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Excellent thermal shock resistant materials with low thermal expansion coefficients

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The high performance of advanced ceramics, fuel cells, and also precision devices for semiconductor systems have been limited by the problem of thermal stresses induced by the thermal expansion between different materials. To avoid this problem, one of the choices is to develop a low or zero-level thermal expansion material, to be used, for instance in diesel particulate filter applications, in which the original dimension of the material is maintained, without being influenced by thermal shock at high temperatures. It appears that the negative thermal expansion of Al_2TiO_5 ceramics are due to the effects of grain boundary micro-cracking caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase. During a reheating run, the individual crystallites expand at low temperature; thus, the solid volume of the specimen expands into the micro cracks, where as the macroscopic dimensions remain mostly unchanged. As a result, the material expanded very little up to 1000 °C and the micro cracks closed at higher temperatures. This result is closely related to thermal expansion curves that were relatively steep. A characterization of the damage induced by thermal shock was conducted by measuring the evolution of the Young's modulus using ultrasonic analysis, aided by the density and thermal expansion coefficients.

Key words: Al_2TiO_5, mullite, nozzle, thermal shock, non-destructive, ultrasonic, Young's modulus.

Introduction

Most ceramics expand on heating, due to increased thermal agitation of atoms and the 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 loops 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 the thermal stabilization of composites [4, 5]. However, the thermal shock resistance of structural ceramics is a property that is difficult to quantify; as such, it is usually expressed in terms of a number of empirical resistance parameters. These are dependant on the conditions imposed, but one method that can be used is the examination of density, including Young's modulus and the thermal expansion retention after thermal shock. Furthermore, for high temperature diesel particulate filter applications, the long-annealing thermal durability, cycle thermal stability and residual mechanical properties are very important if these materials are to be used at temperatures between 1000 °C and 1300 °C [2].

Aluminum titanate (Al_2TiO_5) is well known as an excellent thermal shock-resistant material, resulting from its unique combination of low thermal expansion and low Young's modulus, which, in turn, allows for its applications as an insulating material in engine components such as portliners, piston bottoms, turbochargers, and nozzles [3]. However, Al_2TiO_5 materials have a relatively low mechanical strength as a consequence of micro cracks that are induced by the high anisotropy of the thermal expansion coefficients which are –3.0, +11.8 and +21.8× 10^{-6}/K for its three crystallographic axes, respectively [4, 5]. Furthermore, pure Al_2TiO_5 tends to reversibly decompose into Al_2O_3 and TiO_2 at temperatures ranging from 800 to 1300 °C during cooling below the equilibrium temperature of 1280 °C [6]. Following decomposition, the material no longer exhibits either a low thermal expansion coefficient or favorable thermal shock behavior [7]. The thermal stability 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, Examples of these are Fe_2TiO_5 [8], $MgTi_2O_5$ [9] or Ti_3O_5 (anosovite) [10]. Al_2TiO_5 can also be mechanically stabilized by limiting its grain growth with additives such as SiO_2 [12], ZrO_2 [13], $ZrTiO_4$ [14, 15] or mullite [16], most of which do not form a solid solution with Al_2TiO_5 but rather restrain the

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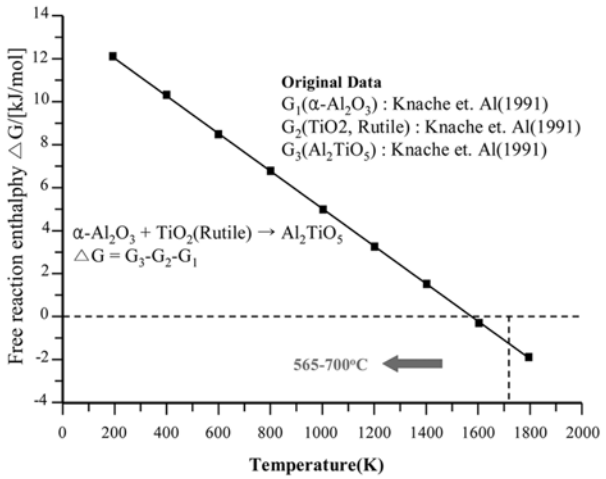

