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Low thermal expansion behavior and thermal durability of $ZrTiO_4$–Al_2TiO_5–Fe_2O_3 ceramics between 750 and 1400 °C

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Abstract

The thermal-shock-resistant materials in the system Al_2TiO_5–$ZrTiO_4$ (ZAT) were synthesized by oxide process. The range of ZAT compositions investigated had showed very low thermal expansions of $0.3\sim1.3\times10^{-6}$/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 composites also had high thermal durability between 750 and 1400° for 100 h. The low thermal expansion and high thermal durability 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 and the limitation of grain growth Al_2TiO_5 by the $ZrTiO_4$. The microstructural degradation of the composites is presented here analyzed by scanning electron microscopy, X-ray diffraction, and dilatometry.

Keywords: Al_2TiO_5; Thermal expansion; Thermal shock resistance

1. Introduction

Aluminum titanate (Al_2TiO_5) is well-known as an excellent thermal shock-resistant material, resulting from its unique combination of low thermal expansion, low thermal conductivity, and low Young's modulus, which, in turn, allows for applications as an insulating material in engines such as portliners, piston bottoms, and turbochargers.[1] However, Al_2TiO_5 materials have a relatively low mechanical strength because of microcracks induced by the high anisotropy of the thermal expansion coefficients along the crystallographic axes.[2]

These polycrystalline ceramics have a much lower thermal expansion coefficient compared with a single crystal of Al_2TiO_5.[3] This particular thermal behavior is characterized by hysteresis loops. 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. But pure Al_2TiO_5 tends to decompose into Al_2O_3 and TiO_2 at temperatures ranging from 750 to 1280 °C during cooling.[4,5] 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 thermal durability of Al_2TiO_5 can be improved by the formation of solid solutions with MgO, Fe_2O_3, or TiO_2, which are isomorphous with the mineral pseudobrookite, such as Fe_2TiO_5,[6] $MgTi_2O_5$,[7,8] or Ti_3O_5 (anosovite).[9] Another source of stabilization is the limitation of microcracks and grain growth of Al_2TiO_5 by the addition of additives such as SiO_2,[10] ZrO_2,[11] $ZrTiO_4$,[12] or mullite,[13] most of which does not form a solid solution with Al_2TiO_5 but rather restrain the tendency of Al_2TiO_5 toward decomposition.

In situ partial reactions during the sintering of Al_2TiO_5 and $ZrTiO_4$ mixtures result in composites that have low coefficient of thermal expansion, high melting point, and high temperature phase stability.[14] The further study on $ZrTiO_4$ showed that the thermal behavior by the microcracking phase is similar to $HfTiO_4$, which also has a low thermal expansion.[15] $ZrTiO_4$ has been used by the electronic industry as a dielectric resonator material in microwaves devices and for high-temperature pigments, but there is moderately little evidence of

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Table 1
Phase composites and physical properties of the ZAT composites

Materials	Phase	Sinter density (g/cm^3)	Relative density (%)	Particle size	$\alpha_{25-1350}$°C ($\times 10^{-6}$/K)
Al_2TiO_5	β-Al_2TiO_5	3.68 (3.70)[a]	93.2	50% < 2.5 μm	0.68
$ZrTiO_4$	High-$ZrTiO_4$	4.85 (5.06)[a]	95.0	100% < 4.0 μm	8.29
Composites					
ZAT5	50 mol% $ZrTiO_4$	50 mol% Al_2TiO_5		5 mol% Fe_2O_3 to Al_2TiO_5	1.3
ZAT7	30 mol% $ZrTiO_4$	70 mol% Al_2TiO_5		5 mol% Fe_2O_3 to Al_2TiO_5	1.2
ZAT8	20 mol% $ZrTiO_4$	80 mol% Al_2TiO_5		5 mol% Fe_2O_3 to Al_2TiO_5	0.9
ZAT9	10 mol% $ZrTiO_4$	90 mol% Al_2TiO_5		5 mol% Fe_2O_3 to Al_2TiO_5	0.3

[a] Theoretical density (g/cm^3).

its use in structural or technical ceramics application.[16] For high temperature applications, long-term thermal durability and mechanical properties are important if these materials are to be used between 750 and 1300 °C. Therefore, in this work, a new low thermal expansion material having the good thermal durability (800–1300 °C) of Al_2TiO_5, based on Al_2TiO_5–$ZrTiO_4$ composites, was fabricated by adjusting the composition of Al_2TiO_5:$ZrTiO_4$.

