Static Fatigue and Fracture Toughness of Mullite Ceramics at 1200°C

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ムライトセラミックスの1200°Cでの静的疲労及び破壊靱性値

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The fatigue behavior for mullite ceramics containing 71, 72 and 74 wt% Al_2O_3 (71A, 72A and 74A) was measured at 1200°C by the static fatigue technique. The fracture toughness was evaluated from the slow crack growth magnitude (fatigue fracture surface) combined with the applied stress. The crack growth parameter (N) of 71A, 72A and 74A was 17, 23–24 and 26, and the fracture toughness (K_{IC}) was 4.3, 2.4 and 1.7 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. These tendencies correspond to a decrease of the glass phase in the grain boundary. The fracture modes of the grains in the fatigue fracture surface for 71A was intergranular fracture in equiaxial crystals and transgranular fracture broken in the rod-like crystals, for 72A intergranular fracture in equiaxial crystals and transgranular fracture broken in slightly remained rod-like crystals, and for 74A only intergranular fracture. The fracture mode in the catastrophic fracture surface was transgranular for 71A, 72A and 74A. It was considered that the fracture toughness of mullite at 1200°C increased with a decrease of Al_2O_3 content because the crack tip became blunter by increasing the glass phase.

Key-words: Mullite, Fatigue, Static fatigue, Slow crack growth, Crack growth parameter, Fracture toughness, Fracture surface, Fracture mode

1. Introduction

High purity mullite ceramics^{1)–3)} have received considerable attention for structural applications in high temperatures because they have excellent high temperature properties with about twice the strength of high purity alumina. We have previously measured the creep in mullite ceramics at 1300 to 1500°C and have reported that the creep rate of 74 wt% Al_2O_3 mullite was very little even at 1400°C.^{4)–6)} If mullite ceramics are used in high temperature, revealing the mechanism of the degradation of strength under stress (the fatigue behavior) and the creep behavior is important.

In this study, the fatigue behavior of mullite containing 71, 72 and 74 wt% Al_2O_3 was measured, and the fracture toughness was evaluated from the slow crack growth region magnitude (fatigue fracture sur-

face) combined with the applied stress. Furthermore, the relation between their properties and microstructures was considered.

2. Experimental procedure

Mullite powder containing 71, 72 and 74 wt% Al_2O_3 (hereafter referred to as 71A, 72A and 74A, respectively) prepared by a coprecipitation method using an aqueous solution of $\text{Al}(\text{NO}_3)_3$ and colloidal SiO_2 ⁷⁾ was compacted isostatically at 300 MPa. The compacted specimens were sintered at 1650°C in air. The sintered specimens were ground to rectangular bars of $3 \times 4 \times 40$ mm with a diamond wheel. The average grain size of 71A, 72A and 74A was 2.2, 1.6, and 2.4 μm , respectively.

Previous papers have already reported the microstructure characteristics of these specimens.^{4),5)} Specimens 71A, 72A and 74A consisted of fine equiaxial crystals and rod-like crystals, fine equiaxial crystals and slightly remained rod-like crystals, and only equiaxial crystals, respectively.^{4),5)} It has been already observed by the transmission electron microscope (TEM) that the glass phase was absent in 74 wt% mullite but present in the grain boundary of mullite containing less than 72 wt% Al_2O_3 .⁵⁾

Fatigue behavior was measured by the static fatigue technique.^{8)–10)} The time-to-failure was measured at several stresses applied by a three-point bending fixture with a span of 30 mm. The fracture toughness was evaluated from the slow crack growth magnitude in the fracture surface and the applied stress by a controlled surface flaw technique.¹¹⁾

3. Experimental results

3.1 Static fatigue

Static fatigue is defined as the degradation behavior of strength under an applied stress. Slow crack growth is responsible for fatigue in ceramics and the time-to-failure (t_f) at a constant applied stress (σ) is expressed as:^{8)–10),12)}

$$t_f = B_1 \sigma^{-N} \quad (1)$$

where N is the crack growth parameter and B_1 is a constant value.

