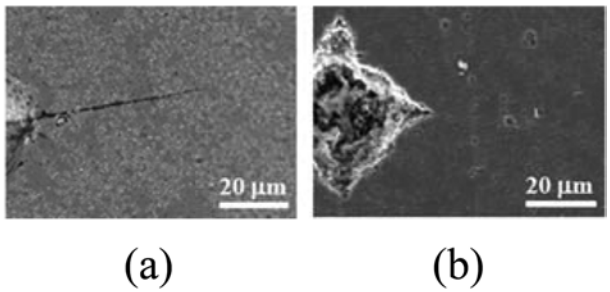

Fig. 7. Appearance of SEM. (a) Cracked specimen, (b) Cracked specimen of 400 hour in alkaline solution.

healed specimens. But, the strength of the crack healed specimen was approximately 1.86 times stronger than that of the smooth specimen. Therefore it is expected that the cracks were healed completely. The surface of

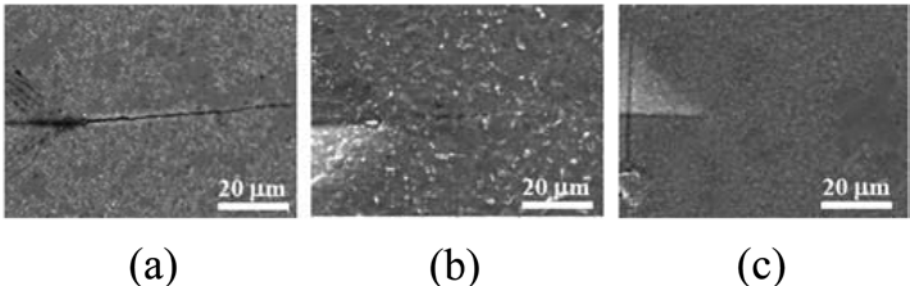

Fig. 8. Appearance of SEM. (a) Cracked specimen, (b) Crack-healed specimen, (c) Crack-healed specimen of 400 hour in acid solution.

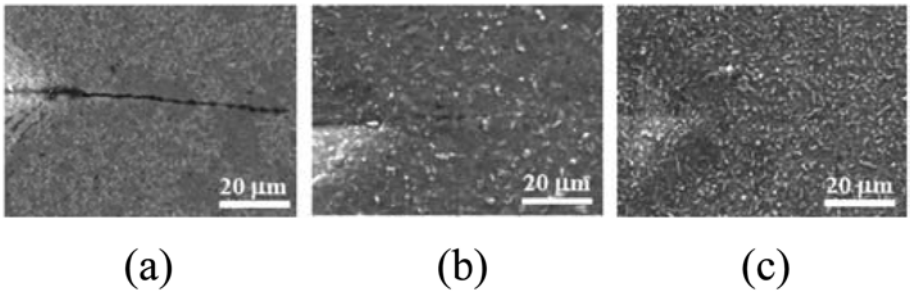

Fig. 9. Appearance of SEM. (a) Cracked specimen, (b) Crack-healed specimen, (c) Crack-healed specimen of 400 hour in alkaline solution.

