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Thermal Durability of Al_2TiO_5-Mullite Composites and Its Correlation with Microstructure

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ABSTRACT

Thermal shock resistance of structural ceramics is a property that is difficult to quantify, and as such 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, Young's modulus and thermal expansion retention after quenching. For high temperature applications, long-annealing thermal durability, cycle thermal stability and residual mechanical properties are very important if these materials are to be used between 1000°C and 1300°C. In this study, an excellent thermal shock-resistant material based on Al_2TiO_5-mullite composites of various compositions was fabricated by sintering reaction from the individual oxides and adjusting the composition of $Al_2O_3/TiO_2/SiO_2$ ratios. The characterization of the damage induced by thermal shock was done by measuring the evolution of the Young's modulus using ultrasonic analysis, density and thermal expansion coefficients.

Key words : Al_2TiO_5, Mullite, Thermal shock, Non-destructive, Ultrasonic, Young's modulus

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 microcracking 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]

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 applications as an insulating material in engine components such as port-liners, piston bottoms, and turbochargers.[6] 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.[7] However, a pure Al_2TiO_5 tends to 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.[8] Following decomposition, the material no longer exhibits either a low thermal expansion coefficient or favorable thermal shock behavior.[9] 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, such as Fe_2TiO_5,[10] $MgTi_2O_5$[11] or Ti_3O_5 (anosovite).[12] Al_2TiO_5 can also be mechanical stabilized by limiting its grain growth with additives such as SiO_2,[13] ZrO_2,[14] $ZrTiO_4$[12,13] or mullite,[14] most of which do not form a solid solution with Al_2TiO_5 but rather restrain the tendency of Al_2TiO_5 toward decomposition.

In this work, several tests were conducted to evaluate the thermal durability of the Al_2TiO_5-mullite composites. First, the specimens were subjected to long-term thermal annealing, at the critical decomposition temperature of Al_2TiO_5 at 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 min. The characterization of the damage induced by thermal shock was done by non-destructive testing methods.

2. Experimental Procedure

Raw materials used in preparing Al_2TiO_5-mullite compos-

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ites were TiO_2 (99.0%, Showa) and 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 the planetary mill (Fritsch, pulveritte) until an average particle size of 3~5 μm was obtained. The chemical composition of each of AT, ATM1, ATM2, ATM3, and ATM5 refer to 0, 10, 20, 30, and 50 vol% addition 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. They were sintered at 1500 and 1600°C for 2 h in air after the calcination in air 600°C for 1 h to remove organic materials. At this stage the heating rate was 10 K min^{-1} and the cooling rate was about 20 K min^{-1}. For density measurements, a gas pycnometer AccuPyc 1330, provided by Micromeritics U.S.A., has been used. The microstructural degradation of the samples were characterized by X-ray diffraction (Rigaku, D/max 2200, Ni-filtered CuKα), scanning electron microscopy (Jeol, JSM-5600) and dilatometer (Netzsch). The thermal expansion coefficient from Room Temperature (RT) to 1350°C was determined for a 5 × 5 × 25 mm specimen, in air, using a dilatometer, at a heating rate of 10 K/min and a cooling rate of 10 K/min. The Young's modulus was measured by an ultrasonic method (Panametric 5800), as a function of quenching number using the test specimens.

After the quenching, the density, the round trip transit time of longitude and transversal ultrasonic waves are measured. Using the values of density, round trip time and thickness of the sample, the Young's modulus can be calculated using formula (1), (2), (3), and (4) as following. The echo pulse technique is used to measure the sound velocity in Al_2TiO_5-mullite ceramics. The propagation velocity depends on the following parameters: Young's modulus (E), Density (ρ) and the Poisson's ratio (υ).

