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Paper

Grain Size Dependence of Thermal Shock Resistance in $KZr_2(PO_4)_3$ Ceramic

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$KZr_2(PO_4)_3$ セラミックの熱衝撃抵抗の粒径依存性

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Thermal shock fracture behavior of $KZr_2(PO_4)_3$ ceramic, which has a near-zero thermal expansion coefficient, was evaluated by the water-quenching test. The specimens having almost the same density, strength, Young's modulus, and thermal expansion coefficient, but different grain sizes, were prepared by adjusting the sintering conditions. The maximum temperature difference (ΔT_{max}), to which the specimens were subjected without failure in the thermal quench test, increased with decreasing grain size. $KZr_2(PO_4)_3$ ceramic composed of fine grains $<3\ \mu m$ withstood the test without lowering of strength even when quenching from 1300°C into water was repeated 20 times. The grain size dependence of ΔT_{max} has been attributed to residual stress caused by the thermal expansion anisotropy. As a result, grain size and thermal expansion anisotropy were incorporated into the equation for the thermal shock resistance.

Key-words : *Thermal shock, Potassium-zirconium-phosphate, Grain size, Water quenching*

1. Introduction

Some compounds in the $NaZr_2(PO_4)_3$ family have been reported in recent years to be low thermal expansion materials.[1)-7)] In particular, $KZr_2(PO_4)_3$ ceramic showed a near-zero thermal expansion, since the thermal expansion coefficients of $KZr_2(PO_4)_3$ crystal were $\alpha_a = -4.4\times10^{-6}$/°C, $\alpha_c = +7.6\times10^{-6}$/°C, and $\alpha_{avg} = -0.4\times10^{-6}$/°C.[4),5)] Consequently, the $KZr_2(PO_4)_3$ ceramic is expected to have an excellent thermal shock resistance. In general, the thermal shock resistance is expressed by

$$\Delta T_{max} = S(1-\mu)/E\alpha \qquad (1)$$

where ΔT_{max} is the maximum temperature difference to which the specimen can be subjected without failure in the thermal quench test, S flexural strength, μ Poisson's ratio, E elastic modulus, and α thermal expansion coefficient.[8)] In Eq. (1), ΔT_{max} increases with decreasing thermal expansion coefficient, and then approaches infinity at $\alpha = 0$. Actually, some $KZr_2(PO_4)_3$ ceramics could withstand the test without lowering of strength upon quenching from 1300°C into 20°C water.[5)] However, other $KZr_2(PO_4)_3$ ceramics cracked upon quenching from only 900°C.[9)] Upon investigation, it was found that the cause for this discrepancy was the difference in the microstructure. Thus, the effect of microstructure on the thermal shock resistance of the $KZr_2(PO_4)_3$ ceramic is discussed in this paper.

2. Experimental procedure

$KZr_2(PO_4)_3$ powder was synthesized by firing a mixture of $(ZrO)_2P_2O_7$ (Nihon Ceramics : industrial grade) and KH_2PO_4 (Wako Pure Chem. Ind. Ltd., reagent grade) at 1400°C for 4h. The obtained powder was ground by ball milling, and two kinds of $KZr_2(PO_4)_3$ powder with average particle sizes of about 1.5 and 3 μm were prepared. Test specimens were formed in the shape of a $5\times5\times60$ mm bar under 50 MPa, and were sintered at temperatures ranging from 1250 to 1400°C for 30 to 120 min. In order to promote densification, 2 wt% MgO was added to the obtained powder as a sintering aid.[5),9)]

The bulk density of the sintered ceramics was determined by the Archimedean method using distilled water as the displacement liquid. The thermal expansion was measured at heating and cooling rates of 10°C/min from room temperature to 800°C with a silica glass differential dilatometer (Shimadzu Co., TMA DT-30). The flexural strength was measured by the three-point bending test on as-sintered specimens over a 20 mm span at a crosshead speed of 0.5 mm/min (Shimadzu Co., S-500′). Young's modulus was measured by the sonic technique (Panametrics, 5055PR). The microstructures were observed by a scanning electron microscope (SEM; JEOL Ltd., JSM-T20). The average grain sizes were determined by the linear intercept technique from SEM micrographs of chemically etched or thermally etched fracture surfaces.[10),11)]

The thermal shock test was carried out as follows: sintered rectangular-shaped bars of $KZr_2(PO_4)_3$ ceramic were held at a desired temperature for 10 min, and quenched into a water bath at 20°C. The time required to transfer specimens to the quenching medium was about 1 to 2s. After quenching, changes in

the strength and Young's modulus were measured.

