

CORROSION AND STRENGTH DEGRADATION OF Si-BASED CERAMICS BY MOLTEN SALT

NAOYA MASUDA¹ and YUJI KIMURA²

¹Graduate Student, Kogakuin Univ.1-24-2 Nishishinjuku,Shinjuku-ku,Tokyo,163-8677, Japan

²Department of Material Science and Technology, Kogakuin Univ.1-24-2
Nishishinjuku,Shinjuku-ku,Tokyo,163-8677, Japan

ABSTRACT

Several trials have been conducted for applying Si-based ceramics as the materials used for the high temperature structure such as gas turbine components, because of their superior fracture toughness and thermal shock resistance under high temperature condition. However, various problems concerning oxidation and corrosion under high temperature environment have been reported. From among various high temperature corrosion problems, the molten salt corrosion has been pointed out as the most important one which caused serious fracture strength degradation. Purpose of this study is to evaluate the corrosion behavior and the degradation in the mechanical property of SiC and Si₃N₄ caused by molten salt. As a result, the influence of molten salt Na₂SO₄ upon the mechanical property of structural ceramics SiC and Si₃N₄ was made clear to be caused by the progressive corrosion reaction, i.e. the successive repetition of the generation and removal of the SiO₂ membrane under the high temperature condition.

KEYWORDS: SiC, Si₃N₄, gas turbine, molten salt Na₂SO₄, corrosion, oxidation, SiO₂, strength degradation,

INTRODUCTION

The application of Si-based ceramics is expected as the material of the high temperature structure such as gas turbine etc. because SiC and Si₃N₄ have excellent fracture strength, fracture toughness and thermal shock resistance under high temperature condition. It was pointed out that the materials used for the high temperature

gas turbine system were seriously corroded by heavy molten salt such as Na_2SO_4 together with the high temperature oxidation[1]. Therefore it becomes important that the materials used in this system must be basically stable under these corrosive environments. Also, they must have superior thermo-mechanical properties. As mentioned before, non-oxide ceramics such as SiC and Si_3N_4 show excellent fracture strength, fracture toughness and thermal shock resistance when used under high temperature condition. However, these non-oxide ceramics fundamentally have unstable oxidizing character especially under heavy molten salt environment. Therefore, it is important to evaluate the effects of molten salt corrosion upon the mechanical properties of non-oxide ceramics.

Therefore in this paper, corrosion characteristics and degradation of mechanical properties of Si-based structural ceramics such as SiC and Si_3N_4 by molten salt of Na_2SO_4 were investigated. Also, degradation mechanism of Si-based ceramics by molten salt was discussed.

EXPERIMENTAL PROCEDURE

Specimen

Materials used in this study are SiC and Si_3N_4 , which are mainly used for various parts of gas turbine engine. Square cross-sectional bar type test specimen ($4 \times 3 \times 40\text{mm}$) with a chamfered edge of 0.1 mm is cut from the sintered plate. Surface of specimen was finished by polishing to obtain mirror surface. The sintering method and chemical composition of Specimen are shown in the following Table 1.

Table 1. Specimen Date

Item	SiC	Si_3N_4
Sintering method	Normal pressure sintering	Gas pressure sintering
Chemical Composition	SiC, Na, Mg, Ca, Fe, Ti, Al, Y, B	Si_3N_4 , Al_2O_3 , Y_2O_3

High Temperature Corrosion Tests and Strength Tests

High temperature corrosion test was conducted employing Na_2SO_4 coated specimens. The Na_2SO_4 coating was conducted as follows. First of all specimen was immersed into the solution that 9.55 g of Na_2SO_4 was mixed to 0.1 liter of pure water. Dip coated layer of Na_2SO_4 was obtained on the surface of the specimen. Then, water molecule in coated layer was evaporated by drying. High temperature oxidation and corrosion tests at 1atm were conducted under various temperature conditions up to 1373K. Holding time for high temperature testing was ranged up to 8 hours. The degrees of progress of high temperature oxidation and molten salt corrosion were evaluated by the change of residual bending strength employing JIS R1601 4 point bending test [2] using each 2 specimens with and without molten salt Na_2SO_4 coating after various high temperature tests. The deflection rate is in bending test selected as 0.5 mm/min. The detailed microscopic observation of specimen surface and fracture surface was conducted by FE-SEM.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The Strength Degradation by Molten Salt Corrosion

