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Oxidation behaviour of Si_3N_4/Y_2O_3 system ceramics and effect of crack-healing treatment on oxidation

M. Nakatani [a], K. Ando [b], K. Houjou [c,*]

[a] *NHK Spring Co., Ltd., 3-10 Fukuura, Kanazawa-ku, Yokohama, Japan*
[b] *Department of Energy & Safety Engineering, Yokohama National University, 79-5 Hodogaya, Yokohama, Japan*
[c] *Oyama National College of Technology, 771 Nakakuki, Oyama, Japan*

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Abstract

This paper describes the oxidation behaviour of Si_3N_4/Y_2O_3-based ceramics. We prepared three kinds of ceramics, which have excellent crack-healing abilities, in different composites – Si_3N_4/Y_2O_3, $Si_3N_4/SiC/Y_2O_3$, and $Si_3N_4/Y_2O_3/Al_2O_3$ – and investigated the effect of crack-healing treatment on their oxidation behaviour. The oxidation tests were carried out at 700–1200 °C for 500 h. Measurements of weight gain and bending strength and observations of the oxidized surfaces were carried out.

The main results obtained are as follows: (1) when Y_2O_3 was used as an additive, Si_3N_4 ceramics exhibited extensive oxidation at low temperatures (700–1000 °C). (2) Si_3N_4/Y_2O_3 ceramics with 3-wt% Al_2O_3 added as an additive showed no extensive oxidation. (3) Crack-healing, as a pre-oxidation treatment, is useful for increasing the oxidation–resistance of ceramics at 1000 °C and for increasing the strength.

Keywords: Si_3N_4; Y_2O_3; Corrosion; Mechanical properties; Crack-healing

1. Introduction

In the recent years, Si_3N_4 ceramics have been used in industrial applications such as ceramic gas turbines and fuel cells because of their excellent properties under high-temperature conditions. However, owing to their low fracture toughness, ceramics are sensitive to flaws. Therefore, the reliability decreases considerably, when cracks grow in machine work or in service.

It is known that Si_3N_4 ceramics are among those ceramics that have a crack-healing ability.[1–4] We had earlier investigated the crack-healing behaviour of Si_3N_4 ceramics; this ability helps in developing their reliability of these ceramics.

Moreover, we had studied the oxidation behaviour of the Si_3N_4 ceramics at 1300 °C,[5] which is the optimum temperature for crack healing. However, an extensive oxidation of $Si_3N_4/SiC/Y_2O_3$ ceramics at about 1000 °C has also been reported.[6–9] Hence, it is important to investigate the oxidation behaviour of ceramics with crack-healing abilities. Therefore, we have investigated the following aspects:

(a) The oxidation behaviour at 700–1200 °C.
(b) The effect of oxidation on the bending strength.
(c) The effect of crack-healing treatment on the oxidation behaviour.

2. Experimental procedures

The samples used in this study involve three types of Si_3N_4/Y_2O_3-based ceramics. The sample names and their properties are as follows:

(1) SN-Y8: additive powder is 8 wt% Y_2O_3;
(2) SNC-Y8: composite powder is 20 vol% SiC, additive powder is 8 wt% Y_2O_3;
(3) SN-Y5A3: additive powder is 5 wt% Y_2O_3 and 3 wt% Al_2O_3.

The Si_3N_4 powder (UBE SN-E-10) has a mean particle diameter of 0.2 μm and an α-ratio of $\alpha/(\alpha+\beta) > 95$ wt%. The

* Corresponding author. Fax: +81 285 20 2884.
E-mail address: houjou@oyama-ct.ac.jp (K. Houjou).

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mean particle diameter of the SiC powder (Ultrafine, Ibiden) and Y_2O_3 powder (Fine grade, Nippon Yttrium Co.) additives are 0.3 μm and 0.5 μm, respectively. The mixtures were hot-pressed at 1850 °C and 35 MPa for 2 h in nitrogen gas. The hot-pressed materials were cut into test specimens measuring 3 mm × 4 mm × 40 mm.

The oxidation tests were carried out in air environment in an electric furnace at elevated temperatures (700–1200 °C) for 500 h. Further, the oxidation of the specimens that were subjected to the crack-healing treatment were also studied; the test conditions were 1100 °C × 20 h, 1200 °C × 5 h and 1300 °C × 1 h in air environment too, which are the almost optimum crack-healing conditions for these samples.[2,4,9] The weight gains resulting from the oxidation were measured by an electric balance with a sensitivity of 0.1 μg in minimum unit. These specimens were subjected to the four-point bending test according to JIS (Japanese Industrial Standards). The oxidation products were identified by scanning electron microscope (SEM) and X-ray diffraction (XRD), and investigated by SEM and Electron Probe Micro Analyzer (EPMA).

