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Low Thermal Expansion of Al_2TiO_5 Ceramics Prepared from Electrofused Powders

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The synthesis of polycrystalline Al_2TiO_5 ceramics with low thermal expansion by fusion in an electric arc furnance was investigated. The thermal expansion curves of Al_2TiO_5 ceramics were lowered because of microcracks caused by the strong thermal expansion anisotropy of the crystal axes and were accompanied by hysteresis curves. These phenomena are explained by the opening and closing of microcracks. The difference in microcracking temperatures of dilatometric cooling curves in the range of 400~620°C is caused by the difference in sintering temperature, grain size and stabilization status.

Key words: Al_2TiO_5, Sintering, Thermal expansion, Hysteresis, Microstructures

I. Introduction

In Al_2TiO_5 polycrystalline ceramics, the thermal expansion anisotropy of the three crystallographic directions causes grain boundary microcracking.[1] These microcracks often result in negative thermal expansion coefficients accompanied by pronounced hysteresis.[2,3] Such anisotropy creates complicate internal stresses during cooling from the sintering temperature.[4] The magnitude of such stresses is a direct function of the degree of anisotropic thermal expansion, which is sufficient to exceed the intrinsic fracture strength of the material. This results in severe microcracking at room temperature and consequently the low mechanical strength and low Young's modulus.[5,6] The development of microcracks also accounts for the low thermal expansion coefficients which are in reality a bulk average value based on the behavior of individual grains. Thus the true thermal expansion coefficient of aluminium titanate is near to $9.7\times10^{-6}K^{-1}$: $\alpha_a = 9.8\times10^{-6}K^{-1}$, $\alpha_b = 20.6\times10^{-6}K^{-1}$, $\alpha_c = -1.4\times10^{-6}K^{-1}$.[7,8]

Low thermal expansion coefficient, low Young's modulus, good thermal insulation, and excellent thermal shock resistance are characteristics of aluminum titanate ceramics. These properties, if property adjusted, allow the application for the insert-casting of ceramic portliners into the cylinder head[alloy AlSi 12(Cu) or cast iron], where they serve as a thermal insulation of the exhaust gas as a means of improving thermal efficiency. It is also under serious consideration for use as exhaust mainfold inserts, piston crowns and turbocharger liners.[9,10] Additionally it finds application in the non-ferrous metallurgical industries.[11] Successful application of the material has depended on the ability to control the microcracking phenomena and use it to advantage, together with an ability to understand the decomposition behaviour. In this paper, the effect of stabilizing aids and sintering temperatures on the thermal expansion hysteresis and microstructure of two aluminium titanate ceramics with different compositions is studied in comparison with their pure components by dilatometry.

II. Experimental Procedure

The ATG powders were prepared through electrofusion in an arc furnance. Table 1 lists the chemical composition of powders. ATG1 and 2 were unstabilized Al_2TiO_5 whereas ATG3 and ATG4 were stabilized during the fusion process through addition of MgO. The later two compositions contain small amounts of ZrO_2 but differ in their SiO_2 content. All powders in the as received condition were milled and seperated and below 4 μm in grain size with an average particle size of 2.5 μm. The specific

Table 1. Chemical Composition of ATG Composites (wt%)

	ATG-1	ATG-2	ATG-3	ATG-4
Al_2O_3	55.50	54.70	53.80	53.00
TiO_2	43.90	43.90	32.75	40.00
ZrO_2	0.05	0.40	3.00	2.30
SiO_2	0.15	0.30	7.90	1.20
MgO	-	-	2.10	3.00
Fe_2O_3	0.20	0.50	0.20	0.25
Na_2O	0.20	0 20	0.20	0.20
CaO	0.01	0.01	<0.05	<0.05

*ATG . Powders of Dynamit Nobel chemicals, D-5210 Troisdorf

surface area(BET) of all materials was 2.3 m^2/g. Sintering experiments in air were done in a muffle furnance at 1400, 1450, 1500 and 1550°C for 2 hrs. Heating and cooling rates were 100°C/h to 500°C(2 hrs) to max. temperature(2hrs) and 600°C/h to room temperature, respectively. The physical properties can be adjusted over in a wide range; apparent density of 3.61~3.68 g/cm^3, thermal expansion coefficient(TEC, RT ~1,000°C) of 1.3~3.0 $\times 10^{-6}$ K^{-1}, and bending strength of 25~49 MPa. The 3-point-bending experiments were performed on unground bars(50 × 4.5 × 3.5 mm), time to fracture about 10 seconds. The thermal expansion was determined on specimens(25 × 5 × 5 mm) by dilatometer with heating and cooling rate 5°C/min in air.

