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Measurement of crack volume due to thermal expansion anisotropy in aluminium titanate ceramics

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Grain-boundary crack onset and crack volume at room temperature resulting from thermal expansion anisotropy in aluminium titanate ceramics were studied by dilatometry. Investigation revealed that specimens with low bulk density have a smaller temperature difference between sintering and crack-onset temperature than those of the specimens with high density and the same grain size. The fracture surface energy of aluminium titanate on the grain-boundary cracking in the present study was about 22 J m^{-2}; the grain-boundary crack volume is proportional to (grain size)$^{0.5}$.

1. Introduction

Some anisotropic ceramics can exhibit grain-boundary cracks caused by thermal expansion anisotropy during cooling from their fabrication temperatures. Aluminium titanate ceramics are among these grain-boundary cracking ceramics [1]. The cracks influence both the mechanical and thermal properties of these ceramics. For high-performance application of aluminium titanate ceramics, the relation between grain-boundary cracks and the mechanical and thermal properties must be explored. Although mechanical and thermal properties can be measured by conventional methods, grain-boundary cracks are more difficult to characterize.

The cracking condition due to thermal expansion anisotropy has been studied by many investigators based on an energy criterion [2–4] and fracture mechanics [5, 6]. Both criteria gave the same formula, indicating the correlation between fracture surface energy, γ_f, cracking temperature difference, ΔT, maximum thermal expansion anisotropy, $\Delta\alpha_{max}$, and critical grain size, G_{cr}, as follows

$$G_{cr} = k\gamma_f / E(\Delta T \Delta\alpha_{max})^2 \qquad (1)$$

where k is a constant and E is Young's modulus. It was reported previously [3] that crack occurrence in dense aluminium titanate ceramics satisfies Equation 1 and is detectable using acoustic emission (AE) and dilatometry. The present paper reports the effects of density on grain-boundary cracking. Furthermore, crack volume in a specimen is evaluated using a dilatometer, and an empirical equation is given relating measured grain size to crack volume. The data used in the present work are based on our previous works [3, 7–9].

2. Experimental procedure

The experimental procedure, preparation of powders, sintering conditions, measurement of grain-boundary cracking during cooling, and microstructural observation, has been described in our previous papers [3, 7–9] in detail. These details can be summarized as follows.

Aluminium titanate ceramics were fabricated from synthesized powders. The raw powders were α-alumina (99.99% pure, 0.5 μm in particle size, AKP-20, Sumitomo Chemical Company Ltd, Tokyo, Japan) and rutile (99.9%, 0.2 μm particle size, TP-13, Fuji Titanium Industry Co. Ltd, Tokyo, Japan). The equimolar powders were mixed for 12 h and then fired at 1500 °C for 1 h in an electric furnace to synthesize aluminium titanate. The fired powder was milled under various conditions in various mills. X-ray powder diffractometry revealed that the powders consist of aluminium titanate and that some contained 2–5 wt % excess α-alumina, which had been introduced from the alumina ball mill and acted as a grain-growth inhibitor [7]. Depending on the milling conditions, the aluminium titanate powders had various particle-size distributions and had mean particle sizes of smaller than 1 μm, as revealed by a scanning electron microscope (SEM). To control the microstructure of the fired specimens, 5 wt % of oxide additive (MgO, Fe_2O_3, Y_2O_3 or ZrO_2) was also added to the synthesized powder. Table I lists the additives and

TABLE I Additives used in the experiment

Additive	Reagent	Solvent	Grade
MgO	$Mg(OH)_2$	HNO_3 aq	> 99.9%
Fe_2O_3	$Fe(NH_4)_3(C_2O_4)_3\cdot 3H_2O$	Ethanol	First grade
Y_2O_3	Y_2O_3	HNO_3 aq	99.9%
ZrO_2	$ZrOCl_2\cdot 8H_2O$	H_2O	Extra pure

solvents used for addition. After the dopant had been mixed, the powders were calcined at 700 °C.

