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Crack healing, reopening and thermal expansion behavior of Al_2TiO_5 ceramics at high temperature

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Abstract

Thermal expansion behavior and its correlation with microstructure of ZAT ($ZrTiO_4$–Al_2TiO_5) composites were investigated. Thermal expansion coefficient increased from 0.05 [mm/(mm°C) × 10^6] at room temperature to 1.6 [mm/(mm°C) × 10^6] at 1100 °C. The low thermal expansion of Al_2TiO_5 ceramics is apparently due to a combination of grain boundary micro-cracking caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase. During the reheating run, the individual crystallites expanded at low temperature; thus, the solid volume of the specimen expanded into the micro-cracks, whereas the macroscopic dimensions remained almost unchanged. As a result, the material expanded very little up to 1000 °C. The micro-cracks closed at higher temperatures. This result is closely related to relatively steeper thermal expansion curves.

Keywords: Al_2TiO_5; $ZrTiO_4$; Grain boundaries; Thermal expansion; Thermal shock resistance

1. Introduction

Most ceramics expand on heating, due to increased thermal agitation of atoms and consequent increase of the bond lengths. However, there are some anisotropic thermal expansion ceramics that exhibit the opposite behavior, i.e., contraction on heating. These structures will expand in one or two dimensions and contract in the other dimension(s).[1] The problem with anisotropic materials is that micro-cracking occurs during the heating cycle. This particular thermal behavior is characterized by a hysteresis loop and by a much lower thermal expansion coefficient compared with dense ceramics.[2,3] As the near-zero 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.[4,5] Al_2TiO_5 ceramics have a very low thermal expansion because of micro-cracks at grain boundaries induced by the high anisotropy of the thermal expansion along −3.0, +11.8 and +21.8 [mm/(mm°C) × 10^6] for its three crystallographic axes.[6,7] In this work, 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 $A1_2TiO_5$–$ZrTiO_4$ in different proportions was studied by reaction-sintering from the individual oxides, adjusting the $Al_2O_3/TiO_2/ZrO_2$ ratios.

2. Experimental

Raw materials used in preparing $ZrTiO_4$–Al_2TiO_5 composites were ZrO_2 (99.0%, Showa), TiO_2 (99.0%, Showa) and Al_2O_3 (99.5%, Showa). Powder mixtures were calcinated at 1000 °C for 1 h in air, and the product was ground using the 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 1, where ZAT5, ZAT6, ZAT7, ZAT8 and ZAT9 refer to as 50, 60, 70, 80 and 90 mol% addition of Al_2TiO_5, respectively, and then

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Table 1
Thermal and physical data of ZAT composites sintered at 1600 °C for 6 h

Materials	Phase	Particle size	Thermal expansion coefficient, $\alpha_{25-1350\,^{\circ}C}$ [mm/(mm°C) × 10^6]	Relative density [%]	Sintered density [g/cm^3]
Al_2TiO_5	β-Al_2TiO_5	50% < 2.5 μm	0.68	93.2	3.68 (3.70)
$ZrTiO_4$	High-$ZrTiO_4$	100% < 4.0 μm	8.29	95.0	4.85 (5.06)
ZAT5[a]	50 mol% $ZrTiO_4$	50 mol% Al_2TiO_5	1.3	96.3	4.40
ZAT6[a]	40 mol% $ZrTiO_4$	60 mol% Al_2TiO_5	1.2	98.7	4.36
ZAT7[a]	30 mol% $ZrTiO_4$	70 mol% Al_2TiO_5	0.9	97.3	4.09
ZAT8[a]	20 mol% $ZrTiO_4$	80 mol% Al_2TiO_5	0.81	98.5	3.95
ZAT9[a]	10 mol% $ZrTiO_4$	90 mol%Al_2TiO_5	0.2	98.1	3.84

( ): Theoretical density (g/cm^3).
[a] $ZrTiO_4$–Al_2TiO_5 composites.

mixed with zirconia balls for at least 30 min. Bar specimens (5 mm × 5 mm × 25 mm) and pellet specimens (2.86 cm diameter × 0.32 cm thickness) were made by pressing at 150 N/mm^2, and sintered at 1400–1600 °C for 2–6 h in air. The microstructure of ZAT samples was characterized by X-ray diffraction (Rigaku, D/Max 2200 Ultima, Ni-filtered Cu Kα) and environmental scanning electron microscopy (ESEM, XL-30, FEG). The thermal expansion coefficient from room temperature (RT) to 1350 °C was determined for a bar specimen in air, using a dilatometer, at a heating rate of 10 °C min^{-1} and a cooling rate of 10 °C min^{-1}.