The results of 4 point bending test obtain using non-oxidized and oxidized specimens of both SiC and Si_3N_4 under various high temperature conditions were shown in Figure 1. Both SiC and Si_3N_4 specimens without

Na₂SO₄ coated layer showed little change in their bending strength. On the contrary, these specimens with Na₂SO₄ coated layer showed remarkable degradation in bending strength as the corrosion temperature became higher. In case of Si₃N₄, bending strength after high temperature corrosion test under 1273 K and 1373 K with Na₂SO₄ coating dropped down till about the half of that of non-corroded specimen.

Therefore, the oxidation did not play an important role in strength degradation after high temperature test up to 1373K. On the contrary, high temperature corrosion by the molten salt such as Na₂SO₄ play an dominant role in the degradation of Si-based ceramics of SiC and Si₃N₄ under the temperature condition up to 1373K.

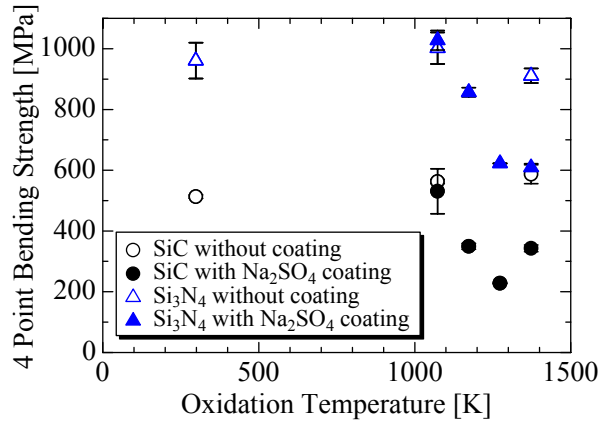
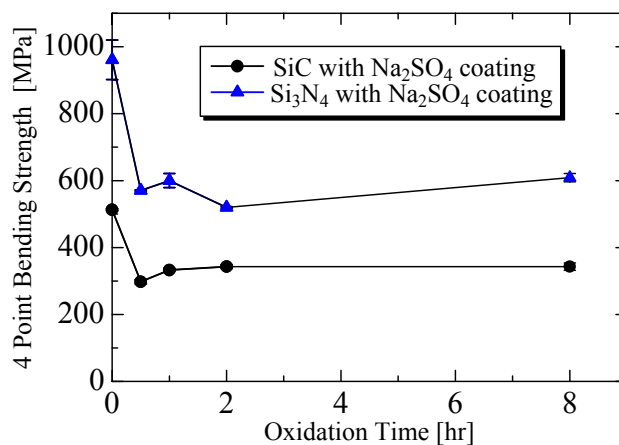


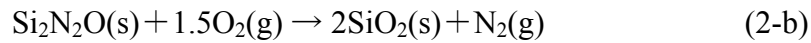
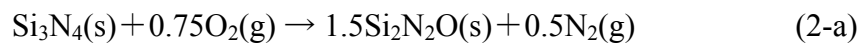
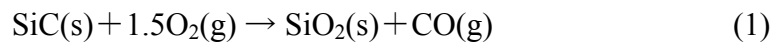
Figure 1: 4 Point Bending Strength after Oxidation Tests under Various Temperature

Also, it was understood that the strength drop of Si₃N₄ is by molten salt corrosion was remarkable compared with that of SiC specimen. Therefore, Si₃N₄ ceramic was more susceptible to molten salt corrosion than SiC.

