JOURNAL OF

Ceramic Processing Research

# Zero level thermal expansion materials based on ZrTiO<sub>4</sub>-Al<sub>2</sub>TiO<sub>5</sub> ceramics synthesized by reaction sintering

## Ik Jin Kim\* and Hyung Chul Kim

Institute for Processing and Application of Inorganic Materials (PAIM), Department of Materials Science and Engineering, Hanseo University, Seosan city, Chungnam 356-820, Korea

Low thermal expansion materials based on  $Al_2TiO_5$  ceramics are of great importance because they can be mixed with other materials having positive thermal expansion coefficients to make composites which have a zero or negative thermal expansion coefficient. Zero level thermal expansion materials based on  $Al_2TiO_5$ -ZrTiO<sub>4</sub> (ZAT) composites up to 1000°C were synthesized by reaction sintering. The ZAT composites also had a much lower thermal expansion coefficient (0.2~1.3×10<sup>-6</sup>/K) than that of polycrystalline  $Al_2TiO_5$  (1.5 × 10<sup>-6</sup>/K). These low thermal expansion coefficients are apparently due to a combination of microcracking caused by the large thermal expansion anisotropy of the crystal axes of the  $Al_2TiO_5$  phase. The thermal properties of the ZAT composites were analyzed after various thermal treatment by scanning electron microscopy, X-ray diffraction, and a dilatometer.

Key words: negative thermal expansion, Al<sub>2</sub>TiO<sub>5</sub>, ZrTiO<sub>4</sub>, anisotropy, grain-boundary microcracks.

## Introduction

Most ceramics expand on heating, due to increased thermal agitation of atoms and a consequent increase of the bond lengths. However, there are some anisotropic thermal expansion ceramics that exhibit the opposite behaviour, i.e., contraction on heating. These structures will expand in one or two dimensions and contract in the other dimension (s) [1]. Examples of anisotropic materials are Al<sub>2</sub>TiO<sub>5</sub>, ZrTiO<sub>4</sub>,  $\beta$ -eucryptite, cordierite, and NZP (NaZr<sub>2</sub>P<sub>3</sub>O<sub>12</sub>) [2-6] as shown in Table 1. The problem with anisotropic materials is that microcracking occurs during the heating cycle. This particular thermal behavior is characterized by a hysteresis loops and by a much lower thermal expansion coefficient compared with dense ceramics. 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 which is the rational approach to thermal stabilization of composites [7, 8]. Al<sub>2</sub>TiO<sub>5</sub> ceramics have a very low thermal expansion because of microcracks at grain boundaries induced by the high anisotropy of the thermal expansion coefficients along the crystallographic axes [9, 10]. But pure Al<sub>2</sub>TiO<sub>5</sub> tends to decompose into Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> at temperatures ranging from 800 °C to 1300 °C during cooling [11]. Following decomposition, the material no longer exhibits either a low thermal expansion coefficient or favorable thermal shock behavior. For high temperature applications, low thermal expansion behaviour is important if these materials are to be used between 25 and 1000 °C [12]. Therefore, in this study, in an attempt to tailor a new low (close to zero or negative) thermal expansion material up to about 1000 °C consisting of a two phase material based on A1<sub>2</sub>TiO<sub>5</sub>-ZrTiO<sub>4</sub> different proportions were studied by reaction-sintering from the individual oxides, an adjusting the Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/ZrO<sub>3</sub> ratios.