If the relation between the applied stress and the time-to-failure is plotted in a logarithmic coordination, the gradient corresponds to the N value. The N value magnitude indicates the fatigue behavior. The larger the N value is, the larger the fatigue resistance is. The N value was calculated by the least-square method. Brittle fracture occurring immediately after elastic deformation is a prerequisite for applying the Eq. (1). As previously reported, the creep rate became lower at 1400°C for 74A and 1350°C for 71A.^{4,5} It is estimated that creep behavior is negligible in this study because the fatigue measurement was performed at 1200°C.

Generally, the strength of ceramics shows a large scatter, because they are sensitive to the magnitude of flaws in a sintered body. The fatigue behavior for 71A was measured for specimens precracked by a Vickers indenter and uncracked specimens. Figure 1 shows the relation between the applied stress and the time-to-failure for 71A. The symbol "□" shows the results for specimens not precracked and their values were remarkably scattered on the lower side of the time-to-failure than line A. However, if the applied stresses was below 204 MPa, the value was between lines A and B, and the scatter was small. The symbol "◆" shows the results for specimens precracked by a Vickers indenter at 300 g. Some of the values existed between lines A and B. The symbol "○" shows the results for the Vickers indenter at 500 g. The values were independent of the scatters for specimens not precracked. The N value for specimens precracked by the Vickers indenter at 500 g was 17.

Figure 2 shows the relation between the applied stress and the time-to-failure for 72A. The symbols "○" and "●" are the results for specimens precracked by the Vickers and the Knoop indenters at 500 g, respectively. Results for both indenters were not remarkably different in their scatters. The N values were 23 for the Vickers and 24 for the Knoop indenters.

Figure 3 shows the relation between the applied stress and the time-to-failure for 74A. The symbol "●" is for the Knoop indenter at 500 g. The relation between $\log \sigma$ and $\log t_f$ was linear above the applied stresses of about 108 MPa, but the specimens were not broken below stresses of about 106 MPa, even if they were held for a long time. The N value from the linear relation was 26. The 74A specimen unbroken after 2h at applied stresses between 107 and 108 MPa was not broken, even if held for 1 to 10 d. The relation between $\log \sigma$ and $\log t_f$ became horizontal at applied stresses of 107 to 108 MPa and showed a tendency equal to fatigue limit. The static fatigue at 200°C for 2 mol%Y₂O₃-containing tetragonal zirconia polycrystals showed the horizontal behavior in the relation between $\log \sigma$ and $\log t_f$.¹³

The symbol "○" in Fig. 3 shows the relation between $\log \sigma$ and $\log t_f$ measured after holding for

Fig. 1. The relation between the time-to-failure and the applied stress (σ_t) at 1200°C for 71 wt%Al₂O₃-mullite. "□" is not precracked. "◆" and "○" are precracked by a Vickers indenter at 300 and 500 g, respectively.

Fig. 2. The relation between the time-to-failure and the applied stress (σ_t) at 1200°C for 72 wt%Al₂O₃-mullite. "○" and "●" are precracked by a Vickers and a Knoop indenter at 500 g, respectively.

Fig. 3. The relation between the time-to-failure and the applied stress (σ_t) at 1200°C for 74 wt%Al₂O₃-mullite precracked by a Knoop indenter at 500 g. "●" is broken and "⊠" is not broken by the static fatigue measurement. "○" is measured after holding for 1 d at the applied stress of 105 MPa.

1 d at an applied stress of 105 MPa below the stress showing the horizontal behavior. This showed that strength increased by preheating for 1 d at 1200°C. However, the gradient (N value) obtained from the relation was similar to that in specimens not preheated.

In summary, N values increased with increasing Al_2O_3 and the resistance to fatigue became much better. This relation between the N value and the Al_2O_3 content corresponds to the relation between the glass phase and the Al_2O_3 content in mullite.

3.2 Observation of fracture surface and fracture toughness

Figures 4 and 5 show the fracture surface of 71A after measuring fatigue behavior. Figure 4 is for specimen not precracked. The applied stress was 161 MPa and the time-to-failure was 13 d 15h and

Fig. 4. The fracture surface of 71 wt% Al_2O_3 -mullite not precracked. The applied stress was 161 MPa and the time-to-failure was 13 d 15h and 52 min. "B" and "D" show the slow crack growth region and the catastrophic fracture surface.

