Erratum

Erratum to: "Grain Boundary Microcracking in $ZrTiO_4$-Al_2TiO_5 Ceramics Induced by Thermal Expansion Anisotropy"

[Journal of the Korean Ceramic Society 40 [2] 109-112 (2003)][1]

Ik Jin Kim,[†] Hyung Chul Kim, Kee Sung Lee,* and In Sub Han*

*Institute for Processing and Application of Inorganic Materials (PAIM), Department of
Materials Science and Engineering, Hanseo University, Chungnam 356-820, Korea
*Energy Materials Research Team, Korea Institute of Energy Research (KIER), Taejeon 305-343, Korea
(Received October 18, 2002; Accepted January 6, 2003)

ABSTRACT

The grain-boundary microcracking materials in the system Al_2TiO_5-$ZrTiO_4$ (ZAT) is influenced by the thermal expansion anisotropy. The range of ZAT compositions investigated had showed very low thermal expansions of $0.3 \sim 1.3 \times 10^{-6}$/K compared to 8.29×10^{-6}/K of pure $ZrTiO_4$ and 0.68×10^{-6}/K of polycrystalline Al_2TiO_5, respectively, compared with the theoretical thermal expansion coefficient for a single crystal of Al_2TiO_5, 9.70×10^{-6}/K. The low thermal expansion and microcraking temperature are apparently due to a combination of thermal contraction and expansion caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase.

Key words : Al_2TiO_5, $ZrTiO_4$, Grain-boundary microcracking, Anisotropic thermal expansion, Hysteresis

1. Introduction

T he average thermal expansion coefficient of polycrystalline Al_2TiO_5 ceramics is much lower than that of the unit cell of Al_2TiO_5.[1] The low thermal expansion is responsible for grain-boundary microcrack formation caused by the high anisotropy of the thermal expansion coefficients of Al_2TiO_5 along the crystallographic axes during solidification and were accompanied by hysteresis loops.[2,3] The grain-boundary microcrack have influence on both Young's modulus and mechanical strength of Al_2TiO_5 ceramics.[4,5]

As the nearzero thermal expansion of the anisotropic material minimizes thermal stress in a body, much effort has been focused upon developing low-expansion materials for severe thermal shock applications. But pure Al_2TiO_5 tends to decompose into Al_2O_3 and TiO_2 in the temperatures range between 750 and 1280°C during cooling, which accompanies by volume contraction according to the increase in densities of products.[6] Following decomposition,

the material no longer exhibits either a low thermal expansion coefficient or favorable thermal shock behavior, rendering it apparently useless for industrial applications.

The present paper reports the ceramic composite system consisting of Al_2TiO_5 and $ZrTiO_4$ having low coefficient of thermal expansion, high melting point, and high temperature phase stability. These phases form by partial in situ reaction of Al_2TiO_5 and $ZrTiO_4$ mixtures. The another study on $ZrTiO_4$ showed that the low thermal expansion by the microcracking phase is similar to that of $HfTiO_4$, which has α-PbO_2 type structure, has a high dielectric constant at microwave frequencies.[7] $ZrTiO_4$ ceramics has been utilized mostly in the electrics industry,[8] but there is little evidence of its use in structural or engineering ceramics for high-temperature applications. Therefore, a new low thermal expansion material, based on Al_2TiO_5-$ZrTiO_4$ composites of various compositions, was fabricated by adjusting the composition of Al_2TiO_5/$ZrTiO_4$ ratios and this paper reports the effects of anisotropic thermal expansion of Al_2TiO_5 on the grain-boundary cracking in Al_2TiO_5 and $ZrTiO_4$.

2. Experimental Procedure

The $ZrTiO_4$ and Al_2TiO_5 (Dynamit Nobel, α-Al_2TiO_5 with SiO_2: 0.3 wt%, ZrO_2: 0.4 wt%, and Fe_2O_3: 0.5 wt%, 50%< 2.5) powders were used for preparing the Al_2TiO_5-$ZrTiO_4$ composites made by combining oxides rather than mixing pre-reacted Al_2TiO_5 and $ZrTiO_4$. Small amounts (5 mol%) of

Table 1. Phase Composites and Physical Properties of the ZAT Composites at 1600°C for 2 h