3. Results

The test specimens were 4 kinds of $KZr_2(PO_4)_3$ ceramics having average grain size ranging from 2.3 to 5.1 μm: KZP-2, 3, 4 and 5. Figure 1 shows the microstructures. The grain size was controlled by adjusting the following: particle size of $KZr_2(PO_4)_3$ powder, sintering temperature and sintering time. The data are summarized in Table 1. If grains grow over 5.5 μm due to excessive sintering, the ceramic suffers from microcracks because of the thermal expansion anisotropy of the crystal, resulting in the lowering of its strength, Young's modulus, and thermal expansion coefficient.[5),12)] Since the test specimens in this run should have almost the same properties except for grain size, ceramics free of microcracks were prepared. The density of the obtained ceramics was about 95% (3.04×10^3 kg·m^{-3}), strength ranged from 80 to 120 MPa, Young's modulus was about 1.1×10^5 MPa, and thermal expansion coefficient was -0.2×10^{-6}/°C which was calculated as a mean over the temperature ranges from room temperature to 800°C from the thermal expansion curves.

Figure 2 shows the strength degradation behavior of thermally shocked $KZr_2(PO_4)_3$ ceramic, where the strength was obtained as the ratio of strength (S_T) after thermal shock to strength (S_0) before thermal shock. The data were plotted as the mean value for 3 to 5 specimens. The deviation was less than 20%. The strengths of KZP-2 and 3 remained constant over the temperature differences investigated. On the other hand, the strengths of KZP-4 and 5 decreased at temperature differences of 980 and 780°C, respectively. The elastic modulus of $KZr_2(PO_4)_3$ ceramics also behaved in a similar manner to the strength, as shown in Fig. 3. Consequently, it was concluded that the maximum temperature difference, ΔT_{max} decreased with increasing grain size.

Figure 4 shows the strength degradation behavior

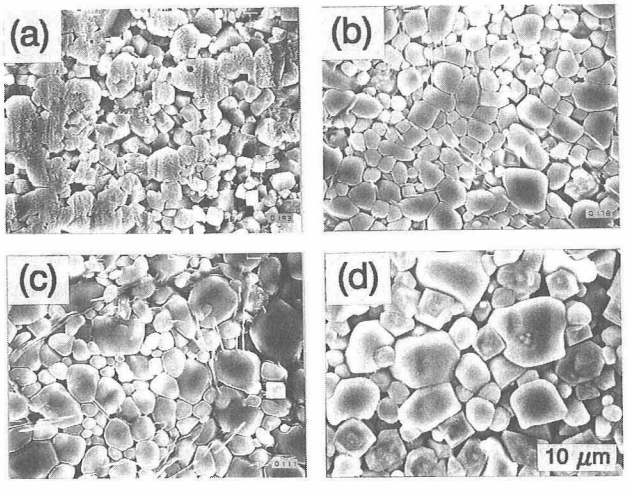

Fig. 1. Microstructures of $KZr_2(PO_4)_3$ ceramics: (a) KZP-2, (b) KZP-3, (c) KZP-4 and (d) KZP-5.

Table 1. Sintering Conditions and Grain Size of Test Specimens

specimen	particle size of $KZr_2(PO_4)_3$ powder (μm)	temperature (°C)	time (min)	grain size (μm)
KZP-2	1.5	1250	30	2.3
KZP-3	1.5	1300	120	3.2
KZP-4	3.0	1300	120	4.1
KZP-5	3.0	1400	60	5.1

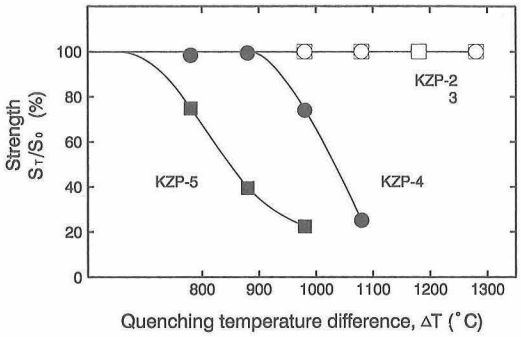

Fig. 2. Strength changes as a function of quenching temperature difference.