Fig. 1. Free energy ΔG of Al_2TiO_5 from α-Al_2O_3 and TiO_2 [16, 18]

tendency of Al_2TiO_5 toward decomposition. These stabilizing effects are related to a decrease in the decomposition temperature induced by the formation of iso-structural compounds during the cooling as shown in Fig. 1. The compounds $MgTi_2O_5$ and Fe_2TiO_5 decompose to $MgTiO_3$ + TiO_2 below 700 °C and Fe_2O_3 + TiO_2 at 565 °C, respectively, whereas Al_2TiO_5 decompose into Al_2O_3 and TiO_2 below 1300 °C [10-13].

In this study, several tests were conducted to evaluate the thermal durability of Al_2TiO_5-mullite composites having an ultra low thermal expansion and high thermal shock resistance, suitable sinter density, and Young's modulus for diesel exhaust filtration applications. First, the specimens were subjected to long-term thermal annealing, at the critical decomposition temperature for Al_2TiO_5 of 1100 °C, for 100 h. Secondly, a cyclic thermal shock test, consisting of 23 cycles of 750-1400-750 °C, was conducted in a two-chamber furnace over an interval of 100 h. Thirdly, the thermal shock resistance of the material was determined by a water-quenching process from 950 °C for 30 minutes. A characterization of the damage of materials induced by thermal shock was conducted through non-destructive testing methods.

Experimental Procedure

Raw materials used in preparing the Al_2TiO_5-mullite composites were TiO_2 (99.0%, Showa), Al_2O_3 (99.5%, Showa) and SiO_2 (99.0%, Showa). Powder mixtures were calcined at 1000 °C for 1 h 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 compositions of the AT, ATM1, ATM2, ATM3, and ATM5 refer to 0, 10, 20, 30, and 50 vol.% additions of mullite, respectively. The powders were dry pressed at 150 N/mm^2 to produce pellets (10 mm in diameter and 15 mm thick) and bar specimens. These were sintered at 1500 and 1600 °C for 2 h in air after the calcination in air at 600 °C for 1 h to remove organic materials. At this stage the heating rate was 10 K minute^{-1} and the cooling rate was approximately 20 K minute^{-1}. For density measurements, a gas pycnometer (AccuPyc 1330, provided by Micromeritics U.S.A) was used. The microstructural degradation of the samples was characterized by X-ray diffraction (Rigaku, D/max 2200, Ni-filtered CuKα), scanning electron microscopy (Jeol, JSM-5600) and through the use of a dilatometer (Netzsch). The thermal expansion coefficient from room temperature (RT) to 1350 °C was determined for a 5 mm × 5 mm × 25 mm specimen, in air, using a dilatometer, at a heating rate of 10 K minute^{-1} and a cooling rate of 10 K minute^{-1}. The Young's modulus was measured by an ultrasonic method (Panametric 5800), as a function of the quenching number using the test specimens.

After the quenching, the density, and the round-trip transit times of longitude and transversal ultrasonic waves were measured. Using the values of density, the round-trip time and thickness of the sample, the Young's modulus could be calculated using formulas (1), (2), (3) and (4) which are explained later. The echo pulse technique was used to measure the sound velocity in the Al_2TiO_5-mullite ceramics. The propagation velocity depends on the following parameters: Young's modulus (E), density (ρ) and the Poisson's ratio (ν) :

$$\nu_p = \sqrt{\frac{E(1-\nu)}{\rho(1+\nu)(1-2\nu)}} \tag{1}$$

The Poisson's ratio (ν) was determined by measuring the longitudinal velocity (V_L) and the shear (transverse) velocity (V_T) in the sample by utilizing an ultrasonic echo. The equation for the Poisson's ratio is given in formula (2) :

$$\nu = \frac{1-2\left(\frac{V_T}{V_L}\right)^2}{2-2\left(\frac{V_T}{V_L}\right)^2} \tag{2}$$