The prepared powders were isostatically pressed into 5 mm × 5 mm × 30 mm bars at 98 MPa pressure, and the specimens were fired in a non-loading type of dilatometer with a heating rate of 6 °C min^{-1}. The sintering temperatures were 1300–1500 °C. After the specimens had soaked for 1.5–20 h, they were cooled at the same rate at which they had been heated. The thermal contraction and expansion curve resulting from grain-boundary cracking during the cooling period was monitored.

The grain size of the sintered specimen was determined from scanning electron micrographs with a correlation based on a report by Fullman [10]. The bulk density was measured using a mercury displacement method or by dividing the weight by the measured dimensions.

The microstructural investigation was also conducted using a transmission electron microscope (TEM) (2000EX, Jeol Co., Tokyo, Japan) for the MgO added and blank samples. The thin sections for TEM observation were prepared by ion-milling.

3. Results and discussion

3.1. Crack onset during cooling

Fig. 1a shows the typical curves of thermal contraction and expansion during cooling from 1500° C, and Fig. 1b shows the effect of sintering conditions, i.e. bulk density, on the curves. The sintering conditions and resultant properties of the samples are listed in Table II. This table contains not only the samples drawn in Fig. 1 but all samples discussed in this paper. Samples A, B, C, and E are from the sample aluminium titanate powder, which has a narrow particle-size distribution, of about 1 μm, powder 1 in Table II. Alpha alumina (5 wt %, 0.5 μm in size) was added into sample C as a grain-growth inhibitor. Starting powders of samples D, F, and G had a wide grain-size distribution, of less than 1 μm, and contained about 5 wt % α-alumina, which was introduced during milling: 4 wt % α-alumina was added to sample G, which contained 9 wt % alumina in total: Sample A was fired at 1500 °C for 20 h and samples B, C and D at 1500 °C for 4 h. The firing conditions of samples E, F, and G were at 1350 °C for 2 h, 1300 °C for 4 h, and 1300 °C for 4 h, respectively. Samples A, B, C, and D were dense, while samples E, F, and G were porous.

During the first stage of cooling, the specimens contracted, with an average thermal expansion coefficient matching that of aluminium titanate. Further cooling increased the grain-boundary thermal stresses and, finally, grain-boundaries began to crack [3]. At this time the specimens began to expand as they reached room temperature.

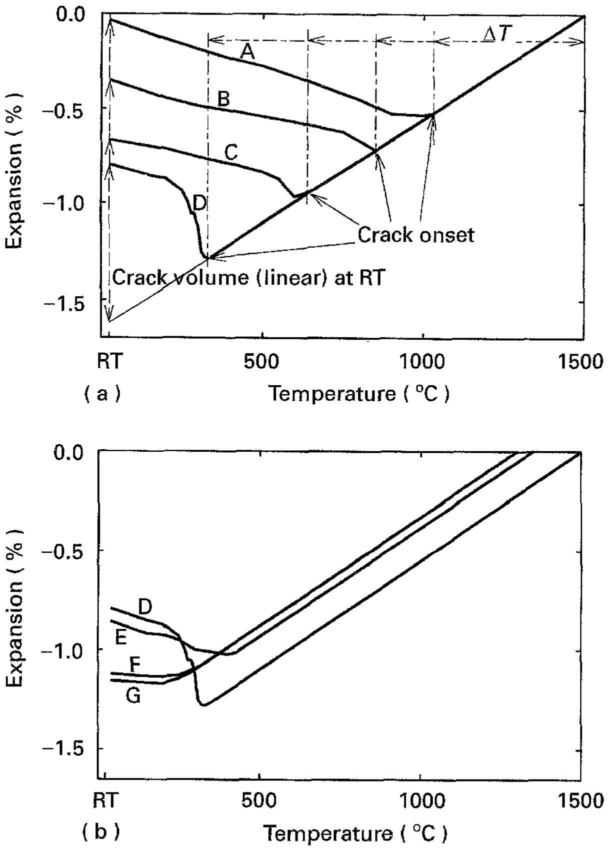

Figure 1 Typical curves of thermal contraction and expansion due to grain-boundary cracking during cooling.

