LOW THERMAL EXPANSION BEHAVIOR AND THERMAL DURABILITY OF AL$_2$TiO$_5$-ZrTiO$_4$ CERAMICS

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Abstract.

Thermal-shock-resistant materials, Al$_2$TiO$_5$-ZrTiO$_4$ (ZAT) composites, were synthesized by oxide process. The range of ZAT compositions investigated had very low average thermal expansions as low as only 0.3 – 1.3 x 10$^{-6}$/K combined with 8.29 x 10$^{-6}$/K of pure ZrTiO$_4$ and 0.68 x 10$^{-6}$/K of polycrystalline Al$_2$TiO$_5$, respectively, compared with the theoretical thermal expansion coefficient for a single crystal of Al$_2$TiO$_5$, 9.7 x 10$^{-6}$/K. The composites also had high thermal durability at 1100 °C for 100h. 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 titanate phase and a contractive phase transformation by the ZrTiO$_4$. The microstructural degradation of the composites is presented here analyzed by scanning electron microscopy, X-ray diffraction, and dilatometry.

Resumen

Materiales compuestos de Al$_2$TiO$_5$-ZrTiO$_4$ (ZAT) resistentes al choque térmico, fueron sintetizados a partir de óxidos. El rango de composiciones ZAT investigado tiene un promedio de expansión térmica muy bajo, tanto como, 0.3 – 1.3 x 10$^{-6}$/K combinando 8.29 x 10$^{-6}$/K para ZrTiO$_4$ puro y 0.68 x 10$^{-6}$/K para Al$_2$TiO$_5$ policristalino, en comparación con el coeficiente de expansión térmica para un monocristal de Al$_2$TiO$_5$, de 9.7 x 10$^{-6}$/K. Los materiales compuestos mostraron también una alta durabilidad térmica a 1100°C por 100h. La baja expansión térmica y la alta durabilidad térmica son debidas aparentemente a una combinación de microgrietas causadas por la amplia anisotropía en la expansión térmica de los ejes cristalinos de la fase de titanato y a la contracción ocurrida por la transformación del ZrTiO$_4$. La degradación microestrutural de los materiales compuestos se presenta y es analizada por microscopía electrónica de barrido, difracción de rayos X y dilatometría.
1. Introduction

Some anisotropic ceramics produce cracks at grain-boundaries due to thermal expansion anisotropy during cooling from their sintering temperature. These polycrystalline ceramics have a much lower thermal expansion coefficient compared with dense ceramics. 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. Al$_2$TiO$_5$ is well known as a material with a low thermal expansion coefficient ($0.5\sim1.5 \times 10^{-6}$/K), low Young’s modulus (15~25 KN/mm$^2$), and high thermal shock resistance. However, it has low mechanical strength (20~25 N/mm$^2$) due to the presence of microcracks developed by the large difference in thermal expansion coefficients along crystallographic axes. Such microcrack formation is largely a function of the magnitude of thermal expansion anisotropy and the grain size. These microcracks provide a cushion effect when adjacent grains expand. Such materials generally have low room-temperature strength which is slightly increased at elevated temperatures because of the rehealing of microcracks. This property allows for its application as an insulating material for engines, portliners, piston bottoms, and turbochargers.

However, pure Al$_2$TiO$_5$ tends to decompose into Al$_2$O$_3$ and TiO$_2$ at temperatures ranging from 800°C to 1300°C during cooling. The decomposition occurs when adjacent aluminum(53pm) and titanium(61pm) octahedra collapse because the lattice site occupied by the aluminum is too large. The thermal energy available from this collapse permits the aluminum to migrate from its position and causes structural dissolution to rutile and corundum. 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 stability of Al$_2$TiO$_5$ can be improved by the formation of solid solutions with MgO, Fe$_2$O$_3$, or TiO$_2$, which are isomorphous with the mineral pseudobrookite, such as Fe$_2$TiO$_5$,[12] MgTi$_2$O$_6$, [13, 14] or Ti$_3$O$_5$ (anosovite).[15] Polycrystalline Al$_2$TiO$_5$ can also be stabilized by limiting its grain growth. Another source of stabilization is the limitation of microcracks by the addition of additives such as SiO$_2$, [16] ZrO$_2$, [17] ZrTiO$_4$, [18, 19] or mullite,[20] most of which do not form a solid solution with Al$_2$TiO$_5$ but rather restrain the tendency of Al$_2$TiO$_5$ toward decomposition. However, the additives of SiO$_2$ and ZrO$_2$ do not have a significant effect on the thermal stability of Al$_2$TiO$_5$, even after a long annealing test at 1100°C for 100h.[21] On the other hand, the addition of mullite or ZrTiO$_4$ not only restrains the decomposition but also increases the thermal stability at 1100°C.

