JOURNAL OF MATERIALS SCIENCE 31 (1996) 1361–1365

Thermal expansion of grain-boundary cracked aluminium titanate ceramics

Y. OHYA, Y. TAKAHASHI
Department of Applied Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-11, Japan
Z. NAKAGAWA
Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Yokohama 227, Japan

The relation between thermal expansion coefficient and grain-boundary crack volume of aluminium titanate ceramics has been calculated based on the thermal expansion data of a single crystal. The calculation began with the drawing of a frequency distribution curve of the thermal expansion coefficient for a single grain. Using the single-grain distribution curve, a distribution curve of an average coefficient for two adjacent grains was derived. The thermal expansion with a partially grain-boundary cracked body was calculated in relation to the amount of cracked boundary from the average distribution curves. The expected relation between crack volume and thermal expansion was close to that of the experimental data.

1. Introduction

Generally, the thermal expansion coefficient is a unique value for a monolithic ceramic material. Therefore, the coefficient is usually independent of microstructure of the ceramics. One of the exceptions is that of anisotropic materials, such as aluminium titanate and other pseudobrookite-type ceramics. In these ceramics, the enormous anisotropy in thermal expansion introduces grain-boundary cracking during the cooling period from their fabricating temperatures [1]. This grain-boundary cracking, as is well known, causes low thermal expansion of the materials and induces a dependence of the thermal expansion on microstructure [2–4]. As the number of grain-boundary cracks could be influenced by the grain size [5], the thermal expansion coefficient of the ceramics would be a function of the grain size [4]. However, in principle, the thermal expansion should be directly correlated to the grain-boundary cracks and not with the grain size.

Aluminium titanate has a very large anisotropic nature of thermal expansion [1] and has been well studied owing to its very low thermal expansion and high melting temperature [6–8]. In this work, we derived a correlation between the volume of grain-boundary cracks and the thermal expansion coefficient for aluminium titanate ceramics, and examined the validity of the correlation by comparing it with the experimental results.

2. Calculation of the thermal expansion of a cracked body

The method used in the work begins with a calculation of the frequency distribution of thermal expansion coefficient for a single crystal. Using this one-grain distribution curve, a frequency distribution of average thermal expansion coefficient for two adjacent grains with random orientations is calculated. The method up to this step is the same as the work of Buessem [9], but more precise in calculation. From the resulting distribution of the two-grain average coefficient, we evaluate the crack volume at room temperature and the thermal expansion coefficient on heating.

2.1. Distribution of the thermal expansion coefficients of one grain

The thermal expansion coefficient of a non-cubic crystal depends on the crystallographic direction. Aluminium titanate is a crystal of orthorhombic system and its thermal expansion coefficient, α, for a direction $(l_1 l_2 l_3)$ is represented by

$$\alpha = \alpha_a l_1^2 + \alpha_b l_2^2 + \alpha_c l_3^2 \tag{1}$$

where α_a, α_b, and α_c are the principal thermal expansion coefficients along the crystallographic axes a, b, and c, respectively. Before calculation, the coordination system is changed from Cartesian to a polar one (shown in Fig. 1) as follows

$$l_1 = \cos\phi \sin\theta \tag{2a}$$

$$l_2 = \sin\phi \sin\theta \tag{2b}$$

$$l_3 = \cos\theta \tag{2c}$$

The value of the thermal expansion coefficient, α, was calculated for every set of ϕ and θ, which increase from

0022–2461 © *1996 Chapman & Hall*

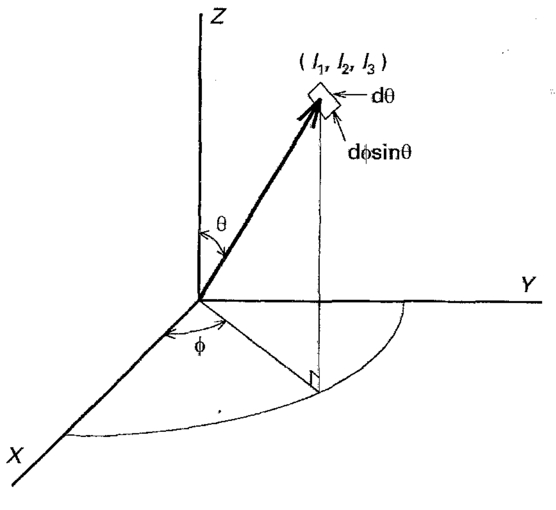

Figure 1 The coordinate system for the calculation.