#### **Experimental procedure**

Raw materials used in preparing ZrTiO<sub>4</sub>-Al<sub>2</sub>TiO<sub>5</sub> composites were ZrO<sub>2</sub> (99.0%, Showa), TiO<sub>2</sub> (99.0%, Showa) and Al<sub>2</sub>O<sub>3</sub> (99.5%, Showa). Powder mixtures were calcined at 1000 °C for 1h in air, and the product was ground using a planet mill (Fritsch, pulveritte) until an average particle size of 3-5 µm was obtained. The chemical composition of each of the compacts is shown in Table 2, where ZAT5, ZAT6, ZAT7, ZAT8 and ZAT9 refer to 50, 60, 70, 80, and 90 mol% additions of Al<sub>2</sub>TiO<sub>5</sub>, respectively and then these were mixed with zirconia balls for at least 30 minutes. Bar specimens (5 mm  $\times$  5 mm  $\times$  25 mm) and pellet specimens  $(2.86 \text{ cm diameter} \times 0.32 \text{ cm thickness})$  were made by pressing at 150 N/mm<sup>2</sup>, and sintered at 1400-1600 °C for 2-6h in air. The microstructure of the samples were characterized by X-ray diffraction (Rigaku, D/Max 2200 Ultima, Ni-filtered CuK $\alpha$ ), scanning electron microscopy (Jeol, JSM-5600) and energy dispersive X-ray spectroscopy (Jeol, ISIS 300). The mean grain sizes of the

<sup>\*</sup>Corresponding author:

Tel:+82-41-660-1441

Fax: +82-41-688-4143

E-mail: ijkim@hanseo.ac.kr

Matarials	Crystallographic th	Crystallographic thermal expansion coefficients $(10^{-6}/K)$			Ref.
Wateriais	$\alpha_{a}$	$\alpha_{\rm b}$	$\alpha_{\rm c}$		
Eucryptite (LiAlSiO <sub>4</sub> )	7.8		-17.5	25.3	3
Codierite (Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub> )	2.9		-1.1	4.0	5
Beryl (Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> )	2.6		-2.9	5.0	6
$Al_2TiO_5$	-3.0	11.8	21.8	24.8	2
H-ZrTiO <sub>4</sub> Quenching at 1300 °C	0.4806	0.5035	0.5498	0.069	4
$L-ZrTiO_4 \qquad 1250 \text{ °C} \rightarrow 750 \text{ °C}, 1 \text{ °C}$	/h 0.4828	0.5035	0.5498	0.067	4

Table 1. Anisotropic Thermal Expansion Materials

 $\Delta \alpha_{max}$ : maximum difference among axial thermal expansion coefficient

Table 2. Thermophysical Data of ZAT Composites Sintered at 1600 °C for 6h

Materials		Phase	Particle size	$\begin{array}{c} {\rm Thermal \ expansion} \\ {\rm coefficient \ } \alpha_{25\text{-}1350^{o}C} \\ (\times \ 10^{-6}/K) \end{array}$	Relative Density (%)	Sintered density (g/cm <sup>3</sup> )
$Al_2$	TiO <sub>5</sub>	$\beta$ -Al <sub>2</sub> TiO <sub>5</sub>	$50\% < 2.5 \ \mu m$	0.68	93.2	3.68(3.70)
Zr	ГіO <sub>4</sub>	High-ZrTiO <sub>4</sub>	$100\% < 4.0 \ \mu m$	8.29	95.0	4.85(5.06)
Com- posites	ZAT5	50 mol%ZrTiO <sub>4</sub>	50 mol%Al <sub>2</sub> TiO <sub>5</sub>	1.3	96.3	4.40
	ZAT6	40 mol%ZrTiO <sub>4</sub>	60 mol%Al <sub>2</sub> TiO <sub>5</sub>	1.2	98.7	4.36
	ZAT7	30 mol%ZrTiO <sub>4</sub>	70 mol%Al <sub>2</sub> TiO <sub>5</sub>	0.9	97.3	4.09
	ZAT8	20 mol%ZrTiO <sub>4</sub>	80 mol%Al <sub>2</sub> TiO <sub>5</sub>	0.81	98.5	3.95
	ZAT9	10 mol%ZrTiO <sub>4</sub>	90 mol%Al <sub>2</sub> TiO <sub>5</sub>	0.2	98.1	3.84

(): theoretical density

sintered Al<sub>2</sub>TiO<sub>5</sub> in ZAT materials were measured by image analysis (Comscope, Sometech vision) using SEM micrographs. The thermal expansion coefficients from room temperature (RT) to 1350 °C were determined for bar specimens in air, using a dilatometer, at a heating rate of 10 Kminute<sup>-1</sup> and a cooling rate of 10 Kminute<sup>-1</sup>.