In situ partial reactions during the sintering of Al$_2$TiO$_5$ and ZrTiO$_4$ mixtures result in composites that have low coefficient of thermal expansion, high melting point, and high temperature phase stability. The further study on ZrTiO$_4$ showed that the thermal behavior by the microcracking phase is similar to HITiO$_4$, which also has a low thermal expansion.[22] ZrTiO$_4$ has been used by the electronic industry as a dielectric resonator material in microwaves devices[23] and for high-temperature pigments,[24] but there is moderately little evidence of its use in structural or technical ceramics application. For high temperature applications, long-annealing thermal stability and mechanical properties are important if these materials are to be used between 1000 and 1300°C Therefore, in this work, in an attempt to improve the thermal durability of aluminum titanate, a new low thermal expansion material consisting of a two phase material based on Al$_2$TiO$_5$ ZrTiO$_4$ in different proportions will be studied after adjusting the Al$_2$TiO$_5$/ZrTiO$_4$ ratios.

2. Experimental procedure

The ZrTiO$_4$ and Al$_2$TiO$_5$ (Dynamit Nobel, 3-Al$_2$TiO$_5$ with SiO$_2$ : 0.3wt%, ZrO$_2$ : 0.4wt%, and Fe$_2$O$_3$ : 0.5wt%, 50%< 2.5μm) powders were used for preparing the ZAT composites made by combining oxides rather than mixing pre-reacted Al$_2$TiO$_5$ and ZrTiO$_4$. Small amounts (5 mol%) of Fe$_2$O$_3$ (Hematite, 96% pure, Riedel-de Haen) were added to the Al$_2$TiO$_5$ 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 amounts of ZrTiO$_4$ and Al$_2$TiO$_5$ powders were then combined as shown in Table I and mixed with zirconia balls for at least 30 min in the planet mill(Fritsch, Pulverisette 6). The powders were die pressed at 150 MPa to produce pellets, approximately 2.86 cm diameter × 0.32 cm thickness. They were sintered at temperatures between 1350 and 1600°C for 2hrs in air. At this time the heating rate was 10°C/min and the cooling rate was about 20°C/min. The final densities of pellets were measured by water-immersion method with an error of ± 0.005 g/cm$^3$ and compared with theoretical densities assumed by XRD density. Samples were characterized by X-ray diffraction (Philips, PW1180/00, Ni-filtered CuKa) and scanning electron microscopy (Cambridge, Stereoscan 250 MK2). The 3-point bending strength of bar specimens (7mm × 7mm × 70mm) at room temperature was measured using a universal testing machine(Instron 1186), with a span length of 40 mm and a crosshead 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 1200°C was...
determined for a 5 mm x 5 mm x 25 mm specimen, in air, using a dilatometer (Netzsch), at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. Cyclic thermal expansion coefficients were also measured, using a dilatometer at up to 1500 °C, before and after the decomposition tests. Long-term thermal durability was studied by annealing the materials at the critical decomposition temperature of Al₂TiO₅ (1100 °C for 100hrs).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Phase</th>
<th>Sinter density (g/cm³)</th>
<th>Relative density (%)</th>
<th>Particle size</th>
<th>α_{25-1350°C} (×10⁻⁶/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂TiO₅</td>
<td>β-Al₂TiO₅</td>
<td>3.68(3.70)</td>
<td>93.2</td>
<td>50%&lt;2.5μm</td>
<td>0.68</td>
</tr>
<tr>
<td>ZrTiO₄</td>
<td>H-ZrTiO₄</td>
<td>4.85(5.06)</td>
<td>95.0</td>
<td>100%&lt;4.0μm</td>
<td>8.29</td>
</tr>
</tbody>
</table>

ZAT5: 50 mol% ZrTiO₄, 50 mol% Al₂TiO₅ + 5 mol% Fe₂O₃ to Al₂TiO₅
ZAT7: 30 mol% ZrTiO₄, 70 mol% Al₂TiO₅ + 5 mol% Fe₂O₃ to Al₂TiO₅
ZAT8: 20 mol% ZrTiO₄, 80 mol% Al₂TiO₅ + 5 mol% Fe₂O₃ to Al₂TiO₅
ZAT9: 10 mol% ZrTiO₄, 90 mol% Al₂TiO₅ + 5 mol% Fe₂O₃ to Al₂TiO₅

( ): Theoretical density[^20,24]

3. Results and Discussion

The relative density of pure ZAT5 (1600 °C) was 97.1% of the theoretical density as shown in Fig. 1.

