High Temperature and Fatigue Strength of crack-healed Mullite/Silicon Carbide Ceramics

균열 치유된 Mullite/SiC 세라믹스의 고온강도와 피로강도

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Key Words : Mullite/SiC ceramics(Mullite/SiC 세라믹스), Crack healing(균열치유), Bending strength(굽힘강도), Recovery of strength(강도회복), High temperature strength(고온강도), Healing condition(치유조건)

Abstract : 본 연구에서는 균열 치유 거동을 가지는 소결된 Mullite/SiC의 모재, 열처리재, 균열재, 치유균열재의 기계적 특성이 논의되었다. 반타원형 균열의 치수는 100㎛과 200㎛이다. 얻어진 결과는 다음과 같다. (a) Mullite/SiC 복합 세라믹스는 균열 치유 능력이 있었다. (b) 최적의 균열 치유 열처리 조건은 1300℃, 1시간이었다. (c) 치유 가능한 최대 균열 길이는 직경 100㎛의 반타원 균열이다. (d) 균열 치유부는 1200℃이상에서 충분한 강도를 가졌고, 대부분의 시험편은 균열 치유부 이외의 영역에서 파단하였다. (e) 공기중에서 예열처리는 본 재료의 피로강도 향상에 유용하였다.

1. INTRODUCTION

Structural ceramics are excellent in heat resistance, corrosion resistance and wear resistance. And it will be the most indispensable material of new millennium. However, the ma chine ability is bad and fracture toughness is low, therefore, the application region has been limited because of its low reliability. It is important to increase the reliability, in other to widen the application area. There are two ways to increase reliability of ceramics; one is to improve fracture toughness in ceramics and the other is that the self crack healing ability is given to the material. It is known that silicon carbide [1], alumina [2,3,6] and silicon nitride [4 6] show very interesting crack healing behavior. However, the maximum size of which crack can be healed, the optimum crack healing condition and heat resistance of the crack healed zone of the crack healed zone have been not yet investigated.

Recently, the authors have clarified the relation between crack healing ability and the chemical composition of silicon nitride [7]. We have also reported that maximum size of a crack can be healed, the best crack healing condition and strength characteristics of the crack healed zone at high temperatures for Si3N4/SiC composite [8 13] and silicon carbide [14].

On the other hand, we discovered that the mullite/SiC showed the interesting crack healing behaviour [15,16]. And, we succeeded in improving the bending strength up to the 900MPa level by utilizing crack healing beha viour and grain growth suppression effect which is resulted by addition of SiC [17]. However, in case of Mullite/SiC, the maximum size of a crack can be healed, the best crack healing condition and strength characteristics of the crack healed zone at high temperatures are

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fatigue not yet investigated.

The above three aspects are investigated in this study.

2. MATERIALS AND TEST METHOD

2.1 Material and sintering method

The mullite powder used is KM101 (average particle size 0.2μm, Al2O3 content 71.8wt%, KIORITZ Co,. Ltd., Japan) and the SiC powder is Ultrafine (average particle size 0.27μm, IBIDEN Co,. Ltd., Japan). Manufacturing proce sses of test specimens are as follows. The mullite powder and SiC powder (20vol.% by volume of mullite powder) were wet blended for 24 hours using nylon balls in alcohol. Then powder was dried in a vacuum furnace, until all the solvent had evaporated. The resulting powder was hot pressed (35MPa at 1650℃) for 4 hours in nitrogen gas and it produced a sintered material with the dimensions of 90×90×5 mm.

2.2 Specimen and experimental method

The bending strength was evaluated by 4 point bending test on 3×4×40mm specimens in accordance to the JIS Standard [13] as shown in Fig. 1. The test specimens were surface ground and polished before testing. A pre crack was