III. Results and Discussion

Table 2 shows the physical properties of the specimens sintered at 1450°C for 2 hrs. The relatively low density level of 92.1 and 93.2% TD of ATG1 and ATG2 samples confirms its poor sinterbility and is connected with a grain growth of Al_2TiO_5. However, the samples of ATG3 and ATG4 containing SiO_2(7.90 wt%), MgO(2.10 wt%) and SiO_2 (1.20 wt%), MgO(3.00 wt%) have reached such high densities as 95.1 and 95.3% of the theoretical density, respectively. The promoting effects of SiO_2 and MgO might be related to the increased contact area between constituent particles and consisting of mainly crystalline phases of Al_2TiO_5, α-Al_2O_3, mullite or MA-spinel, respectively(see Table 3). This phenomena was also obtained by stabilization with Mg-Al-titanate and Mg-Si-titanate in solid solution and by limitaion of grain size and microcracks.[12] When compared with particles ATG3 and ATG4 sintered at 1450°C for 2 hrs a significant grain growth in pure aluminium titanate ATG1 and ATG2, have occured at the sintering temperaure in Fig. 1. Unstabilized ATG1 and ATG2 exhibit a relatively broad spectrum of β-Al_2TiO_5 grain size in the range of 5~40 μm and 5~20 μm with a small amount of dispersed corundum phase, respectively. The stabilized specimen ATG3 and ATG4 appear to have a smaller mean grain size β-Al_2TiO_5. In all cases aluminium titanate grains are surrounded by microcracks. As the grain size of a polycrystalline ceramic becomes larger, microcracks occur, resulting in lowering of thermal expansion coefficient; the extremely low thermal expansion with hysteresis is attributed to the occurrence and healing of internal microcracks.[13] The process of grain spheroidization and neck formation between Al_2TiO_5 grain of heterogeneous array was observed but it was more pronounced in the samples with SiO_2 and MgO. Some of the larger grains created during heating procedure, probably as a consequence of large thermal expansion anisotropy of Al_2TiO_5 crystals. These grains may have behaved as obstacles to the mass transport during the interparticle bonding, due to the presence of microcracks created in the cooling step

Fig. 2 shows the thermal expansion curves of ATG2, ATG3, and ATG4 sintered at 1500°C for 2 hrs. The ther-

Table 2. Physical Data of the Sintered Specimens (1450/2 hrs.)

Physical Data	ATG	ATG 2	ATG 3	ATG 4
Geeen density (g/cm^3)	2.10	2.16	2.11	2.15
Sintered density (g/cm^3)	3.39	3.43	3.44	3.49
True density (g/cm^3)	3.68	3.68	3.61	3.67
Relative density (% TD)	92.1	94 8	95.3	95.1
Apparent porosity (%)	-	3.98	3.7	4.7
Total porosity (vol. %)	7.9	6.8	4.7	4.9
Firing shrinkage (%)	15.5	15.	15.0	15.1
Heating/Cooling rate (°C/min)	10.0	10.0	10.0	10.0
Coefficient of thermal expansion ($1/K10^{-6}$, RT~1273K)	-	3.0	3.28	2.56
Thermal expansion, RT~1273K (%)	-	0.35	0.28	0.22
Bending strength (MPa)	-	25.0	48.0	29.0

Table 3. Phase Composition of ATG Composites after Various Thermal Treatments

Phase composition	ATG-1 (unstabilized)	ATG-2 (unstabilized)	ATG-3 (fused-stabilized)	ATG-4 (fused-stabilized)
After fusion process	β-AT	β-AT	β-AT MA-Spinel m-ZrO_2	β-AT α-Al_2O_3 MA-Spinel m-ZrO_2
Sintering at 1450°C/2 hrs	β-AT Rutile	β-AT Rutile	β-AT α-Al_2O_3 Mullite m-ZrO_2	β-AT α-Al_2O_3 MA-Spinel m-ZrO_2