3. Result and discussion

3.1. Microstructure

The pure $ZrTiO_4$ appeared to have a wide grain size of 5–20 μm interlinked fine-$ZrTiO_4$ particles at the grain boundaries would accompany grain growth as shown in Fig. 1. On the other hand, the pure Al_2TiO_5 sintered at 1500 °C for 4 h exhibited significant grain boundary micro-cracks with grain sizes of about 5–7 μm and also abnormal Al_2TiO_5 grain growth. These micro-cracks at the grain boundary observed at the Al_2TiO_5

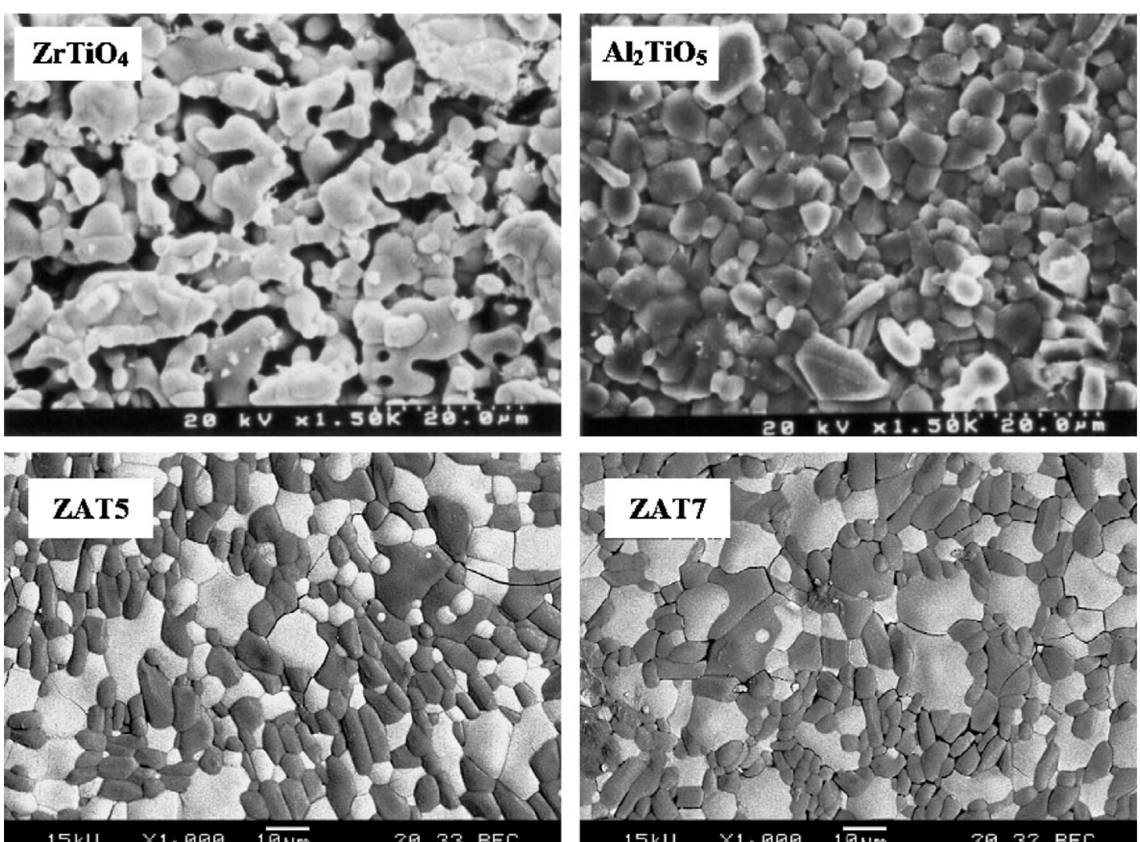

Fig. 1. Microstructure of pure Al_2TiO_5 and $ZrTiO_4$ sintered at 1500 °C for 4 h, ZAT5 and ZAT7 sintered at 1600 °C for 6 h.

grains are expected to be highly thermal anisotropic Al_2TiO_5 crystal. The microstructure of the sintered ZAT5 composite at 1600 °C for 6 h consists of a narrow size distribution of $ZrTiO_4$ and Al_2TiO_5 grains. The EDX analysis indicates that the dark grains are in Al_2TiO_5 and the gray phase is in $ZrTiO_4$. The average grain sizes of Al_2TiO_5 phase of ZAT5 are in the range of 3 μm. The microstructure of sintered ZAT7 phase at same conditions consists of discontinuous larger grain of Al_2TiO_5 and this grain showed abnormal grain growth to 5–20 μm in microstructure. With increasing Al_2TiO_5 contents, the abnormal grain growth of Al_2TiO_5 phase increased as shown in Fig. 1.

