General paper

FATIGUE CRACK PROPAGATION BEHAVIOR OF Si_3N_4 CERAMICS IN CORROSIVE ENVIRONMENTS

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Abstract: The effect of corrosion on fatigue fracturing of silicon nitride ceramics was investigated in 1N and 3N H_2SO_4 solutions. The crack propagation rate da/dt increased when the stress ratio R under cyclic loading was decreased. The higher concentrated solution enlarges the stress ratio dependence of da/dt . Therefore, it is considered that corrosion increases the effect of cyclic loading on da/dt . According to results of an energy dispersive X-ray spectroscopy(EDX) analysis, it was found that the sintering additive components of Al and Y decreased at the crack tip. This suggests that the grain boundary phase at the region dissolved. In addition, a similar effect was also observed by scanning electron microscopy(SEM). Consequently, it is concluded that the dissolution of the grain boundary phase contributes to the increase of da/dt in H_2SO_4 solutions.

Key words: Fatigue, Corrosion, Silicon nitride, Crack propagation, Sulfuric acid solution

1 INTRODUCTION

Ceramics are applied to many structural members in high temperature and chemical corrosive environments, because they are superior in heat and corrosion resistance to conventional metallic materials [1]. Such applications will be extended in the future, making it necessary to develop higher reliable ceramics and to construct fundamental data bases concerning their strength properties in various environments. Up to now, there has been limited study on the corrosion of ceramics [2,3]. Since ceramic components are also subjected to cyclic loading, it is important to estimate their strength under fatigue in corrosive environments. Few studies, however, have been carried out about the influence of environments on fatigue fracture in corrosive solution, though some studies have been done at high-temperature oxidation atmospheres [4,5].

The present investigation studies fracture behavior of Si_3N_4 ceramics in sulfuric acid solution under cyclic loading.

2 EXPERIMENTAL PROCEDURES

The material was a normal-sintered Si_3N_4 with sintering additives of Y_2O_3 and Al_2O_3 . The material properties at room temperature($293 \pm 5\text{K}$) are shown in Table 1. The test samples were flexural specimens 10mm wide, 5mm thick and 50mm long. After mirror finishing by using diamond abrasive powder #2000, a pre-crack 2-3mm long was made at the center of the specimen using

Table 1. Material properties.

Density ρ , Mg/m^3	Young's modulus E , MPa	Poisson's ratio ν	Grain size d , μm
3.3	2.7×10^5	0.3	1.5

a pre-cracking device (BI method[6]). The cyclic fatigue test was carried out by fatigue testing apparatus with a piezoelectric bimorph as a motor [7], a symmetric four point bending jig and a test tank made of Teflon, as shown in Fig.1. Corrosive environments were H_2SO_4 solutions of 1 and 3 normals (1N and 3N) at a temperature of $293 \pm 5\text{K}$. The crack tip was immersed in the environment by dropping the solution continuously. The crack length was measured using a traveling microscope with a magnification of 200. Fracture surfaces were observed using a scanning electron microscope (SEM), and the composition change at the fracture surface was analyzed using an energy dispersive X-ray spectroscopy (EDX).

3 RESULTS

3.1 Weight Loss of the Specimen in H_2SO_4 Solutions

To investigate the corrosion behavior of Si_3N_4 , the relation between weight loss and immersion time was examined for the specimen immersed in 3N- H_2SO_4 . The result is shown in Fig.2, where the weight is found to decrease with an increase in immersion time. In particu

Fig. 1. Fatigue testing apparatus.

Fig. 2. Relation between weight loss and immersion time in 3N-H₂SO₄.

lar, the weight loss is very large the first 0.25×10^5 s after immersion. This suggests much corrosion in the initial stage of immersion. By EDX analysis and SEM observation, it was confirmed that some components (Al in particular) of the grain boundary dissolve and grains break away from the matrix, which is considered to have caused the weight loss [8-10]. The large weight loss at the initial stage ($t_i < 0.25 \times 10^5$ s) is considered to be due to the activation of a mechanochemical reaction by residual stress [9]. The weight loss rate decrease after the subsequent stage ($t_i > 0.25 \times 10^5$ s) may be attributed to the relaxation of residual stress by corrosion.

3.2 Crack Propagation Rate in Various Environments

Figure 3 depicts the crack propagation rate da/dt

under cyclic loading in various environments for $R=0.52$ and $f=300\text{Hz}$, where R is the stress ratio and f is the cyclic frequency. In this figure, $K_{I\text{max}}$ is the initial maximum stress intensity factor. The crack propagation did not occur in N₂ gas up to $N=10^8$ (see symbol $\bullet$), where N is the number of stress cycles. The da/dt in H₂SO₄ ($\circ$, $\square$) was higher than that in water ($\bullet$). Furthermore, it was higher in 3N ($\circ$) than in 1N ($\square$). As previously reported [11], there is no doubt that the environment greatly influences ceramic fatigue fracture. The crack did not propagate under static loading in 3N-H₂SO₄ ($\triangle$), although, in the case of cyclic loading in the same environment, the crack propagated for a short time. This suggests that there is an effect of cyclic loading on the crack propagation in the environment of H₂SO₄ as well.