In order to evaluate the thermal stability of the various compositions, the following tests were carried out: 1) Long-term thermal durability was studied by annealing the materials at the critical decomposition temperature of  $Al_2TiO_5$  (1100 °C for 100 h) because the decomposition rate has a maximum in the range 1100-1150 °C. 2) Cyclic thermal expansion coefficients were also measured, using a dilatometer at up to 1350 °C. 3) The sinter densities and decomposition contents of  $Al_2TiO$  (%) in ZAT composites were measured by a gas pyconometer (Micromeritics, Accupyc 1330) and by XRD (MDI Jade 5.0), before and after the decomposition tests.

## **Results and Discussion**

# Pure Al<sub>2</sub>TiO<sub>5</sub> and ZrTiO<sub>4</sub>

The pure  $Al_2TiO_5$  sintered at 1500 °C for 4h exhibited significant grain boundary microcracks with grain sizes of about 5-7 µm and also abnormal  $Al_2TiO_5$  grain growth. These grain boundary microcracks observed for the  $Al_2TiO_5$  grains are expected due to the highly



Fig. 1. Microstructure of pure  $Al_2TiO_5$  and  $ZrTiO_4$  sintered at 1500 °C for 4h.



Fig. 2. Thermal expansion curves of pure  $Al_2TiO_5$  and  $ZrTiO_4$  sintered at 1500 °C for 4h.

thermal anisotropic  $Al_2TiO_5$  crystal. On the other hand, the pure ZrTiO<sub>4</sub> appeared to have a wide grain size of 5-20 µm which interlinked fine-ZrTiO<sub>4</sub> particles at the grain boundaries and accompanied grain growth as shown in Fig. 1.

The thermal expansion and contraction behavior of the pure Al<sub>2</sub>TiO<sub>5</sub> and ZrTiO<sub>4</sub> materials fabricated at 1600 °C for 2h is shown in Fig. 2. The thermal expansion of the Al<sub>2</sub>TiO<sub>5</sub> phase was between -0.75% and near zero % in the extensive temperature range 25°-830°C. A maximum thermal expansion of pure Al<sub>2</sub>TiO<sub>5</sub> occurred between 1280 and 1300 °C. The pure ZrTiO<sub>4</sub> materials showed a positive thermal expansion up to 1100 °C, but when the temperature was further increased, a thermal hysteresis contraction after 1100°C up to 1250°C due to the presence of a continuous phase transition occurred and then was accompanied by a slight decrease (0.5%) in the length dimension on conversion of the high-temperature form to the low-temperature structure down to about 850 °C during the cooling [13].

The two pure materials showed large hysteresis curves. Such a phenomenon can be explained in terms of the accumulated phase transition of ZrTiO<sub>4</sub> and also the microcrack healing and reopening of the microstructure by thermal expansion anisotropy of the individual  $\beta$ -Al<sub>2</sub>TiO<sub>5</sub> crystals that give rise to stresses on a microscopic scale during cooling, these localized internal stresses were the driving force for microcrack formation. During the reheating run, the individual Al<sub>2</sub>TiO<sub>5</sub> crystallites expanded in the low temperature region; thus, the solid volume of the specimen expanded into the microcracks, whereas the macroscopic dimensions remained almost unchanged. As a result, the material expanded very little [12]. The microcracks are closed at higher temperatures above 850 °C. This result is closely related to the relatively steeper thermal expansion curve as shown in Fig. 2. However, at still higher temperatures, the slope (i.e. expansion coefficient of  $0.2 \times 10^{-6}$ /K for ZAT5) was far below the theoretical value of single crystal Al<sub>2</sub>TiO<sub>5</sub> ( $9.70 \times 10^{-6}$ / K.), suggesting that a large proportion of the microcracks were still open. This result is ascribed to the onset of mechanical healing of the microcracks with heating to  $>800^{\circ}$ C and their reopening or refracturing which occurs when cooling below 750 °C.

