# Review
# Formation, Decomposition and Thermal Stability of $Al_2TiO_5$ Ceramics

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## Abstract

The thermal instability of $Al_2TiO_5$ can be mitigated using solid solutions of MgO, $Fe_2O_3$, $TiO_2$, and $ZrO_2$ in the $Al_2TiO_5$ lattice or grain boundary solutions with additives such as $SiO_2$, $ZrO_2$, $ZrTiO_4$, or mullite, most of which do not form solid solutions with $Al_2TiO_5$ but rather restrain the tendency of $Al_2TiO_5$ toward decomposition. The additives $SiO_2$ and $ZrO_2$ do not have a significant effect on the thermal stability of $Al_2TiO_5$, even after long annealing at the critical temperature of 1100 °C. Mullite retarded decomposition and increased thermal stability between 750 and 1300 °C. Literature regarding the formation, decomposition and thermal stability of $Al_2TiO_5$ ceramics with different inorganic materials exhibiting thermal expansion and excellent thermal shock resistance is discussed with regard to the application of the materials at high temperature, especially as diesel particulate filters.

*Keywords: $Al_2TiO_5$, formation, decomposition, low thermal expansion, thermal stability, thermal shock-resistant, raw materials*

## I. Introduction

Aluminum titanate ($Al_2TiO_5$)-based ceramics are used as excellent thermal-shock-resistant, corrosion-resistant, and insulating materials because of their low thermal conductivity, low thermal expansion, and low Young's modulus. However, they exhibit low mechanical strength. Pure $Al_2TiO_5$ tends to decompose into $Al_2O_3$ and $TiO_2$-rutile at 750–1300 °C, which greatly hampers its industrial application, while $Al_2TiO_5$ ceramics can be made suitable for use as insulating material in engine components such as port liners, piston bottoms, turbochargers, and DPFs, etc. [1–3]. The material's low mechanical strength is due to microcracks induced by the high anisotropy of its thermal expansion coefficients, which are -3.0, +11.8 and $+21.8 \times 10^{-6}$/K in each of its three crystallographic axes [4,5]. The crystal structure of $\beta$-$Al_2TiO_5$ is of pseudobrookite type with a theoretical density of 3.70 g/cm³. The densities of the starting oxides are 3.99 and 4.25 g/cm³. Therefore, reaction (1) is accompanied by an 11-% molar volume increase [6,7].
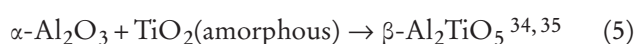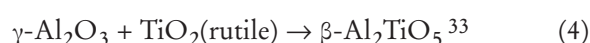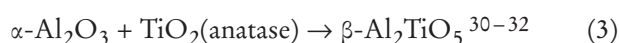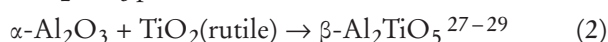
$$\alpha\text{-}Al_2O_3 + TiO_{2\text{-Rutile}} \rightarrow \beta\text{-}Al_2TiO_5 \qquad (1)$$
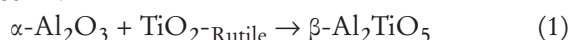
The decomposition of pure $Al_2TiO_5$ into $Al_2O_3$ and $TiO_2$ occurs below the equilibrium temperature, which has been reported to be 1300 °C (Lang, 1952)[53], $1237 \pm 10$ °C (Ki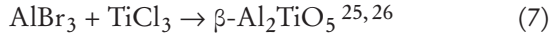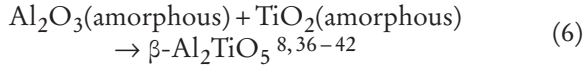m, 1960)[7], 1200 °C (Goldberg, 1968)[54], and 1280 °C (Kato, 1980)[8]. This decomposition occurs when adjacent $Al^{3+}$(0.54 Å) and $Ti^{4+}$ (0.67 Å) octahedra collapse because the lattice sites occupied by the $Al^{3+}$ions are too large [10,11]. The thermal energy available from this collapse allows $Al^{3+}$ to migrate, resulting in structural dissolution to rutile ($TiO_2$) and corundum ($Al_2O_3$) [12]. After decomposition, the material exhibits neither a low thermal expansion coefficient nor favorable thermal shock behavior, rendering it useless for high-temperature applications [13].