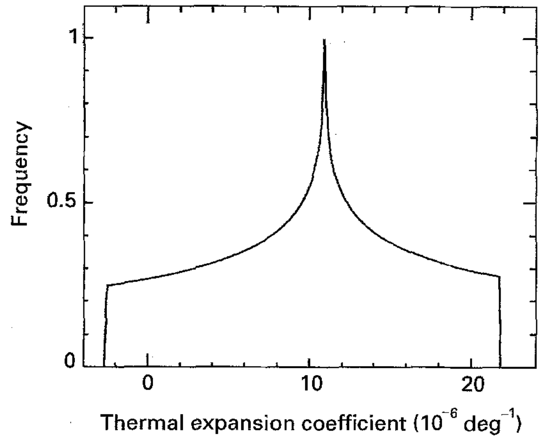

Figure 2 Frequency distribution of the thermal expansion coefficient for a single crystal.

0°–90° by dφ and dθ, respectively. Because the direction of $(l_1 l_2 l_3)$ has an area of $d\phi\, d\theta \sin\theta$ in the polar coordination system, the frequency corresponding to α increases by $d\phi\, d\theta \sin\theta$ when the calculated value is between α and $\alpha + d\alpha$.

In the calculation, the values of α_a, α_b and α_c were cited from Taylor [10] (an average coefficient from room temperature to 1400 °C), i.e. $\alpha_a = 10.9 \times 10^{-6}\,\mathrm{K}^{-1}$, $\alpha_b = 21.5 \times 10^{-6}\,\mathrm{K}^{-1}$, and $\alpha_c = -2.63 \times 10^{-6}\,\mathrm{K}^{-1}$, and $d\phi = d\theta = 0.05°$, $d\alpha = 0.1 \times 10^{-6}\,\mathrm{K}^{-1}$. The result is shown in Fig. 2. This distribution curve is characterized by its steep maximum. To confirm the steep maximum of the curve and to avoid the accumulation of numerical error in calculation, some calculations were conducted under several other conditions, i.e. taking the angle ψ (= 90° − θ) increasing from 0°–90° by dψ = 0.05° instead of θ and exchanging the data of α_a, α_b, and α_c with each other. All results showed the same steep maximum and all data were the same within several percentages.

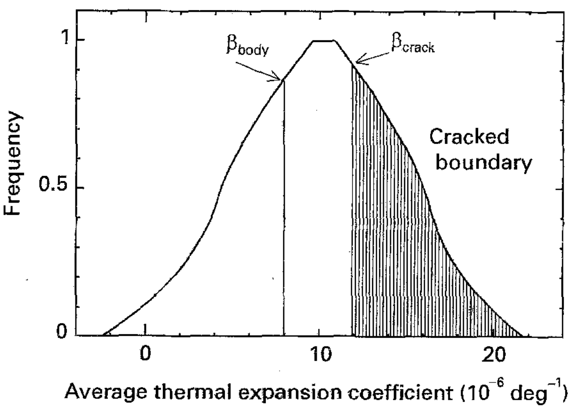

Figure 3 Frequency distribution of the average thermal expansion coefficient for two adjacent grains.