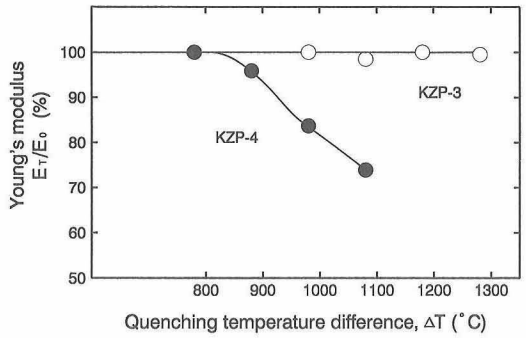

Fig. 3. Young's modulus changes as a function of quenching temperature difference.

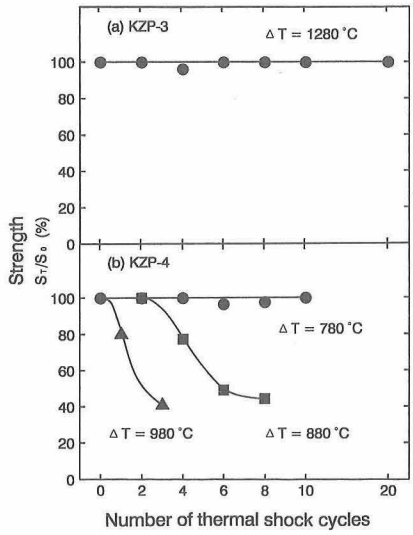

Fig. 4. Strength changes as a function of repeated thermal shock quenching.

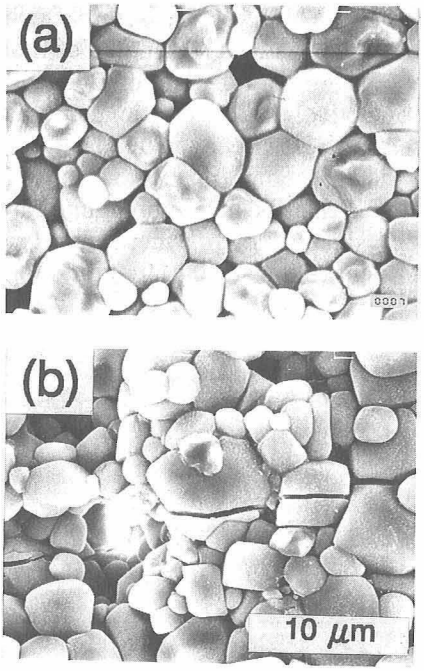

Fig. 5. Microstructures of (a) KZP-3 after 20 times of thermal shock cycles at ΔT=1280℃ and (b) KZP-4 after 8 times of thermal shock cycles at ΔT=880℃.

of KZP-3 and 4, when the thermal quench test was repeated a number of times. The strength of KZP-3 did not decrease even after 20 times of thermal shock cycles at ΔT=1280℃. KZP-4 could withstand repeated thermal shock cycles at ΔT=780℃, but it cracked on the 4th thermal shock cycle at ΔT=880℃, with subsequent thermal shock cycles causing a further reduction of strength. Figure 5 shows the typical microstructures of the specimens after thermal shock. The microstructure of KZP-3 did not change compared with that in Fig. 1(b). On the other hand, it is obvious that larger grains of KZP-4 showed signs of cracking.

4. Discussion

Generally, it is known that microcracks are formed adjacent to the larger grains and not the smaller grains when a ceramic having a high thermal expansion anisotropy is cooled from a high temperature. There is a relationship between grain size and microcracking, that is to say, microcracking occurs at a certain grain size.[13)-15)] From the report of Cleveland and Bradt,[14)] the critical grain size for microcracking is related to the inverse of the square of the maximum thermal expansion difference:

$$G_{cr}=g\gamma/(E\Delta\alpha^2\Delta T^2) \quad (2)$$

where g is a geometry factor, γ fracture surface energy, E Young's modulus, ΔT temperature change and $\Delta\alpha$ the thermal expansion anisotropy which is represented by the maximum difference in the single-crystal thermal expansion coefficient. $KZr_2(PO_4)_3$ crystal has a relatively high thermal expansion anisotropy, as mentioned in the Introduction. The critical grain size of $KZr_2(PO_4)_3$ ceramic for microcracking was 5.5 μm.[12)] The $KZr_2(PO_4)_3$ ceramic with grain size over 5.5 μm exhibited spontaneous microcracking on cooling from the sintering temperature even if it was not quenched, resulting in the lowering of the strength and Young's modulus. On the other hand, even if the specimen with fine grain size is free of microcracks, there must be a residual stress caused by thermal expansion anisotropy between the grains. Since the magnitude of the stress is assumed to depend on grain size, it was thought that ΔT_{max} decreased with increasing grain size in the thermal quench test.