3. Test results and discussion

3.1. Oxidation behaviour of three kinds of Si_3N_4/Y_2O_3 ceramics

Oxidation tests were carried out in air environment for 500 h and the weight gains were measured. Fig. 1 shows the relation between the oxidation temperature and the weight gains of sample. It is recognized that the weight gains at elevated temperatures vary with the sample components. The weight gain of SNC-Y8 (●) at 700–1000 °C is considerably high. In particular, the oxidation is extensive at 800–1000 °C. However, above 1100 °C, the sample develops resistance to oxidation, and then there is no significant weight gain. The oxidation peak of SN-Y8 (■) appears at a slightly higher temperature than that of SNC-Y8 (●). However, the weight gain of SN-Y5A3 (♦) is not significant

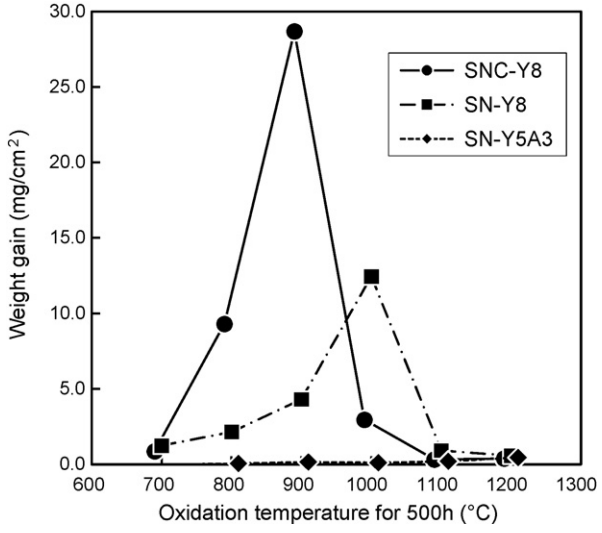

Fig. 1. Relationship between the oxidation temperature for 500 h and weight gain.

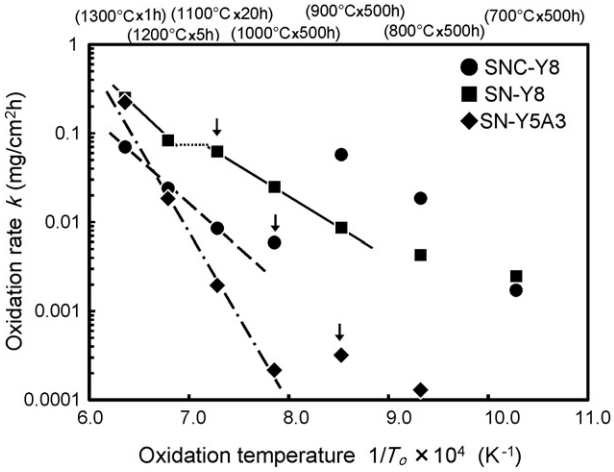

Fig. 2. Relationship between oxidation temperature (T_o) and rate (k).

up to 1100 °C, and slightly increases above 1200 °C. The oxidation behaviour of SN-Y5A3 (♦) is clearly different from those of the other ceramics, despite the addition of Y_2O_3. It is considered that the oxidation rate of the surface was accelerated by adding Al_2O_3[5]; therefore, the oxide layer protects its base material from another oxidation at low temperatures (700–1000 °C). An observation of the surfaces of the specimens, as mentioned later, revealed that only SN-Y5A3 (♦) forms a coherent oxide layer of 5–10 μm thickness. Therefore, SNC-Y8 (●) and SN-Y8 (■) are excellent in oxidation resistance on the high-temperature side, whereas SN-Y5A3 (♦) is excellent on the low temperature side.