The velocity is defined as follows:

$$V = \frac{\text{Thickness}}{\frac{1}{2}[(\text{Round}-\text{trip})-(\text{transit}+\text{time})]} \tag{3}$$

A gas pycnometer was used to determine the volume of the sample. After cradling the sample, the density could be calculated. The gas pycnometer compares the pressures before and after the insertion of the sample. From the difference in this measure, the volume can be calculated. After determining Poisson's ratio and density, the Young's modulus can easy be calculated using formula (1) and solving for E :

$$E = \frac{\nu_p \rho(1+\nu)(1-2\nu)}{1-\nu} \tag{4}$$

The velocity is expressed in cm/s, density in g/cm^3 whereas the Young's modulus is expressed in N/cm^3.

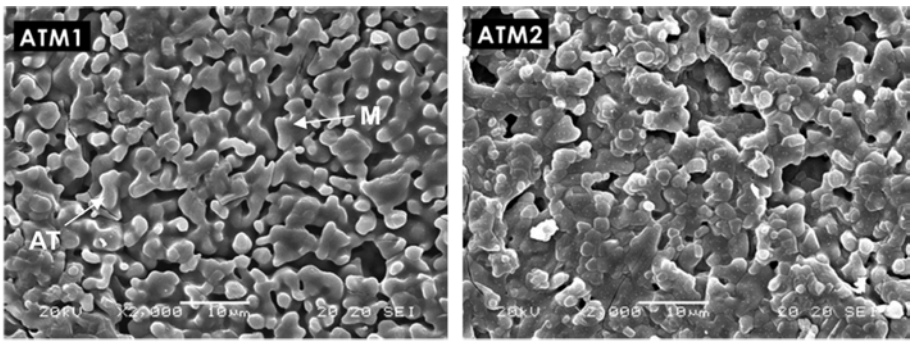

Fig. 2. SEM image of micro cracks at the grain boundary in the ATM1 and ATM2 composite (1600 °C/2 h), AT : Al_2TiO_5, M : Mullite.