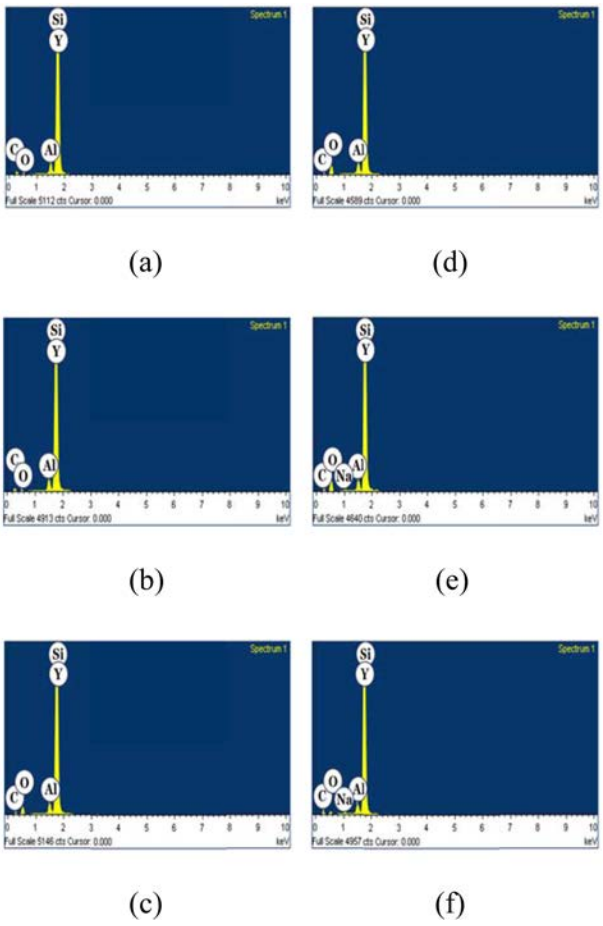

Fig. 10. Example of component analysis by EDS. (a) Cracked specimen, (b) Cracked specimen of 400 hour in acid solution, (c) Crack healed specimen, (d) Crack healed specimen of 400 hour in acid solution, (e) Cracked specimen of 400 hour in alkaline solution, (f) Crack healed specimen of 400 hour in alkaline solution.

Figure 8(c) shows a smooth appearance, unlike the appearance of (b). The surface of Figure 9(c) has many white spots, and is rough. It is considered that this is due to corrosion. In particular, there was no change in the indentation part, unlike in Figs. 6 and 7. It is considered that residual stress due to the indentation had disappeared, and the micro cracks were healed.

Fig. 10 shows the components of the surface by EDS, in order to observe the effect of corrosion on the surface. (a), (b), (c), (d), (e) and (f) show the cracked specimen, cracked specimen of 400 hour in acid solution, crack healed specimen, crack healed specimen of 400 hour in acid solution, cracked specimen of 400 hour in alkaline solution and crack healed specimen of 400 hour in alkaline solution, respectively. The components of Si, Al, C, Y and O were detected in (a), (b), (c) and (d). Na was detected in (e) and (f) of the alkaline solution (NaOH), in addition to the five components, but only five components were detected in (b) and (d) of the acid solution (H_2SO_4). In other words, the surface components show Si and C of the major component, SiC, Al and Y of the additives, Al_2O_3 and Y_2O_3, O of the crack healing material, SiO_2, and Na of the alkaline solution, NaOH. However, the S components of the acid solution, H_2SO4 did not show.

Table 1 shows the composition of the surface of the cracked specimen and crack healed specimen. The components of (a) ~ (f) are the same as described in Fig. 10. The cracked specimen (b) of acid solution showed increased O of 9% over the cracked specimen (a). In the cracked specimen (e) of alkaline solution, the O was increased by about 106%. In the crack healed specimen, the O was increased to 420%, and the C was reduced to 47% of that of the cracked specimen.

Table 1. Component analysis by EDS.

	(a)	(b)	(c)	(d)	(e)	(f)
Element	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
C	32.43	29.62	17.16	10.08	29.24	16.33
O	3.69	4.03	19.22	22.95	7.60	23.98
Na	–	–	–	–	0.82	0.22
Al	2.64	2.82	2.69	2.88	2.44	2.44
Si	56.77	58.71	57.02	60.07	55.76	52.82
Y	4.47	4.81	3.91	4.03	4.14	4.21
Totals	100.00	100.00	100.00	100.00	100.00	100.00

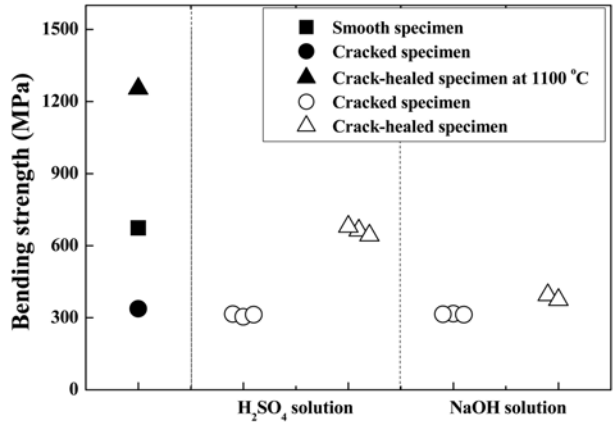

Fig. 11. Bending strength of SiC corroded in both solutions.