2. Experimental procedure

The Al_2TiO_5 (β-Al_2TiO_5 with SiO_2: 0.3 wt.%, ZrO_2: 0.4 wt.%, and Fe_2O_3: 0.5 wt.%, 50% < 2.5 μm) powders was suppied by Dynamit Nobel. Small amounts (5 mol%) of Fe_2O_3 (Hematite, 96% pure, Riedel-de Haen) were added to the Al_2TiO_5 as a stabilizer. The $ZrTiO_4$ sintered at 1600 °C for 4 h was made by mixing ZrO_2 (99.0% pure, Fluka Chemie) and TiO_2 (99.0%, E-Merck). The $ZrTiO_4$ and Al_2TiO_5 powders were used for preparing the ZAT composites made by mixing $ZrTiO_4$ and Al_2TiO_5 powders. Powder mixtures were calcined at 1000 °C and the product was ground until an average particle size of 3∼5 μm was obtained. Appropriate amounts of $ZrTiO_4$ and Al_2TiO_5 powders were then combined as shown in Table 1 and 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. They were sintered at temperatures between 1400 and 1600 °C for 2 h in air. At this time the heating rate was 10 °C/min and the cooling rate was about 20°/min. The sintered densities were measured by the water-immersion method. The three-point bending strength of three bar specimens (7×7×70 mm) of each compostion at room temperature was measured using a universal testing machine (Instron 1186), with a span length of 40 mm and a cross head speed of 0.2 mm/min. The Young's modulus was measured by the resonance-frequency method, as a function of sintering temperature using the bending-test specimens. The thermal expansion coefficient from room temperature to 1350 °C was determined for a specimen (5×5×25 mm), in air, using a dilatometer (Netzsch), at a heating rate of 10 °C/min and a cooling rate of 10 °C/min.

In order to evaluate the thermal durability of the various compositions, the following tests were carried out: (1) Cyclic thermal shock in a two-chamber furnace between 750 and 1400 °C. The total number of cycles was 23 with a cyclic interval of 100 h. (2) Cyclic thermal expansion coefficients were also measured, using a dilatometer at up to 1500 °C, before and after the decomposition tests. 3) Long-term thermal durability was studied by annealing the materials at the critical decomposition temperature of Al_2TiO_5 (1100 °C for 100 h). The microstructural degradation of the samples were characterized by X-ray diffraction (Philips, PW1180/00, Ni-filtered CuK_α) and scanning electron microscopy (Cambridge, Steroscan 250 MK2).

3. Results and discussion

Table 2 summarizes physical properties of the 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 ZAT sintered at 1600° was 97.1% of the theoretical density. The relative density of the ZAT composition decreased with increasing Al_2TiO_5 content because the densities of the

Table 2
Physical data of ZAT composites after various heat treatment temperature for 2 h

Physical data		ZAT 5	ZAT 7	ZAT 8	ZAT 9
Relative density (%)	1400 °C	75	76	78	77
	1500 °C	93	88	87	87
	1600 °C	95	94	93	92
Bending strength (MPa)	1400 °C	22	16	15	15
	1500 °C	30	27	17	19
	1600 °C	35	27.5	23	22
Elastic modulus (GPa)	1400 °C	10	7	7	5
	1500 °C	18	16	13	12
	1600 °C	17	15	12	12

starting oxides α-Al_2O_3 and TiO_2 (rutile) are 3.99 and 4.25 g/cm^3, respectively. Therefore, the formation of pseudobrookite type β-Al_2TiO_5 with a theoretical density of 3.70g/cm^3 is accompanied by an about 11% molar volume increase.[17] 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 as shown in Table 1. As the firing temperature increased, the density of ZAT materials was normally higher. On the other hand, higher sintering temperature resulted in grain growth of Al_2TiO_5. A relatively high bending strength of 35.0 MPa and a moderately high Young's modulus of 18.0 KN/mm^2 were found in ZAT5 (50 mol% of $ZrTiO_4$) sintered at 1500 °C. This result can be attributed to the limitation of grain growth and microcracks with $ZrTiO_4$, which does not form a solid solution with Al_2TiO_5. This material shows results, that is, the bending strength of ZAT5 sintered at 1500 °C showed higher strength than those at sintered at 1600 °C, average 30 MPa. This result could be possibly explained by an increase of grain boundary microcracking in Al_2TiO_5 with sintering temperature and increased abnormal grain size of Al_2TiO_5 in ZAT composites to 10∼30 μm (see Fig. 1). the Young's modulus was measured as a function of quenching number by the resonance method. ZAT5 having 50 mol% $ZrTiO_4$ has a relatively higher Young's modulus (17 KN/mm^2) than the others. However, it gives a decrease of Young's modulus with increasing Al_2TiO_5 content.