## II. Formation and Decomposition of $Al_2TiO_5$ Ceramics

Most studies of $Al_2TiO_5$ systems concern the high-temperature preparation of these materials from oxide powders. In this conventional processing, the reactions between the oxides to complete reaction are not sufficiently fast [14,15]. Therefore, pre-synthesis processes have been developed, incorporating the use of stabilizers [16,17], electrofused powders [54,18], sol-gel methods [19–22], semi-sol-gel methods [23,24], and CVD [25,26], to produce mainly uniform $Al_2TiO_5$ phases.

$$\alpha\text{-}Al_2O_3 + TiO_2(\text{rutile}) \rightarrow \beta\text{-}Al_2TiO_5 \ ^{[27-29]} \qquad (2)$$

$$\alpha\text{-}Al_2O_3 + TiO_2(\text{anatase}) \rightarrow \beta\text{-}Al_2TiO_5 \ ^{[30-32]} \qquad (3)$$

$$\gamma\text{-}Al_2O_3 + TiO_2(\text{rutile}) \rightarrow \beta\text{-}Al_2TiO_5 \ ^{[33]} \qquad (4)$$

$$\alpha\text{-}Al_2O_3 + TiO_2(\text{amorphous}) \rightarrow \beta\text{-}Al_2TiO_5 \ ^{[34,35]} \qquad (5)$$

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$$Al_2O_3(\text{amorphous}) + TiO_2(\text{amorphous})$$
$$\rightarrow \beta\text{-}Al_2TiO_5 \quad [8, 36-42] \tag{6}$$

$$AlBr_3 + TiCl_3 \rightarrow \beta\text{-}Al_2TiO_5 \quad [25, 26] \tag{7}$$

The formation of $Al_2TiO_5$ from individual oxides occurs at over 1200 °C as a result of solid-state reactions of the crystalline components [40-42]. The formation of $Al_2TiO_5$ can be achieved at low temperature, at over 600 °C via non-hydrolytic synthesis [43] and at approx. 800 °C using alkoxides stabilized with acetylacetone [44]. Acid-catalyzed solutions of aluminum and titanium alkoxides have been used to synthesize $Al_2TiO_5$ films at approx. 700 °C [45]. These low-temperature formations are attributed to a diffusion-limited crystallization process, which takes place in conditions of high homogeneity reached in the material at the molecular level [19]. The molar free energy of $Al_2TiO_5$ formation can be estimated with a third-law treatment of the available heat capacity and the equilibrium temperature; it has been confirmed experimentally [28, 46].

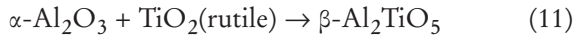$$\Delta G° = \Delta H° - \Delta S°T \quad [\text{Gibbs-Helmholtz}] \tag{8}$$

with: $\Delta G$ = free enthalpy of reaction
     $\Delta H$ = enthalpy
     $\Delta S$ = entropy

$$\Delta G° = \Sigma \Delta G°_{\text{pro.}} - \Sigma \Delta G°_{\text{react}} = 0, \text{ equilibrium} \tag{9}$$

$$\Delta G°_T < 0: \text{ The product is stable} \tag{10}$$

$$\alpha\text{-}Al_2O_3 + TiO_2(\text{rutile}) \rightarrow \beta\text{-}Al_2TiO_5 \tag{11}$$

$$\Delta G = G_3(Al_2TiO_5) - G_2(TiO_2, \text{rutile})$$
$$- G_1(\alpha\text{-}Al_2O_3) \tag{12}$$

$$G_3(Al_2TiO_5) = \Delta H° - \Delta S°T \tag{13}$$

$$\Delta G° = -3.20 - 12{,}89 \cdot 10^{-3} \, T \, \text{kJ/mol}$$
$$[\text{Barin-Knacke } 28, 47-50] \tag{14}$$

In general, above 1280 °C additive reaction takes place in an oxidizing atmosphere resulting in the formation of $Al_2TiO_5$ as in Eq. (1) and it is only thermodynamically stable above 1280 °C and undergoes a eutectoid-like decomposition to $\alpha\text{-}Al_2O_3$ and $TiO_2$(rutile) within the temperature range of 900 – 1280 °C. The eutectoid decomposition occurs at 1280 °C (equilibrium), but takes place upon undercooling [7-12, 28]. $\beta\text{-}Al_2TiO_5$ has a pseudobrookite crystal structure with an orthorhombic lattice with a *Cmcm* space group, with the following lattice constants: $a = 0.3591$ nm, $b = 0.9429$ nm, and $c = 0.9636$ nm [4, 8, 16]. The molar free energy of the $Al_2TiO_5$ formation can be estimated with a third-law treatment of the available heat capacity data and the equilibrium temperature and it has been confirmed experimentally (Fig. 1).