Here, the increase of the O components and the reduction of the C components were caused by the SiO_2 oxide that formed on the surface, and the CO emission due to heat treatment at 1373 K for 1 hour in air, respectively. The crack healed specimen (d) of acid solution showed increased O of 19%, and decreased C of 41% over the crack healed specimen (c). On the other hand, some Na was detected in the crack healed specimen (f) of alkaline solution , and the O of 25% was increased, but the C of 5% was decreased. Thus, the increase of O formed the oxide on the surface by corrosion. The increase of oxygen was greater in alkaline solution than in acid solution.

By the above-mentioned reasons, Fig. 11 shows the bending strength of specimens immersed in the acid solution (H_2SO_4) and alkaline solution (NaOH). In the figure, the black symbols (■, ●, ▲) show the average strength of the smooth specimen, cracked specimen, and crack-healed specimen for 1 hour at 1373 K, respectively. The strength of the smooth specimen showed 674 MPa. That of the cracked specimen showed half of the smooth specimen strength, at 337 MPa. But, that of the crack-healed specimen was increased by approximately 270% over that of the cracked specimen, to 1254 MPa. The strength of the cracked specimen immersed in acid and alkali solution showed 310 and 314 MPa, respectively. This was slightly lower than that of the cracked specimen. However, the crack-healed specimen immersed in the acid and alkali solution showed 661 and 384 MPa, respectively. This was a decrease of about 47 and 70% over that of the crack-healed specimen, respectively. The strength of the crack-healed specimen in acid solution was similar to that of the smooth specimen, but that of the alkaline solution was similar to that of the cracked specimen. Therefore, the corrosion of SiC ceramics is faster in alkaline solution than in acid solution [15].

Fig. 12 shows the fracture surface. (a) is the cracked specimen of as-received material, (b) and (c) are immersed in the acid solution, (d) and (e) are immersed in the alkaline solution. The cracked specimen (a) shows a semi-elliptical crack. The corroded cracked-specimen (b) and (d) showed a lot of corrosion at the part of the Vickers indentation. Corrosion was also found in the crack part. But, the corroded crack-healed specimen (c) and (e) maintained the shape of the Vickers indentation by the heat treatment.

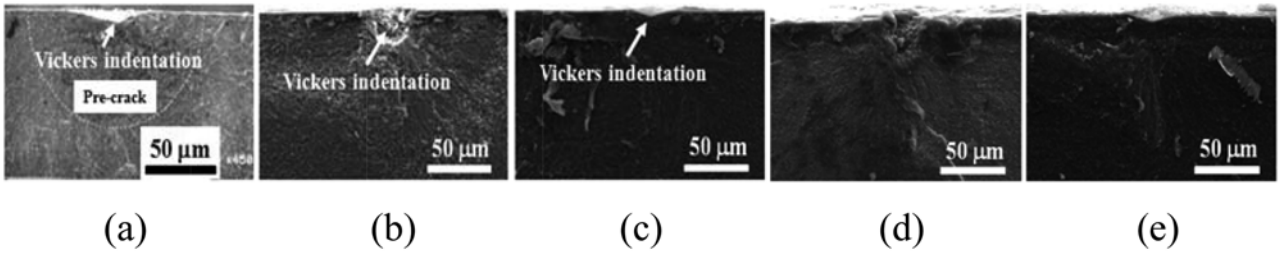

Fig. 12. SEM photograph of fracture surface. (a) Cracked, (b) Cracked in H_2SO_4, (c) Crack healed in H_2SO_4, (d) Cracked in $NaSO_4$, (e) Crack healed in $NaSO_4$.

Conclusions

This study evaluated the crack healing strength and corrosion properties of silicon carbide ceramics. The results were as follows:

(1) The optimum crack healing temperature of SiC ceramics is for one hour at 1373 K. The strength of the crack-healed specimen showed good strength of 86% over that of the smooth specimen.

(2) The cracked specimen observed by optical microscopy and SEM showed the crack was blurred according to the corrosion time, regardless of the acid and alkali solution. The crack-healed specimen had a surface of slightly black, and increased white spots.

(3) The cracked specimen of acid solution and alkaline solution showed an increase of O of 9 and 106%, respectively. The crack-healed specimen of acid solution and alkaline solution increased the O by 19% and 25%, respectively. Thus, the O component was the oxide of corrosion. The increase of O is greater in alkaline solution, than in acid solution.