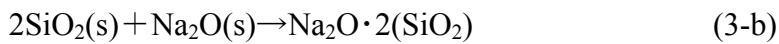
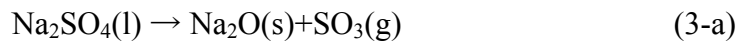
The results of 4 point bending tests of specimen with Na₂SO₄ coated layer after high temperature corrosion under 1373K with various different holding times were obtained and Shown in Figure 2. These results of bending test after high temperature corrosion showed that the remarkable strength degradation was recognized even after 30 minutes molten salt corrosion. Therefore, molten salt corrosion by Na₂SO₄ was expected to cause serious damage on the Si-based ceramics especially Si₃N₄ even when exposure time of those material to the molten salt is relatively short. Then, no more serious progress in strength degradation was recognized after high temperature corrosion test under longer holding time conditions than 30 minutes. These bending test results showed that the degradation in bending strength caused by Na₂SO₄ corrosion might be saturated in the high temperature test under the above-mentioned conditions.



To make clear the corroded morphology and to investigate the mechanism of molten salt Na₂SO₄ corrosion in Si-based ceramics, detailed FE-SEM observation of specimen surface and fractured surface was conducted. In Figure 3, the fractured surface morphologies of oxidized and non-oxidized specimen with and without Na₂SO₄ coating were indicated. From Figure 3 it was understood that the fracture of specimen was initiated from original micro-void in specimen when bending test was conducting for non-oxidized specimens. In contrast, on the fracture surface of Na₂SO₄ corroded specimen after high temperature test under 1273K, bubble formation was recognized. Also, crack initiation from these bubbles formed on the specimen surface by molten salt corrosion was observed. The liquid phase Na₂O·2(SiO₂) formation due to the chemical reaction between molten salt Na₂SO₄ and SiO₂ under the high temperature oxidation condition may play an important role in the high temperature corrosion process of Si-based ceramics caused by Na₂SO₄. Namely the Si-based ceramics are oxidized under high temperature environment and cause the reaction of SiO₂ generation [3] as shown in the following.



Solid phase SiO₂ formed by the reaction shown by equations (1) and (2-b) reacted with Na₂O and then liquid phase Na₂O·2(SiO₂) was generated.



As a result, oxidation reactions of Si-based ceramics were continued successively. Therefore, continuous formation of N₂ and CO was resulted. These gas formations caused bubble generation that became the initial site for crack formation under bending stress. For this reason, remarkable degradation in room temperature residual bending strength after high temperature corrosion was brought about.

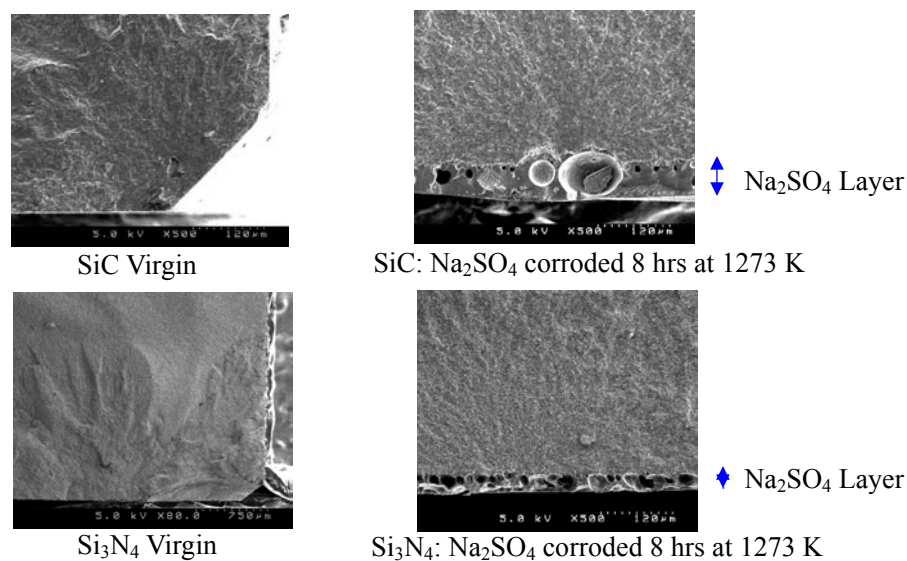


Figure 3: FE-SEM Micrographs of Fracture Surfaces

Governing Factor for Residual Bending Strength after High Temperature Corrosion

To investigate the governing factor for residual bending strength of Si-based ceramics after high temperature test from the fracture mechanics view point, correlation between the inverse square root depth (d) of bubble