Lange[16)] discussed the grain-size dependence of fracture energy in ceramics with dispersed second-phase particles, and showed that crack extension will occur if

$$\sigma_i^2 G>k \text{ (a constant)} \quad (3)$$

where σ_i is the highly localized residual stress caused by the thermal expansion mismatch ($\Delta\alpha$) between matrix and second-phase particles, and G is the particle size. Since the residual stress by thermal expansion mismatch is given by

$$\sigma_i=E\Delta\alpha\Delta T \quad (4)$$

condition for crack extension can be rewritten as

$$E^2\Delta\alpha^2\Delta T^2 G>k \quad (5)$$

Rearranging Eq. (5) gives

$$G>(k/E)/(E\Delta T^2\Delta\alpha^2) \quad (6)$$

This equation is consistent with the relationship between the critical grain size and the thermal expansion anisotropy on microcracking, Eq. (2). Furthermore, Lange showed that the externally applied stress, σ_a, can be superposed onto the residual stress caused by thermal expansion mismatch.[16)] Thus Eq. (3) can be rewritten as

$$(\sigma_a+\sigma_i)^2 G>k \quad (7)$$

Supposing that the externally applied stress is the thermal shock stress,

$$\sigma_a=E\alpha\Delta T \quad (8)$$

and that cracking occurs at ΔT_{max}, Eq. (7) can be rewritten as

$$(E\alpha\Delta T_{max}+E\Delta\alpha\Delta T_{max})^2 G=k \quad (9)$$

Here, Poisson's ratio is disregarded to simplify the expression. By rearranging Eq. (9), ΔT_{max} is given by

$$\Delta T_{max}=k'/E(\alpha+\Delta\alpha)G^{1/2} \quad (10)$$

It is noted ΔT_{max} depends on grain size G and $\Delta\alpha$ as well as α. However, when there is no thermal expansion anisotropy ($\Delta\alpha=0$),

$$\Delta T_{max}=k'/E\alpha G^{1/2} \quad (11)$$

This equation does not agree with the general thermal shock equation, Eq. (1).

Next, the effect of grain size on thermal shock behavior was considered from another viewpoint. The factor of grain size was introduced into the thermal shock resistance equation as expressed by

$$\Delta T_{max}=\{S(1-\mu)/E\alpha\}\times f(G) \quad (12)$$

The experimental result showed that ΔT_{max} decreased with increasing grain size. Hence, the

function, $f(G)$, must decrease with increasing grain size, G. In a uniform solid body ($G=0$), $f(0)=1$. When the grain size is the critical grain size at which spontaneous failure occurs in the absence of the thermal shock stress, $f(G_{cr})=0$. Consequently, $f(G)$ can be expressed as

$$f(G)=(1-G/G_{cr})^m \quad (13)$$

where m is assumed to be 1/2 on the analogy of the former discussion, in order to simplify the equation. Since the critical grain size is given by Eq. (2), combining these equations gives

$$\Delta T_{max}=S(1-\mu)/E(\alpha^2+K\Delta\alpha^2G)^{1/2} \quad (14)$$

where $K=S^2(1-\mu)^2/g\gamma E$. Equation (14) shows that ΔT_{max} depends on grain size and $\Delta\alpha$ as well as on α. Here, $\alpha=0$ expresses the relationship of the critical grain size to microcracking. On the other hand, $\Delta\alpha=0$ expresses the original equation for thermal shock resistance.

5. Conclusions

Since $KZr_2(PO_4)_3$ ceramic had a near-zero thermal expansion coefficient, it exhibited an excellent thermal shock resistance. However, the maximum temperature difference (ΔT_{max}) to which the specimen could be subjected without failure in the thermal quench test depended on the microstructure of the ceramic. It was found that ΔT_{max} increased with decreasing grain size. The strength of $KZr_2(PO_4)_3$ ceramic composed of fine grains $<3\,\mu$m did not decrease even after repeated quenching from 1300°C into water.

The dependence of grain size cannot be predicted from the general thermal-shock-resistance theory, because the factor of grain size is not included. Thus, the dependence of ΔT_{max} on grain size was discussed, and it was found to be due to a residual stress caused by the thermal expansion anisotropy between the crystal orientations. As an equation for the thermal shock resistance in the case of ceramics having thermal expansion anisotropy,

$$\Delta T_{max}=S(1-\mu)/E(\alpha^2+K\Delta\alpha^2G)^{1/2}$$

was presented, where ΔT_{max} was expressed as a function of grain size and thermal expansion anisotropy as well as the thermal expansion coefficient.

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