#### Physical properties and microstructure

The physical properties of the materials sintered at 1600 °C for 6h are summarized in Table 3. In the as sintered state, the final phases consisted mainly of two crystalline phases: Al<sub>2</sub>TiO<sub>5</sub> and ZrTiO<sub>4</sub> as shown in Table 3. The theoretical densities of ZAT materials were calculated from the XRD density using the unit cell volumes [14]. The relative density of ZAT5 sintered at 1600 °C for 6 h was 96.3% of the theoretical density. The sinter density of the ZAT composition decreased with increasing Al<sub>2</sub>TiO<sub>5</sub> content because the densities of the starting oxides  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (rutile) are 3.99 and 4.25 g/cm<sup>3</sup>, respectively. Therefore, the formation of pseudobrookite type Al<sub>2</sub>TiO<sub>5</sub> with a theoretical density of 3.70 g/cm<sup>3</sup> is accompanied by an approximately 11% molar volume increase [15]. However, the density of ZAT materials increased with ZrTiO<sub>4</sub> content up to 40-50 Mol% and then showed decreased densities for ZAT7, ZAT8 and ZAT9 at higher temperatures and also longer reaction times, which indicates an increase in the volume induced by the formation and the grain growth of the Al<sub>2</sub>TiO<sub>5</sub>



Fig. 3. Sinter density of ZAT ceramics as a function of  $ZrTiO_4$  content and reaction temperature before and after a thermal durability test. (1100 °C for 100h).

Table 3.	. Physical	Properties.	Phase Com	position and	Thermal H	Expansion	Coefficient	after Durability	Test
		· · · · · · · · · · · · · · · · · · ·				<b>P</b>			

Phase compositions	ZAT 5	ZAT 6	ZAT 7	ZAT 9	
Sintering at 1600 °C/6h	High-ZrTiO <sub>4</sub> , β-Al <sub>2</sub> TiO <sub>5</sub>				
Temperature (°C)	1100 °C/100h				
Durability test	$\begin{array}{c} \text{High-ZrTiO}_4\\ \beta\text{-Al}_2\text{TiO}_5\\ \text{TiO}_2\\ \text{Al}_2\text{O}_3 \end{array}$	$\begin{array}{c c} \text{High-ZrTiO}_4 & \text{High-ZrTiO}_4 \\ \beta\text{-Al}_2\text{TiO}_5 & \beta\text{-Al}_2\text{TiO}_5 & \text{TiO}_2 \\ \text{TiO}_2 & \text{TiO}_2 & \text{TiO}_2 & \text{Al}_2\text{O}_3 \end{array}$		ZrTiO <sub>4</sub> O <sub>2</sub> <sub>2</sub> O <sub>3</sub>	
Decomposition content of Al <sub>2</sub> TiO <sub>5</sub> (%)	50.7	20.5	85.3	95.6	
Thermal expansion coefficient ( $\times 10^{-6}/K$ )	8.87	8.70	9.02	8.91	
Increase of sinter density (%)	5.84	4.51	7.17	6.59	

phase as shown in Fig. 3.

The microstructure of the ZAT5 and ZAT6 composites sintered at 1600°C for 6h consists of a narrow size distribution of ZrTiO<sub>4</sub> and Al<sub>2</sub>TiO<sub>5</sub> grains. The EDX analysis indicates that the dark grains are Al2TiO5 and the gray phase is ZrTiO<sub>4</sub>. The average grain sizes of the  $Al_2TiO_5$  phase in ZAT5 are in the range around 3  $\mu$ m. The grain boundary microcracks observed in the ZATcomposites are expected to be due to the presence of the highly anisotropic  $\beta$ -Al<sub>2</sub>TiO<sub>5</sub> crystal as shown in Table 1. The microstructure of ZAT7 and ZAT9 sintered at same conditions consists of discontinuous larger grains of Al<sub>2</sub>TiO<sub>5</sub> and these grains showed abnormal grain growth to 5-20 µm in the microstructure. This result is also closely related with a slightly lower density as well as a lowering of the thermal expansion coefficient due to more developed microcracking at grain-boundaries. With increasing amount of Al<sub>2</sub>TiO<sub>5</sub>, the abnormal grain growth of Al<sub>2</sub>TiO<sub>5</sub> phase increased, accounting for the observed decrease in the thermal expansion coefficient.