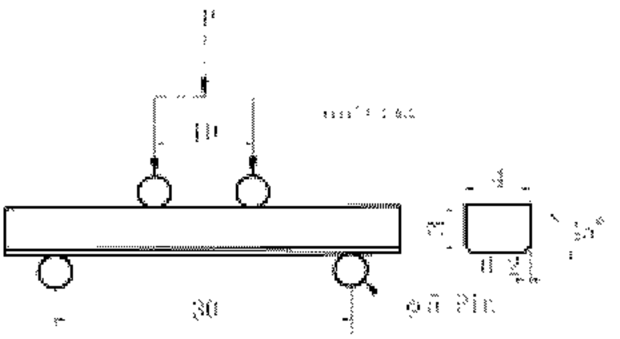

Fig. 1 Specimen dimension and loading system

introduced onto the specimens by indentation method using Vickers indenter. Semi elliptical crack length (2C) of the surface were about 100 μm or 200μm, and Vickers load was 9.8N or 29.4N. The shape of the crack has been shown

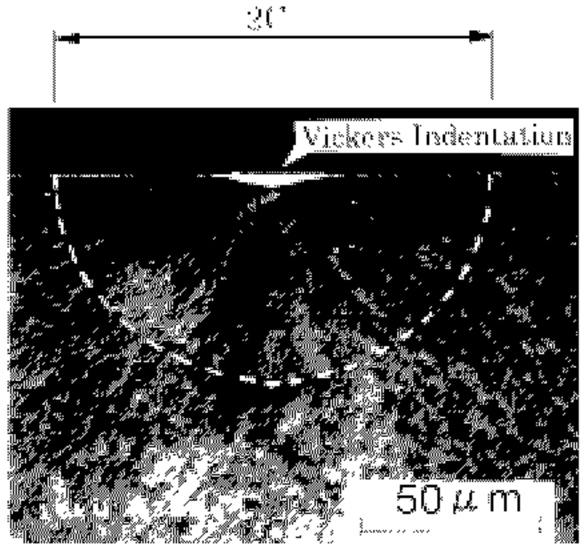

Fig. 2 A SEM photograph

in Fig.2. The cracks were semi elliptical with aspect ratio of 0.8~0.9. The specimens were heat treated in air at 1000℃ for 20h, 1100℃ for 10h, 1200℃ for 5h and 1300℃ for 1h in order to heal the crack. The heating rate was 10℃/min and cooling was done spontaneously in the furnace. The bending test was carried out at R.T, 800℃, 1000℃, 1100℃, 1200℃ and 1300℃. The cross head speed of the test was 0.5mm/min. Fatigue test was conducted at room temperature at a stress ratio R 0.2 and a frequency 5 Hz using sine wave.

Crystal phases of sintered material and surface oxides were investigated by X ray diffraction method. The X ray diffraction analysis condition was cookα radiation (30kV accelerated voltage and 30mA electric current) and detector scanning speed of 0.5deg/min. The crack healing at elevated temperature was observed directly using ultrahigh temperature scanning laser microscope (1LM21H LK1500 LASER TECH Co., Ltd. Japan).

3. RESULT AND DISCUSSION

3.1 Crack healing behaviour

Fig.3 shows the experimental data of crack healing behavior of the mullite/SiC composite ceramics. This is a result of the bending test carried out at room temperature. The symbols (○) in the figure is the result of the as received specimens which did not conduct the heat treatment and the bending strength was about 340MPa. The symbol (△) shows the bending strength of the as cracked specimens which are introduced the crack of surface length about 100μm. By cracking, the bending strength has decreased up to about 140MPa. Next, the symbols (●,▲) illustrate the bending strength of heat treated smooth specimens and cracked and heat treated specimens. The heat treatment was done in air at temperature 1300℃ for 1 h. After the heat treatment, bending strength of as received specimens and as crack specimens (2C 100μm) have increased significantly to about 520MPa. Both of them show a bending strength higher than that of the as received smooth specimens.