The curves in this study are characterized by the temperature differences between sintering and crack onsets, i.e. ΔT in Equation 1, and by total expansion at room temperature (see Fig. 1a). In terms of temperature difference, the relation between grain size and ΔT is shown in Fig. 2. Data for specimens F and G are not shown in the graph, because the grain size of those specimens was too small and the grain-boundary not obvious enough to allow determination of grain size by a conventional method. This graph contains more data than that of the previous report [3]. The "dense" specimens fit the straight line, but the data on "porous" specimens with densities of 89%, 89%, and 91% theoretical density (open squares) are not on the line. These porous specimens have lower ΔT value than the dense specimens of the same grain size. This low ΔT value can be understood in terms of the energy criterion as follows. Porous specimens have lower grain-boundary area than dense specimens of the same grain size, because they have large pores at the boundaries or at three-grain junctions. Such porous specimens therefore exhibit a lower increase in surface energy with grain-boundary cracking. Consequently, the grain-boundary can crack with less strain energy during cooling, i.e. with a low ΔT, than that of dense specimens of the same grain size.

The fracture surface energy, γ_f, of aluminium titanate ceramics can be estimated as 22 J m^{-2} from the straight line in Fig. 2, using Equation 1 and assuming

TABLE II Sintering conditions and cracking features of fired samples

Powders and additives[a] (wt%)	Sintering (°C)(h)	Density (%)	Grain size (μm)	Expansion (%)	Cracking temp. (°C)	Sample[b]
#1 –	1350°C 2 h	90.9	1.5	0.57	430	E
#1 –	1400 2	95.4	3.5	0.96	550	
#1 Al_2O_3 5%	1500 4	92.6	4.9	0.98	650	C
#1 Al_2O_3 1%	1500 4	93.2	7.1	1.18	830	
#1 –	1500 4	91.3	9.8	1.38	925	
#1 –	1500 4	91.8	7.2	1.33	850	B
#1 –	1500 20	91.8	12.7	1.60	1030	A
#2 Al_2O_3 2%	1500 4	93.0	3.2	1.07	660	
#4 Al_2O_3 5%	1400 4	92.6	1.9	1.18	200	
#3 Al_2O_3 5%	1400 4	89.1	1.4	0.64	390	
#4 Al_2O_3 5%	1450 4	95.8	2.6	0.79	340	
#4 Al_2O_3 5%	1500 1.5	96.1	2.5	0.76	320	
#4 Al_2O_3 5%	1500 4	95.0	2.3	0.83	340	D
#1 MgO 5%	1400 2	97.1	2.2	0.32	100	
#1 ZrO_2 5%	1400 2	89.3	1.6	0.51	400	
#1 Y_2O_3 5%	1400 2	98.3	2.1	0.55	250	
#1 Fe_2O_3 5%	1400 2	96.9	2.8	0.71	440	
#4 Al_2O_3 5%	1300 4	78.3	–	0.32	330	F
#4 Al_2O_3 9%[c]	1300 4	79.0	–	0.30	280	G

[a] Particle size of powders; #4 < #3 < #2 < #1 ≈ 1 μm. Powders #2, #3 and #4 contain α-Al_2O_3 as a contamination from the used mill, which was listed in the column of additives.

[b] Samples as in Fig. 1

[c] 5% from ball mill and 4% addition of alumina powder.