This calculated frequency distribution curve is for one grain. In a ceramic body, many grains are in contact with random orientations. Therefore, from the frequency distribution curve shown in Fig. 2 and assuming the same grain size, the average thermal expansion of two-faced grains having expansion coefficients α and α′ is defined as $\beta = (\alpha + \alpha')/2$. The value of β is an average thermal expansion coefficient between the centres of two-faced grains. The calculation was conducted using all sets of α and α′ in Fig. 2, and the value β increases by $f(\alpha)f(\alpha')$, when $(\alpha + \alpha')/2$ is between β and $\beta + d\beta$, where $f(\alpha)$ is a frequency distribution curve of α, Fig. 2, and dβ is $0.1 \times 10^{-6}\,\mathrm{K}^{-1}$. Fig. 3 shows the calculated frequency distribution curve of β.

2.2. Estimation of crack volume

During cooling from the fabricating temperature, the specimen contracts with an average thermal expansion coefficient, leaving stresses at grain boundaries. The average thermal expansion coefficient of the ceramic body should be about the middle of the frequency distribution curve of β. The grain boundaries, having larger β than the average thermal coefficient of the ceramic body, are under tensile stresses, because two-faced grains having these large β tend to contract at a larger rate than the body does on cooling. When the grain-boundary stress reaches some critical value, which is determined by an energy criterion, [10–14], the grain boundary begins to crack to release elastic energy at the boundary. The cracking should start from the boundaries having the maximum β ($\beta_{\max}$ in Fig. 3), because the boundaries are under the maximum tensile stress and therefore have maximum elastic energy, which can be released by grain-boundary cracking. On further cooling, the cracking boundaries shift to those having smaller β, right to left in Fig. 3. At room temperature, all grain boundaries having larger β than β_{crack} are cracked, leaving uncracked boundaries, which have β less than β_{crack} (as in Fig. 3). The crack opening of a cracked grain boundary having β is $(\beta - \beta_{\mathrm{crack}})l\Delta T$ at room temperature, where l is the grain size and ΔT the temperature difference between sintering and room temperature. This crack has volume of $(\beta - \beta_{\mathrm{crack}})l\Delta T l^2 k'$, where k' is a factor relating to the shape of the grain boundary. The crack volume should be thought of as the volume fraction to total volume. So we can define the crack volume in unit volume, V_{crack}, in the specimen at room temperature

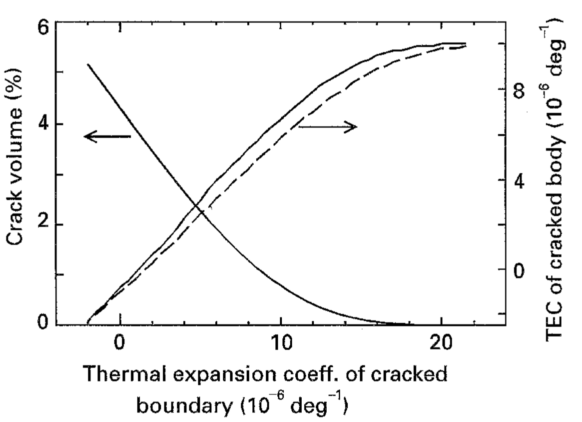

Figure 4 Crack volume per unit volume and thermal expansion coefficients (TEC) of a grain-boundary cracked body plotted against the minimum thermal expansion coefficient of cracked grain boundaries. (——) Simple average of the thermal expansion coefficient; (– – –) minimizing the elastic energy.

as follows

$$V_{\text{crack}} = k \int_{\beta_{\text{crack}}}^{\beta_{\max}} g(\beta)(\beta - \beta_{\text{crack}})\Delta T \, d\beta \qquad (3)$$

where $g(\beta)$ is the frequency distribution curve of β shown in Fig. 3 and k is a constant.