The microstructure of the sintered ZAT composites at 1500 °C consists of a narrow size distribution of $ZrTiO_4$ and Al_2TiO_5 grains. The average grain sizes of Al_2TiO_5 are in the range of 3 μm. The grain boundary microcracks observed at the ZAT-grains are expected to be highly anisotropic β-Al_2TiO_5 crystal (Fig. 1). With increasing Al_2TiO_5 contents and sintering temperature, the abnormal grain growth of Al_2TiO_5 phase and the thermal expansion hysteresis areas also increased as shown in Figs. 2 and 3. This result may be attributed to the lower mechanical strength and Young's mouduls of ZAT-composites as shown in Table 2. The microstructure of sintered ZAT-phase at 1600 °C for 2 h consists of abnormal grains of Al_2TiO_5 and these ranging 5∼20 μm in $ZrTiO_4$ phase as shown clearly in Fig. 1. This result is also closely related with a slightly lower density as well as a lowering of the thermal expansion due to microcracking.

All ZAT composites with increasing Al_2TiO_5 content exhibit reduced thermal expansion. On the other hand, the composites showed large hysteresis areas. Such a phenomenon can be explained in terms of accumulated microcracking of the microstructure by thermal expansion anisotropy of the individual β-Al_2TiO_5 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

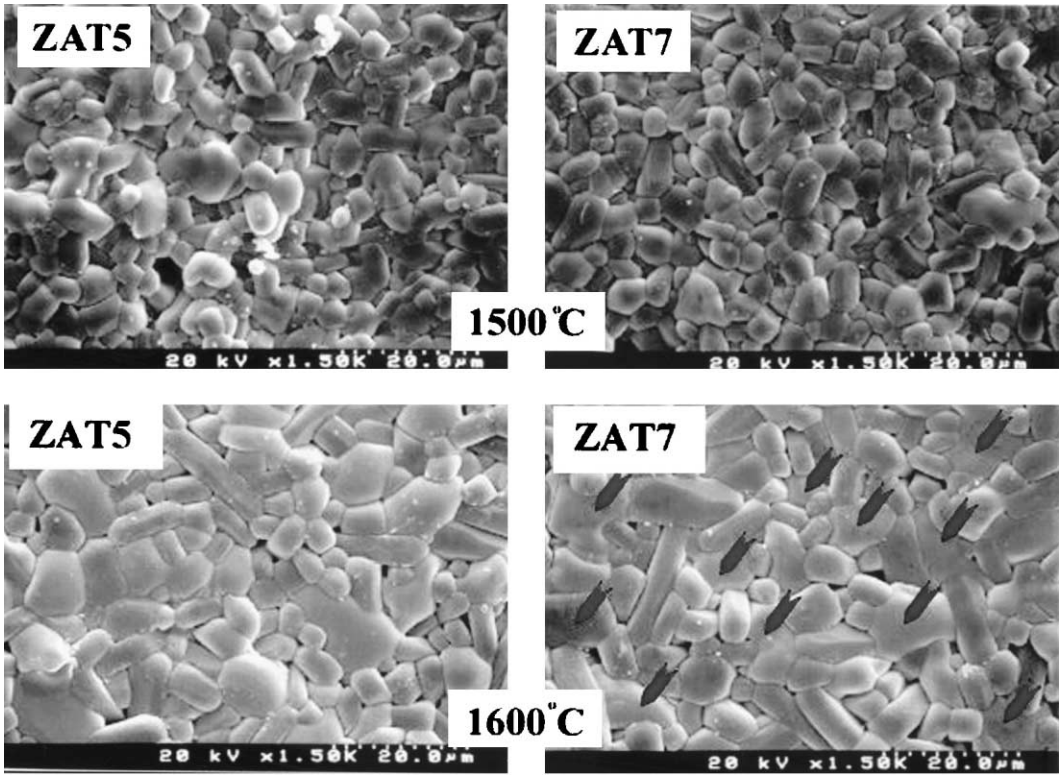

Fig. 1. Microstructure of ZAT composites sintered at 1500 and 1600 °C for 2 h (←: $ZrTiO_4$).