$$\Delta G° = 17.00 - 10.95 \cdot 10^{-3} \, T \, \text{kJ/mol}$$
$$[\text{Freudenberg and Mocellin } 16] \tag{15}$$

$$\Delta G° = 14.68 - 12.76 \cdot 10^{-3} \, T \, \text{kJ/mol}$$
$$[\text{Kubaschewski } 51] \tag{16}$$

$$\Delta G° = 13.39 - 8.049 \cdot 10^{-3} T \, \text{kJ/mol} \, [\text{Knacke } 52] \tag{17}$$

Where $\Delta T = T - 1553(K)$ in Eq. (2). The endothermic reaction is feasible because of the positive entropy contribution, $\Delta S°$, which is of similar magnitude to that of isotypic pseudobrookite phase with entropy contributions from cation disorder oxygen vacancies. The positive entropy might be further enhanced through additional entropy of mixing, upon the formation of $Al_2TiO_5$ solid solution containing $Mg^{2+}$, $Fe^{3+}$, or $Cr^{3+}$, which provide a lower decomposition temperature, i.e. increased stability.
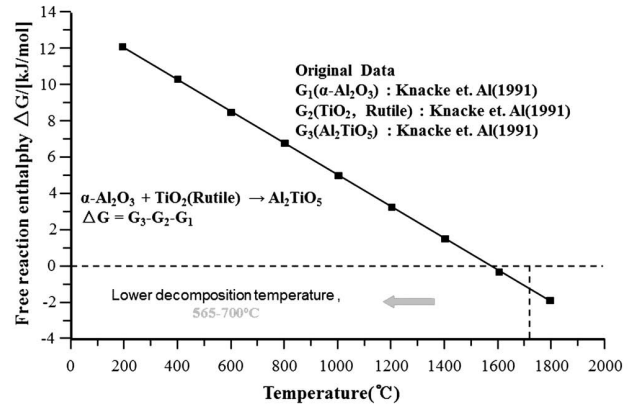


**Fig. 1:** Free energy $\Delta G$ of $Al_2TiO_5$ from $\alpha\text{-}Al_2O_3$ and $TiO_2$ [54, 90].

Eqs. (2), (3), and (4), show that the stable temperatures of the products were 1280, 877, and 1356 °C, respectively [16, 51, 52]. However, pure $Al_2TiO_5$ can reversibly decompose into $\alpha\text{-}Al_2O_3$ and $TiO_2$ (rutile). This thermal behavior of $Al_2TiO_5$ is due primarily to the complex system of internal stresses and fractures that develop in the material during cooling from elevated temperatures, and thus are the result of the anisotropic thermal expansion properties of individual grains which form the bulk of $Al_2TiO_5$ ceramics [4, 10].

Many equilibrium temperatures of pseudobrookite-type crystals related to this have been reported, e.g. 1237 °C and 1200 °C as lower limits at which $\beta\text{-}Al_2TiO_5$ is stable above 1356 °C (Table 1) [53]. In addition, Lang *et al.* reported the existence of two allotropic forms of $Al_2TiO_5$, which they termed β or low-temperature- and α or high-temperature-modifications [54]. Lejus and Goldberg compared different $Al_2O_3\text{-}R_2O_3$ systems and discussed new phases formed in the $Al_2O_3\text{-}TiO_2$ system during reduction by $H_2$ and C at high temperatures [55]. This temperature can be modified with the use of additives for increased stability of $Al_2TiO_5$ ceramics during cooling.