The oxidation temperature (T_o) and rate (k) are plotted on an Arrhenius graph as shown in Fig. 2. The test temperatures are 700–1300 °C including crack-healing conditions. The oxidation rates (k) are scattered as a whole. At higher temperature side, rates (k) obey a linear law comparatively. However, at lower side, plots are out of lines considerably, and show the high rates (k) because of containing an extensive oxidation. The symbols (↓) in Fig. 2 indicate the temperatures of turning points of rates (k). And the temperatures of turning point are 1100 °C, 1000 °C and 900 °C for SN-Y8 (■), SNC-Y8 (●) and SN-Y5A3 (♦), respectively. However, in case of SN-Y5A3 (♦), the values of (k) at lower temperature side are relatively small, therefore they are not defined the "extensive oxidation". This implies that the mechanism of the oxidation reaction in the low-temperature range differs from that in the high-temperature range. These oxidations are more complex than the diffusion reaction that follows a single mechanism. This result corresponds with the tendency depicted in Fig. 1.

3.2. Effect of crack-healing conditions on oxidation

All the Si_3N_4 ceramics tested in this study have crack-healing abilities in the order SNC-Y8 > SN-Y8 > SN-Y5A3.[4] In an earlier study, the authors have proposed a methodology to guarantee the reliability of the ceramics components based on their crack-healing abilities.[3] Thus, if ceramics are used as structural members in a high-temperature environment, it is

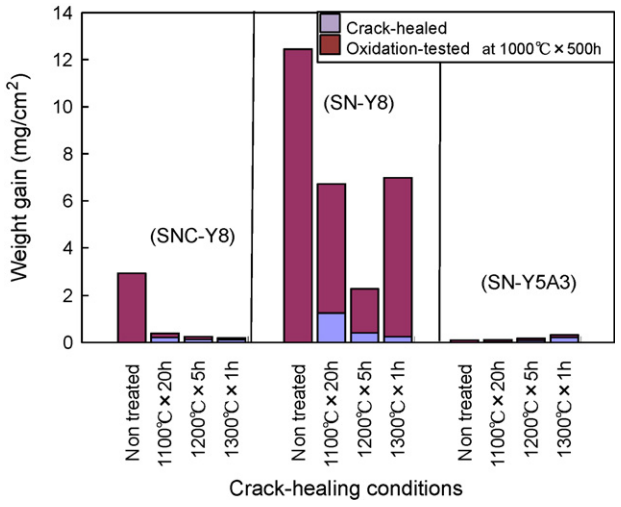

Fig. 3. Effect of crack-healing conditions on weight gain in oxidation test. The weight gain shows a total of crack-healing treatment and oxidation test.

desirable that the ceramics are crack-healed before use, even if they had no damages. The samples were subjected to the crack-healing treatment, and then oxidation-tested at 1000 °C × 500 h. Fig. 3 shows the effect of the crack-healing conditions on the weight gains. The crack-healing conditions used in this test are 1100 °C × 20 h, 1200 °C × 5 h and 1300 °C × 1 h. As mentioned before, these conditions are almost optimum healing conditions.

For comparison, the results of the specimens that were not subjected to the crack-healing treatment are shown on the left side of the figure. SNC-Y8 exhibits the most remarkable effect of crack-healing treatment on oxidation at 1000 °C. When the specimen was subjected to the crack-healing treatment before the tests, extensive oxidation is not observed. Among all the crack-healing conditions mentioned above, the condition 1300 °C × 1 h is especially effective.

The crack-healing treatment reduces the weight gain of SN-Y8 by about half. The optimum condition is 1200 °C × 5 h; however, the weight gain is 2.3 [mg/cm^2]. Therefore, the treatment cannot retard the extensive oxidation completely.

In the case of SN-Y5A3, the effect of crack-healing treatment is small. Thus, extensive oxidation is not observed with or without the crack-healing treatment.

The order of the effect of the crack-healing treatment on the weight gain is SNC-Y8 > SN-Y8 > SN-Y5A3; this corresponds to the order of the crack-healing ability.

3.3. Observations of the samples

Pictures of the specimens (SN-Y8 and SNC-Y8) are shown in Fig. 4. In the case of SN-Y5A3, a no change in the appearance was observed. Fig. 4(a) shows the initial condition. The as-received specimens are blackish brown in color. Fig. 4(b) represents the pictures of the oxidation-tested specimens without crack-healing treatment. The samples show a tendency to change to a white color. The extensive oxidation is distinguished by this color.[6–9] Fig. 4(c) shows the pictures of the oxidation-tested specimens with crack-healing treatment at1300 °C for 1 h. Observations revealed that the SNC-Y8 specimen does not show a change in the color; however, in the case of SN-Y8, the color changed to white after the oxidation. In addition, cracks on the surface and expansion of the volume were also observed. These occurred as a result of the extensive weight gain in the oxidation test stages.