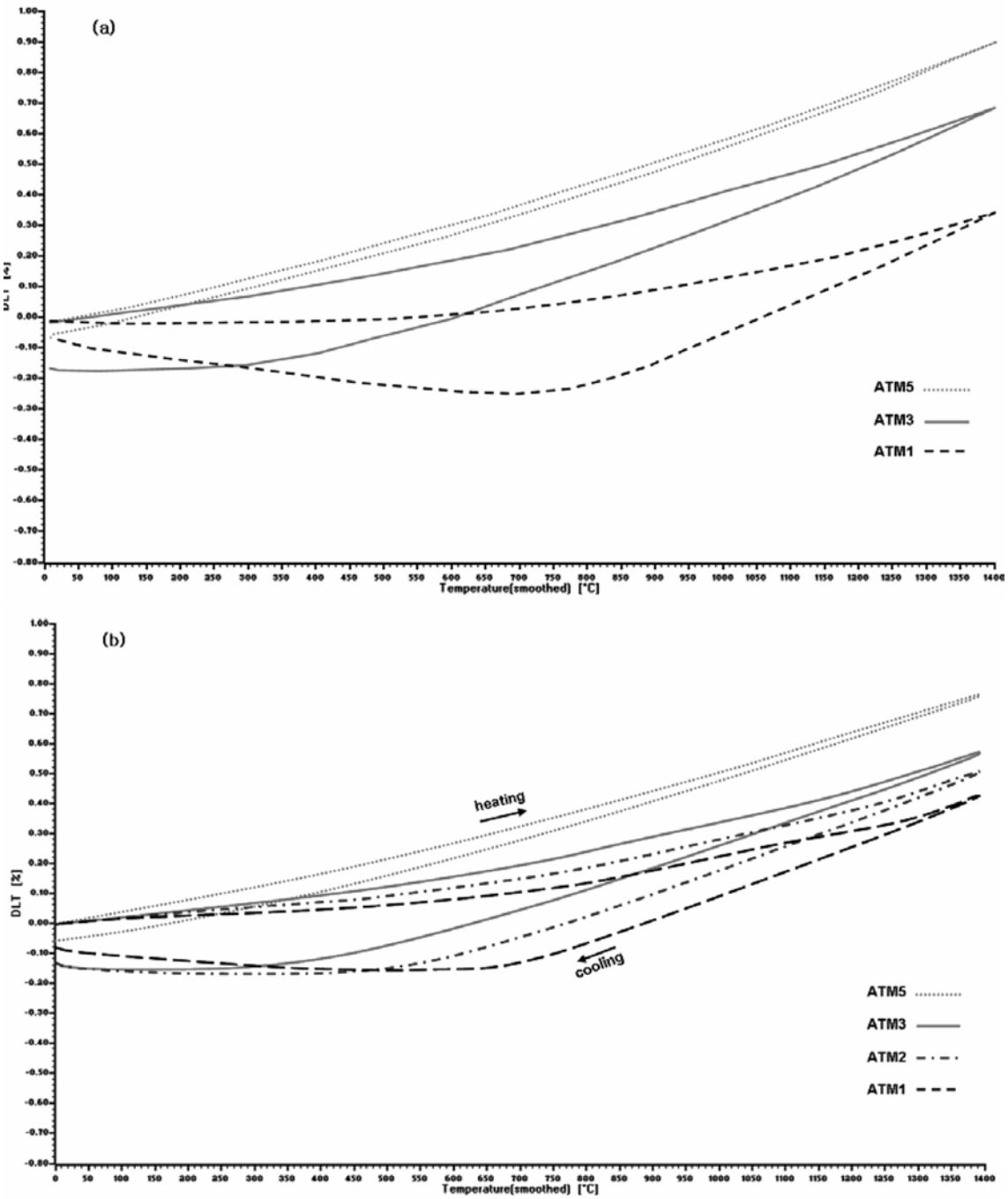

Fig. 3. Thermal expansion curves of the ATM ceramics sintered at 1600 °C for 2 h (a) and after a decomposition test at 1100 °C for 100 h (b).

Results and Discussion

Microstructure

The positive effects of the thermal treatment and thermal expansion are due to the microstructural system of the Al_2TiO_5-mullite composites as shown in Fig. 2. The bright structure illustrates the dominating Al_2TiO_5 grains, whereas the dark spots display the mullite phase. Similar to all other materials the Al_2TiO_5 expands during the thermal treatment. However, the evident expansion is nearly zero at low temperatures and increases only at higher temperatures (> 600 °C). During heating, the Al_2TiO_5 grains will expand anisotropically into these cracks until they are closed. After closing the change in volume becomes noticeable by continuous heating. During cooling the micro-cracks will open again, as shown in Fig. 3. The ATM composites also had a much lower thermal expansion coefficient (0.68-5.48 × 10^{-6}/K) than that of a single-crystal Al_2TiO_5 (9.70 × 10^{-6}/K) [8]. It appears that these low thermal expansion coefficients are due to the effects of the micro cracking caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase [15].