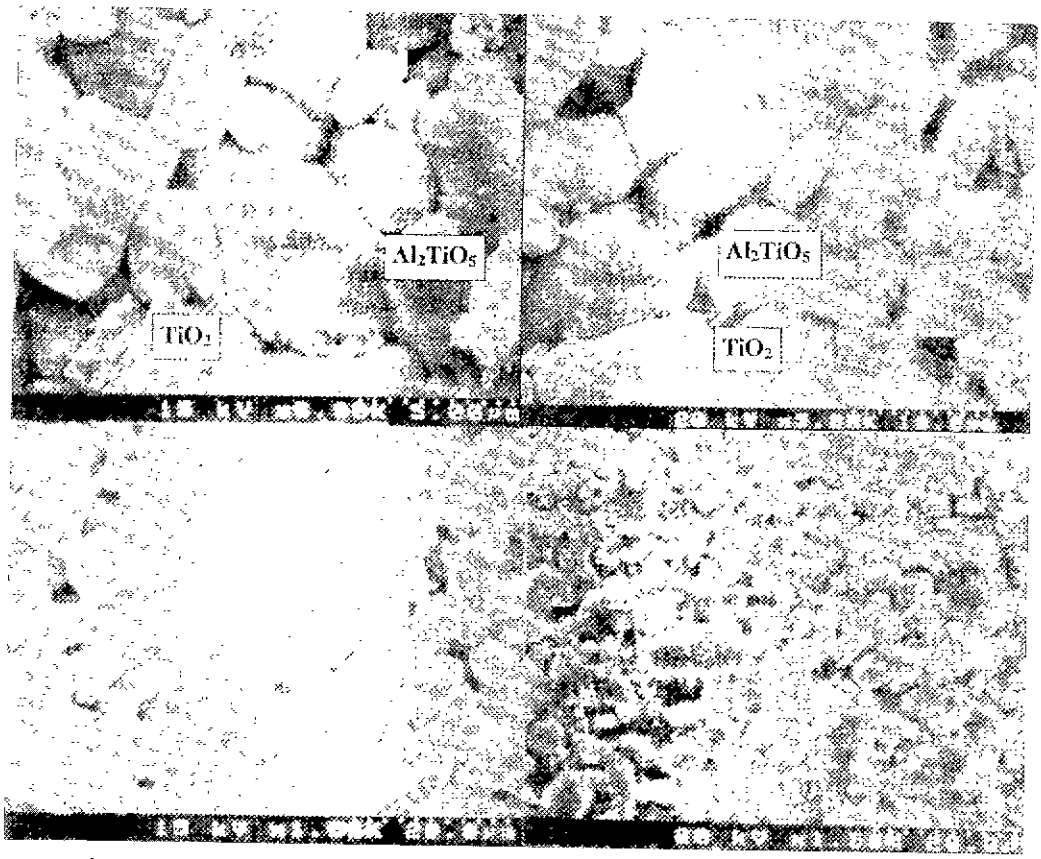

Fig. 1. Microstructure of sintered ATG-1, 2, 3 and 4 at 1450 for 2 hrs.

mal expansion of these materials lies between 0.41% and 0.50% in the temperature range of 25-1500°C. Maxium thermal expansion coefficient of ATG2($2.95 \times 10^{-6}K^{-1}$), ATG3($3.55 \times 10^{-6}K^{-1}$), and ATG4($3.95 \times 10^{-6}K^{-1}$) occurs between 1250 and 1350°C, respectively. This can be compared with a theoretical expansion coefficient for single phase β-Al_2TiO_5 of $9.7 \times 10^{-6}K^{-1}$[2]. It is the pronounced in the thermal anisotropy expansion of individual Al_2TiO_5 grains that gives rise to internal stresses on a microscopic scale during cooling from the firing temperature. These localized internal stresses are the driving force for microcrack formation. During reheating, the individual crystallites expand at a lower temperatures, thus the solid volume of sample expands to the smaller sized microc-