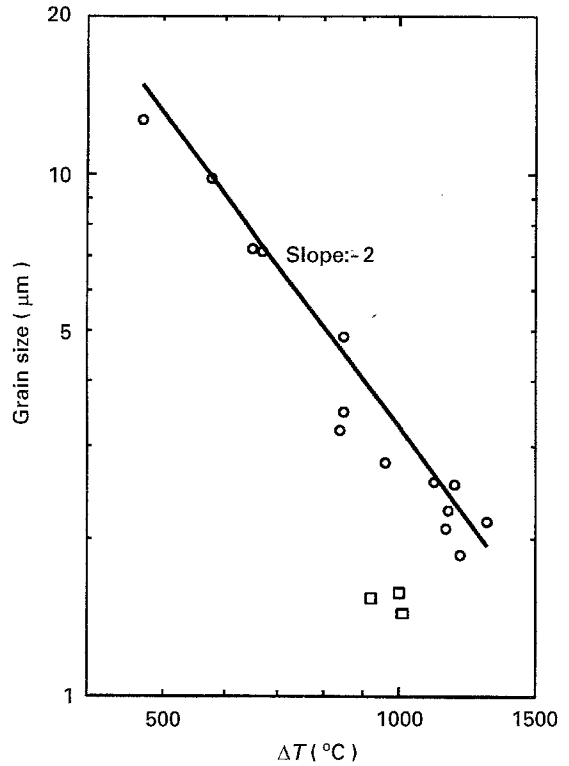

Figure 2 Relationship between grain size and ΔT : (○) dense specimens, (□) porous specimens.

$E = 200$ GPa, $\Delta\alpha_{max} = 22 \times 10^{-6}$ deg^{-1} [11], and $k = 14.4$, which is a constant after Cleveland and Bradt [4]. The present value is for initial grain-boundary cracking in an uncracked specimen and is as large as the γ_{wof} of alumina ceramics, 20 J m^{-2} [12]. In one report [12], the γ_{wof} values of aluminium titanate ceramics were less than 3 J m^{-2}, such low γ_{wof} data were not for the initial crack onset in a crack-free body, but rather for crack propagation in grain-boundary cracked ceramics. The two values thus differ in nature.

3.2. Crack volume at room temperature

Crack volume is defined as (see Fig. 1a) the straight line of intrinsic thermal contraction before cracking extrapolated to room temperature. The difference between the extrapolated line and the actual expansion of the specimen at room temperature represents the linear expansion caused by the grain-boundary cracking. Multiplying this linear expansion by three gives the grain-boundary crack volume at room temperature. The linear extrapolation can be done because the thermal expansion of aluminium titanate is almost linear in the temperature range between room temperature and 1000 °C [13], which is the range of the present extrapolation, though the thermal expansion of aluminium titanate has been reported as second-degree functions of temperature between room temperature and 1500 °C [13]. Additionally, the dopants in the present study hardly affect the thermal expansion of aluminium titanate [8]. However, there is another problem of decomposition of aluminium titanate into rutile and corundum in the temperature range between 750 and 1300 °C [14], which accompanies volume contraction according to the increase in densities of products. However, the fact that the contraction rate during the decomposition range on cooling matches the average thermal expansion of

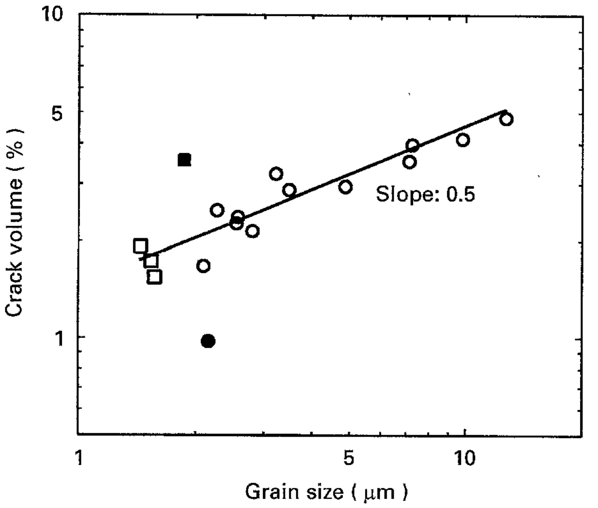

Figure 3 Dependence of crack volume on grain size: (○) dense specimens, (□) porous specimens.

aluminium titanate and decomposition could not be detected by X-ray diffractometry for the specimens fired above 1350 °C [8], confirm that the decomposition of aluminium titanate never influenced the determination of crack volume in the present study.