Fig. 5. The fracture surface of 71 wt% Al_2O_3 -mullite precracked by a Vickers indenter at 500 g. The applied stress was 183 MPa and the time-to-failure was 53 min and 4 s. "A", "B" and "D" in (a) show the Vickers indentation, the slow crack growth region and the catastrophic fracture surfaces, respectively. (b) and (d) are enlarged photographs corresponding to regions "B" and "D" in (a), and (c) shows the boundary of them.

52 min. Figure 5 is for specimens precracked with a Vickers indenter at 500 g. The applied stress was 183 MPa, and the time-to-failure was 53 min and 4 s.

The slow crack growth region spread semielliptical from the origin and the catastrophic fracture surface followed. The origin was a natural flaw on the specimen surface for Fig. 4 and the Vickers indentation for Fig. 5. Figures 5(b) and (d) are enlarged photographs of the slow crack growth region (region B) and the catastrophic fracture region (region D) in Fig. 5(a), respectively. Figure 5(c) shows the boundary of the slow crack growth and the catastrophic fracture surface regions. The fracture mode of grains in the slow crack growth region was intergranular fracture in equiaxial crystals and transgranular fracture broken in the rod-like crystals. However, the fracture mode in the catastrophic fracture region was transgranular.

Figures 6 and 7 show the fracture surfaces of 72A precracked by a Vickers indenter at 500 g and 74A precracked by a Knoop indenter at 500 g, respectively. They show the fracture surfaces broken after holding 22h 40 min and 58 s at an applied stress of 115 MPa, and 9 min and 20 s at an applied stress of 110 MPa, respectively.

The slow crack growth region spread semielliptical from the Vickers or the Knoop indentation, and the catastrophic fracture surface followed similar to the 71A-mullite. Figures (b) and (d) in Figs. 6 and 7 are enlarged photographs of the slow crack growth (region B) and the catastrophic fracture regions (region D), respectively. Figures 6(c) and 7(c) show the boundary of the slow crack growth and the catastrophic fracture surface regions. The fracture

Fig. 6. The fracture surface of 72 wt% Al_2O_3 -mullite precracked by a Vickers indenter at 500 g. The applied stress was 115 MPa and the time-to-failure was 22h 40 min and 58 s. "A", "B" and "D" in (a) show the Vickers indentation, the slow crack growth region and the catastrophic fracture surface, respectively. (b) and (d) are enlarged photographs corresponding to region B and D in (a), and (c) shows the boundary of them.

Fig. 7. The fracture surface of 74 wt% Al_2O_3 -mullite precracked by a Knoop indenter at 500 g. The applied stress was 110 MPa and the time-to-failure was 9 min and 20 s. "A" "B" and "D" in (a) show the Knoop indentation, the slow crack growth region and the catastrophic fracture surface, respectively. (b) and (d) are enlarged photographs corresponding to region "B" and "D" in (a), and (c) shows the boundary of them.

Fig. 8. The fracture toughness of 71, 72 and 74 wt% Al_2O_3 -mullite as a function of the time-to-failure.

mode of grains in the slow crack growth region of 72A was intergranular fracture in equiaxial crystals and transgranular fracture broken in the rod-like crystal. However, the slow crack growth region of 74A was intergranular fracture. All the fracture modes in the catastrophic fracture regions in 72A and 74A were transgranular and similar to 71A.

The K_{IC} was evaluated by a controlled surface flaw technique combining the slow crack growth region magnitude with the applied stress.⁷⁾ Figure 8 shows the results. The K_{IC} was 4.3, 2.4 and 1.7 $\text{MPa} \cdot \text{m}^{1/2}$ for 71, 72 and 74 wt% Al_2O_3 , respectively.

4. Discussion

4.1 Fatigue behavior

The flaws that exist in sintered bodies are divided into microcracks which exist exclusively along the grain boundaries and macroflaws such as pores developed in the manufacturing process.^{14),15)} Generally, the strength of a material is scattered, if the pore size is larger than the grain size of the material. Figure 4 shows that the slow crack growth region in 71A not precracked has grown from a microcrack on the specimen surface at maximum stress point, and the specimen is broken when the stress intensity factor from the combination of the slow crack growth region magnitude and the applied stress were equal to the critical stress intensity factor (fracture toughness).