Thermal expansion behavior of ATM composites

All ATM composites with increasing Al_2TiO_5 content exhibit a reduced low thermal expansion coefficient accompanied by a pronounced large hysteresis area as the Al_2TiO_5 content is increased, as shown in Fig. 3(a). The ATM materials showed no low thermal expansion up to 700 °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 as the temperature is raised to > 900 °C such as in Fig. 4 and their the reopening or refracturing of the cracks which that occurs when cooled to below 730 °C. Even at 1000 °C the slope of the ATM1 materials sintered at 1600 °C remains flat in terms of a zero level thermal expansion when heating, suggesting that an important percentage of the micro cracks remain open. The thermal expansion coefficient of ATM materials sintered at 1600 °C for 6 h are 1.09 × 10^{-6}/K for ATM1, 2.50 × 10^{-6}/K for ATM2, 4.06 × 10^{-6}/K for ATM3 and 5.48 × 10^{-6}/K for ATM5 at temperatures that increased from 20 to 1000 °C.

Figure 3(b) shows the thermal expansion curves of the ATM composites after the durability test at 1100 °C for 100 h, which resulted in a mean thermal expansion coefficient between 1.49 × 10^{-6}/K and 5.36 × 10^{-6}/K at room temperature to 1350 °C. Additionally, little change in thermal hysteresis behavior during the heating and cooling cycles was found. These materials have slightly larger hysteresis areas, in addition to somewhat higher densities and thermal expansion coefficients than those before the durability test, clearly indicating the influences of the change of microstructure and the decomposition of the Al_2TiO_5 into its component oxides after the test [16]. This result is in good agreement with the thermo-physical results in Table 1. On the other hand, severe decomposition occurred for the AT materials.

Micro crack healing and reopening

The positive effects of the thermal treatment and thermal expansion behavior are due to the micro crack system of the Al_2TiO_5-mullite at grain boundaries as shown

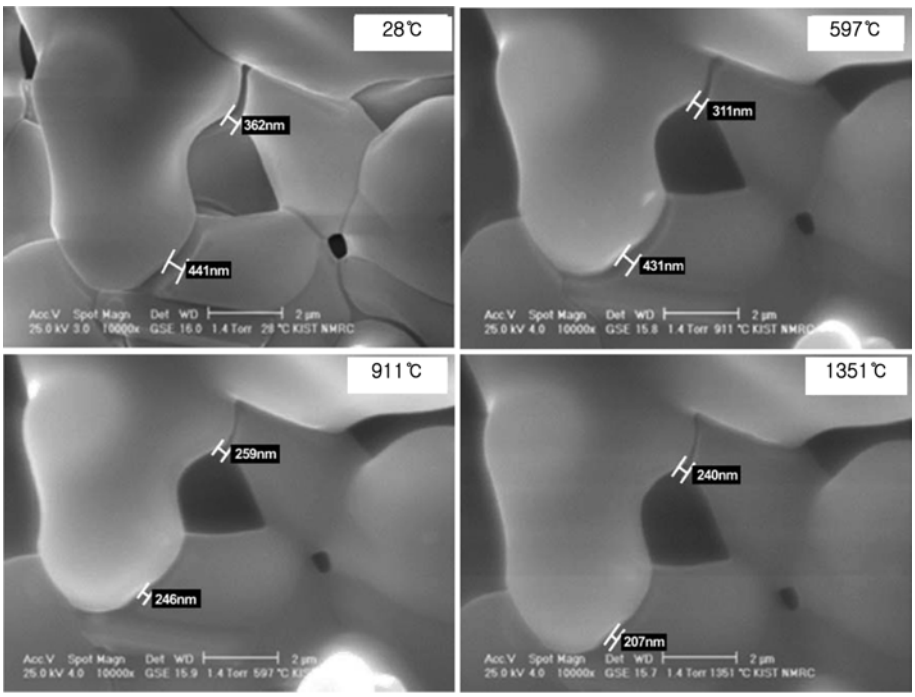

Fig. 4. Microstructure of ATM1 sintered at 1600 °C for 6 h during heating.

in Fig. 4. The bright structure shows the dominating Al_2TiO_5 grains, whereas the dark spots display the mullite. Similar to all other materials the Al_2TiO_5 expands during thermal treatment. However, the evident expansion of ATM1 is nearly zero for low temperatures; it increases only at higher temperature (> 600 °C). During heating, the Al_2TiO_5 grains will expand anisotropically into these cracks until they are closed. After closing a change in volume becomes noticeable after continuous heating. During cooling the micro-cracks will open again. The ATM1 composites also had a much lower thermal expansion coefficient (1.09×10^{-6}/K) than that of single-crystal Al_2TiO_5 (9.70×10^{-6}/K). These low thermal expansion coefficients are apparently due to the effect of the micro cracking caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase [17].