**Table 1:** Decomposition temperature of pseudobrookite-type crystals [8, 53].

| Crystal | Name | Decomposition temperature | Decomposition phase |
|---|---|---|---|
| $Fe_2TiO_5$ | pseudobrookite | 585 °C | rutile + hamatite |
| $Al_2TiO_5$ | tialite | 1280 ± °C | rutile + corundum |
| $MgTi_2O_5$ | karrooite | 620 °C | rutile + geikielith |
| $FeTi_2O_5$ | ferropseudo-brookite | 1140 °C | rutile + ilmenite |

This $\beta\text{-}Al_2TiO_5$ is stable from room temperature to 750 °C and from 1200 °C up to the inversion tempera-

ture at 1820 °C. The $\alpha$-$Al_2TiO_5$ form is thermodynamically stable from 1280 °C to the melting temperature ($T_m = 1860$ °C). In general, below 1280 °C, it decomposes into the parent oxides $\alpha$-$Al_2O_3$ and $TiO_2$ as the result of an eutectoid reaction; the decomposition rate is very low, below about 800 °C [51–53, 56] (Fig. 2).
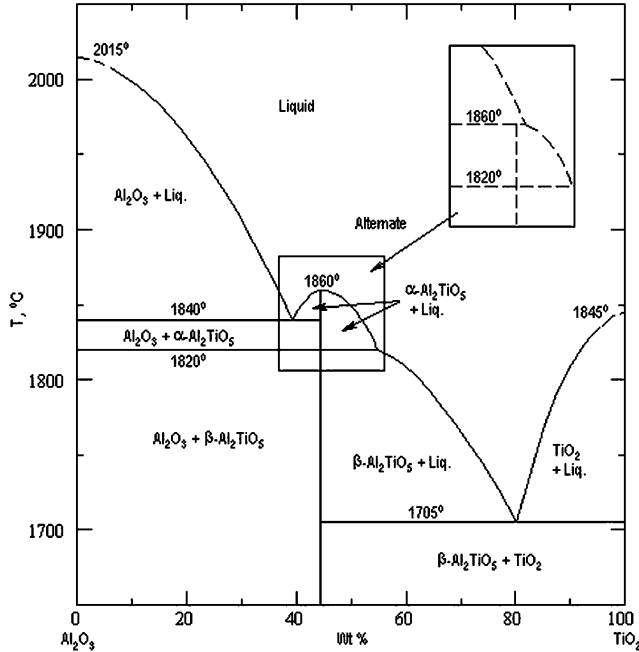


**Fig. 2:** Phase diagram of $Al_2O_3$ – $TiO_2$ system as proposed by P. Pena and S. DeAza [55].

The decomposition of both sintered and powdered $Al_2TiO_5$ has been widely studied [57], and its nucleation and growth reaction kinetics can be described with the Avrami model [58]. However, Hennicke and Lingenberg suggested that the decomposition occurred via metastable phases, the most likely of which being annosovite ($Ti_3O_5$), which is known to exhibit a complete range of solid solutions with $Al_2TiO_5$ [59]. The following mechanism was proposed as the most likely explanation of the decomposition of $Al_2TiO_5$:

$$Al_2TiO_5 = [(Al_2TiO_5)_{1-3x} (Ti_2TiO_5)_x] + x/2+3_x Al_2O_3 \qquad (18)$$
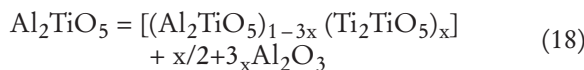
This mechanism fitted microstructural observations that showed the formation of small, irregular, $Al_2O_3$ particles and the appearance of small intracrystalline pores, as would be produced by gas evolution (e.g. $O_2$).

The decomposition is quickest between 1100 and 1150 °C, reaching completion within 5 – 50 h, depending on the average grain size and annealing time above the decomposition temperature. Considering the nucleation of a single grain, Kato derived a kinetic equation to fit the two regions of decomposition. It describes an early acceleration period, where the kinetics follow [9, 56, 57]:

$$t \leq \tau: \quad \alpha = -\frac{1}{\kappa\tau} - [\kappa t - (1 - e^{-\kappa t})] \qquad (19)$$

and a subsequent "deceleration period":

$$t \geq \tau: \quad \ln(1-\alpha) = \ln\left[-\frac{1}{\kappa\tau} - (e^{-\kappa\tau} - 1)\right] - \kappa t \qquad (20)$$

where $\alpha$ is the fraction decomposed, t the decomposition time, k is the nucleation time constant, and $\tau$ is the average time for decomposition to initiate and complete in one grain.