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

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

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

The velocity is defined as follows:

$$V = \frac{Thickness}{\frac{1}{2}Round\text{-}trip\text{-}transit\text{-}time} \tag{3}$$

A gas pycnometer is used to determine the volume of the sample. After cradling the sample, the density can be calculated. The gas pycnometer compares the pressures before and after putting inside the sample. Out of the deviation, the volume can be calculated. After determine Poisson's ratio and density, the Young's modulus can easy be calculated by using formula (1) and solving for E.

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

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

3. Results and Discussion

3.1. Microstructure

The positive effects of thermal treatment and thermal expansion are due to the microstructure system of Al_2TiO_5-mullite composites as shown in Fig. 1. The bright structure shows the dominating Al_2TiO_5 grains, whereas the dark spots display mullite phase. Like all other materials the Al_2TiO_5 expands during thermal treatment. But the noticeable expansion is nearly zero for low temperatures and increase only at higher temperature (>600°C). During heating, the Al_2TiO_5 grains will expand anisotropic into these cracks until they are closed. After closing a change in volume will be 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 single crystal Al_2TiO_5 (9.70 × 10^{-6}/K).[8] These low thermal expansion coefficients are apparently due to a combination of micro crack-

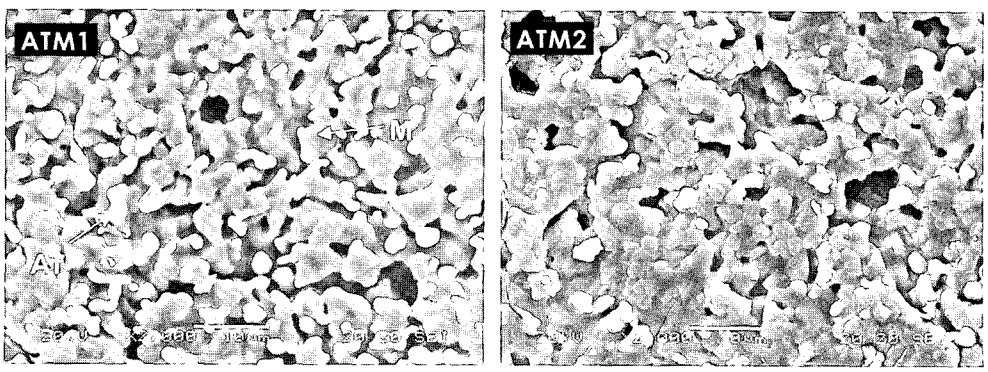

Fig. 1. SEM image of micro cracks at the grain boundary in ATM1 and ATM2 composite (1600°C/2 h).
AT : Al_2TiO_5, M : Mullite

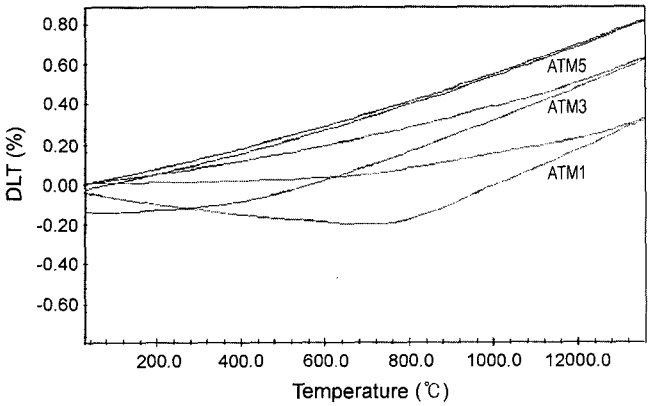

Fig. 2. Thermal expansion coefficient of ATM ceramics sintered at 1600°C for 2 h.

ing caused by the large thermal expansion anisotropy of the crystal axes of the Al_2TiO_5 phase.[15]

3.2. Thermal Expansion Behavior of ATM Composites

All ATM composites with increasing Al_2TiO_5 content exhibit reduced a low thermal expansion coefficients accompanied by pronounced large hysteresis area as shown in Fig. 2. The ATM materials showed a zero level 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 with heating to >900°C and their reopening or refracturing which occurs when cooling below 730°C.