The micro cracks observed by ESEM between grain boundaries at 28 °C was 362-441 nm as shown in Fig. 4. In the first run to 597 °C the length of the micro crack at a grain boundary was 311-431 nm, and the specimen exhibited negative thermal expansion. During the second run to 911 °C, the individual Al_2TiO_5 crystallites expanded into the micro cracks, whereas the macroscopic dimensions remained nearly unchanged. As a result, the material expanded very little. The micro cracks were closed at temperatures higher than 1351 °C; however, at still higher temperatures, the slope (i.e. expansion coefficient of 1.09×10^{-6}/K for ATM1) was far below the theoretical value and that of single-crystal Al_2TiO_5 (9.70×10^{-6}/K.), suggesting that a large proportion of the micro cracks were still open. The reopening of the cracks would promote the thermal hysteresis during cooling on the third run.

Non-destructive testing

Figure 5 shows the average residual density of the ATM composites as a function of the quenching cycles. The density differences for the ATM composite after 30 quenching cycles were marginal. Although the ATM shows a difference on the chart during the test, the relative deviation for these samples was below 1.5%. Perhaps the most significant aspect of the density data lies in the fact that while the ATM-1, -2 and -3 materials have a relatively higher density of 3.55-3.80 gcm^{-3} after 7 or 11 quenching cycles, the fine-grained materials exhibit respectable residual densities and no crack extension. This result is the foundation of the lower Young's modulus and lower flexural strength, while simultaneously providing an excellent level of thermal shock resistance.

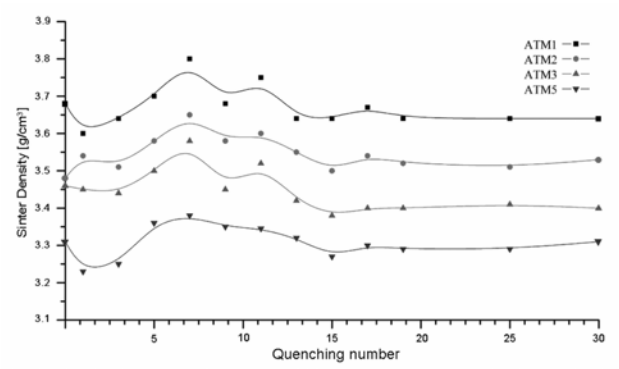

Fig. 5. Average sintered density of the ATM materials as a function of the quenching number, 950 °C/30 cycles.

As shown in Fig. 6. the Young's modulus was measured as a function of the number of quenching cycles. The ATM5 material had a higher Young's modulus, 80 GPa, than did the other specimens, which, although denser, contained appreciable amounts of cracks on their grain boundaries. The Young's modulus values of the ATM composites containing micro cracks at grain boundaries were influenced by the constant area of contact across the

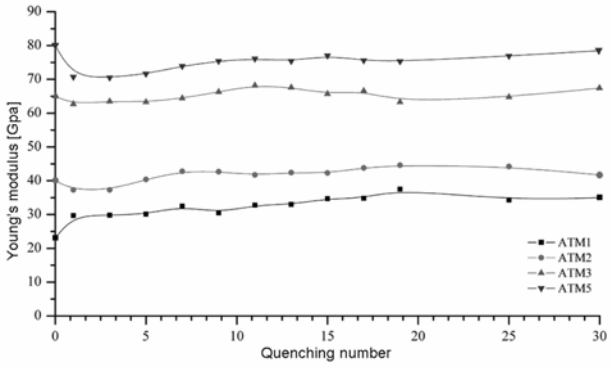

Fig. 6. Average Young's modulus of ATM composites as a function of quenching number.