The decomposition of $Al_2TiO_5$ can be controlled with the addition of MgO or $Fe_2O_3$, which leads to solid solutions $Al_2TiO_5$ and isostructural $MgTi_2O_5$ or $Fe_2TiO_5$ during sintering. The stabilization is due to the improved thermodynamic stabilities of $MgTi_2O_5$ and $Fe_2TiO_5$ over $Al_2TiO_5$. $MgTi_2O_5$ decomposes to $MgTiO_3 + TiO_2$ below 700 °C [55], and $Fe_2TiO_5$ decomposes to $Fe_2O_3 + TiO_2$ at 565 °C, (Table 1) [59].

### (1) Thermal expansion behavior

Most ceramics expand on heating, as a result of the thermal agitation of atoms, which increases their bond lengths. However, some anisotropic thermal expansion ceramics contract on heating. Upon heating, these structures will expand and contract in their various dimensions [60], making them susceptible to microcracking during the heating cycle. This thermal behavior is characterized by hysteresis loops and by much lower thermal expansion coefficients than in dense ceramics [4, 61]. As near-zero thermal expansion can minimize thermal stress, much effort has focused on developing low-expansion materials for severe thermal shock applications [12, 62].

$Al_2TiO_5$ is highly anisotropic ($\Delta\alpha_{max}^3 = 22.0 \cdot 10^{-6}$/K). Therefore, despite its average crystallographic thermal expansion being slightly higher than that of alumina ($\alpha_{-Al_2O_3, 25-1000°C} = 8.7 \cdot 10^{-6}$/K, $\alpha_{-Al_2TiO_5, 25\_1000°C} = 9.7 \cdot 10^{-6}$/K)[5 – 8, 63, 64], high compressive residual stresses on $Al_2TiO_5$ grains are expected to develop during cooling from the sintering temperature, at least for some grain-matrix crystallographic orientations. Consequently, $Al_2TiO_5$ grains may act as bridges during fracture [65, 66]. Microcracking may also occur as a result of fractures caused by the residual stresses. The positive effects of thermal treatment and thermal expansion behavior are due to microcrack systems at the grain boundaries of $Al_2TiO_5$ ceramics.

The high thermal expansion of $Al_2TiO_5$ single crystal ($9.70 \times 10^{-6}$/K) and the low thermal expansion of sintered $Al_2TiO_5$ ceramics (Fig. 3) are due to the effects of grain boundary microcracking caused by the high anisotropy of thermal expansion along the crystal axes of $Al_2TiO_5$. During reheating, individual crystallites expand at low temperature and the solid volume expands into microcracks, leaving the macroscopic dimensions relatively unchanged.

As a result, the material expanded slightly up to 1000 °C and the microcracks closed at higher temperatures. This is closely related to the relatively steep thermal expansion curves [6, 35–37, 67, 68], which are ascribed to the mechanical closing of microcracks on heating to > 800 °C and their reopening that occurs on cooling below 900 °C

The ESEM images show microcracks of 362–448 nm between grain boundaries at 28 °C (Fig. 4). Sintering at 597 °C reduced their lengths to 310–429 nm, and the specimens exhibited negative thermal expansion. Sintering at 911 °C allowed individual $Al_2TiO_5$ crystallites to expand into the microcracks, and the macroscopic dimensions remained nearly unchanged. The microcracks were closed upon sintering at 1351 °C; however, at still higher temperatures, the expansion coefficient ($1.09 \cdot 10^{-6}$/K for ATM1) was far below the theoretical value of single-crystal $Al_2TiO_5$ ($9.70 \cdot 10^{-6}$/K.), suggesting that a large proportion of the microcracks were still open. The reopening of the cracks led to the thermal hysteresis during cooling on the third run [69].
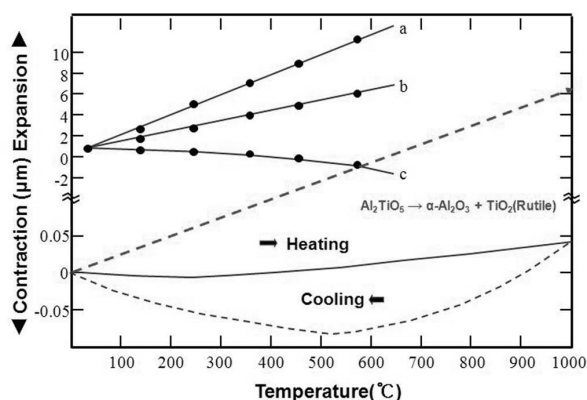


**Fig. 3:** Thermal expansion of single crystal (top), sintered $Al_2TiO_5$ (bottom), and fully decomposed pure $Al_2TiO_5$ into $Al_2O_3$ and $TiO_2$ (red dotted line).