Even at 1000°C the slope of ATM1 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 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 temperature from 20 to 1000°C, respectively.

3.3. Micro Crack Healing and Reopening

Microstructure of ATM composite during the heat treatment was shown in the Fig. 3. The observed micro cracks by ESEM between grain boundaries at 28°C was 362~441 nm. In the first run to 597°C the length of micro crack at grain boundary was 311~431 nm, and the specimens exhibited negative thermal expansion. The second run to 911°C, the individual Al_2TiO_5 crystallites 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 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 than 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 crack reopening would promote the thermal hysteresis during cooling on the third run.

3.4. Non-Destructive Testing

Fig. 4 shows the average residual density of the ATM com-

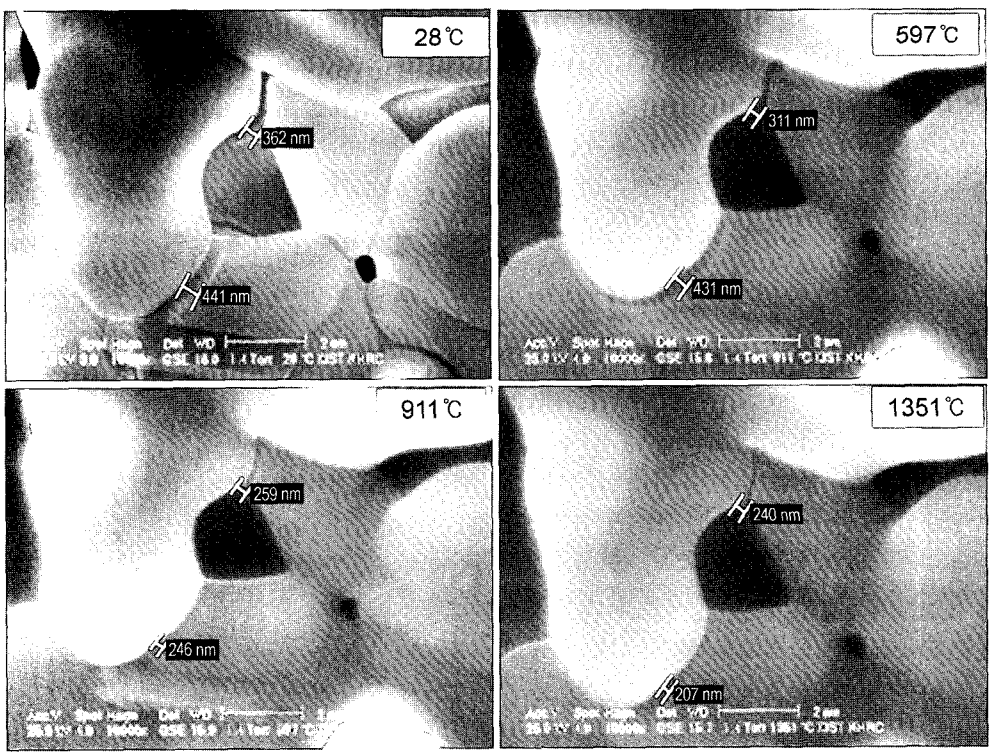

Fig. 3. Microstructure of ATM1 sintered at 1600°C for 6 h during the heating.

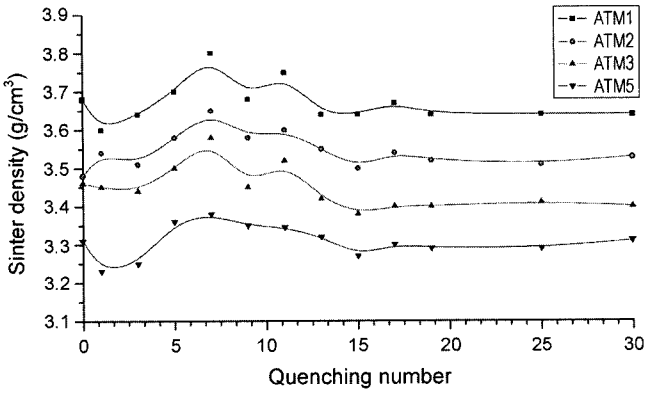

Fig. 4. Density of ATM materials as a function of quenching number, 950°C/30 cycles.