3.4. Bending strength after oxidation

The strengths of the specimens that were oxidation-tested at elevated temperatures were measured by the four-point bending test at room temperature. The relation between oxidation-tested temperatures which were applied for 500 h and the bending strength is shown in Fig. 5. The bending strength of the as-received specimens is shown on the left side in the figure. In the case of SN-Y8 (■) and SNC-Y8 (●), the specimens that were oxidation-tested at low temperatures (800–1000 °C) exhibited a considerable decline in the bending strengths. However, at high oxidation temperatures, the bending strengths recovered up to the level of those of the as-received specimens. Moreover, the temperatures at the maximum weight gain point, as shown in Fig. 1 corresponds to those at the minimum bending strength point. However, the values of weight gain did not always correspond to the decrease in those of the bending strength. In Fig. 1, the weight gain of SNC-Y8 (●) at 700 °C is lower than that at 1000 °C; however, the bending strength at 1000 °C is higher than that at 700 °C. From the SEM observations of the oxides, it is evident that the surface of the specimen oxidized at 700 °C is porous, and it is considered that the many small pores contribute to the fracture. However, fewer pores are found on the surface of the specimen oxidized at 1000 °C. In case of SN-Y5A3 (♦), the bending strengths slightly decreased with an increase in the oxidation temperature.

As mentioned before, crack-healing treatment before oxidation is useful to decrease the weight gain. Subsequently, we investigated the bending strengths of the specimens that were oxidation-tested at 1000 °C for 500 h as functions of the crack-healing conditions. Fig. 6 shows the effect of crack-healing conditions on the bending strengths after oxidation. The bending strengths of the as-received specimens and non-healed specimens are shown on the left side in the figure. In the case of SNC-Y8 (●) and SN-Y5A3 (♦), it is recognized that the crack-healing conditions have little effect on the bending strength of the specimens oxidized at 1000 °C. In the case of SN-Y8 (■), the bending strengths of the samples that were not subjected to the crack-healing treatment decrease considerably; however, the bending strengths of the samples with crack-healing treatment improve, although the bending strengths vary widely. The crack-healing treatment performed on SN-Y8 (■) led to an improvement in the bending strength after oxidation (1000 °C × 500 h). The optimum crack-healing condition is found to be 1200 °C × 5 h.

3.5. SEM observation of oxide layers

The fracture surfaces of the oxidation-tested specimens were observed using a SEM. The samples observed were