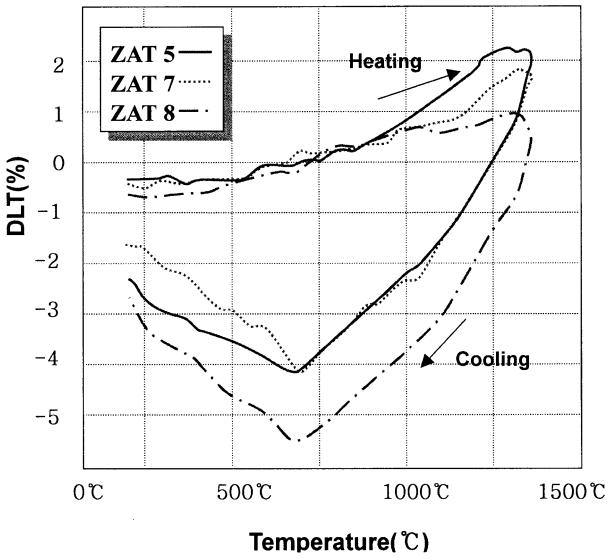

Fig. 2. Thermal expansion curves of ZAT composites sintered at 1500 °C/2 h.

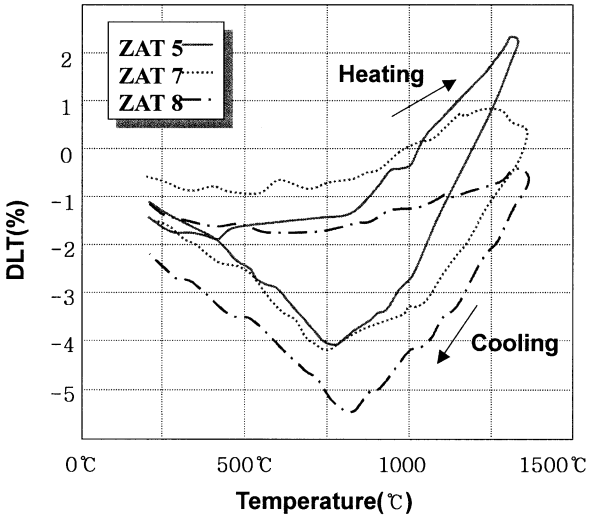

Fig. 3. Thermal expansion curves of ZAT composites sintered at 1600 °C/2 h.

run, the individual 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.[18] The microcracks are closed at higher temperatures. This result is closely related to the relatively steeper thermal expansion curve in Figs. 2 and 3. However, at still higher temperatures, the slope (i.e. expansion coefficient) was far below the theoretical value, suggesting that a large proportion of the microcracks were still open.

The thermal expansion and contraction behavior of the ZAT materials fabricated at 1500 °C for 2 h are shown in Fig. 2. The thermal expansion of the specimens was between 2.3 and 0.8% in the temperature range

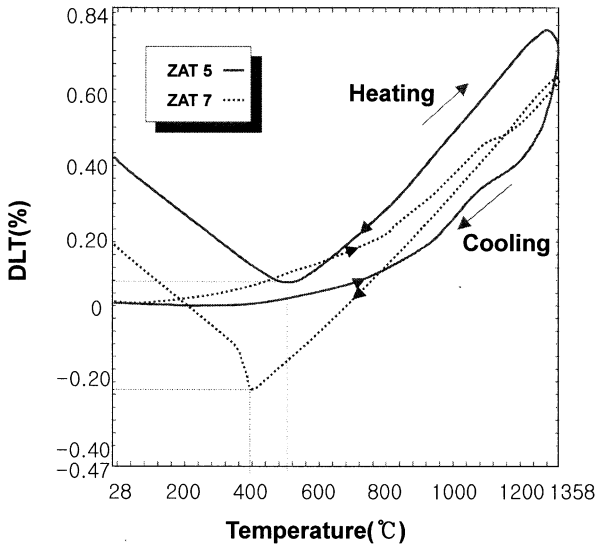

Fig. 4. Thermal expansion curves of ZAT5 and ZAT7 sintered at 1500 °C/2 h cyclic thermal shock test between 750 and 1400 °C for 100 h.