#### Thermal expansion behaviour

The thermal expansion and contraction behavior of the ZAT5, ZAT6 and ZAT7 materials fabricated at 1600°C for 6h are shown in Fig. 5. All ZAT composites with increasing Al2TiO5 content exhibit reduced low thermal expansion coefficients accompanied by a pronounced large hysteresis effect. The ZAT5 materials showed a low thermal expansion coefficent up to 600 °C, but when the temperature was further increased, the thermal hysteresis increased relatively. This result is ascribed to the onset of mechanical healing of the microcracks with heating to >600 °C and their reopening or refracturing which occurs when cooling below 730 °C. This phenomenon of microcrack healing was previously reported from studies using acoustic emission by Wright [16]. Furthermore the thermal contraction temperature difference,  $\Delta T$ , as defined by Ohya and Nakagawa [8], between sintering and the crack onset temperatures, increased with an increasing ZrTiO<sub>4</sub> content. However, even at 1000 °C the slope of ZAT5 material sintered at 1600 °C still give zero level thermal expansion when heating, suggesting that an important fraction of the microcracks is also still open. The thermal expansion coefficient of ZAT materials sintered at 1600 °C for 6 h are  $0.2 \times 10^{-6}/K$ for ZAT9,  $0.81 \times 10^{-6}$ /K for ZAT8,  $0.93 \times 10^{-6}$ /K for ZAT7,  $1.2 \times 10^{-6}$ /K for ZAT6 and  $1.3 \times 10^{-6}$ /K for ZAT5 respectively at temperatures from 20 to 1000 °C. The hysteresis areas, which were integrated with a planimeter, showed a distinct maximum hysteresis area for the ZAT9 material sintered at 1600 °C for 6h, whose average grain size is 20-30 µm (Fig. 4). These thermal expansion curves are in good agreement with the results of Buessem et al. [17] and with the tendency of the grain size effect on the thermal expansion of MgTi<sub>2</sub>O<sub>5</sub> reported by Kuzyk and Bradt [18]. On the other hand, fine-grained materials exhibited small hysteresis areas.

#### Decomposition

The changes of the physical properties, phase compositions and thermal expansion coefficients due to long-term thermal loading tests are given in Table 3. The relative amounts of decomposed composition after tests were calculated from XRD (MDI, Jade 5.0) measurements. The Al<sub>2</sub>TiO<sub>5</sub> phase in ZAT8 and ZAT9 composites containing 20 and 10 mol% ZrTiO<sub>4</sub> decomposed to Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> in the main, and partial decomposition was observed in the ZAT5 and ZAT7 composites sintered at 1600 °C for 6h after the annealing tests. However, the final phase of ZAT6 sintered at 1600 °C consisted in the main of two phases: Al<sub>2</sub>TiO<sub>5</sub> and ZrTiO<sub>4</sub> as shown in Table 3. The decomposition content of Al2TiO5 decreased with increased ZrTiO4 content by limiting the grain growth of Al<sub>2</sub>TiO<sub>5</sub>, and thus the compositions with 30 and 50 mol% of ZrTiO<sub>4</sub>



**Fig. 4.** Microstructure of ZAT5 (a), ZAT7 (b), ZAT8 (c) and ZAT9 (d) ceramics sintered at 1600 °C for 6h.



Fig. 5. Thermal expansion curves of ZAT ceramics sintered at 1600  $^{\circ}\mathrm{C}$  for 6h.

still retained above 60% of the Al<sub>2</sub>TiO<sub>5</sub> phase. These decompositions result in an increase of the thermal expansion coefficients and an increase of densities of about 4.51-7.20% compared to the samples sintered at 1600 °C for 6h, corresponding to a decreased volume of the Al<sub>2</sub>TiO<sub>5</sub> phase as shown in Fig. 3. These volume contractions occur after the Al<sub>2</sub>TiO<sub>5</sub> decomposes into Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> at 1100 °C. However, the addition of ZrTiO<sub>4</sub> partially prevented the decomposition of the Al<sub>2</sub>TiO<sub>5</sub> materials.