![Fig. 1. Relative density of ZAT Composites](image)

The relative density of the ZAT compositions decreased with increasing Al₂TiO₅ content because the densities of the starting oxides α-Al₂O₃ and TiO₂ (rutile) are 3.99 and 4.25 g/cm³, respectively. Therefore, the formation of pseudobrookite type β-Al₂TiO₅ with a theoretical density of 3.70g/cm³ is accompanied by an about 11% molar volume increase.[^1] A relatively high bending strength of 35.0MPa was found in ZAT5 (50 mol% of ZrTiO₄) at 1500 °C. This result can be attributed to the limitation of grain growth and microcracks with ZrTiO₄ which does not form a solid solution with Al₂TiO₅. As the firing temperature increased, the density was normally higher. On the other hand, higher sintering temperature resulted in grain growth.

The microstructure of the sintered ZAT-composites at 1500 °C consists of a narrow size distribution of ZrTiO₄ and Al₂TiO₅ grains. The grain sizes are in the range of 3 μm. The grain boundary microcracks observed at the ZAT-grains are expected due to the presence of the highly anisotropic β-Al₂TiO₅ crystal (Fig. 2). With increasing Al₂TiO₅ contents, the abnormal grain growth of Al₂TiO₅ phase and the thermal expansion hysteresis areas also increased. This result may be attributed to the lower mechanical strength and Young’s modulus of ZAT-composites. The microstructure of sintered ZAT-phase at 1600 °C for 2h consists of discontinuous larger grain of ZrTiO₄ and Al₂TiO₅ grains. The micrograph showed abnormal grains to 5 ~ 40 μm and considerable intergranular microcracking in ZrTiO₄ phase as shown clearly in Fig. 3.
Fig. 2. Microstructure of sintered at 1500°C for 2 hrs ZAT composites showing grain boundary microcracks and grain growth. (\(\Rightarrow\): ZrTiO_4 grains)

Fig. 3. Microstructure of sintered at 1500°C for 2 hr ZAT composites showing grain boundary microcracks and grain growth (\(\Rightarrow\): ZrTiO_4 grains)
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 aluminum titanate 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 $\beta$-Al$_2$TiO$_5$ 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 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.[3, 20] The microcracks are closed at higher temperatures. This result is closely related to the relatively steeper thermal expansion curve in Fig. 4 and 5.

Fig. 4. Thermal expansion curves of ZAT composites (a) ZAT5, (b) ZAT7
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 $\text{ZAT5}$ and $\text{ZAT7}$ materials fabricated at 1500 and 1600 °C for 2 h are shown in Fig. 4. 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 $\text{ZAT}$ materials sintered at 1500 °C showed 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 °C-820 °C. This phenomenon of microcrack healing was reported previously using acoustic emission by R.E. Whight [25]. Furthermore the thermal contraction temperature difference, $\Delta T$, as defined by Y. Ohya et al [3], between sintering and crack onset

![Fig. 5. Thermal expansion curves of ZAT composites. (a) ZAT8, (b) ZAT9](image-url)
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 during heating. The result indicates that an important fraction of the microcracks is still open. At the beginning of the cooling cycle, a higher crack-onset temperature in the range of 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 x 10^{-6}/K for ZAT9 and 1.76 x 10^{-6}/K for ZAT5 from 20 to 1200 °C, respectively. The thermal expansion coefficients of ZAT Materials (1600 °C for 2h) were between 1.63 x 10^{-6}/K and -0.35 x 10^{-6}/K (RT-1200 °C) only (Fig 4 and 5), compared with the thermal expansion coefficient of 0.5 - 1.0 x 10^{-6}/K for polycrystalline Al2TiO5 ceramics. [1,2]

The hysteresis areas, which were integrated with a planimeter, showed a distinct maximum for the ZAT9 material sintered at 1600°C for 2 h in Fig. 5, whose average grain size is 20-30μm in Fig. 3. These thermal expansion curves are good agreement with the results of Buessem [26] and with the tendency of grain size effect on the thermal expansion of Mg2TiO3 reported by Kuzyk et al. [5] On the other hand, fine-grained materials exhibited small hysteresis areas.