Fig. 3. Relation between da/dt and $K_{I\text{max}}$ in various environments.

3.3 Effect of the Stress Ratio on the Crack Propagation Rate

Figure 4 shows the relation between da/dt and $K_{I\text{max}}$ in 3N-H₂SO₄ under the stress ratio R is from 0.5 to 0.9. It is found that the da/dt increases with decreasing R , and Fig. 5 represents that in 1N-H₂SO₄. It can be seen that the tendency of the result is the same as that in 3N-H₂SO₄. The stress ratio dependence of da/dt is, however, larger in 3N-H₂SO₄ than in 1N-H₂SO₄. The stress ratio depen-

dence of da/dt in H_2O increases in air, because the corrosive action in H_2O was stronger than that in air[12].

Fig. 4. Relation between da/dt and $K_{I\max}$ in 3N- H_2SO_4 .

Fig. 5. Relation between da/dt and $K_{I\max}$ in 1N- H_2SO_4 .

Therefore, it is thought that the effect of cyclic loading on the crack propagation rate increases with increasing corrosion. The above results suggest that the combination of corrosion and cyclic loading promote the fatigue of ceramics.

4 DISCUSSION

4.1 Effect of Corrosion on Fatigue Crack Propagation

The effect of corrosive action on the fatigue crack propagation under cyclic loading in H_2SO_4 was investigated based on EDX analysis. The line analysis of EDX was carried out for fatigue fracture surfaces in 3N- H_2SO_4 and in air. The analytical procedure is as follows. First, a crack 0.8mm in length was made under cyclic loading ($R=0.5$) in 3N- H_2SO_4 . The test was then stopped and the specimen was removed from the testing apparatus immediately. Next, to remove the corrosive solution between crack surfaces completely, the specimen was cleaned in acetone by an ultra-sonic cleaner. Moreover, after drying the specimen sufficiently, the specimen was equipped with the apparatus again. The crack was then propagated in air until the final fracture, and the fracture surface was analyzed by EDX.

Figure 6 is the result of line analysis, where (a) is for Al, (b) for Si, and (c) for Y. The vertical center lines in Fig.6 divide the region of slow crack growth (SCG) in 3N- H_2SO_4 (the left side) and that in air (the right side). The corrosion time becomes short as the line on the left side approaches the center line, since the crack propagates to the right in this figure. Therefore, the corrosion time corresponding to the center line is zero in practice. According to the result on Al(Fig.6(a)), the upper peaks (maximum points) of EDX line analysis on the left side (in 3N- H_2SO_4) are low on the whole. This means that the component Al dissolved. It should be noted that the peaks are very low in the region just on the left of the line where the corrosion time is very short, and there is a remarkable difference to that of air. According to a quantitative analysis of this region, the amount of Al in 3N- H_2SO_4 is about 16 percent lower than the amount in air. This suggests that the component Al dissolved for a short time by a mechanochemical reaction. The measured data also confirms a slight decrease in Y in terms of the EDX line analysis illustrated in Fig.6(c). This shows that Y dissolved in the same way, though the degree of dissolution is less. On the other hand, there was little difference in the peak of Si between the H_2SO_4 region and the air region in Fig.6(b). Since Si is a basal component, it was thought that the peak change did not appear.

Next, to investigate the influence of stress on the dissolution phenomenon, we analyzed quantitatively the results for the specimens fractured in air before and after

Fig. 6. Line analysis by EDX on fracture surface.

immersion in 3N-H₂SO₄, where the specimens were under no stress during immersion. The result is shown in Table 2, where only the components Si and Al are analyzed. As seen in the table, the quantity of components did not change before or after immersion, suggesting the degree of dissolution to be very low under no stress. Moreover, Fig.6 and Table 2 supports that dissolution (i.e., corrosive reaction) is apparent under high stress.

Table 2. Quantitative analysis on fracture surface.

	Air (Before immersion)	3N-H ₂ SO ₄ (After immersion)
Si/wt%	94.10	94.10
Al/wt%	5.90	5.90

Immersed time $\approx 10^4$ s (in 3N-H₂SO₄)

Note: Only the components Si and Al are analyzed.