(4) The strength of the corroded cracked specimen was similar to that of the cracked specimen. But, that of the corroded crack-healed specimen was decreased by 47 and 75% over that of the crack-healed specimen, respectively. Therefore, the corrosion of SiC ceramics is faster in alkaline solution, than in acid solution.

Acknowledgments

This work was supported by the Pukyong National University Research Fund in 2011(PK-2011-2-24)

References

1. Snead, L.L., Jones, R.H., Kohyama, A. and Fenici, P. “Status of silicon carbide composites for fusion”, J. Nucl. Mater., Vol 233-237 (1996) pp. 26-36.
2. Giancarli, L., Bonal, J.P., Caso, A., Marois, G. Le., Morley, N. B. and Salavy, J. F. “Design requirements for SiC : SiC composites structural material in fusion power reactor blankets”, Fusion Engineering and Design, Vol 41 (1998) pp. 165-171.
3. Raffray, A.R., Jones, R., Aeill, G., Billone, C., Giancarli, L., Golfer, H., Hasegawa, A., Katoh, Y., Kohyama, A., Nishio, S., Riccardi, B. and Tillack, M.S. “Design and material issues for high performance SiCf/SiC-based fusion power cores”, Fusion Eng. Des., Vol 55 (2001) pp. 55-95.
4. Saddow, S.E. and Agarwal, A. “Advances in Silicon Carbide Processing and Applications”, Artech House, Inc., Boston (2004).
5. Ando, K., Ikeda, T., Sato, S., Yao, F. and Kobayasi. A.“A preliminary study on crack healing behavior of Si3N4/SiC composite cermiacs”, Fatigue & Fracture of Engineering Materials & Structures, Vol 21 (1998) pp. 119-122.
6. Lee, S.K., Ishida, W., Lee, S.Y., Nam, K.W. and Ando, K. “Crack-healing behavior and resultant strength properties of silicon carbide ceramic”, Journal of the European Ceramic Society, Vol 25 (2005) pp. 569-576.
7. Takahashi, K., Uchiide, K., Kimura, Y., Nakao, W. and Ando, K. “Threshold Stress for Crack Healing of Mullite Reinforced by SiC Whiskers and SiC Particles and Resultant Fatigue Strength at the Healing Temperature”, J. Am. Ceram. Soc., Vol 90 (2007) pp. 2159-2164.
8. Nam, K.W., Lee, K.C. and Kohyama, A. “A Feasibility Study on the Application of Ultrasonic Method for Surface Crack Detection of SiC/SiC Composite Ceramics”, KSNT, Vol 29 (2009) pp. 479-484.
9. Nam, K.W. and Kim, J.S. “Critical Crack Size of Healing Possibility of SiC ceramics”, Materials Science and Engineering A, Vol 527 (2010) pp. 3236-3239.
10. Nam, K.W., Kim, J.S. and Park, S.W. “The high temperature strength of SiC ceramics based on SiO2 nano-colloidal employed” Materials Science and Engineering A, Vol 527 (2010) pp. 5400-5404.
11. Nam, K.W., Kim, J.S. and Park, S.W. “Crack-Healing Behavior and Bending Strength Properties of SiC Ceramics based on the Type of Additive SiO2 Employed”, International Journal of Modern Physics B, Vol 24 (2010) pp. 2869-2874.
12. Nam, K.W., Kim, J.W., Hinoki, T., Kohyama, A., Murai, J. and Murakami, T. “Application of ultrasonic inspection to characterization of advanced SiC/SiC composites”, Journal of Nuclear Materials, Vol 417 (2011) pp. 353-355.
13. Nam, K.W., Moon, C.K. Seo, I.S. “A fundamental study for the crack healing of SiC ceramics and SiCf/SiC composite ceramics” Journal of Ceramic Processing Research. Vol 12 (2011) pp. 646-649.
14. Sembokuya, H., Kubouchi, M., Oshida, Y. and Tsuda, K. “Corrosion Behavior of Alumina or Silicon Carbide Filled Epoxy Resin Immersed in Alkaline Solution”, Journal of Network Polymer (Japan), Vol 23 (2002) pp. 72-80.
15. Sydow, U., Schneider, M., Herrmann, M., Kleebe, H.J. and Michaelis, A., “Electrochemical corrosion of silicon carbide ceramics. Pt.1: Electrochemical investigation of sintered silicon carbide (SSiC)”, Materials and corrosion, Vol 61 (2010) pp. S.657-664.