formed layer by Na_2SO_4 corrosion $1/\sqrt{\pi d}$ and residual 4 point bending strength σ_R was investigated and shown in Figure 4. Also in this figure, fracture toughness data [4,5], i.e., $K_{IC}=3.5 \text{ MPa}\sqrt{m}$ for SiC and $K_{IC}=6 \text{ MPa}\sqrt{m}$ for Si_3N_4 were indicated by solid lines. As a result, it was indicated that the residual bending strength of Si_3N_4 decreased as the increase of square root depth of bubble formed layer in case when the fracture of specimen was initiated from formed bubble. For this reason, the residual bending strength of Si_3N_4 ceramic was controlled by K_{IC} value calculated based on depth of bubble formed layer. On the contrary, in case of SiC ceramic, the residual bending strength data can not plotted on any straight line which showed $K_{IC}=\sigma_R\sqrt{\pi d}=\text{Const}$, where σ_R means residual bending strength. Therefore, it becomes clear that the residual bending strength after high temperature corrosion can not be uniquely evaluated from the fracture mechanics view point evaluated based on the bubble formed layer depth in case of Si-based ceramics.

In the followings, detailed examinations of fracture surface morphologies especially bubble shape which governed the residual bending strength after high temperature corrosion test were conducted and shown in Figure 5. From the results shown in this figure, it was recognized that there was clear difference between the corroded morphology and bubble morphology formed on Si_3N_4 and SiC ceramics. In case of Si_3N_4 ceramics corroded by molten salt, continuous bubble formation was usually recognized in entire coated molten salt surface layer. On the contrary, local single bubbles were generated discontinuously in the coated molten salt layer in case of SiC ceramics. Therefore, the fracture of specimen was initiated from the local single bubble. For this reason, in case of SiC ceramics, K_{IC} value evaluation based on fracture origin defect area was introduced employing the following equation [6].

$$K_{IC} = K_{I \max} = 0.629\sigma_0\sqrt{\pi\sqrt{area}} \quad (4)$$

Then, correlation between K_{IC} values evaluated based on defect area and residual bending strength were obtained and shown in Figure 6. Judging from the results shown in Figure 6, the residual bending strength after high temperature corrosion can be plotted around the straight line showing $K_{IC}=0.629\sigma_0\sqrt{\pi\sqrt{area}}=3.5 \text{ MPa}\sqrt{m}$ in case of SiC. Therefore in this case, it was indicated that the residual bending strength of SiC decreased as the increase of square root defect area. For this reason, the residual bending strength of SiC ceramic was controlled by K_{IC} value calculated based on defect area.