Materials		Phase	Sinter density (g/cm³)	Particle size		Relative density (%)		$\alpha_{25\text{-}1350°C}(\times 10^{-6}/K)$
Al_2TiO_5		β-Al_2TiO_5	3.68(3.70)	50% < 2.5 μm		93.2		0.68
$ZrTiO_4$		High-$ZrTiO_4$	4.85(5.06)	100% < 4.0 μm		95.0		8.29
Composites	ZAT5	50 mol% Al_2TiO_5 to $ZrTiO_4$	5 mol% Fe_2O_3 to Al_2TiO_5		1400°C	75		1.3
					1500°C	93		
					1600°C	95		
	ZAT7	70 mol% Al_2TiO_5 to $ZrTiO_4$	5 mol% Fe_2O_3 to Al_2TiO_5		1400°C	76		1.2
					1500°C	88		
					1600°C	94		
	ZAT8	80 mol% Al_2TiO_5 to $ZrTiO_4$	5 mol% Fe_2O_3 to Al_2TiO_5		1400°C	78		0.9
					1500°C	87		
					1600°C	93		
	ZAT9	90 mol% Al_2TiO_5 to $ZrTiO_4$	5 mol% Fe_2O_3 to Al_2TiO_5		1400°C	77		0.3
					1500°C	87		
					1600°C	92		

*( ): Theoretical density [g/cm³]

Fe_2O_3 (Hematite, 96% pure, Riedel-de Haen) were added to the Al_2TiO_5 as a stabilizer. Raw materials used in preparing $ZrTiO_4$ were ZrO_2(99.0% pure, Fluka Chemie) and TiO_2 (99.0%, E-Merck). Powder mixtures were calcined at 1000°C, and the product was ground until an average particle size of 3~5 μm was obtained. Appropriate ratios of $ZrTiO_4$ and Al_2TiO_5 powders were combined between 10/90 mol% and 50/50 mol% $ZrTiO_4$/Al_2TiO_5 as shown in Table 1 and mixed with zirconia balls for at least 30 min in the planet mill (Fritsch, pulveritte and then mixed with zirconia balls for at least 30 min in the planet mill (Fritsch, pulveritte). The powders were dry pressed at 150 MPa to produce pellets, approximately 2.86 cm diameter × 0.32 cm thickness. The pellets were sintered at temperatures between 1400°C and 1600°C for 2 h in air, in which the heating and cooling rate was 10°C/min and 20°C/min, respectively. The grain size of the sintered samples was determined from scanning micrographs with a correlation based on a report by Fullman.[9] The density was measured by using a mercury displacement method. The thermal expansion coefficient from room temperature to 1350°C was determined for a specimen (5 mm × 5 mm × 25 mm) in air, using a dilatometer (Netzsch), at a heating rate of 10°C/min and a cooling rate of 10°C/min. The crystalline structure of the samples was characterized by X-ray diffraction (Philips, PW1180/00, Ni-filtered CuKα) and scanning electron microscopy (Cambridge, Steroscan 250 MK2).

3. Results and Discussion

3.1. Phase composition and physical properties of Al_2TiO_5-$ZrTiO_4$ composites

Table 1 summarizes phase composition and physical properties of the ZAT materials sintered at 1400, 1500, and 1600°C for 2 h. The final phase consisted mainly of two crystalline phases: Al_2TiO_5 and $ZrTiO_4$. The relative density of

ZAT5 sintered at 1600°C was 95.0% of the theoretical density. The relative density of the ZAT composition decreased with increasing Al_2TiO_5 content because the densities of the starting oxides α-Al_2O_3 and TiO_2 (rutile) are 3.99 and 4.25 g/cm³, respectively. Therefore, the formation of pseudobrookite type β-Al_2TiO_5 with a theoretical density of 3.70 g/cm³ is accompanied by an about 11% molar volume increase.[6] The low relative density of ZAT9 (90 mol% Al_2TiO_5) sintered at 1600°C is related to the grain growth of Al_2TiO_5 with increasing temperature, as shown in Fig. 1, the grain sizes of β-Al_2TiO_5 decreased with increased $ZrTiO_4$ content, accounting for the observed increase in the thermal expansion coefficient of ZAT composites from 0.3 × 10⁻⁶/K to 1.3 × 10⁻⁶/K.

3.2. Anisotropic thermal expansion of Al_2TiO_5-$ZrTiO_4$ crystal lattice

Table 2 shows the thermal expansion of crystal axes of Al_2TiO_5 and $ZrTiO_4$ unit cell. Al_2TiO_5 crystal showed large anisotropic thermal expansion behavior, therefore it could be deduced that the low thermal expansion curves exhibiting hysteresis loops were due to the grain-boundary microcracks caused by the large thermal expansion anisotropy of Al_2TiO_5 in the system Al_2TiO_5-$ZrTiO_4$ as shown in Figs. 2 and 3. The calculated average linear thermal expansion coefficients of the Al_2TiO_5 and $ZrTiO_4$ unit cell were 9.70 ×10⁻⁶/K and 5.10 × 10⁻⁶/K, respectively.[1,8] However, the thermal expansion coefficient of polycrystalline ZAT8 composites sintered at 1600°C for 2 h showed up to 1000°C negative and zero level in Fig. 3.

