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Low Thermal Expansion Behavior of $ZrTiO_4$-Al_2TiO_5 Ceramics Having High Thermal Durability Between 750 and 1400°C

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Abstract. The thermal-shock-resistant materials in the system Al_2TiO_5-$ZrTiO_4$ (ZAT) with low average thermal expansions as low as only $0.3 \sim 1.3 \times 10^{-6}$/K were synthesized by oxide process. Sintered bodies were subjected to prolonged durability test - on the one hand cyclic thermal shock between 750 and 1400°C for 100h and on the other annealing at critical decomposition temperature of 1100°C for 100h. The low thermal expansion and high thermal durability of ZAT7 composite 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 samples, studied with the help of scanning electron microscopy, dilatometer and X-ray diffraction, is presented here.

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 [1]. However, Al_2TiO_5 materials tends to decompose fully in the range 800-1300°C [2,3] and also have a relatively low mechanical strength because of microcracks induced by the high anisotropy of the thermal expansion coefficients along the crystallographic axes [4,5]. This phenomenon has been investigated by several authors [6,7]. The thermal durability and also the service life of Al_2TiO_5 ceramics are dependent on the stabilization status and the processing route. 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 [8]. $ZrTiO_4$ 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 its use in structural or technical ceramics application [9]. 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, in an attempt to improve the thermal durability of Al_2TiO_5, a new low thermal expansion material consisting of a two-phase material based on Al_2TiO_5-$ZrTiO_4$ in different proportions will be studied after adjusting the Al_2TiO_5/$ZrTiO_4$ ratios.

Experimental procedure

The $ZrTiO_4$ and Al_2TiO_5 (Dynamit Nobel, β-Al_2TiO_5 with SiO_2 : 0.3wt%, ZrO_2 : 0.4wt%, and Fe_2O_3 : 0.5wt%, 50%< 2.5 μm) powders were used for preparing the ZAT composites made by combining oxides rather than mixing pre-reacted Al_2TiO_5 and $ZrTiO_4$ between 10/90 mol% and 50/50 mol%. Small amounts (5 mol%) of 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 mixed with zirconia balls in the planet mill (Fritsch, pulveritte) until an average particle size of 3 ~ 5 μm. The powders were dry pressed at 150 MPa to produce pellets, approximately 2.86 cm diameter × 0.32 cm thickness. Table I summarizes physical properties of the materials sintered at 1400, 1500, and 1600°C for 2 h. 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) 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 CuKα) and scanning electron microscopy (Cambridge, Steroscan 250 MK2).

Table 1. Physical data of the sintered specimens

Physical data	Al_2TiO_5(AT)	$ZrTiO_4$(ZT)
Relative density [%]	93.2(3.70)	95.0(5.06)
Particle size [μm]	50% < 2.5 μm	100% < 4.0 μm
Thermal expansion coefficient [10^{-6}/K]	0.68	8.29

Physical data		ZAT 5	ZAT 7	ZAT 8	ZAT 9
Thermal expansion coefficient [$\alpha_{25\text{-}1250}$°C (x 10^{-6}/K)]		1.3	1.2	0.9	0.3
Relative density [%]	1400°C	75	76	78	77
	1500°C	93	88	87	87
	1600°C	95	94	93	92
Bending strength [N/mm^2]	1400°C	22	16	15	15
	1500°C	35	27	17	19
	1600°C	30	27.5	23	22
Elastic modulus [KN/mm^2]	1400°C	10	7	7	5
	1500°C	18	16	13	12
	1600°C	17	15	12	12

* ( ): Theoretical density[g/cm^3]

Results and Discussion

As the firing temperature increased, the density of ZAT materials was normally higher as shown in Table I. On the other hand, higher sintering temperature resulted in grain growth of Al_2TiO_5 (see Fig. 1). A relatively high bending strength of 35.0MPa and a moderately high Young's modulus of 18.0 KN/mm^2 were found in ZAT5 (50 mol% of $ZrTiO_4$) at 1500°C. This result can be attributed to the limitation of grain growth and microcracks with $ZrTiO_4$. 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, 30 MPa. This result could be possibly explained by an increase of grain boundary microcracking in Al_2TiO_5 with higher 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 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-Al_2TiO_5 crystal. 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 Fig. 2. This result may be attributed to the lower mechanical strength and Young's mouduls of ZAT-composites as shown in Table I. The microstructure sintered ZAT at 1600°C for 2h 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.