Instead of determining k and the vertical scale of the distribution curve in Fig. 3, it is convenient to calculate the maximum crack volume, $(V_{\text{crack}})_{\text{maximum}}$, at which β_{crack} reaches the minimum value of β, or all grain boundaries are cracked. This value gives a new factor to the numerical integration of Equation 3. In this work, we calculated the maximum crack volume as three times the difference of linear thermal expansion between the non-cracked body $[(\alpha_a + \alpha_b + \alpha_c)/3]\Delta T$, and the all-cracked body having the largest expansion (or the smallest coefficient of c-axis), as follows

$$(V_{\text{crack}})_{\text{maximum}} = 3[(\alpha_a + \alpha_b + \alpha_c)/3 - \alpha_c]\Delta T. \qquad (4)$$

In the equations, the value of ΔT is 1375° C, because the experimental data of the crack volume, which have been described in our previous papers [15, 16] in detail and will be discussed later in the paper, were obtained for specimens fired at 1300–1500 °C, mainly at 1400 °C. Fig. 4 is a result of the above calculation and V_{crack} is shown as a function of β_{crack} in the graph.

2.3. Estimation of average thermal expansion coefficient

When the grain-boundary cracked specimen is heated, it expands with an average thermal expansion coefficient, β_{body}. The next step in our work was to determine β_{body} from Fig. 3 for a given β_{crack}. The simplest solution for β_{body} could be obtained by calculating the average expansion coefficient of an uncracked area in Fig. 3. The values of β_{body} can be defined as the β value that divides the uncracked region in Fig. 3 into two parts of equal area. The value of β_{body} can be obtained as a function of β_{crack} by numerical integration as follows. First we select the value of β_{crack} and then integrate numerically the area of $g(\beta)$ from $\beta_{\min}$ to β_{crack}. Then we integrate again the area of $g(\beta)$ from $\beta_{\min}$ to increase the β value until the integrated value reaches a half of the area from $\beta_{\min}$ to β_{crack}, and the β value gives β_{body}

$$\int_{\beta_{\min}}^{\beta_{\text{body}}} g(\beta)\,d\beta = \int_{\beta_{\text{body}}}^{\beta_{\text{crack}}} g(\beta)\,d\beta = \int_{\beta_{\min}}^{\beta_{\text{crack}}} g(\beta)\,d\beta/2 \qquad (5)$$

Another rather precise solution could be obtained by minimizing the elastic energy on heating. This solution could be calculated by making the following assumptions: the crystal is isotropic in its elastic nature and the increase in strain energy due to the normal stresses of adjacent grains on heating is only taken into account. Assuming a grain boundary to have a thermal expansion coefficient of β and a thermal expansion coefficient of a ceramic body of β_{body}, the elastic energy in unit volume is represented by $E[(\beta_{\text{body}} - \beta)\Delta T]^2/2$, where E is an elastic constant and ΔT is the temperature difference of interest. The average thermal expansion coefficient, β_{body}, is determined by

$$\frac{d}{d\beta_{\text{body}}} \int_{\beta_{\min}}^{\beta_{\text{crack}}} \{E[(\beta_{\text{body}} - \beta)\Delta T]^2/2\} g(\beta)\,d\beta = 0 \qquad (6a)$$

and hence

$$\frac{E(\Delta T)^2}{2} \frac{d}{d\beta_{\text{body}}} \left(\beta_{\text{body}}^2 \int_{\beta_{\min}}^{\beta_{\text{crack}}} g(\beta)\,d\beta - 2\beta_{\text{body}} \int_{\beta_{\min}}^{\beta_{\text{crack}}} \beta g(\beta)\,d\beta + \int_{\beta_{\min}}^{\beta_{\text{crack}}} \beta^2 g(\beta)\,d\beta \right) = 0 \qquad (6b)$$

We get

$$\beta_{\text{body}} = \int_{\beta_{\min}}^{\beta_{\text{crack}}} \beta g(\beta)\,d\beta \Big/ \int_{\beta_{\min}}^{\beta_{\text{crack}}} g(\beta)\,d\beta \qquad (7)$$

In Equation 7, β_{body} can also be calculated numerically against a given value of β_{crack}. In this way, we can obtain the value of β_{body} as a function of β_{crack}.

The relations of β_{body} and β_{crack} are also shown in Fig. 4, where we obtain two quantities, β_{body} and V_{crack}, as functions of β_{crack}. A new relation is found between the two quantities, β_{body} and V_{crack}, by eliminating a common parameter, β_{crack}, from the two relations. The change in β_{body} with V_{crack} is shown in the next section.