3.2. Thermal expansion behavior of pure $ZrTiO_4$ and Al_2TiO_5

The pure $ZrTiO_4$ materials showed a positive thermal expansion up to 1100 °C, but when the temperature was further increased, the thermal hysteresis contracted after 1100 °C relatively up to 1250 °C due to the presence of continuous phase transition and then accompanied a slight decrease (0.5%) in the length of dimension on conversion of the high-temperature form to the low-temperature structure up to about 850 °C during the cooling.[8] The two pure materials showed large hysteresis curves as shown in Fig. 2. Such a phenomenon can be explained in terms of accumulated phase transition of $ZrTiO_4$ and also the micro-crack healing and reopening of the microstructure by thermal expansion anisotropy of the individual Al_2TiO_5 crystals that give rise to stresses on a microscopic scale during cooling, respectively; these localized internal stresses were the driving force for micro-crack formation.

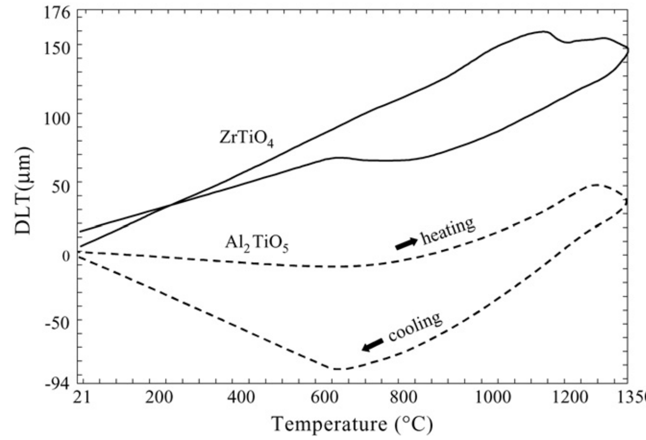

Fig. 2. Thermal expansion curves of pure Al_2TiO_5 and $ZrTiO_4$ sintered at 1500 °C for 4 h.

3.3. Micro-crack healing and reopening

Microstructure of ZAT5 composite during the heat treatment is shown in Fig. 3. The observed micro-cracks by ESEM between grain boundaries at 26 °C were 233–244 nm. In the first run to 681 °C, the length of micro-crack at grain boundary was 52 nm, and the specimens exhibited negative thermal expansion. The second run to 900 °C, the individual Al_2TiO_5 crystal-