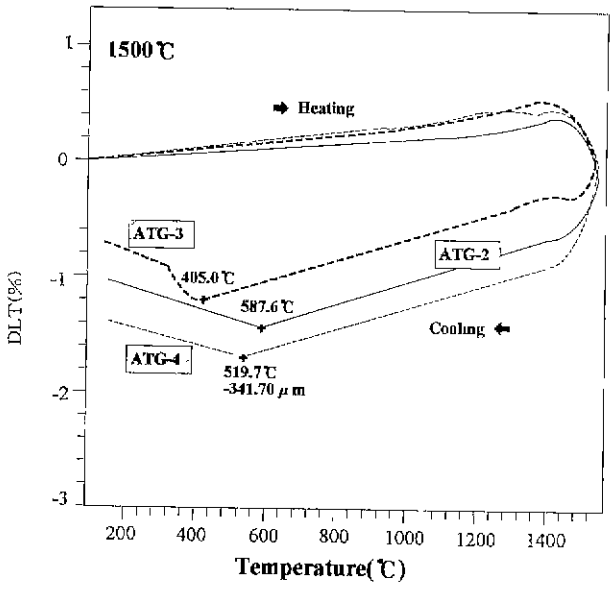

Fig. 2. Thermal expansion curves of sintered ATG-2, -3 and -4 at 1500°C for 2 hrs.

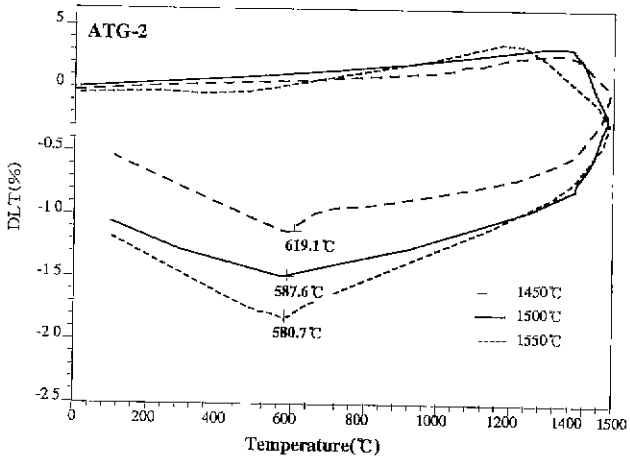

Fig. 3. Thermal expansion curves of sintered ATG2 at 1450, 1500 and 1550°C for 2 hrs.

racks, while the macroscopic dimensions remain almost constant. As a result, the material expands very little. The higher the temperature, the more cracks are closed, the steeper the thermal expansion curve becomes. However, even at 1250°C the slope is far below the theoretical value, suggesting that high fractions of the microcracks are still open. The thermal expansion curves of ATG materials demonstrated nearly the same hysteresis with internal rupture or microcracking created during cooling. The difference in the microcracking temperature, such as 587.6, 405.0 and 519.7°C, for the specimens ATG2, ATG3 and ATG4 respectively, was caused by the difference in grain size of β-Al_2TiO_5 and additive contents.

The thermal expansion curves of sintered ATG2 at 1450, 1500 and 1550°C for 2 hrs showed negligible expansion from room temperature to 650°C, but as the temperature is raised above this level, the hysteresis curves increase markedly as show in Fig. 3. This is ascribed to the onset of mechanical healing of microcracks above 700°C on heating and their reopening or refracturing on cooling, being delayed until the temperature was below 650°C. It is pronounced that stresses on the microstructure of all composites build up only below about 650°C. The difference in the microcraking temperature, which were 550, 587.6 and 619.10°C, for the specimens 1450, 1500 and 1500°C, respectively, was caused by differene in grain size as show in Table 4. The thermal expansion coefficents of sintered ATG2 at 1450, 1500 and 1550°C for 2 hrs lies 2.45 and $1.18 \times 10^{-6} K^{-1}$(RT ~ 1000°C). Fig. 4 and 5 show typical thermal expansion curves of ATG3 and ATG4 at various sintering temperature. The dependence of the thermal expansion of Al_2TiO_5 ceramics on grain size has been shown previously,[14] where it decreases with increasing grain size(see Table 3). The presence of mullite in ATG3 also shows relatively lower microcracking temperature. these are ranged between 402.1 and 467.0°C. The microcracking temperature of lower sintered samples were lower and ranged from 402.1 up to 497.4°C. This could be connected with the lower sensitivity to

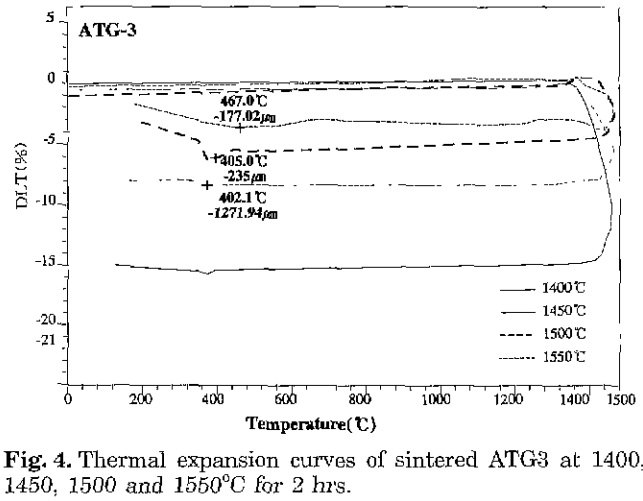

Fig. 4. Thermal expansion curves of sintered ATG3 at 1400, 1450, 1500 and 1550°C for 2 hrs.