Table 1. The phase compositions, thermal and physical properties of the ATM materials (1600 °C for 2 h).

Material	Mullite content [%]	Phase		Sinter density [g/cm^3]			Thermal expansion coefficient [10^{-6}/K]		Young's modulus [GPa]		
		1600 °C /6 h	1100 °C /100 h	1600 °C /6 h	1100 °C /100 h	*cycles	1600 °C /6 h	1100 °C /100 h	1600 °C /6 h	1100 °C /100 h	*cycles
AT	0	AT	*A+T	3.1	-	-	0.68	6.15	20	-	-
ATM1	10	*AT+M	*AT+M	3.3	3.71	3.63	1.09	1.49	23	38.9	35.0
ATM2	20	*AT+M	*AT+M	3.5	3.57	3.53	2.50	3.03	40	44.7	41.7
ATM3	30	*AT+M	*AT+M	3.41	3.46	3.40	4.06	3.59	65	70.9	67.4
ATM5	50	*AT+M	*AT+M	3.4	3.50	3.30	5.48	5.36	80	78.8	78.5

A : Al_2O_3, T : TiO_2, AT: Al_2TiO_5, M : Mullite

sintered grain boundaries. This result not only brings about the lower and constant Young's modulus, but simultaneously provides excellent thermal shock resistance as well. Although several samples show a similar evolution, no overall trend is noticeable.

According only to the density, the grain boundary micro cracks were influenced by the constant area of contact across the sintered grain boundaries.

Table 1 summarizes the phase compositions, thermal and physical properties of the ATM materials (1600 °C/2 h) after various heat treatments. The final materials consisted mainly of two phases: Al_2TiO_5 and mullite. The low density of pure Al_2TiO_5 of 3.1 g/cm^3 is related to the grain growth of Al_2TiO_5 with a higher porosity as Al_2TiO_5 has a lower theoretical density of 3.70 g/cm^3, compared to an equimolar Al_2O_3/TiO_2 mixture (4.19 g/cm^3), accompanied by nearly a 11% molar volume increase [7].

This phenomenon can be explained by comparing the density of Al_2TiO_5 and mullite. The density of the ATM materials increased as the mullite content increased, reaching a maximum at 20 vol% of mullite, and then decreased as the mullite content was increased further. The Young's modulus of Al_2TiO_5 increased as the mullite content increased, accounting for the observed increase in the thermal expansion coefficient. The AT material decomposed to corundum and rutile in both cases, and partial decomposition was observed in the ATM2, ATM3, and ATM5 composites after annealing at 1100 °C. The amount of decomposition of Al_2TiO_5 decreased as the mullite content increased, thus the composition with 20-50 vol% mullite continued to retain ~90% of Al_2TiO_5. The changes caused in the phase compositions by cyclic thermal shock illustrate a similar trend.

Conclusions

Homogeneously-dispersed and narrowly distributed Al_2TiO_5 and mullite grains with a complex system of micro cracks were sintered at 1600 °C for 6 h. The thermal expansion hysteresis curves of ATM1 remained flat to 700 °C for ATM1, but as the temperature was raised above this level, hysteresis increased slightly due to a crack-healing effect. A good thermal durability was achieved for the compositions containing 70 and 80 vol% Al_2TiO_5, which showed little change in their microstructure and thermal properties during the tests. The Young's modulus and thermal expansion coefficient were highest at a mullite content of 50 vol%, but these maximum values were accompanied by a relative lower thermal shock resistance, a result attributed to fewer grain-boundary micro cracks acting as stress absorbers.

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