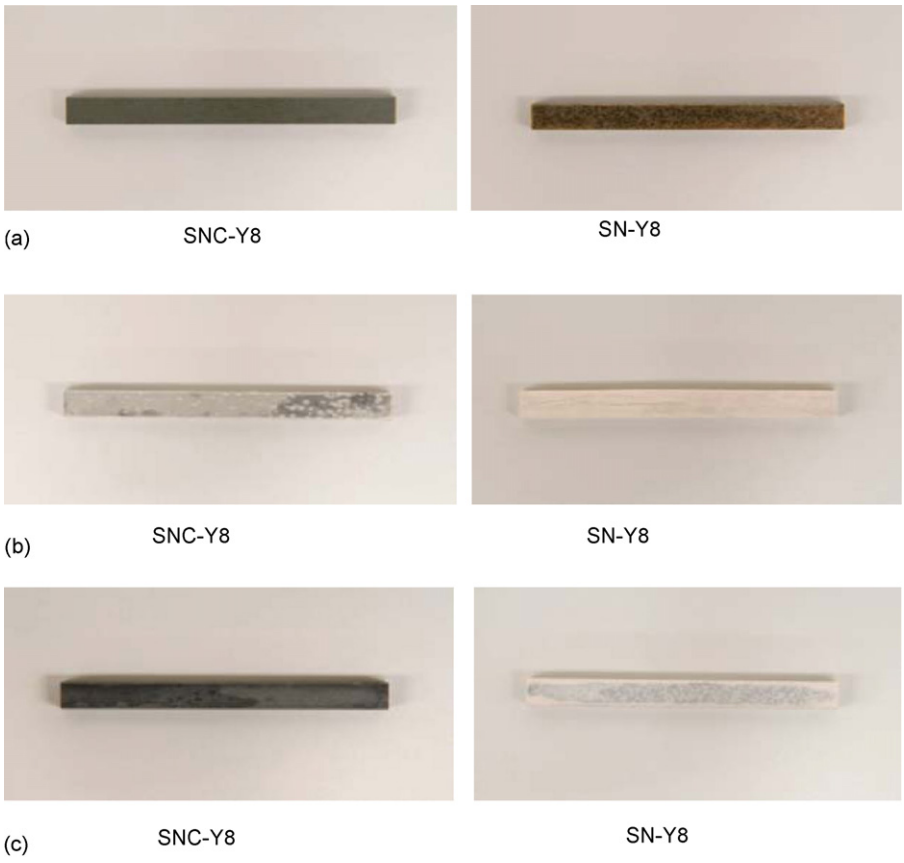

Fig. 4. Pictures of the specimens (SN-Y8, SNC-Y8): (a) before oxidation test, (b) after oxidation test (no crack-healed) and (c) after oxidation test (crack-healed at 1300 °C × 1 h). The oxidation condition is (1000 °C × 500 h).

SNC-Y8, SN-Y8 and SN-Y5A3. The crack-healing condition was 1300 °C × 1 h, and the oxidation condition was 1000 °C × 500 h. For comparison, the specimens that were not subjected to the crack-healing treatment were also observed.

Fig. 7 shows the SEM images of the fracture surface. The arrows in the figure represent the oxide area. Fig. 7(a) shows the image of SNC-Y8 that was subjected to the crack-healing treatment. A coherent and thin oxide layer of 5 μm thickness was clearly formed on the surface of the specimen that was pre-oxidized by the crack-healing treatment. On the other hand, an oxide layer of 30 μm thickness, shown in Fig. 7(b), is observed on the surface of the specimen was not subjected to the crack-healing treatment. In addition, the boundary line of the oxide layer is not clearly visible. It is found that the oxide layer produced during the crack-healing treatment at 1300 °C × 1 h acts

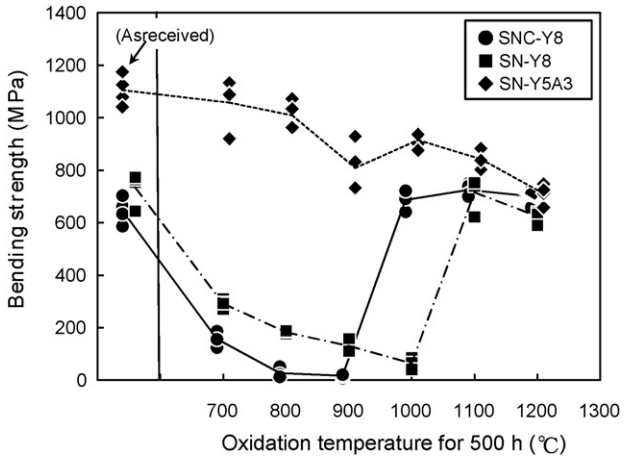

Fig. 5. Relationship between oxidation temperature for 500 h and the bending strength.

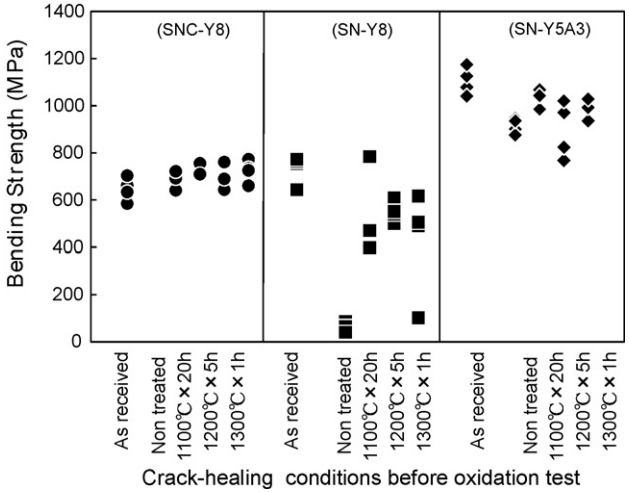

Fig. 6. Effect of crack-healing conditions on the bending strength after oxidation.