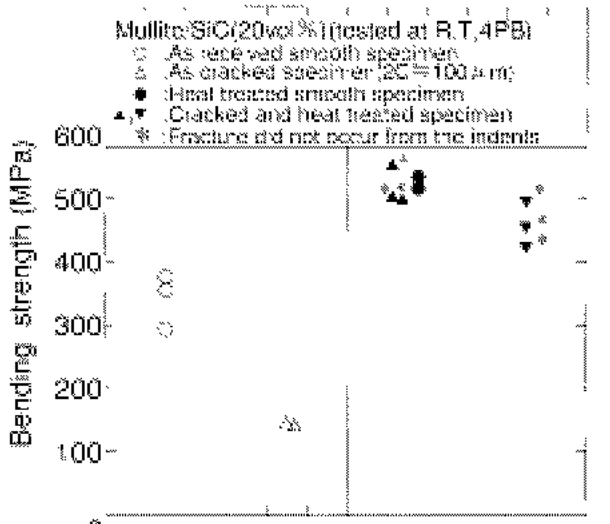

Fig. 3 The effect of heat treament on room temperature bending strength of mullite /SiC complsite

Fig. 4 shows the surface condition of the heat treated specimens. As shown in the Fig. 4, the marks like water droplet can be seen on the surface of the specimens. These deposits were removed by polishing the surface longitudinally using the abrasive paper of #1000 and #2000. The bending strengths of these polished specimens have shown in Fig. 3 by the inverted solid triangles. After polishing the bending strength decreased up to 460MPa, that is somewhat less than un polished heat treated specimens, but considerably higher than as cracked (△) specimens. The marks of * in Fig. 3 indicate specimens that fracture was occurred from outside the Vickers indent. All specimens of cracked and heat treated specimens had been failed from outside of the pre crack zone.

To investigate the reason of the recovery in strength, the pre crack zone was observed directly during the heat treatment process using a laser microscope. The result is shown in Fig. 5. At 1000℃, see Fig. 5 (a), the crack is clearly observed, and any change is not yet recognized. However, when it passed 10 minutes after it reached at 1300℃, see Fig. 5 (c), the crack can not be clearly distinguished. And then, when it passed 1 hour at 1300℃, see Fig. 5 (d), the

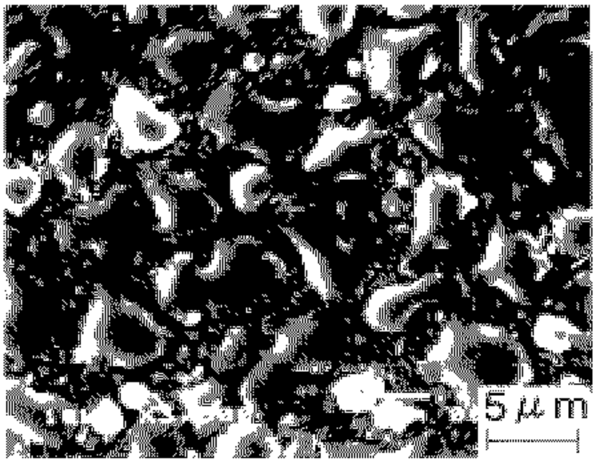

Fig. 4 A SEM photograph of surface of which specimen was heat treated at 1300℃ for 1 hr in air

crack can not be hardly observed because the surface is covered with some new created phases. It was investigated by the X ray diffraction method in order to investigate what these material has been composed. The X ray patterns are shown in Fig. 6. Fig 6 (a) and (b) show result of as received and heat treated specimens, respectively. In comparison with Fig. 6 (a) and (b), it can be seen that mullite and