In an attempt to improve the mechanical strength and thermal stability (800–1300 °C) of $Al_2TiO_5$, a new thermal-shock-resistant material consisting of a two-phase material based on $Al_2TiO_5$-mullite in different proportions was investigated by reducing the particle size (0.3~0.5 μm) for adjusting the $Al_2O_3/SiO_2/TiO_2$-ratios to form the main phase of $Al_2TiO_5$-mullite content 10 vol% for ATM, 20 vol% for ATM2, 30 vol% for ATM3, and 50 vol% for ATM5, respectively [24].

All ATM composites exhibit reduced thermal expansion coefficients with increasing $Al_2TiO_5$ content, accompanied by large hysteresis areas (Fig. 5). ATM materials show low thermal expansion up to 700 °C. However, temperature hysteresis increases when the temperature rises further.

This was attributed to the mechanical filling of the microcracks as the temperature was raised above 900 °C, and the re-opening or refracturing of the cracks upon cooling < 730 °C. Even at 1000 °C the slope of ATM1 sintered at 1600 °C remained flat, i.e. zero thermal expansion during heating, suggesting that a significant proportion of the microcracks remained open (Fig. 5). The thermal expansion coefficients at increasing temperature from 20 to 1000 °C of ATM materials sintered at 1600 °C for 6 h were $1.09 \cdot 10^{-6}$/K for ATM1, $2.50 \cdot 10^{-6}$/K for ATM2, $4.06 \cdot 10^{-6}$/K for ATM3 and $5.48 \cdot 10^{-6}$/K for ATM5 [37, 70].

All $ZrTiO_4$-$Al_2TiO_5$(ZAT) composites with increasing $Al_2TiO_5$ content exhibit reduced low thermal expansion coefficients accompanied by a pronounced large hysteresis area as shown in Fig. 6. The ZAT5 materials sintered at 1600 °C for 2 h showed negative thermal expansion up to 600 °C, but when the temperature was further increased, the thermal hysteresis increased relatively [96, 117].

This result is ascribed to the onset of mechanical healing of the microcracks with heating up to > 1000 °C and their reopening or refracturing which occurs on cooling below 730 °C. Even at 1000 °C the slope of ZAT5 materials sintered at 1600 °C is still at zero level thermal expansion when heating, suggesting that an important fraction of the microcracks is also still open. The thermal expansion coefficients of ZAT materials sintered at 1600 °C for 6 h are $0.2 \cdot 10^{-6}$/K for ZAT9-$Al_2TiO_5$ content 90 vol%, $0.81 \cdot 10^{-6}$/K for ZAT8-$Al_2TiO_5$ content 80 vol%, $0.93 \cdot 10^{-6}$/K for ZAT7-$Al_2TiO_5$ content 70 vol%, $1.2 \cdot 10^{-6}$/K for ZAT6-$Al_2TiO_5$ content 60 vol%, and $1.3 \cdot 10^{-6}$/K for ZAT5-$Al_2TiO_5$ content 50 vol%, at a temperature from 20 to 1000 °C, respectively.
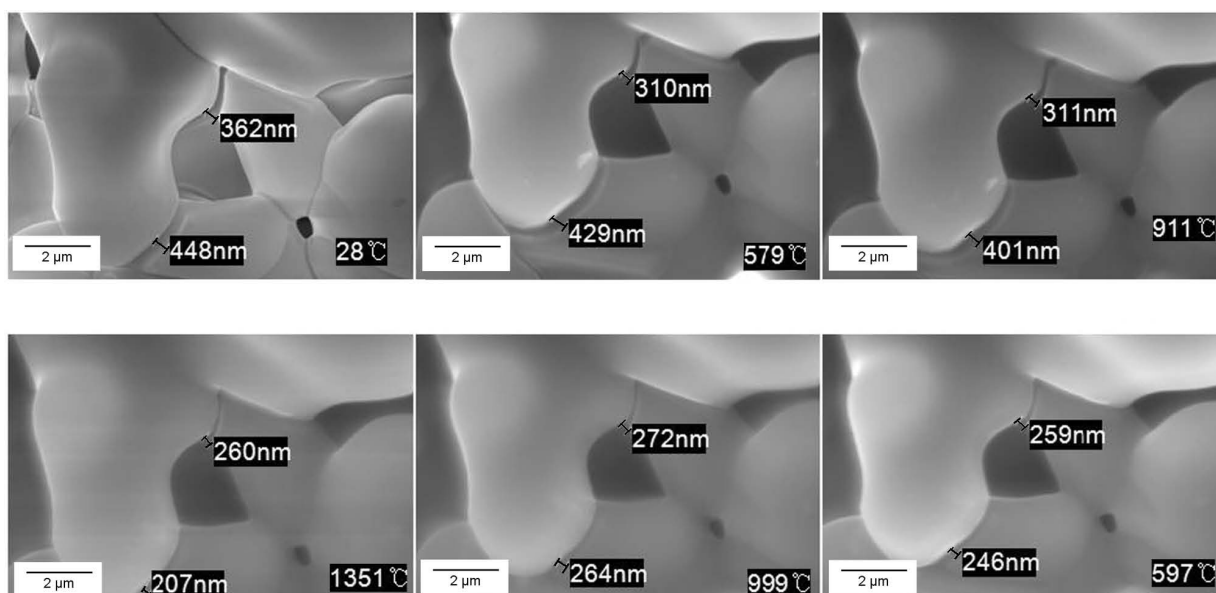