## Conclusions

Materials fired at 1600 °C for 6h consisted of homogeneously-dispersed and narrowly distributed ZrTiO<sub>4</sub> and Al<sub>2</sub>TiO<sub>5</sub> grains with a complex system of microcracks at grain boundaries. The thermal expansion hysteresis curves showed a zero or negative level to 650 °C for ZAT5 (1600 °C/6h), and above 800 °C for ZAT7 (1600 °C/6h), respectively, but as the temperature is raised above this level, the hysteresis increased slightly due to the crack healing effect. The thermal expansion coefficient and sinter density increased with increasing ZrTiO<sub>4</sub> content. ZAT6 containing 60 vol% Al<sub>2</sub>TiO<sub>5</sub>, which showed little change in microstructure, density and thermal expansion coefficient during the tests, showed good thermal durability after a long-term annealing test at 1100 °C for 100 h. However, to tailor the new zero level thermal expansion materials based on ZrTiO<sub>4</sub>-Al<sub>2</sub>TiO<sub>5</sub> ceramics, the Al<sub>2</sub>TiO<sub>5</sub> phase in the composites should be stabilized by the formation of a solid solution and by limitation of its grain growth.

# Acknowledgement

This work was supported by Frontier 21C, Carbon Dioxide Reduction & Sequestration R&D Center, Korea Institute of Energy Research.

## References

- 1. H.D. Megaw, Mat. Res. Bull. 6 (1971) 1007-1018.
- I.J. Kim and H.S. Kwak, Canadian Metallugical Quarterly. (2000) 39[4] 387-395.
- 3. F.J. Parke, J. Am. Ceram. Soc. 73[4] (1990) 929-932.
- 4. H. Schulz, J. Am. Ceram. Soc. 60[7] (1974) 313-327.
- M. Lachman, R.D. and R.M. Lewis, Am. Ceram. Soc. Bull. 60[2] (1981) 202-205.
- D.K. Agrawal and J.H. Adair, J. Am. Ceram. Soc. 73[7] (1990) 2153-2155.
- I.J. Kim, F. Zhao, J. Gong, K.S. Lee, I.S. Han, and W.S. Kuk, J. of Ceramic Processing Research 4[2] (2003) 71-79.
- Y. Ohya and Z. Nakagawa, J. Am. Ceram. Soc. 70[8] (1987) C184-186.
- 9. B. Morosin and R.W. Lynch, Acta Cryst. B28 (1972) 1040-1046.
- G. Bayer and J. Less, Common. Met. 24[2] (1971) 129-134.
- V. Buscaglia and P. Nanni, J. Am. Ceram. Soc. 81[10] (1998) 2645-2653.
- 12. E. Gugel, Keramische Zeitschrift. 36[9] (1984) 477-479.
- A.E. Machale and R.S. Roth, J. Am. Ceram. Soc. 69[11] (1986) 827-832.
- L.M.D. Cranswick. "To solve structure from powder diffraction, first they must be indexed!" School of crystallography, Birkbeck university of Landon, U.K.
- 15. H.A.J. Thomas and R. Sterens, Br. Ceram. Trans. J. 88 (1989) 144-151.
- 16. R.E. Wright, J. Am. Ceram. Soc. 5[5] (1972) 54-56.
- 17. W.R. Buessem, N.R. Thielke, and R.V. Sarakauskas, Ceram. Age. 60 (1952) 38-40.
- J.K. Kuszyk and R.G. Bradt, J. Am. Ceram. Soc. 56[8] (1973) 420-423.