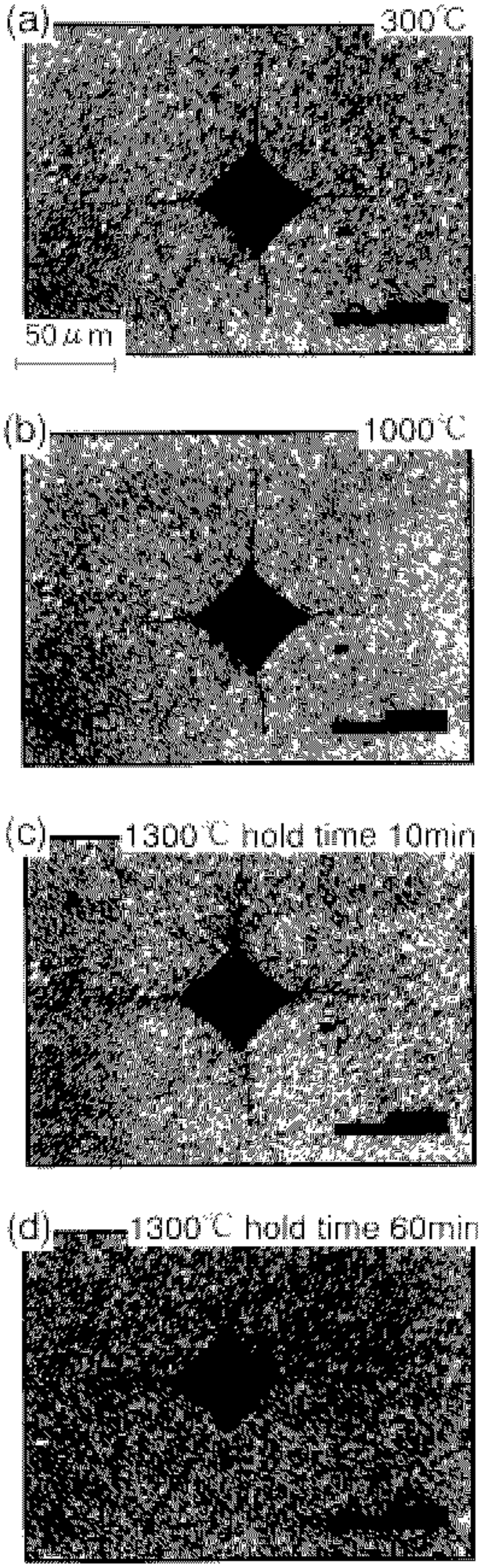

Fig. 5 Observation of crack healing process using a laser microscope

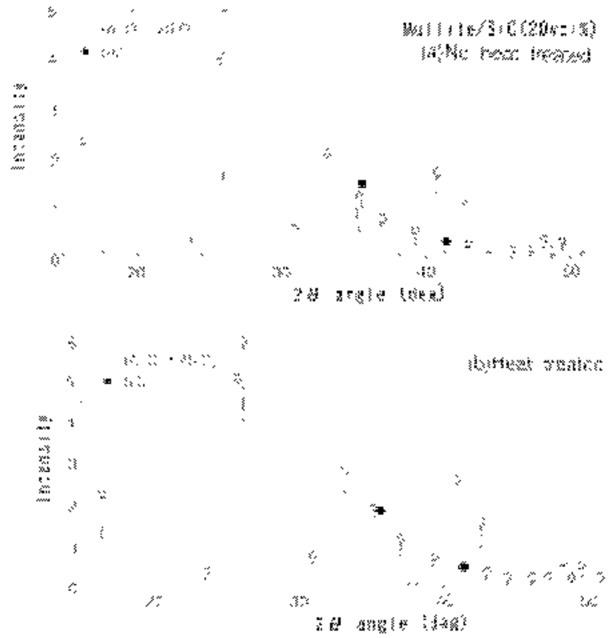

Fig. 6 X ray diffraction patterns of (a) no heat treated specimen and (b) heat treated specimen

SiC were only detected and any difference did not discovered from the figures. And, another crystalline phase has not been observed. From this fact, it seems that the new phases are non crystalline phases and contribute to heal the pre crack. From Fig. 3 to 6, it is concluded that the improvement of strength is resulted in healing of the pre crack and a surface crack due to pre oxidation process.

3.2 Effect of healing condition on bending strength

The effect of the crack healing condition on bending strength was investigated. The test result is shown in Fig. 7.

The bending strength of cracked and heat treated specimen is not dependent on the crack healing condition in this experimental range, and all cracked and heat treated specimens showed higher bending strength than that of the as received specimens. It is considered that there are two reasons for this. One is a residual stress due to mismatching of the thermal expansion coefficient and the elastic modulus between matrix and the surface oxides that have been created during heat treatment in air. As mentioned in the section 3.1, see Fig. 3, the strength of the specimen removed surface oxides is higher than that of the as received specimen. So, this is not a reason for that. The other is healing of both a pre crack and another cracks that would be made in the specimen surface during machining. This material has a low fracture toughness of about 2.8MPa√m. So, it is easy to create crack during machining and it seems that the cracks affected to strength of the as received specimen. From this fact, it is considered that the increase in strength is resulted in healing the cracks that was created by machining.