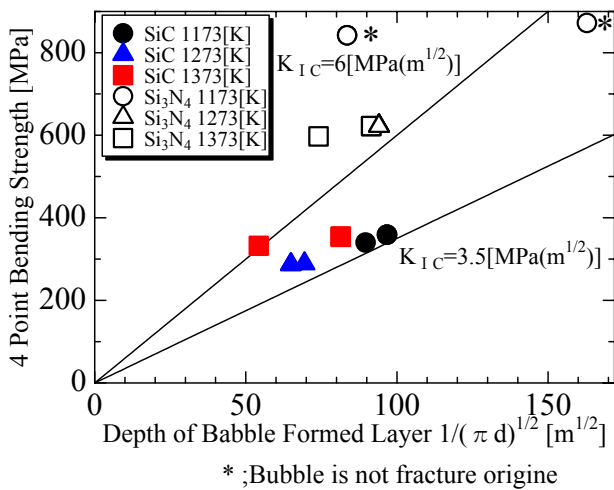


Figure 4: Relation Between Depth of Bubble Formed Layer and Strength

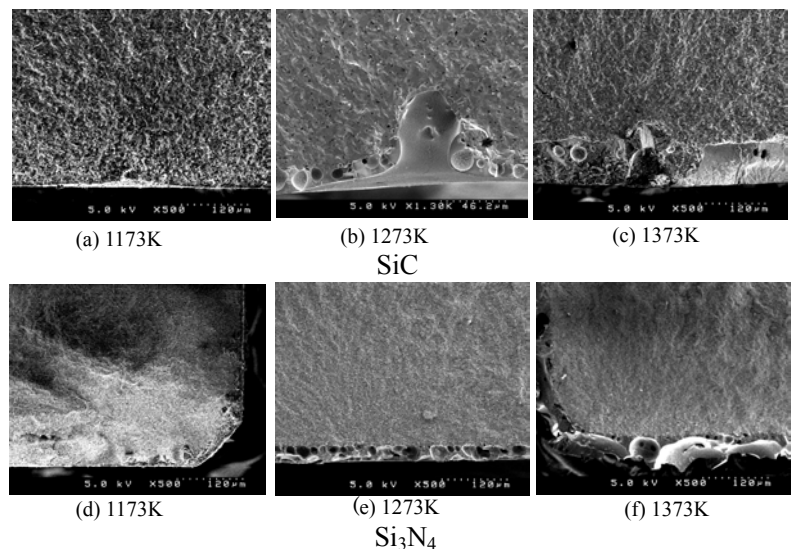


Figure 5: FE-SEM Photographs of Fracture Surface

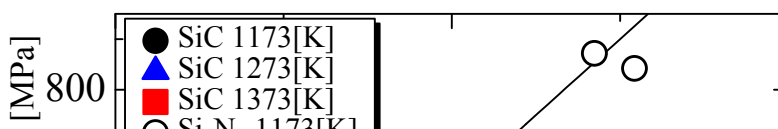


Figure 6: Relation Between Defect Area and Strength

CONCLUSIONS

Corrosion characteristics and degradation in the mechanical properties of Si-based structural ceramics such as SiC and Si₃N₄ by molten salt of Na₂SO₄ were investigated.

Results obtained are summarized as follows:

1. The influence of molten salt Na₂SO₄ upon the mechanical property of structural ceramics SiC and Si₃N₄ was made clear to be caused by the progressive corrosion reaction, i.e. the successive repetition of the generation and removal of the SiO₂ membrane under the high temperature condition.
2. Also, the degradation of the mechanical property by the progress of the molten salt corrosion under high temperature environment became clear to be saturated within 0.5 hours.
3. Furthermore, the residual bending strength after molten salt corrosion can be investigated on the basis of fracture mechanics view point. In case of Si₃N₄ ceramics, K_{IC} can be evaluated on the basis of square root depth of bubble formed layer. On the other hand, in case of SiC ceramics, it can be evaluated based on fracture origin defect area.

Accordingly, it is required to pay sufficient attentions to the existence of the molten salt when Si-based ceramics such as SiC and Si₃N₄ are used under the high temperature environment.

REFERENCES

1. T Sato, Y Koike, T Endo, M Shimada, (1988) J. Soc. Mat. Sci., Japan, Vol.38, No.424, 39-43
2. JIS R 1601, (1994) Testing method for flexural strength of high performance ceramics
3. Nathan S. Jacobson, (1993) J. Am. Ceram. Soc., 76(1)3-28
4. Catalog of Sintered SiC "CERASIC B", Toshibaceramics Co. Ltd.
5. Catalog of Gasometrical sintering Si₃N₄, NTK Co. Ltd.
6. Y Murakami, S Nemat-Nasser, (1983) Engineering Fracture Mechanics, Vol.17, No.3, 193-210