3. Experimental data

The experimental procedure on aluminium titanate ceramics and some of the resultant data on thermal expansion of fired bodies were shown previously [15, 16]. Fig. 5 shows examples of the thermal expansion of fired ceramics with some additives. The thermal expansion and average thermal expansion coefficients of these ceramics from room temperature to 500° C and from room temperature to 1000° C were determined. Fig. 6 shows the relation between percentage crack volume at room temperature and percentage linear thermal expansion of the ceramics at 500 and 1000° C. The grain-boundary crack volume was measured as shown in Fig. 7, which also gives

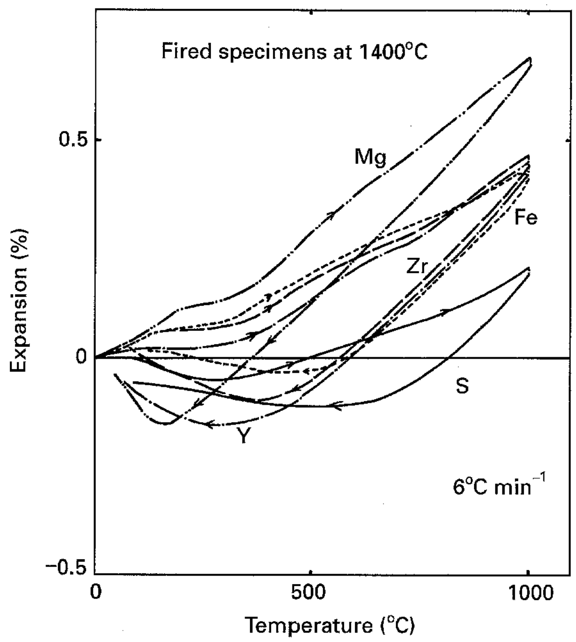

Figure 5 Thermal expansion curves of doped aluminium titanate ceramics; Mg, MgO 5 wt %; Y, Y_2O_3 5 wt %; Fe, Fe_2O_3 5 wt %; Zr, ZrO_2 5 wt %; S. blank specimen. Experimental procedures are given in [16].

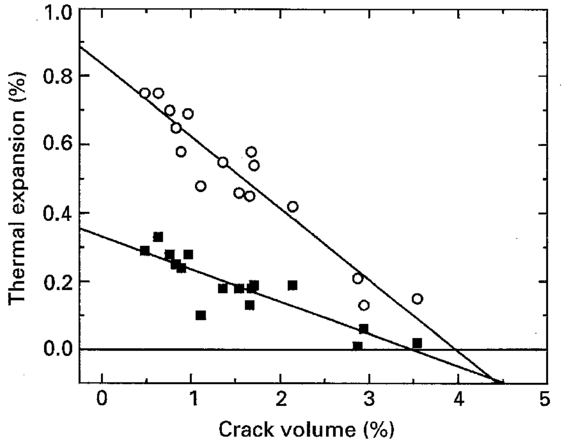

Figure 6 Thermal expansion at (■) 500 and (○) 1000° C plotted against grain-boundary crack volume.

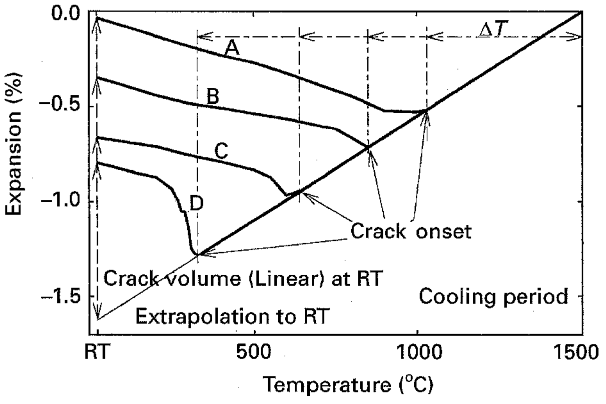

Figure 7 Measurement of crack volume during the cooling period of fabrication of the ceramics. Samples A–D differ in grain size. Three times the linear expansion represents the crack volume at room temperature.