On the other hand, the bending strength shows the highest value of about 520MPa when a pre cracked specimen has been heat treated at 1300℃ for 1 hour in air. So, that condition was applied in this study as the standard crack healing condition of this material.

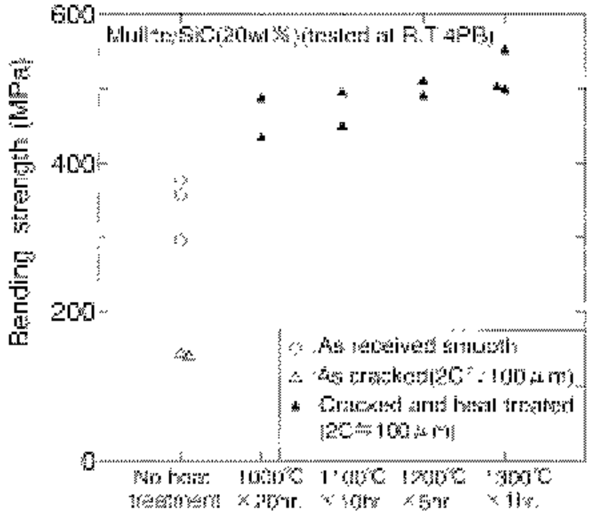

Fig. 7 The effect of heat treatment condition on room temperature bending strength

3.3 Maximum crack size can be healed under the standard crack healing condition

It is important to determine the maximum size of crack that can be healed perfectly. The maximum crack size was investigated using specimens with a surface pre crack, which was introduced by a Vickers indenter. The test result is shown in Fig. 8. The bending strength of as received specimen is about 340MPa. By heat treating, the strength is increased and showed a value of 520MPa. It seems that this improvement in strength is caused by healing a crack presented the specimen surface, which was introduced in machining. In case of as cracked specimens, the bending strength is 140MPa and 100MPa at 100μm and 200μm in crack diameter, respectively. By heat treating, the strength is increased and showed a value of 520MPa and 420MPa, respectively. And, all of the two case, the strength is higher than that of as received smooth specimen. However, in case of 200μm, the strength showed as low as 100MPa in compare with that of heat treated smooth specimen. In this case, all of three

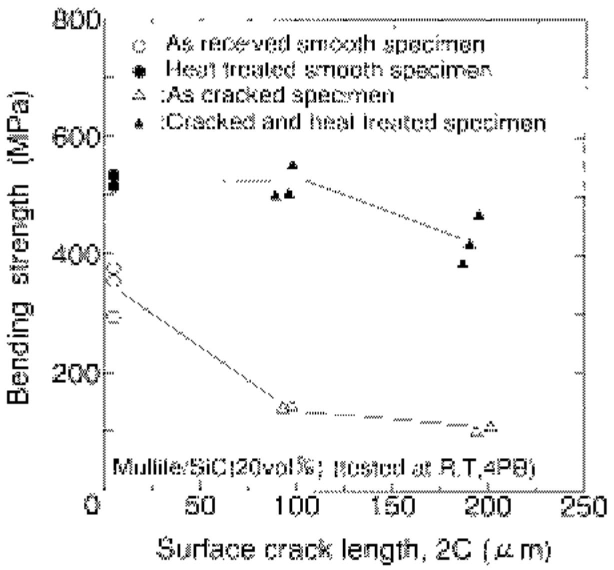

Fig. 8 Effect of pre crack size on room temperature bending strength of cracked and heat treated specimen

specimens have been failed from the Vickers indentation. The indentation size is about 60μm and this is enough to decrease the strength of heat treated pre cracked specimen. From these facts, it can be concluded that this material has an ability to heal the surface semi elliptical cracks with 200μm in diameter.