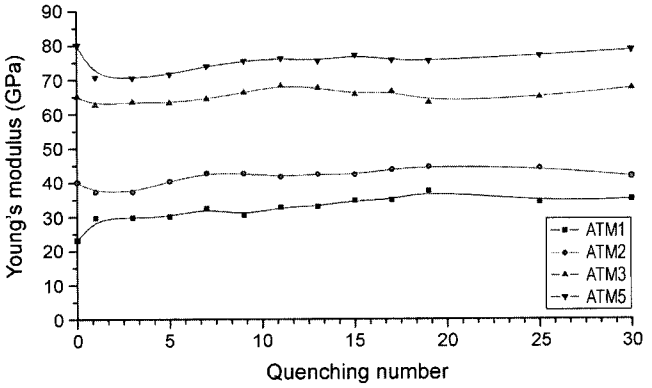

Fig. 5. Young's modulus of ATM composite as a function of quenching number.

posites after thermal shock. The low density of pure Al_2TiO_5 of 3.1 g/cm^3 is related to the grain growth of Al_2TiO_5 and higher porosity because Al_2TiO_5 has a lower theoretical density of 3.70 g/cm^3, in comparison with an equimolar Al_2O_3/TiO_2 mixture (4.19 g/cm^3), accompanied by an about 11% molar volume increase.[7] This phenomenon can be explained by comparing the density of Al_2TiO_5 and mullite. With increasing amount of mullite, the density decreases. Because of the theoretical density of Al_2TiO_5 (3.75 g/cm^3) is higher than mullite.

The density differences for ATM composite after 30 quenching cycles are marginal. Even if ATM shows a difference on the chart during the test, the relative deviation for these samples laid below 1.5%. Perhaps the most significant aspect of the density data is that, although 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 grounds for the lower Young's modulus and lower flexural strength, but simultaneously provides excellent thermal shock resistance.

As shown in Fig. 5, Young's modulus was measured as a function of the number of quenching. 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 the grain-boundary were influenced by the constant area of contact across the sintered grain boundaries. This result is grounds for the lower and constant Young's modulus, but simultaneously provides excellent thermal shock resistance. Although some samples show similar evolution, no overall trend is noticeable, just according to the density containing grain boundary micro cracks were influenced by the constant area of contact across the sintered grain boundaries.

Table 1 summerizes the phase compositions, thermal and physical properties of ATM materials (1600°C/2 h) after various heat treatment. The final materials consisted mainly of two phases: 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 with further increased mullite contents. Young's modulus of Al_2TiO_5 increased with increased mullite content, 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 with increased mullite content, so that the composition with 20~50 vol% mullite still retained ~90% of Al_2TiO_5. The changes caused in the phase compositions by

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 ($10^{-6}k^{-1}$)		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

*AT : Al_2TiO_5, M : Mullite, A : Al_2O_3, T : TiO_2
**cycles : 750 – 1400 – 750°C for 23 cycles

cyclic thermal shock illustrate a similar trend.

4. Conclusions

Materials sintered at 1600°C for 6 h consisted of homogeneously-dispersed and narrow distributed Al_2TiO_5 and mullite grains with a complex system of micro cracks. The thermal expansion hysteresis curves of ATM1 showed a zero level to 700°C for ATM1, but as the temperature was raised above this level, hysteresis increased slightly due to the crack healing effect. The good thermal durability was achieved for the compositions containing 70 and 80 vol% Al_2TiO_5, which showed little change in 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 those maximum values were accompanied by relative lower thermal shock resistance, a result attributed to fewer grain-boundary micro cracks acting as stress absorbers.

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