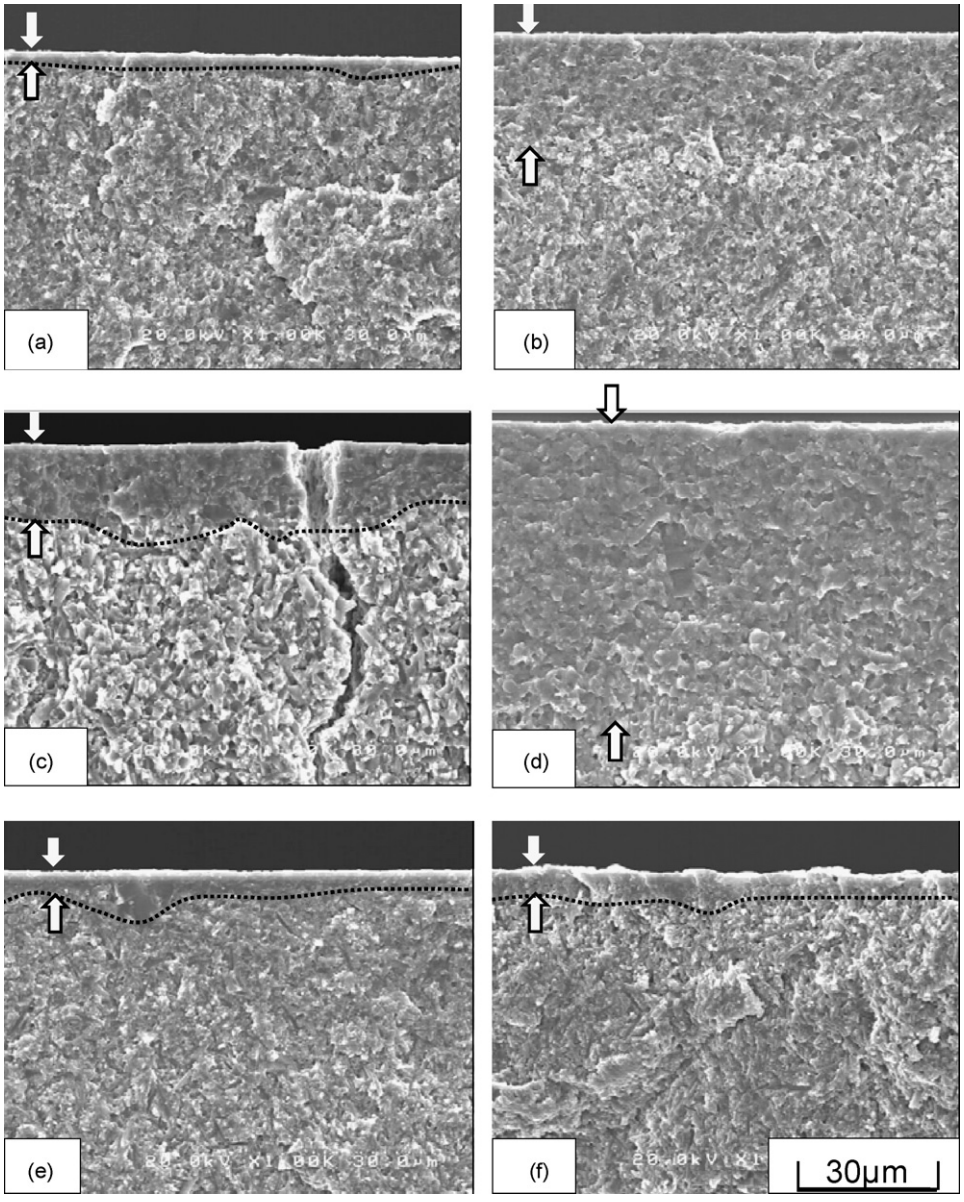

Fig. 7. SEM images of fracture surface of the specimen oxidation-tested at 1000 °C for 500 h: (a) SNC-Y8 with crack-healing; (b) SNC-Y8 without crack-healing; (c) SN-Y8 with crack-healing; (d) SN-Y8 without crack-healing; (e) SN-Y5A3 with crack-healing; (f) SN-Y5A3 without crack-healing. Crack-healing condition is (1300 °C × 1 h).

as a protective layer and reduces further oxidation during the test stage (1000 °C × 500 h). On the other hand, deep oxidation is observed in the case of SNC-Y8 that was not subjected to the crack-healing treatment.