200∼1400 °C. Maximum thermal expansion occurred between 1350 and 1400 °C. The ZAT materials sintered at 1500 °C showed zero level low thermal expansion up to 650∼750 °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 >650 °C and their reopening or refracturing which occurs when cooling below 750∼820 °C. This phenomenon of microcrack healing and reopening was reported previously using acoustic emission by R.E. Whight.[19] Furthermore the thermal contraction temperature difference, ΔT, as defined by Y. Ohya et al.,[3] between sintering and crack onset temperatures, increased with an increasing mullite content. However, even at 1100 °C the slope of ZAT materials sintered at 1600 °C is still zero level 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 (RT-1200 °C) only (Fig. 2 and 3), compared with the theoretical thermal expansion coefficient for single crystal of Al_2TiO_5 ceramics, 9.70×10^{-6}/K. 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[18] and Kim[20] and with the tendency of grain size effect on the thermal expansion of $MgTi_2O_5$ reported by

Table 3
Phase composition and thermal expansion coefficient after various thermal treatment

Phase compositions	ZAT 5		ZAT 7		ZAT 8		ZAT 9	
Sintering at 1500 °C/2 h				High-$ZrTiO_4$, β-Al_2TiO_5				
Temperature (°C)	1500	1600	1500	1600	1500	1600	1500	1600
Cyclic thermal shock test (750–1400–750 °C/100 h)			High-$ZrTiO_4$, corundum,		β-Al_2TiO_5, Rutile			
Decomposition content of Al_2TiO_5 (wt.%)	5.0 (5.28)[a]	10.0 (4.31)[a]	7.0 (1.51)[a]	15.0 (4.57)[a]	10.0 (4.89)[a]	15.0 (2.27)[a]	15.0	20.0
Durability test (annealing at 1100 °C/100 h)	High-$ZrTiO_4$, β-Al_2TiO_5 rutile corundum	H-ZT β-AT	H-ZT β-AT rutile		High-$ZrTiO_4$, β-Al_2TiO_5 rutile corundum			
Decomposition content of Al_2TiO_5 (wt.%)	15.0	20.0	5.0 (4.60)[a]	10.5 (5.11)[a]	50.3 (7.30)[a]	65.0 (6.45)[a]	60.0 (7.11)[a]	70.2 (9.12)[a]

[a] Thermal expansion coefficient ($\times 10^{-6}$/K).

Kuzyk et al.[5] On the other hand, fine-grained materials exhibited small hysteresis areas.

Fig. 4 shows the thermal expansion characteristics of the ZAT composites sintered at 1500 °C after the cyclic thermal shock test between 750 and 1400 and 750 °C, which show a mean thermal expansion coefficient of 5.28×10^{-6}/K for ZAT5 and 1.51 for ZAT7 between 25 and 1350 °C, respectively. Moreover, it was found some change in thermal hysteresis behavior during the heating and cooling cycles. These materials have slightly smaller hysteresis areas and a higher thermal expansion than those before the cyclic test (Figs. 2 and 3), clearly indicating the influences of decomposition of the Al_2TiO_5 into its component oxides after test as shown in Table 3. The mean thermal expansion coefficient of ZAT7, ZAT8 and ZAT9 after the decomposition test at 1100 °C for 100 h were 4.60×10^{-6}/K, 7.30×10^{-6}/K and 7.11×10^{-6}/K (RT–1350 °C), respectively, the results indicate much changes of the thermal hysteresis behavior in the heating and cooling cycles. However, only 5% of Al_2TiO_5 in the ZAT7 is decomposed to their components of Al_2O_3 and TiO_2. Fig. 5 shows the thermal expansion characteristics of the ZAT7 composites sintered at 1500 °C after decomposition test. This material has also slightly smaller hysteresis areas of and a moderately higher thermal expansion of 4.60×10^{-6}/K than those before the test, Furthermore, the microstructure of ZAT7 sintered at 1500 and 1600×°C for 2 h after cyclic test and durability test is a little changed as shown in Fig. 6.

The changes in the phase compositions and thermal expansion coefficient due to cyclic thermal shock and thermal loading tests are given in Table 3. The relative amount of decomposed composition after test were calculated with an internal standard samples by quantitative XRD measurement. The Al_2TiO_5 phase in ZAT8 and ZAT9 composites containing 20 and 10 mol% $ZrTiO_4$ decomposed to Al_2O_3 and TiO_2 mostly, and partial decomposition was observed in the ZAT5 and ZAT7 composites sintered at 1600 °C for 2 h after annealing test. But the final phase of ZAT7 sintered 1500 °C consisted mainly of two phases: Al_2TiO_5 and $ZrTiO_4$ as shown in Table 3. The decomposition content of Al_2TiO_5 decreased with increased $ZrTiO_4$ content by limiting grain growth of Al_2TiO_5, thus the composition with 30 and 50 mol% of $ZrTiO_4$ still retained above 80% of Al_2TiO_5 phase. The change of phase composition in ZAT composites illustrates a similar trend after cyclic thermal shock test between 750 and 1400 °C. $ZrTiO_4$ addition prevented Al_2TiO_5 materials.