3.4 Effect of testing temperature on the bending strength of pre-crack healed specimen

Fig. 9 shows the effect of testing temperature on the bending strength In the experiment ranging from room temperature to 1300℃, the bending strength of as received smooth specimens(○) is independent of testing temperature. In case of cracked and heat treated specimen(▲), the bending strength decreased slightly with increasing testing temperature up to 1200℃. And, at 1300℃, the strength is decreased dramatically and showed a value of 290MPa. The value is approximately same to that of as received smooth specimen as well as the heat treated one. On the other hand, the strength behaviour of heat treated smooth specimen(●) was similar to that of cracked and heat treated specimen in this experimental

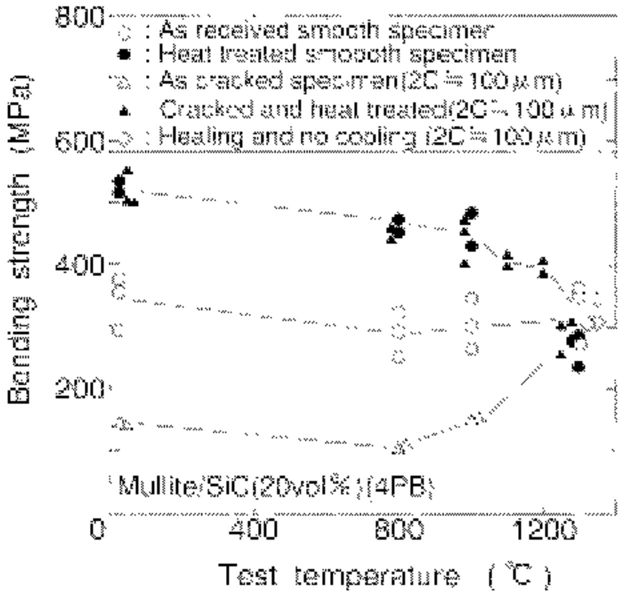

Fig. 9 Effect of testing temperatures on room temperature bending strength of the heat treated specimen

range. In the as cracked specimen(△), the bending strength is 140 MPa at R.T and decreased slightly at 800℃. However, above it, the strength is increased with increasing test temperature, and showed a value of about 310 MPa, which is the same one of as received specimens.

The schematic illustration of heat treatment and testing process are shown in Fig 10. In case of process A, Fig. 10 (a), the specimen was tested in bend at each temperature after heat treatment (crack healing process). By contrast, in case of process B, Fig. 10 (b), the specimen was tested in bend without any pre heat treatment. In results of Fig. 9, both the symbols of ▲ and ● indicate test results that were carried out using the process A. On the one hand, both the symbols of △, ◇ and ○ in Fig.9 show datum that test was performed by the process B. The difference of △ and ◇ is duration time at test temperature and the time is 20 min and 60 min in case △ and ◇, respectively. In Fig. 9, the bending strength of as cracked specimen at 1300℃(◇) recovered perfectly to that of as received smooth

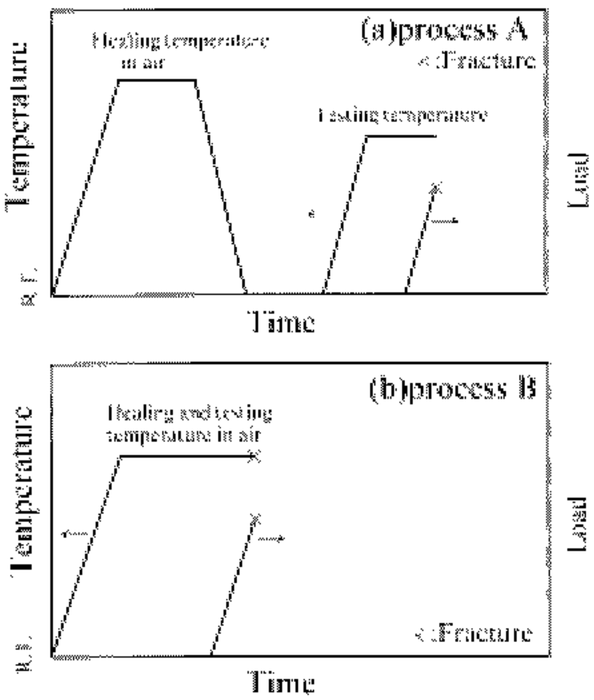

Fig. 10 Schematic illustration of crack healing and testing process

specimen. From this result, it seems that a surface crack could be healed in service in this material, if a condition would be satisfied.