Fig. 7(c) and (d) show the fracture surface of the oxidation-tested SN-Y8. In Fig. 7(c), an oxide layer of 20 μm thickness is clearly observed on the crack-healed specimen. The oxide layer was produced during crack healing (1300 °C × 1 h); however, it has a lesser ability to function as a protective layer against secondary oxidation, as compared with SNC-Y8. Therefore, oxygen penetrates the oxide layer and oxidizes the base material. Subsequently, cracks at the grain boundary were formed due to the volume expansion of oxidation. Furthermore, it is recognized by oxygen mapping (EPMA) that oxidation forced its way through the grain boundary. Fig. 7(d) shows the specimen that was not subjected to the crack-healing treatment. An oxide layer of 60 μm thickness is observed, and the boundary line of the oxide layer is not clearly visible. In addition, many deep and serious cracks are observed.

Fig. 7(e) and (f) show the fracture surfaces of SN-Y5A3. Both the oxide layers are thin and clearly visible. However, in the case of the specimen that did not undergo the crack-healing treatment, the surface of the oxide layer is slightly uneven.

A clear boundary line of the oxide layer is formed by the crack-healing treatment at a temperature higher (1300 °C) than the oxidation temperature (1000 °C). The coherent oxide layer takes effect on the resistance to oxidation. In the case of SNC-Y8, the crack-healing treatment is especially effective. The weight

Table 1
XRD results of surface of specimens

Sample	Before oxidation As received	After oxidation Crack-healed 1300 °C × 1 h	1000 °C × 500 h No-treated
SNC-Y8	β-Si_3N_4 SiC $Y_{20}N_4Si_{12}O_{48}$ $YNSiO_2$	β-Si_3N_4 SiC $Y_{20}N_4Si_{12}O_{48}$ $YNSiO_2$	β-Si_3N_4 SiC $Y_2Si_2O_7$ SiO_2
SN-Y8	β-Si_3N_4 $Y_{20}N_4Si_{12}O_{48}$	β-Si_3N_4 $YNSiO_2$ $Y_2Si_2O_7$ SiO_2	*β*-Si_3N_4 $Y_2Si_2O_7$ SiO_2
SN-Y5A3	β-Si_3N_4	β-Si_3N_4 $Y_2Si_2O_7$ SiO_2	β-Si_3N_4 $Y_2Si_2O_7$

gain is reduced because the diffusion rate of oxygen is slow in a coherent oxide layer produced by the crack-healing treatment at 1300 °C for 1 h. SEM observations lead us to these considerations.

3.6. Results of XRD

In order to study the oxidation mechanism, the oxidation products were investigated by XRD. The results of XRD with regard to the specimen surfaces are shown in Table 1. The crystalline phases of the oxidation-tested SNC-Y8 that was subjected to the crack-healing (1300 °C × 1 h) are β-Si_3N_4, SiC, $Y_{20}N_4Si_{12}O_{48}$ and $YNSiO_2$. Moreover, these crystalline phases are the same as those of the specimen before the experiments.

However, in the case of SNC-Y8 was not subjected to the crack-healing treatment, β-Si_3N_4, SiC, $Y_2Si_2O_7$ and SiO_2 are detected. It is considered that composite SiC, and $Y_{20}N_4Si_{12}O_{48}$, $YNSiO_2$ crystallized in the grain boundary are oxidized to $Y_2Si_2O_7$ and SiO_2. It has been pointed out that if $Y_{20}N_4Si_{12}O_{48}$ and $YNSiO_2$ are oxidized, they expand by 4% and 12% in volume,[10] respectively. Extensive oxidation then penetrates the base material because of numerous cracks formed during the oxidation of the grain boundary. In the case of Si_3N_4/Y_2O_3 ceramic systems, if a melilite ($Y_2N_4Si_3O_4$) is crystallized at the grain boundary, extensive oxidation occurs by a 30% expansion in the volume[10] at 1000 °C. However, in this study of SNC-Y8, a coherent oxide layer is produced owing to the SiC addition and crack-healing treatment. Furthermore, the oxides such as melilite are not produced. Therefore, the resistance to oxidation is improved.

However, the grain boundary of the as received SN-Y5A3 mainly comprises of a glassy phase. $Y_2Si_2O_7$ is diffracted after the oxidation test. This is crystallized in the oxide layer[5] in a different way from that of SN-Y8. The results of the specimens subjected to crack-healing treatment before oxidation shows an intensive diffraction peak of SiO_2 (1 0 1). It is considered that SiO_2 was produced during the crack-healing process and remained until the test was completed.