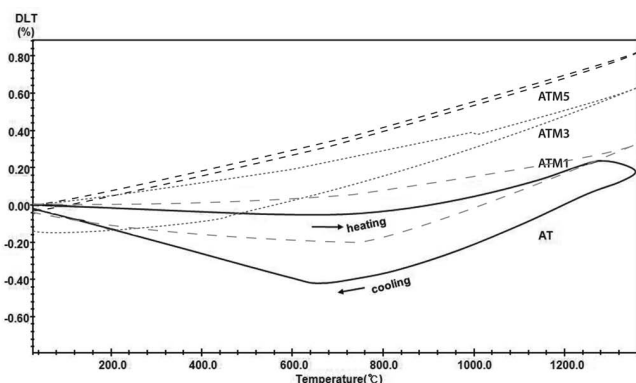**Fig. 4:** Microstructure of ATM sintered at 1600 °C for 6 h.

**Fig. 5:** Thermal expansion curves of AT and ATM ceramics sintered at 1600 °C for 6 h.
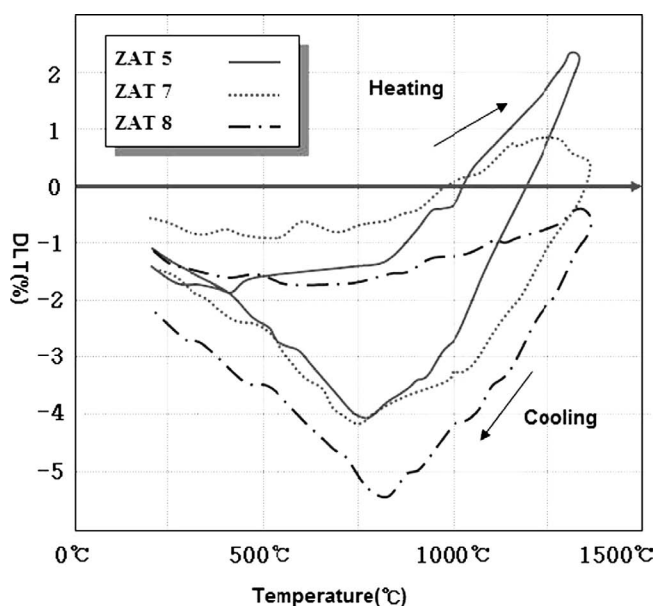


**Fig. 6:** Thermal expansion curves of ZAT ceramics sintered at 1600 °C for 6 h.

*(2)  Thermodynamic thermal stability*

The thermodynamic thermal stability of $Al_2TiO_5$ can be improved by the formation of solid solutions with MgO, $Fe_2O_3$, or $TiO_2$, which have pseudobrookite structures, Examples include $Fe_2TiO_5$ [11,30,71,72], $MgTi_2O_5$ [66,67,73–80], $Ti_3O_5$ (anosovite) [81] and $MgAl_2O_4$ (spinel) [82–87]. This thermodynamic stabilization is related to the materials' decreased decomposition temperature during cooling (see Fig. 2). $MgTi_2O_5$ and $Fe_2TiO_5$ decompose to $MgTiO_3 + TiO_2$ below 700 °C and to $Fe_2O_3 + TiO_2$ at 565 °C, respectively, whereas $Al_2TiO_5$ decomposes to $Al_2O_3$ and $TiO_2$ below 1300 °C [12–15,88].