All ZAT composites with increasing Al_2TiO_5 content exhibit reduced thermal expansion. On the other hand, the composites showed large hysteresis areas. Such phenomenon can be explained in terms of accumulated grain-boundary microcracking of the microstructure by thermal expansion anisotropy of the individual α-Al_2TiO_5 crystals
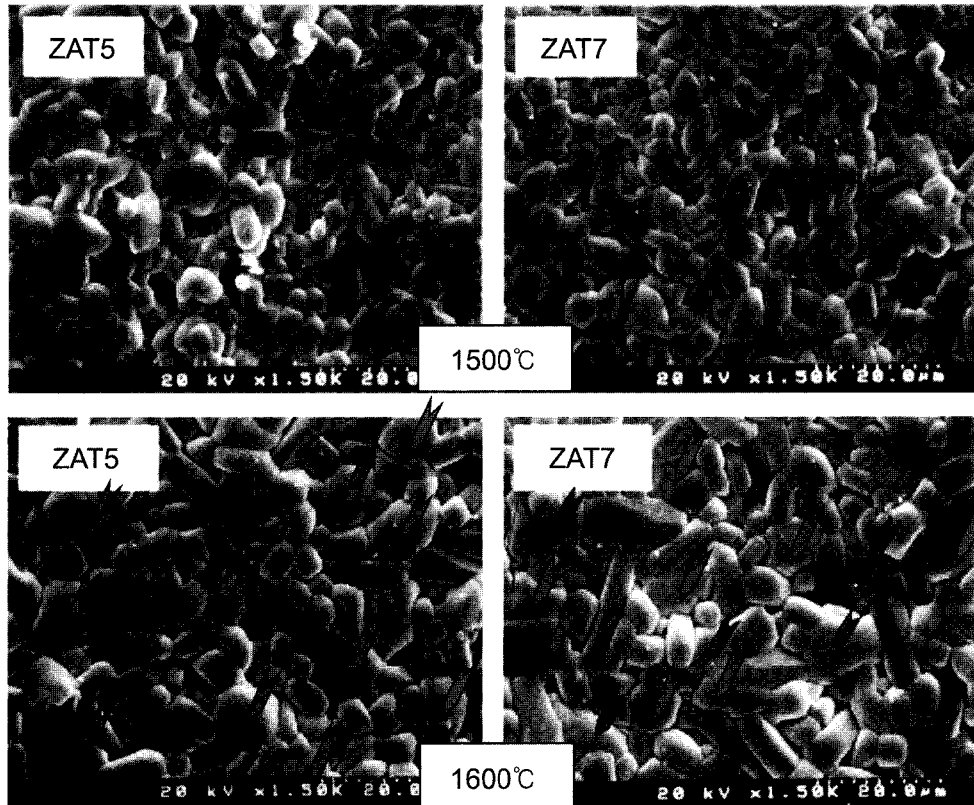
Fig. 1. Microstructure of ZAT composites sintered at 1500 and 1600°C for 2 h ($\Longrightarrow$: $ZrTiO_4$).

Table 2. Thermal Expansion Anisotropic of Al_2TiO_5 and $ZrTiO_4$

Materials	Crystallographic thermal expansion coefficients [$10^{-6}K^{-1}$]			
	a-axis	b-axis	c-axis	*$\Delta\alpha_{max}$
Al_2TiO_5	$\alpha_a = 9.40$	$\alpha_b = 9.68$	$\alpha_c = 3.60$	6.08
H-$ZrTiO_4$	$\alpha_a = 4.80$	$\alpha_b = 5.03$	$\alpha_c = 5.49$	0.69
L-$ZrTiO_4$	$\alpha_a = 4.83$	$\alpha_b = 5.03$	$\alpha_c = 5.35$	0.52

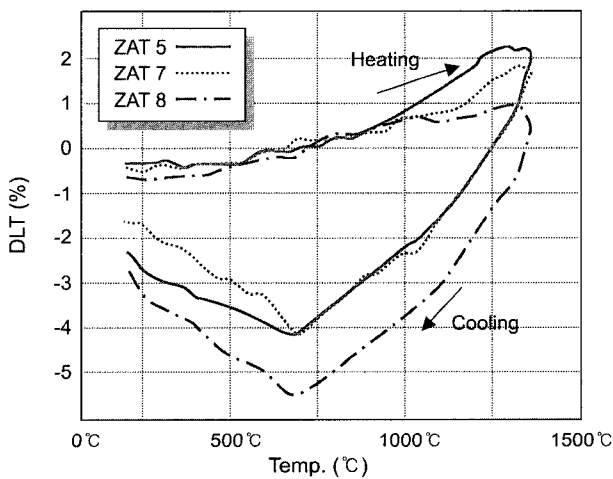*$\Delta\alpha_{max}$: Maximum anisotropic thermal expansion