In Fig. 9, in comparison with the bending strength of the as received smooth specimens (○) and cracked and heat treated specimens (▲) , the strength of heat treated specimen is higher than that of as received one up to 1200 ℃. At 1300℃, however, both specimens is the same in strength. Therefore, it can be seen that a crack healing effect is remarkable up to 120 0℃ in this material. Matrix of mullite does not degrade in strength up to 1300℃[2,4]. From this fact, it is considered that the degradation above 1200℃ is resulted in the crack healing material composed of glassy phases to be weaken at that temperature.

On the other hand, the crack healing material in silicon nitride/silicon carbide composite is a crystalline phase. In that reason, the bending strength of pre crack healed specimens was equal to that of the matrix up to 1400℃[7,8].

3.5 Fatigue strength of pre-crack healed specimen

The relationship between maximum stress, σ max, and number of cycles to failure, Nf, is shown in Fig. 11. The bending test results indicated in the left side of Fig. 11, and symbol of → in the figure indicates data that specimen did not failed during the fatigue testing till cycle numbers of 2x106. The stress value of these data designated in this study as σf0 . In the case of as received specimen, symbols of ○, σ f0 is about 200MPa. On the other hand, σf0 of heat treated smooth specimen shows 350MPa and is higher than that of as received specimen by 150MPa. It is suggested that pre heat treatment is useful to improve fatigue strength of this material.

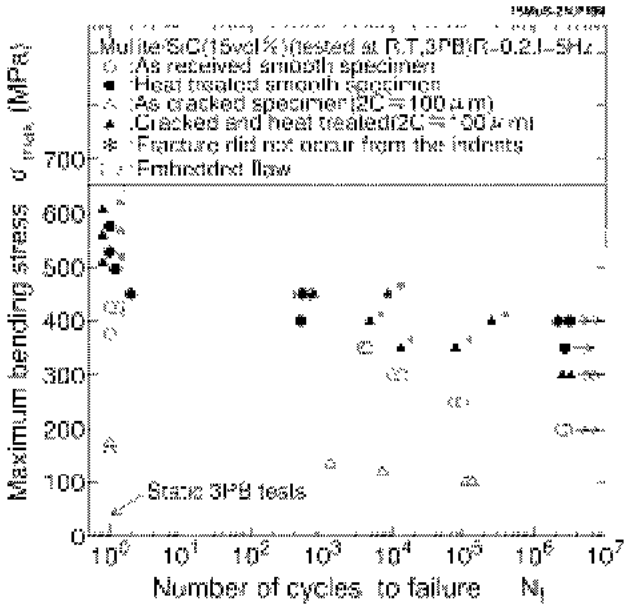

Fig. 11 Relationship between maximum bending stress(σmax) and number of cycles to failure(Nf)

The fatigue strength of as cracked specimen, symbols of △, is much lower than that of as received specimen. However, in the case of cracked and heat treated specimen, symbols of ▲, the fatigue strength is improved compare to that of as cracked specimen as well as as received specimen by pre heat treatment in air. And the σf0 is about 300MPa which is higher than that of as received specimen by 100MPa and is about three times value as high as as creaked specimens. And five of six specimens have been failed from outside of the crack healed zone(symbols of * in Fig. 11). It is considered that this improvement in fatigue strength results in healing both pre crack and surface crack would be produced while test pieces was machined. From this result, it can be concluded that crack healed zone has enough the fatigue strength in comparison with the matrix zone.

4. CONCLUSIONS

Using the hot pressed mullite/SiC composite ceramics, crack healing behavior, high tempera ture strength and fatigue characteristics were investigated systematically. As the result, this material shows a very interest of crack healing behavior. The main results of this experiment are as follows:

1) The strength of pre cracked specimen was recovered due to healing the pre crack by a pre oxidation at elevated temperature in air.
2) The optimum crack healing condition in this experiment range is at 1300℃ for 1 h in air. In this conditions, a semi elliptical crack of 200μm in diameter could be healed perfectly.
3) The crack healed zone has a sufficient in bending strength in compared with that of matrix up to about 1200℃.
4) The pre heat treatment in air is useful to improve fatigue strength of this material and crack healed zone has enough the fatigue strength in comparison with the matrix zone.