A crack developed under an applied stress, that is, the slow crack growth region, is equal to fatigue crack. The fatigue crack magnitude was large in low applied stresses, because the time-to-failure was long. The strength of the specimen not precracked in 71A was slightly scattered at low applied stresses because it was controlled by the fatigue crack magnitude and not by the macroflaws such as pores. However, the fatigue crack magnitude was small in high applied stresses, because the time-to-failure was short. The strength of the specimen not precracked in 71A was scattered at high applied stresses, because it was controlled not only by fatigue crack but also by macroflaws such as pores. If the flaw produced by the Vickers or the Knoop indenter at 500 g (Figs. 1, 2 and 3) was used as the initial crack in static fatigue measurement, the scatter of the result was small because the growth of the fatigue crack initiated from the controlled flaw.

It is considered that crack healing arise simultaneously with crack growth, if a stress is applied at a high temperature such as 1200°C. Figure 3 shows that the relation between the applied stress and the time-to-failure after holding for 1 d at 105 MPa. The relation had shifted to the high strength side because of crack healing. That is, it is estimated that the crack growth in the measurement of static fatigue at 1200°C was the result that the crack growth under an applied stress was interrupted by the crack healing resisting to the crack growth. The 74A specimens unbroken after 2h at applied stresses of 107 to 108 MPa were not broken, even if they were held for 1 to 10 d, because the crack growth at this applied stress is in equilibrium with crack healing at 1200°C.

The fatigue behavior in oxide ceramics such as Al_2O_3 is affected by the glass phase in the grain boundary.^{5),12)} Generally, the N value decreases with increasing the glass phase. In this study, the N value at 1200°C decreased with decreasing Al_2O_3 , that is, increasing the glass phase in the grain boundary. The fatigue behavior of glass or oxide ceramics in room temperature was interpreted by the mechan-

ism of stress corrosion caused by water vapor. More studies are required to determine whether the fatigue mechanism of mullite ceramics at high temperatures such as 1200°C is the same as oxide ceramics in room temperature or not.

4.2 Fracture toughness

In the previous paper the glass phase was slightly present in the grain boundary triple point of 72A, increased in the grain boundary of 71A and was absent in 74A.⁵⁾ Figure 8 shows that the K_{IC} of mullite ceramics at 1200°C increased with decreasing Al_2O_3 . That is, the K_{IC} of mullite at 1200°C increased with increasing glass phase.

The K_{IC} of these mullite ceramics was about 2 MPa·m^{1/2} at room temperature. That is, K_{IC} of 74A at 1200°C was similar to room temperature. However, the K_{IC} of 71A at 1200°C was larger than at room temperature. The similar effects of the glass phase to the K_{IC} at high temperature was previously reported for Si_3N_4 .^{16),17)}

It is considered that the K_{IC} of mullite ceramics at 1200°C is increased by the glass phase, and the K_{IC} of mullite containing the glass phase at 1200°C is larger than at room temperature because the crack tip becomes blunter by increasing the glass phase.

5. Conclusions

The fatigue behavior of mullite ceramics containing 71, 72 and 74 wt% Al_2O_3 (71A, 72A and 74A) was measured at 1200°C by the static fatigue technique. The fracture toughness at 1200°C was evaluated from the fatigue fracture surface magnitude combined with the applied stress by using the controlled surface flaw technique. Results obtained are as follows:

(1) The crack growth parameter (N) of 71A, 72A and 74A was 17, 23–24, and 26, respectively. The resistance to fatigue increased with increasing Al_2O_3 . The fracture toughness (K_{IC}) of 71A, 72A and 74A was 4.3, 2.4 and 1.7 MPa·m^{1/2}, respectively. These tendencies correspond to a decrease of the glass phase in the grain boundary.

(2) The fracture modes of the grain in the slow crack growth region (fatigue fracture surface) for 71A was intergranular fracture in equiaxial crystals and transgranular fracture broken in rod-like crystals, for 72A intergranular fracture in equiaxial crys-

tals and transgranular fracture broken in slightly remained rod-like crystals, and for 74A only intergranular fracture. The fracture mode in the catastrophic fracture surface was transgranular for 71A, 72A and 74A.

(3) It was considered that the fracture toughness of mullite at 1200°C increased with decreasing Al_2O_3 content, because the crack tip became blunter by increasing the glass phase.

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