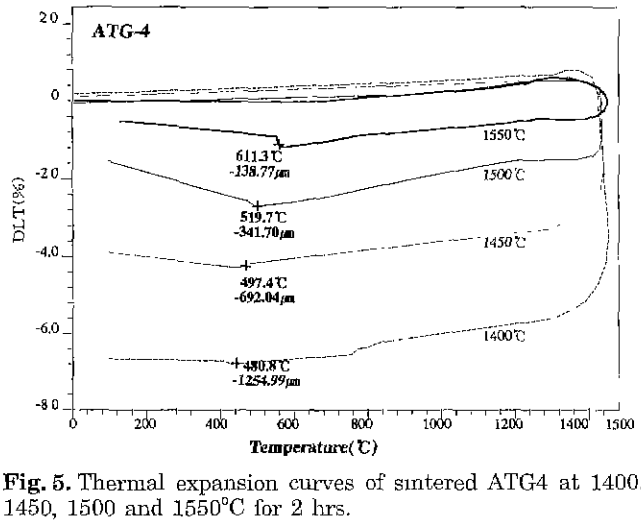

Fig. 5. Thermal expansion curves of sintered ATG4 at 1400, 1450, 1500 and 1550°C for 2 hrs.

Table 4. The Densification, the Thermal Expansion Behavior, and the Grain Size of ATG Ceramics, after Sintering at Various Temperatures

Materials	Sintering temperature (2 hrs)	Relative density (%)	Grain size (μm)	Maxium expansion (%)	Thermal expansion coefficient, $\alpha_{25\text{-}1000°C}$ ($10^{-6}K^{-1}$)	Microcracking temperature(°C)
ATG2	1400°C	94.72	3~12			0
	1450°C	94.80	3~15	0.40	3.00	580.7
	1500°C	94.42	5~15	0.40	2.45	587.6
	1550°C	93.78	5~17	0.26	1.18	619.10
ATG3	1400°C	92.43	2~7	0.80	4.71	0
	1450°C	95.30	2~7	0.50	3.28	402.1
	1500°C	92.40	10	0.50	2.35	405.0
	1550°C	92.86	10~20	0.30	0.83	467.0
ATG4	1400°C	94.95	2~5	0.51	4.02	480.8
	1450°C	95.10	2~5	0.41	2.56	497.4
	1500°C	94.85	5~10	0.41	2.79	519.7
	1550°C	92.10	10~15	0.40	1.22	611.3

microcracking of the relatively fine grained microstructure typical of ATG3 samples if ATG3 sintered at 1400°C does not show the inflection temperature of the cooling curves. Table 4 shows the densification, the thermal expansion behaivor and the grain size of ATG ceramics, after sintered vaious temperature. As the firing temperature higher, the density was higher On the other hand, the relative density of ATG1 and ATG2 increased initially, then reached a maximum at 1450°C for 2 hrs of 93.1 and 94.80%, respectively, and decreased. Higher sintering resulted in grain growth and corresponding microcracking, as shown clearly in Fig. 2, and resulting in a slight lower of the relative density as well as a lowering of the thermal expansion due to microcracking.

IV. Conclusions

The thermal expansion properties of the investigated ATG composites show the hysterisis due to the strong anisotropy of Al_2TiO_5. These phenomena are explained by the opening and closing of microcracks. With decreasing the average grain size, the thermal expansion decreased. The difference in microcracking temperatures, e.g. 587.6, 405.0 and 519.7°C, for the sintered specimens ATG2, ATG3 and ATG4 at 1500°C for 2 hrs respectively, was caused by the difference in grain size of β-Al_2TiO_5 and additive content. The lowest thermal expansion coefficient of studied materials was found from ATG3 and lies between 0.83 and 3.28×10^{-6} K^{-1} in the temperature range of RT~1000°C.

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