4. Summary

Materials fired at 1500 °C consisted of homogeneously-dispersed and narrowly distributed $ZrTiO_4$ and Al_2TiO_5 grains with a complex system of grain boundary microcracks. Thermal expansion hysteresis showed zero negative level to 750 °C (1500 °C/2), and above 1000 °C (1600 °C/h), but as the temperature is raised above this level, hysteresis increased markedly caused by the crack healing effect. The thermal expansion coefficient and

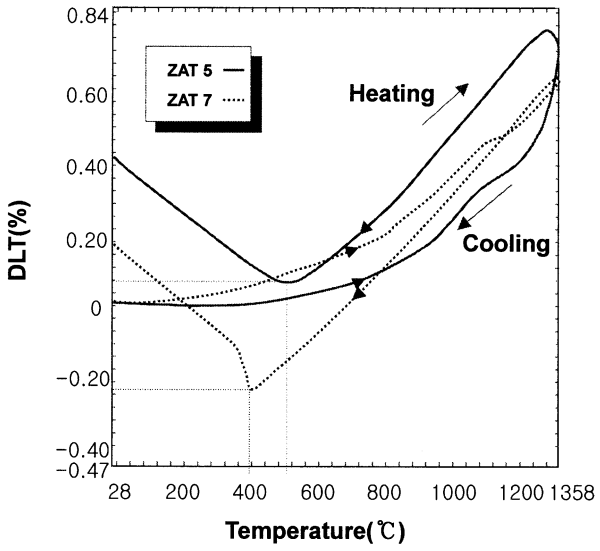

Fig. 5. Thermal expansion curves of ZAT7 sintered at 1500 °C/2 h after durability test at 1100 °C for 100 h.

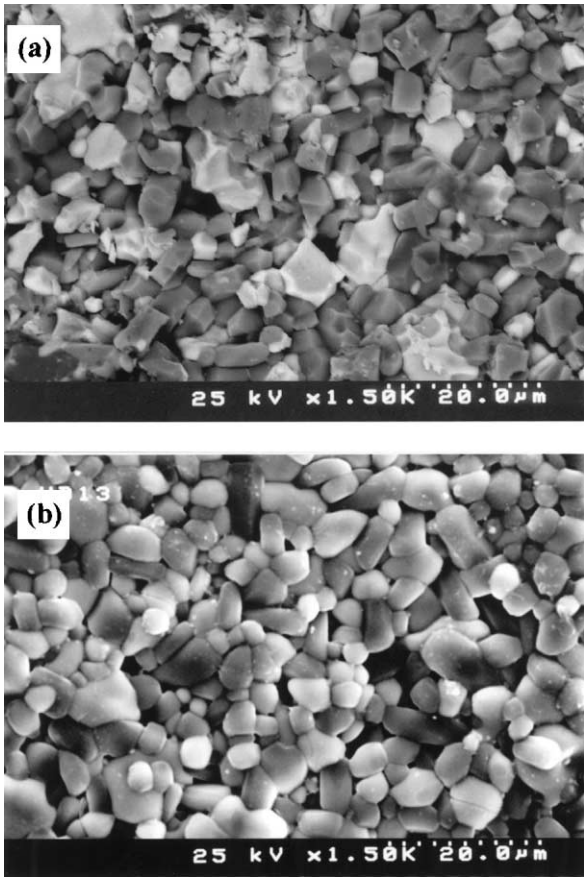

Fig. 6. Microstructure of ZAT7 sintered at 1500 °C/2 h after cyclic thermal shock between 750 and 1400 and 750 °C (a) and after durability test at 1100 °C for 100 h (b).

room temperature strength increased with increasing $ZrTiO_4$ content. ZAT7 containing 70 vol% Al_2TiO_5, which showed increased thermal expansion coefficients from 0.62×10^{-6}/K to 4.60×10^{-6}/K and a slightly smaller hysteresis area than those before the thermal shock test, clearly indicating the influence of decomposition of Al_2TiO_5 into its component oxides. But these materials showed moderately good thermal durability after a long-term annealing test at 1100 °C for 100 h and also the cyclic thermal shock test between 750 and 1400 °C.

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