The expansion rate after cracking depends on porosity. This rate for the dense specimens, A–D in Fig. 1, increased with increasing ΔT or grain-boundary stress. On the other hand, the rate for the porous specimens, E–G in Fig. 1, was low. This low expansion rate after crack onset suggests that the crack tip was blunted by pores and hardly propagated to neighbouring boundaries. Crack volume is plotted versus grain size on logarithmic scale in Fig. 3. All of the data except two, which are shown as a solid square and a solid circle and will be discussed later, fit on a straight line with a slope of 0.5. The crack volume at room temperature is proportional to the square root of grain size. Although the porous specimens have smaller ΔT values than do the dense specimens with the same grain size as shown in Fig. 2, both the dense and the porous specimens fall on the same line. This is because the porous specimens have a lower expansion rate after cracking than do the dense specimens of the same grain size, as shown in Fig. 1b. An empirical relation between grain size and crack volume is derived as follows

$$V_{cr} = 10^{0.16} G^{0.5} \qquad (2)$$

where V_{cr} is the crack volume (%), and G the grain size (μm). Equation 2 can be used to estimate the amount of crack volume in an aluminium titanate ceramic.

One exception to this equation (the solid square in Fig. 3) is the specimen from the powder 4 fired at 1400 °C with 5 wt % excess alumina (see Table II). This specimen broke spontaneously into several pieces because of transverse cracking during cooling [7]. Fig. 4 shows a photograph of a cross-section of the broken surface. Circular cracks can be observed in the cross-section.

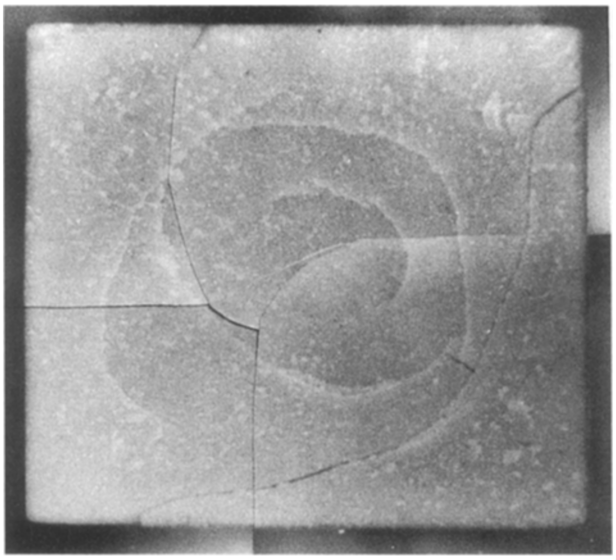

Figure 4 Optical photograph of a spontaneously cracked surface of a specimen having a large grain-boundary crack volume. Specimen size 4.0 mm × 3.6 mm.

One explanation for these transverse and circular cracks would lie in the difference in mean grain size between the centre and the outside portion of the specimen. The average grain size of the present specimen was 1.9 μm, measured at the centre of the specimen. If the outer edge had an average grain size of 2.0 μm, the cracking temperatures of the centre and outside parts are calculated to be 88 and 120 °C, respectively, assuming the sintering temperature is 1400 °C and γ_f is 22 J m^{-2}, and using Equation 1. The grain size of the outer edge of a specimen would become larger than that of the inside through a thermal gradient. Once the small difference in average grain size was introduced into the aluminium titanate ceramics, the small difference in grain size leads to a difference of 30 °C in cracking temperature in this case. In these specimens, the outer edge will first start to crack and expand on cooling; the remaining inside portions are uncracked and continue to undergo thermal contraction. The difference in expansion temperature then induces thermal stresses on a large scale and results in the transverse and circular cracks.