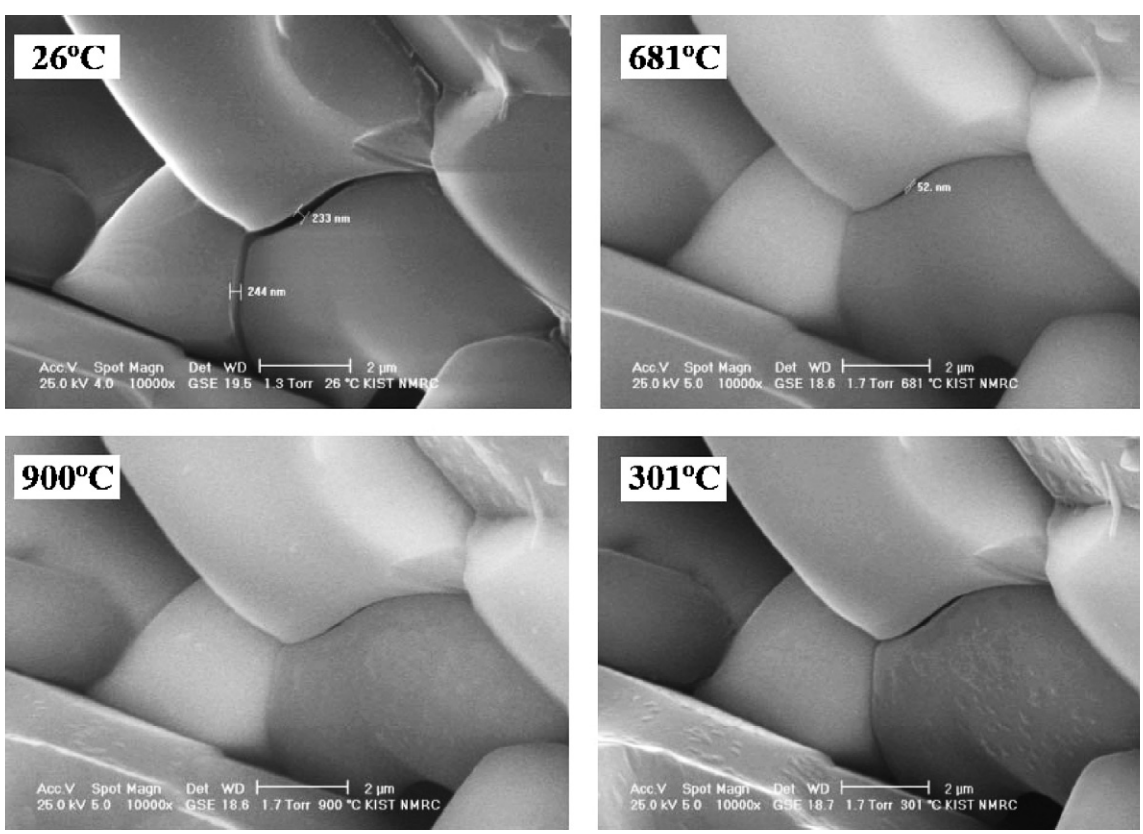

Fig. 3. Microstructure of ZAT5 sintered at 1600 °C for 6 h.

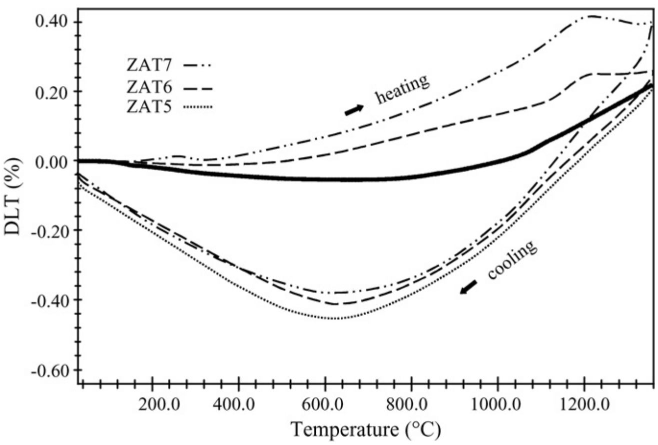

Fig. 4. Thermal expansion curves of ZAT ceramics sintered at 1600 °C for 6 h.

lites expanded into the micro-cracks, whereas the macroscopic dimensions remained almost unchanged. As a result, the material expanded very little. The micro-cracks are closed at higher temperatures above 950 °C. However, at still higher temperatures, the slope (i.e., expansion coefficient of 0.2 [mm/(mm°C) × 10^6] for ZAT5) was far below the theoretical value than that of single crystal Al_2TiO_5 (9.70 [mm/(mm°C) × 10^6]), suggesting that a large proportion of the micro-cracks were still open. The crack reopening would promote the thermal hysteresis during cooling on the third run.

3.4. *Thermal expansion behavior of ZAT composites*

All ZAT composites with increasing Al_2TiO_5 content exhibit reduced low thermal expansion coefficients accompanied by pronounced large hysteresis area as shown in Fig. 4. The ZAT5 materials showed a low thermal expansion 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 micro-cracks with heating to >600 °C and their reopening or refracturing which occurs when cooling below 730 °C.

Even at 1000 °C the slope of ZAT5 materials sintered at 1600 °C is still zero level thermal expansion when heating, suggesting that an important fraction of the micro-cracks is also still open. The thermal expansion coefficients of ZAT materials sintered at 1600 °C for 6 h are 0.2 [mm/(mm°C) × 10^6] for ZAT9, 0.81 [mm/(mm°C) × 10^6] for ZAT8, 0.93 [mm/(mm°C) × 10^6] for ZAT7, 1.2 [mm/(mm°C) × 10^6] for ZAT6 and 1.3 [mm/(mm°C) × 10^6] for ZAT5 at temperature from 20 to 1000 °C, respectively.

4. Conclusions

Materials fired at 1600 °C for 6 h consisted of homogeneously dispersed and narrow distributed $ZrTiO_4$ and Al_2TiO_5 grains with a complex system of micro-cracks. The thermal expansion hysteresis curves showed a zero or negative level to 950 °C for ZAT5, and above 600 °C for ZAT6, respectively, but as the temperature is raised above this level, hysteresis increased slightly due to the crack healing effect. The thermal expansion coefficient and sinter density increased with increasing $ZrTiO_4$ content.

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