REFERENCES

1. J. J. Petrovic, and L. A. Jacobson, Controlled surface flaws in hot pressed SiC. J. Am. Ceram. Soc., 59 [1 2], pp. 34 37, 1976
2. J. E. Moffatt, W. J. Plumbridge and R. Hermann, , High temperature crack annealing effect on fracture toughness of alumina and alumina SiC composite. British Ceramics Transaction, 95 [1], pp. 23 29, 1996
3. T. K. Gupta, Crack healing and streng sthening of thermally shocked alumina. J. Am. Ceram. Soc., 59 [5 6], pp. 259 262, 1976
4. S. R. Choi and V. Tikare, Crack healing behaviour of hot pressed silicon nitride due to oxidation. Scripta Metallurgica et Mate rialia, 26, pp. 1263 1268, 1992
5. Y. Z. Zhang, L. Edwards and W. J. Plum bridge, Crack healing in a silicon nitride ceramics. J. Am. Ceram. Soc., 81, pp. 34 37, 1998
6. M. Mitomo, T. Nishihara and M. Tsutsumi, Crack healing in silicon nitride and alumina ceramics. J. Mat. Sci. Lett., 15[22], pp. pp. 1976 1978, 1996
7. M. C. Chu, K. Ando, T. Hirasawa, S. Sato and Y. Kobayashi, Crack healing behaviour of silicon nitride ceramics (Effect of chemical composition on crack healing ability). High Pressure Institute of Japan., 36, pp. 82 89, 1996
8. K. Ando, M. C. Chu, S. Sato, F. Yao and Y. Kobayashi, The study on crack healing behaviour of silicon nitride ceramics. Jpn. Soc. Mech. Engng., 64, pp. 1936 1942, 1998
9. K. Ando, T. Ikeda, S. Sato, F. Yao and Y. Kobayashi, A preliminary study on crack healing behaviour of Si3N4/SiC composite ceramics. Fatigue Fract. Engng. Mater. Struct., 21, pp. 119 122, 1998
10. K. Ando, M. C. Chu, Y. Kobayashi, F. Yao, and S. Sato, Crack healing behaviour and high temperature strength of silicon nitride ceramics. Jpn. Soc. Mech. Engng., 65, pp. 1132 1139, 1999
11. K. Ando, M. C. Chu, F. Yao and S. Sato, Fatigue strength of crack healed Si3N4/SiC ceramics, Fatigue Fract. Engng. Mater. Struct, 22, pp. 897 903, 1999
12. F. Yao, K. Ando, M. C. Chu and S. Sato, Crack healing behavior, high temperature and fatigue strength of SiC reinforced silicon nitride composite. J. Mat. Sci., Lett., 12, pp. 1081 1084, 2000
13. F. Yao, K. Ando, M. C. Chu and S. Sato, Static and cyclic behaviour of crack healed Si3N4/SiC composite ceramics. J. European Ceramics Society(accpted)
14. J. Korous, M. C. Chu, M. Nakatani and K. Ando, Crack healing behavior of silicon carbide ceramics. J. Am. Ceram. Soc., 83, pp. 2788 2792, 2000
15. M. C. Chu, S. Sato, Y. Kobayashi and K. Ando, Damage healing and strengthening behaviour in intelligent Mullite/SiC ceramics. Fatigue Fract. Engng., Mater. Struct., 18, pp. 1019 1029, 1995
16. M. C. Chu, S. Sato, Y. Kobayashi and K. Ando, Study on strengthening of mullite by dispersion of carbide ceramics particles. Jpn. Soc. Mech. Engng., 60, pp. 2829 2834, 1994
17. S. Sato, M. C. Chu, Y. Kobayashi and K. Ando, Strengthening of mullite by dispersion of carbide ceramics particles. Jpn. Soc. Mech. Engng., 61, pp. 1023 1030, 1995