3.3. Stress relaxation in an MgO-doped body

Another exception to the present calculation (solid circle in Fig. 3) is the specimen with MgO added and fired at 1400 °C (see Table II). This specimen exhibited the lowest grain-boundary crack volume in the present work.

Fig. 5 shows transmission electron micrographs of the MgO-doped specimen: many dislocations and transgranular cracks were observed in the specimen. On the other hand, no contrasts caused by dislocations were revealed in the blank specimen. In the MgO-doped specimens, the formation of dislocations released the thermal stresses during cooling from the fabrication temperatures. The reason for these dislocations that were formed in an MgO-doped body must be closely connected with the formation of a solid solution between Al_2TiO_5 and $MgTi_2O_5$ [8], but remains uncertain. In any case, increasing grain-boundary

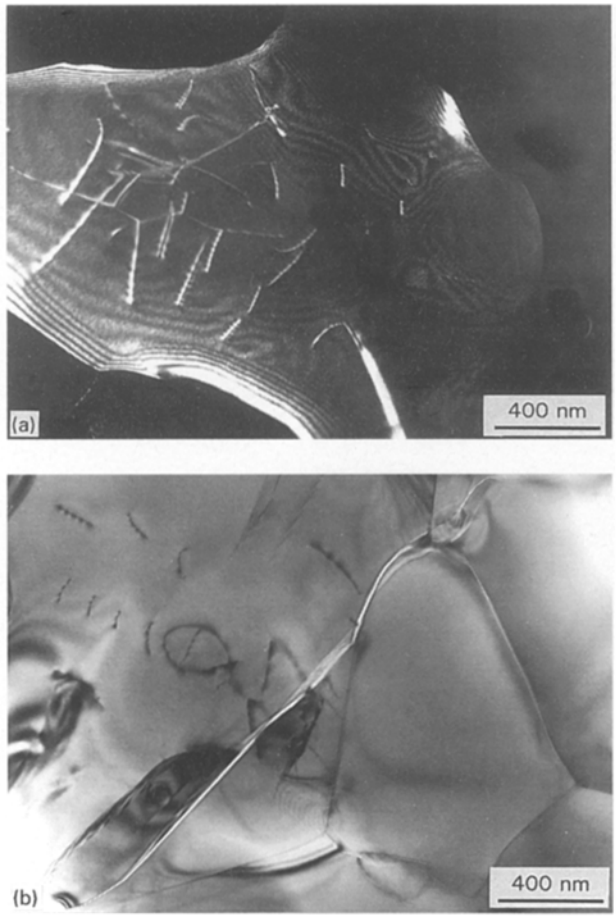

Figure 5 Transmission electron micrographs of MgO-doped specimens: (a) fired at 1350° C, dark field; (b) fired at 1400° C, bright field.

stresses during cooling do introduce dislocations, and consequently, the stresses are partially released, with the resulting small crack volume. That the crack-onset condition for the MgO-doped specimen is the same as that for the blank specimen suggests that stress relaxation did not occur at all grain boundaries, but the occurrence of relaxation depends on the crystallographic direction of the faced grains. Stress relaxation by dislocation formation gives a high bending strength and high thermal expansion to the MgO-doped specimens, as we reported previously [8].

4. Conclusion

Grain-boundary cracking caused by thermal expansion anisotropy was influenced by porosity, according to the present study. Porous specimens cracked with a rather low temperature difference, because of the small increase in surface energy during cracking. The grain-boundary crack volume, V_{cr} (%), was measured using a dilatometer, and can be shown as a function of grain size, G (μm) as

$$V_{cr} = 10^{0.16} G^{0.5}$$

Only two exceptions to this equation have been observed: one caused by nonuniformity in grain size and the other by stress relaxation with the formation of dislocations.

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