4.2 Fracture Surfaces

Figure 7 shows the fracture surfaces observed by SEM, where (a) is the fracture surface under cyclic loading in 3N-H₂SO₄, (b) under static loading in 3N-

H₂SO₄, (c) under cyclic loading in the air and (d) under static loading in the air. Though the figures are not clear, with 3N-H₂SO₄ (Fig.7(a) and (b)), it is found that the grain boundary dissolved and the grain boundary of each grain is distinct. Furthermore, we can find that there is an evidence of columnar grains pulling-out. On the other hand, for the fracture surfaces in air (Fig.7(c) and (d)), the outlines of grains become a little indistinct due to the existence of the grain boundary phase, and we can partially see the transgranular fracture. EDX analysis suggests the above results are due to the difference of the degree of dissolution. Thus, it is thought that the dissolution of the grain boundary phase in H₂SO₄ makes grain boundaries very weak, so that the pulling-out of columnar grains, the crack initiation, and its growth at the boundaries occur easily. Naturally, it is considered that these phenomena greatly influence fatigue crack propagation in H₂SO₄. Since it is not confirmed that there is a considerable difference between cyclic and static fatigue fracture surfaces both in 3N-H₂SO₄ and in air, the crack propagation mechanism is thought to be almost the same in both of the cyclic and static fatigues.

4.3 The Mechanism of Crack Propagation under Cyclic Loading in H₂SO₄ Solutions

The fatigue crack propagation of normal-sintered Si₃N₄ is caused by stress corrosion cracking(SCC) at the crack tip [13]. As mentioned above, the SCC occurs easily especially at grain boundaries, because the fracture surfaces offer almost intergranular fracture (Figs.7(c) and (d)). On the other hand, the microstructure of Si₃N₄ consisting of columnar grains causes the bridging easily between the crack surfaces behind the crack tip. This results in the stress shielding and suppresses crack propagation. These relations are represented by the following equation [14];

$$K_{tip} = K_{app} - K_s, \quad (1)$$

where K_{tip} is the effective stress intensity factor at the crack tip, K_{app} the applied stress intensity factor and K_s the K -value due to the stress shielding effect. The bridging effect increases K_s and decreases K_{tip} . Under cyclic loading the K_{tip} increases, and crack propagation is enhanced since the bridging effect corresponding to K_s decreases by fretting damage in the bridging portion. Generally, the mechanisms as mentioned above are supported for crack propagation [13].

The experimental results in H₂SO₄ solutions revealed the following: (1) the grain boundary phase is dissolved and partially weakened (Fig.6 and Table 2); (2) pulling-out of columnar grains takes place easier(Figs.7(a) and (b)); and (3) the mechanochemical reaction activates under high stress in the crack tip stress field.

Figure 8 is a flow chart depicting the mechanism of

 (a) Cyclic loading in 3N- H_2SO_4 for 1.346×10^3 s.

 (b) Static loading in 3N- H_2SO_4 for 2.720×10^3 s.

(c) Cyclic loading in air.

(d) Static loading in air.

Fig. 7. SEM observation of fracture surface. The arrow indicates the direction of crack propagation.

fatigue crack propagation that we can expect from the above results. The increase of the crack propagation rate in H_2SO_4 solutions due to both corrosion and stress is clearly shown here. First, corrosion makes the grain boundary phase dissolve and weakens the boundary. This factor is considered to make crack propagation at the grain boundary easier and to promote pulling-out of the columnar grains (decrease of K_s and increase of K_{tip} , see Eq.(1)). That is, these factors make the fatigue resistance low and promote fatigue, so that the crack propagation rate increases. In addition, the mechanochemical reaction at the crack tip will promote dissolution, weakening, and fatigue. On the other hand, fretting damage in the bridging portion due to cyclic loading will be promoted further by dissolution and weakening (more decrease of K_s). Consequently, in H_2SO_4 solutions, the crack propagation rate increases in combination with these factors caused by corrosion and stress. That is, the increase of K_{tip} ($=K_{app} - K_s$) due to the decrease of K_s , which is caused by the dissolution of the grain boundary phase (i.e., the weakening of the boundary), the mechanochemical reaction, the cyclic loading effect etc., is considered to be the reason for increasing the crack propagation rate under cyclic loading in H_2SO_4 solutions.

 Fig. 8. Flow chart of crack propagation mechanism in H_2SO_4 solutions.

5 CONCLUSIONS

The effect of corrosion on fatigue fracture of silicon nitride ceramics was investigated in 1N and 3N H₂SO₄. The results obtained are as follows.

(1) The weight of Si₃N₄ ceramics decreased when the immersion time in H₂SO₄ solutions was increased. In particular, the weight loss was very large at the initial stage ($t < 0.25 \times 10^5$ s), which was thought to be caused by a mechanochemical reaction due to residual stress.

(2) The crack propagation rate da/dt in H₂SO₄ solutions was higher than that in H₂O, and higher in 3N-H₂SO₄ than in 1N-H₂SO₄.

(3) The stress ratio dependence of da/dt increased with an increase in the corrosive reaction.

(4) The dissolution of the grain boundary phase occurred easily under high stress in H₂SO₄ solutions.

(5) The reason for increasing da/dt under cyclic loading in H₂SO₄ solutions was considered to be due to the decrease of the stress shielding effect such as the dissolution of the grain boundary phase that weakens the boundary, the promotion by the mechanochemical reaction and the cyclic loading.

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