Figure 6 shows the flexural strength of the specimens with various compositions and sintered at different temperatures. The room-temperature strength decreased with increasing aluminium titanate content because of the presence of large-grained microcracks. Materials having 50 mol% aluminium titanate shows interesting results, that is, the flexural strength of the ZAT5 composites sintered at 1500 °C showed much higher flexural strength, 35 MPa than those at sintered at 1600 °C, 30 MPa. This result could possibly be explained by an increase of grain boundary microcracking in the aluminium titanate with sintering temperature and increased abnormal grain size of Al2TiO5 in ZAT composites to 10-30 μm (see Fig. 2 and 3).

Figure 7 shows the thermal expansion characteristics of the ZAT7 composites after the decomposition test at 1100 °C for 100 h. As the mean thermal expansion coefficient of ZAT7 and ZAT8 were 4.60 x 10^{-6}/K and 7.11 x 10^{-6}/K (RT-1350 °C), respectively, the results indicate changes of the thermal hysteresis behavior in the heating and cooling cycles. Moreover, these materials have slightly smaller hysteresis areas and a higher thermal expansion than those before the test, clearly indicating the influences of decomposition of the Al2TiO5 into its component oxides.

The change in the phase composition caused by the decomposition test at 1100 °C for 100 h are given in Table II. The relative amount of decomposed composition after test were calculated with an internal standard samples by quantitative XRD measurement. The Al2TiO5 phase in ZAT8 and ZAT9 composites containing 20 and 10 mol% ZrTiO4 decomposed to corundum and rutile mostly, and partial decomposition was observed in the ZAT5 and ZAT7 composites sintered at 1600°C after annealing test. But the final phase of ZAT7 sintered at 1500 °C consisted mainly of two phase : the Al2TiO5 and ZrTiO4, compared with the decomposed phase of ZAT7 sintered at 1600 °C for 2 h in Table II. The decomposition content of Al2TiO5 decreased with increased ZrTiO4 content by limiting grain growth of Al2TiO5, thus the composition with 30 and 50 mol% ZrTiO4 still retained above 80% of Al2TiO5 phase. The change of phase compositions in ZAT composites sintered at 1600 °C illustrates a similar trend. ZrTiO4 addition prevented Al2TiO5 materials from decomposing during the test.
Table II. Phase Composition of ZAT Composites after Various Thermal Treatment.

<table>
<thead>
<tr>
<th>Phase compositions</th>
<th>ZAT 5</th>
<th>ZAT 7</th>
<th>ZAT 8</th>
<th>ZAT 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintering at 1500, 1600°C/2h.</td>
<td>β-AT H-ZT</td>
<td>β-AT H-ZT</td>
<td>β-AT H-ZT</td>
<td>β-AT H-ZT</td>
</tr>
<tr>
<td>Decomposition test [Annealing at 1100°C/100h.]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500°C</td>
<td>1600°C</td>
<td>1500°C</td>
<td>1600°C</td>
<td>1500°C</td>
</tr>
<tr>
<td>Decomposition content of Al₂TiO₅ [%]</td>
<td>15.0</td>
<td>20.0</td>
<td>5.0</td>
<td>10.5</td>
</tr>
</tbody>
</table>


As shown in Fig 8, the Young’s modulus was measured as a function of quenching number by the resonance method. ZAT5 having 50 mol% ZrTiO₄ has a relatively higher Young’s modulus (17 kN/mm²) than the others. However, it showed a decrease of Young’s modulus with increasing Al₂TiO₅ content.

![Fig. 8. Elastic Modulus of ZAT Composites.](image)

4. Conclusion

Materials fired at 1500 °C consisted of homogeneously-dispersed and narrowly distributed ZrTiO₄ and Al₂TiO₅ grains with a complex system of grain boundary microcracks. Thermal expansion hysteresis showed zero negative level to 750 °C (1500 °C/2hrs), and above 1000 °C(1600 °C/hrs), but as the temperature is raised above this level, hysteresis increased markedly caused by the crack healing effect. The thermal expansion coefficient and room temperature strength increased with increasing ZrTiO₄ content. ZAT7 containing 70 mol % Al₂TiO₅ 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 annealing test at 1100 °C for 100hrs. The result indicates the influence of decomposition of Al₂TiO₅ into its component oxides. High thermal durability in the present study was achieved for the compositions containing 30 mol % ZrTiO₄, which consisted mainly of two phases; the Al₂TiO₅ and ZrTiO₄ after test.

5. References

4. G. Bayer, "Thermal Expansion Characteristics and Stability of