Fig. 2. Thermal expansion curves of ZAT composites sintered at 1500°C for 2 h.
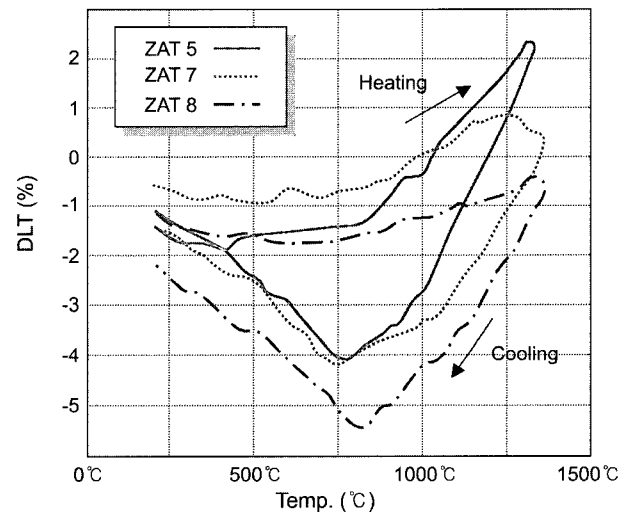

Fig. 3. Thermal expansion curves of ZAT composites sintered at 1600°C for 2 h.

that give rise to stresses on a microscopic scale during cooling; these localized internal stresses were the driving force for grain-boundary microcrack formation. During the reheating run, the individual crystallites expanded in the low temperature region; thus, the solid volume of the specimen expanded into the microcracks up to the temperature range 600 – 1000°C, whereas the macroscopic dimensions remained almost unchanged. As a result, the material

expanded very little.[10] The microcracks are closed at higher temperatures. This result is closely related to the relatively steeper thermal expansion curve. However, at still higher temperatures, the slope (i.e. expansion coefficient) was far below the theoretical value, suggesting that a large proportion of the grain-boundary microcracks were still open.

3.3. Microcracking at grain-boundary

The microstructure of the sintered ZAT composites at 1500°C consists of a narrow size distribution of $ZrTiO_4$ and Al_2TiO_5 grains as shown in Fig. 1. The average grain sizes of Al_2TiO_5 in the sintered at 1500°C are in the range of 3–5 µm. The grain-boundary microcracks observed at the ZAT-grains as shown in Fig. 1 are expected due to the presence of the highly anisotropic β-Al_2TiO_5 crystal. With increasing Al_2TiO_5 contents and sintering temperature, increased the abnormal grain growth of Al_2TiO_5 phase in ZAT5 from 3–5 µm at 1500°C for 2 h to 10–20 µm at 1600°C for 2 h, respectively, and the thermal expansion hysteresis areas of ZAT composites also increased as shown Figs. 2 and 3. The microstructure of the sintered ZAT-phase at 1600°C for 2 h consists of discontinuous larger grain of Al_2TiO_5 and this grains showed abnormal grain growth to 5–20 µm in $ZrTiO_4$ phase as shown clearly in Fig. 1.

3.4. Thermal contraction and expansion

The thermal expansion and contraction behavior of the ZAT materials fabricated at 1500°C for 2 h is shown in Fig. 2. The thermal expansion of the specimens was between 2.3% and 0.8% in the temperature range 200~1500°C. Maximum thermal expansion occurred between 1350 and 1400°C. The ZAT materials sintered at 1500°C showed almost zero level thermal expansion up to 650~750°C, though it increased by further heating, the thermal expansion increased relatively. This result is ascribed to the onset of mechanical healing of the microcracks at temperature of >650°C (1500°C/2 h) and 1000°C (1600°C/2 h), respectively and their reopening or refracturing which occurs during cooling in the temperature range between 750 and 820°C. This phenomenon of microcrack healing and reopening was reported previously using acoustic emission by R.E. Whight.[11] Furthermore the thermal contraction temperature difference, ΔT, as defined by Y. Ohya *et al.*,[2] between sintering and crack onset temperatures, increased with decreasing the grain size. However, even at 1100°C the slope of ZAT materials sintered at 1600°C is still zero level in thermal expansion when heating, suggesting that an important fraction of the microcracks is also still open in Fig. 3. At the beginning of the cooling cycle, a higher crack-onset temperature in the range 750~780°C is observed (comparable to 1500°C).