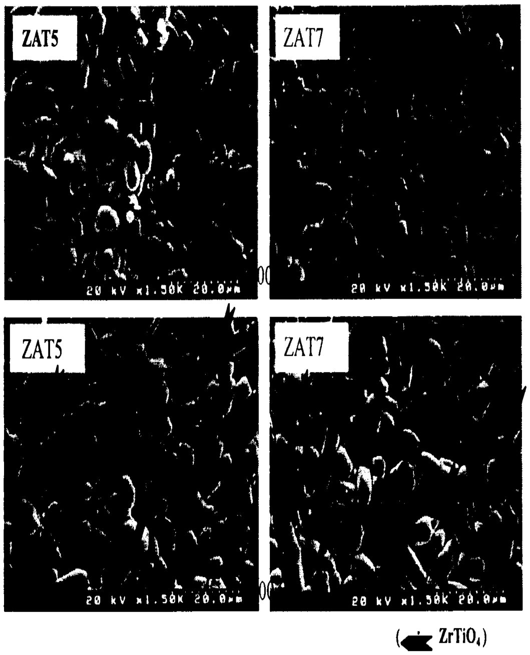

Fig. 1 Microstructure of ZAT composites sintered at 1500°C and 1600°C for 2h.

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 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 [10]. The microcracks are closed at higher temperatures. This result is closely related to the relatively steeper thermal expansion curve in Fig. 2. 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.

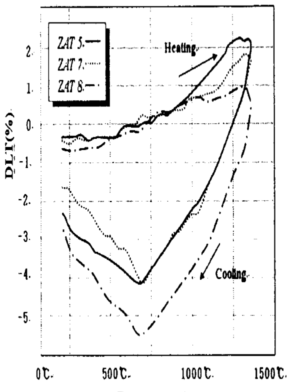

Fig. 2 Thermal expansion curves of ZAT composites sintered at 1500°C/2h.

The ZAT materials sintered at 1500°C showed

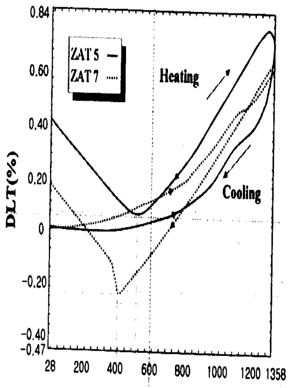

Fig. 3 Thermal expansion curves of ZAT5 and ZAT7 sintered at 1500°C/2h after cyclic thermal shock test between 750-1400°C for 100h.

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. 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 2h) were between 1.63×10^{-6} /K and -0.35×10^{-6}/K (RT–1200°C) only.

Figure 3 shows the thermal expansion characteristics of the ZAT composites sintered at 1500°C after the cyclic thermal shock test between 750 - 1400 -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, clearly indicating the influences of decomposition of the Al_2TiO_5 into its component oxides after test as shown in Table II.

Table II. Phase composition and thermal expansion coefficient after various thermal treatment

Phase compositions	ZAT 5		ZAT 7		ZAT 8		ZAT 9	
Sintering at 1500°C/2h	High-$ZrTiO_4$, Al_2TiO_5							
Temperature (°C)	1500	1600	1500	1600	1500	1600	1500	1600
Cyclic Thermal Shock Test (750-1400-750°C/100h)	High-$ZrTiO_4$, Al_2TiO_5, Corundum, Rutile							
Decomposition content of Al_2TiO_5(%)	5.0 (5.28)	10.0 (4.31)	7.0 (1.51)	15.0 (4.57)	10.0 (4.89)	15.0 (2.27)	15.0	20.0
Durability Test (Annealing at 1100°C /100h)	High-$ZrTiO_4$, 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 (%)	15.0	20.0	5.0 (4.60)	10.5 (5.11)	50.3 (7.30)	65.0 (6.45)	60.0 (7.11)	70.2 (9.12)

* ( ): Thermal expansion coefficient [$x10^{-6}$/k]

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 expansion coefficients 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. The changes in the phase compositions and thermal expansion coefficient due to cyclic thermal shock and thermal loading tests 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 Al_2TiO_5 phase in ZAT8 and ZAT 9 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 hours after annealing test. But the final phase of ZAT7 sintered 1500°C consisted mainly of two-phase: Al_2TiO_5 and $ZrTiO_4$. 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 750-1400°C. $ZrTiO_4$ addition prevented Al_2TiO_5 materials.

Conclusion

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/h), and above 1000°C (1600°C/h), but as the temperature is raised above this level, hysteresis in creased markedly caused by the crack healing effect. The thermal expansion coefficient and 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 100hrs and also the cyclic thermal shock test between 750-1400°C.

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