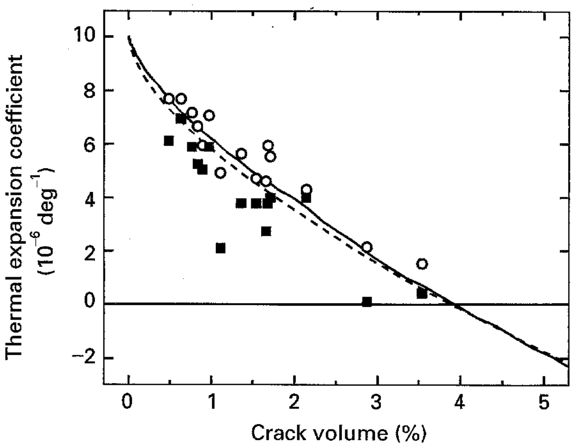

Figure 8 Thermal expansion coefficients: (——) simple average, (– – –) minimizing the elastic energy, experimental data from (○) room temperature to 1000° C, and (■) room temperature to 500° C.

some experimental data. Details of the measurement of crack volume were given elsewhere [5]. Both the experimental data and the calculated values of thermal expansion coefficient are shown in Fig. 8 as a function of the crack volume. It is clear that the experimental data closely fit with the calculated data. The graph also indicates that the two calculations based on the simple average of thermal expansion and on minimizing the elastic energy show little difference between the results, and the former assumption is sufficient to calculate the average thermal expansion coefficients of a sintered body.

4. Conclusion

The distribution curve of the thermal expansion coefficient for aluminium titanate was calculated and characterized by the steep maximum. The distribution of two-faced grains average of the coefficients was also calculated. Using this two-grain average, a relationship between grain-boundary crack volume at room temperature and the thermal expansion coefficient of grain-boundary cracked aluminium titanate ceramics, was evaluated making certain assumptions. The relation between crack volume and thermal expansion coefficients of the experimental data fit very closely to that of the calculated values.

References

1. G. BAYER, *J. Less-Common Metals* **24** (1971) 129.
2. S. M. LANG, C. L. FILLMORE and L. H. MAXWELL, *J. Res. Nat. Bur. Stand.* **48** (1952) 298.
3. W. R. BUESSEM, N. R. THIELKE and R. V. SARAKAUSKAS, *Ceram. Age* **60** (5) (1952) 38.
4. F. J. PARKER and R. W. RICE, *J. Am. Ceram. Soc.* **72** (1989) 2364.
5. Y. OHYA and Z. NAKAGAWA, *J. Mater. Sci.*, in press.
6. H. A. THOMAS and R. STEVENS, *Br. Ceram. Trans. J.* **88** (1989) 145.
7. *Idem. ibid.* **88** (1989) 184.
8. *Idem. ibid.* **88** (1989) 229–233.
9. W. R. BUESSEM, in "Mechanical Properties of Engineering Ceramics", edited by Kreigel and Palmour (Interscience, New York, 1961) pp. 127–47.

10. D. TAYLOR, *Br. Ceram. Trans. J.* **87** (2) (1987) 39.
11. J. A. KUSZYK and R. C. BRADT, *J. Am. Ceram. Soc.* **56** (1973) 420.
12. J. J. CLEVELAND and R. C. BRADT, *ibid.* **61** (1978) 478.
13. R. W. DAVIDGE, *Acta Metall.* **29** (1981) 1695.
14. Y. OHYA, Z. NAKAGAWA and K. HAMANO, *J. Am. Ceram. Soc.* **70** (1987) C184.
15. Y. OHYA, K. HAMANO and Z. NAKAGAWA, *Yogyo-Kyokai-Shi* (*J. Ceram. Soc. Jpn.*) **91** (1983) 289.
16. *Idem. ibid.* **94** (1986) 665.

Received 11 July 1994
and accepted 8 September 1995