The thermal expansion coefficient of ZAT materials sintered at 1500°C for 2 h lies between 0.62×10^{-6}/K for ZAT9 and 1.76×10^{-6}/K for ZAT5 from 20 to 1200°C, respectively. The thermal expansion coefficients of ZAT Materials (1600°C for 2 h) were between 1.63×10^{-6}/K and 0.35×10^{-6}/K

(RT1200°C) only compared with the theoretical thermal expansion coefficient for single crystal of Al_2TiO_5 ceramics, 9.70×10^{-6}/K.[1] The hysteresis areas, which were integrated with a planimeter, showed a distinct maximum for the ZAT8 material sintered at 1600°C for 2 h. These thermal expansion curves are good agreement with the results of Buessem[10] and Kim[12,13] and with the tendency of grain size effect on the thermal expansion of $MgTi_2O_5$ reported by Kuzyk *et al.*[4] On the other hand, a fine-grained materials exhibited small hysteresis areas.

4. Conclusions

Materials fired at 1500°C consisted of narrowly distributed $ZrTiO_4$ and Al_2TiO_5 grains with a complex system of grain-boundary microcracks. These grain-boundary microcracks in the ZAT system are expected due to the presence of the highly anisotropic β-Al_2TiO_5 crystal. The thermal expansion hysteresis of ZAT ceramics showed zero negative level to 750°C (1500°C/2 h), and above 1000°C (1600°C/2 h), but as the temperature is raised above this level, hysteresis increased markedly caused by the crack healing effect.

Acknowledgement

REFERENCES

1. Morosin and R. W. Lynch, "Structure Studies on Al_2TiO_5 at Room Temperature and at 600°C," *Acta Cryst.*, **B28** 1040-46 (1972).

2. Y. Ohya and Z. Nakagawa, "Grain Boundary Microcracking due to Thermal Expansion Anisotropy in Aluminium Titanate Ceramics," *J. Am. Ceram. Soc.*, **70** [8] C184-86 (1987).

3. G. Bayer, "Thermal Expansion Characteristics and Stability of Pseudobrookitetype Compounds M_3O_5," *J. Less. Common. Met.*, **24** [2] 129 (1971).

4. J. K. Kuszyk and R. G. Bradt, "Influence of Grain Size on Effects of Thermal Expansion Anisotropy in $MgTi_2O_5$," *J. Am. Ceram. Soc.*, **56** [8] 420-23 (1973).

5. I. J. Cleveland and R.C. Bradt, "Grain size/Microcracking Relations for Pseudobrookite Oxides," *J. Am. Ceram. Soc.*, **61** [11-12] 478-81 (1978).

6. I. J. Kim and H. S. Kwak, "Thermal Shock Resistance and Thermal Expansion Behaviour with Compostion and Microstructure of Al_2TiO_5 Ceramics," *Canadian Metallugical Quarterly*, **39** [4] 387-95 (2000).

7. A. H. Michale and R. S. Roth, "Investigation of the Phas Transformation in $ZrTiO_4$ and $ZrTiO_4$-SnO_2 Solid Solutions," *J. Am. Ceram. Soc.*, C-18 (1983).

8. Fred J. Parke, "Al_2TiO_5 -$ZrTiO_4$-ZrO_2 Composites : A New Familiy of Low-thermal-expansion Ceramics," *J. Am. Ceram. Soc.*, **73** [4] 929-32 (1990).

9. R. L. Fullman, Trans AIME **197** 447 (1953).
10. W. R. Buessem, N. R. Thielke, and R. V. Sarakauskas, "Thermal Expansion Hysteresis of Aluminiumn Titanate," *Ceram. Age,* **60** 38-40 (1952).
11. R. E. Wright, "Acoustic Emission of Aluminium Titanate," *J. Am. Ceram. Soc.,* **5** [5] 54-56 (1972).

12. I. J. Kim, O. S. Kweon, Y. S. Ko, and C. Zogarfou, "Effect of Grain Size on the Thermomechanical Properties of Al₂TiO₅ Ceramics," *J. of the Kor. Ceram.,* **2** [4] 246-50 (1996).
13. I. J. Kim and C. Zogarfou, "Thermal Shock Resistance of Al₂TiO₅ Ceramics Prepared from Electrofused Powders," *J. of the Kor. Ceram. Soc.,* **35** [10] 1061-69 (1998).