4. Conclusions

The oxidation behaviour of three types of Si_3N_4/Y_2O_3 system ceramics with crack-healing abilities was investigated in the temperature range 700–1200 °C for 500 h. The main conclusions obtained in this work are as follows:

(1) The oxidation behaviour differed greatly depending on the additives (Y_2O_3, Al_2O_3) or the composite (SiC). The specimens with Y_2O_3 as an additive exhibited an extensive oxidation on the low temperature side (700–1000 °C). Moreover, the bending strengths decreased considerably after the oxidation tests.
(2) The specimens with 3-wt% Al_2O_3 added as an additive showed no extensive oxidation in the entire temperature range. However, the bending strengths slightly decreased with an increase in the oxidation temperature.
(3) Extensive oxidation at low temperatures was caused by the expansion of the grain boundaries due to oxidation. Oxygen penetrated the base material along the cracks. This oxidation was more complex than diffusion which follows a single mechanism.
(4) In the case of Si_3N_4/Y_2O_3/SiC oxidation, the effects of the crack-healing treatment before oxidation were remarkable, in the test at 1000 °C. The weight gain was reduced, and the oxide layer was coherent and very thin.
(5) It was revealed that the oxide layer produced by the crack-healing treatment acted as a protective layer and improved the resistance to oxidation. A part of the extensive oxidation of Si_3N_4/Y_2O_3 system ceramics was reduced by the crack-healing treatment.
(6) It was recognized that the use of different ceramics at each service temperature is necessary; therefore, the use of $Si_3N_4/Y_2O_3/Al_2O_3$ at comparatively low temperatures (up to 1000 °C) and Si_3N_4/Y_2O_3/(SiC) at comparatively high-temperatures (beyond 1000 °C) is recommended.

From the above-mentioned results, we propose the practice of choosing ceramics as a function of the service temperature. Moreover, the crack-healing treatment of ceramics before their use is beneficial.

References

1. Zhang, Y. Z., Edwards, L. and Plumbridge, W. J., Crack healing in a silicon nitride ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 1861–1868.
2. Ando, K., Houjou, K., Chu, M. C., Takeshita, S., Takahashi, K., Sakamoto, S. and Sato, S., Crack-healing behavior of Si_3N_4/SiC ceramics under stress and fatigue strength at the temperature of healing (1000 °C). *J. Eur. Ceram. Soc.*, 2002, **22**, 1339–1346.
3. Ando, K., Shirai, Y., Nakatani, M., Kobayashi, Y. and Sato, S., (Crack-healing + proof test): a new methodology to guarantee the structural integrity of a ceramics components. *J. Eur. Ceram. Soc.*, 2002, **22**, 121–128.
4. Houjou, K., Ando, K., Liu, S. P. and Sato, S., Crack-healing and oxidation behavior of silicon nitride ceramics. *J. Eur. Ceram. Soc.*, 2004, **24**, 2329–2338.

5. Houjou, K., Ando, K., Chu, M. C., Liu, S. P. and Sato, S., Effect of sintering additives on the oxidation behavior of Si_3N_4 ceramics at 1300 °C. *J. Eur. Ceram. Soc.*, 2005, **25**, 559–567.
6. Lange, F. F., Singhal, S. C. and Kuznicki, R. C., Phase relations and stability studies in the Si_3N_4–Y_2O_3–SiO_2 pseudoternary system. *J. Am. Ceram. Soc.*, 1977, **60**, 249–252.
7. Patel, J. K. and Thompson, D. P., The low-temperature oxidation problem in yttria-densified silicon nitride ceramics. *Br. Ceram. Trans. J.*, 1988, **87**, 70–73.
8. Yamashita, H., Sano, H., Uchiyama, Y., Kobayashi, K. and Wada, S., Abnormal oxidation behavior of Si_3N_4–SiC–Y_2O_3 composite at about 1000 °C. *J. Ceram. Soc. Jpn.*, 1997, **105**, 31–36 (in Japanese).
9. Takahashi, K., Murase, H., Yoshida, S., Houjou, K., Ando, K. and Sato, S., Improvement of static fatigue strength of Si_3N_4/SiC crack-healed under cyclic stress. *J. Eur. Ceram. Soc.*, 2005, **25**, 1953–1959.
10. Lange, F. F., Importance of phase equilibria on process control of Si_3N_4 fabrication. *Ceram. High Perform. Appl. III Reliability*, 1983, 275–291.