This stabilization of $Al_2TiO_5$ ceramics is not only due to the intrinsic stability of $MgTi_2O_5$ and other pseudobrookite phases, but also due to increased entropy caused by cation disorder. It is conceivable that positive entropy might be further enhanced by additional entropy of mixing term, that is by the formation of $Al_2TiO_5$, as confirmed by thermodynamic properties and X-ray diffraction patterns [89,90].

The thermal stability of $Al_2TiO_5$ ceramics with solid solutions of $Fe_2TiO_5$, $MgTi_2O_5$, or $Ti_3O_5$ was studied by annealing at the critical temperature of 1100 °C for 100 – 300 h [20,54,91,92].

For a solid solution to form, the solute element must have a similar ionic radius and similar atomic charge (valence) as the element that it is replacing (Table 2). Similar crystal structures are helpful but not always necessary. $Fe^{3+}$ with a radius of 0.64 Å, readily forms solid solutions with $Al^{3+}$ in $Al_2TiO_5$, which has a radius of 0.54 Å. Other elements include $Cr^{3+}$ (0.69 Å) and $Mg^{2+}$ (0.72 Å). Elements such as $Si^{4+}$ and $Zr^{4+}$ would be suitable for substituting $Ti^{4+}$. Small amounts of oxide elements may diffuse between the phases during sintering and calcining, resulting in more complex solid solutions than intended for the stability of $Al_2TiO_5$-$ZrTiO_4$ (ZAT) composites [63].

The addition of excess starting oxides can also give desired phase assemblies and subsequently beneficial properties. Small quantities of such as $Fe_2O_3$ and MgO can be added to $Al_2TiO_5$ via any of the routes described above. And they maintain the properties of $Al_2TiO_5$, 1 – 5 wt% addition of, for example, $Fe_2O_3$, MgO, or mixtures thereof can result in phase stability and controlled microcracking behavior because of decreased crystal anisotropy. In addition, cation diffusion between components can occur during calcining or sintering such that a small amount of $ZrO_2$ for a solution of $Al_2Ti_{1-x}Zr_xO_5$ can impart beneficial properties.

*(3)  Kinetic thermal stability*

Polycrystalline $Al_2TiO_5$ can also be stabilized by limiting its grain growth [93–95] with the addition of, for example, $SiO_2$ [26,96], $ZrO_2$ [97,98], mullite [7,33,71,99–116], or $ZrTiO_4$ [58,117–119], most of which do not form solid solutions with $Al_2TiO_5$ but rather inhibit its decomposition. However, $ZrO_2$ and $ZrTiO_4$ do not have a significant effect on the thermal stability of $Al_2TiO_5$, even after a long annealing at 1100 °C for 100 – 300 h [13,15,59]. A second mullite phase can reduce microcracking and grain growth in $Al_2TiO_5$, improving mechanical behavior at 1300 and 1450 °C, according to a compressive mechanical test that was correlated to the microstructure.

In general, most $Al_2TiO_5$-mullite (ATM) ceramics used in high-temperature applications are prepared with an oxide method after sintering reactions of the individual minerals and after adjusting the main composition of $Al_2O_3/TiO_2/SiO_2$ to form $Al_2TiO_5$-mullite and a glass phase such as; kaolin [120], feldspar [74,76,77,121–126], SrO feldspar [97,103,107,108], amorphous $SiO_2$ [126], boehmite [109], inorganic micro-balloons [110], $SE_2O_3$ ($SE_2O_3$:0.1–10 wt%, SE:Y, Yb, Dy, Ho, Tm, Lu) [126], cordierite-spinel [110,127], spinel [128,129], $Na_{0.6}K_{0.4}AlSi_3O_8$ [80,86] and $Al_2O_3$ [130,131].

**Table 2:** Influence of additives on properties of $Al_2TiO_5$, $A_2BO_5$ solid solutions [Ion A: $Al^{+3}$ (0.54Å), Ion B: $Ti^{4+}$ (0.61 Å)] [34].

| Additives | Ionic Radius (Goldschmidt) in A or in B | Solid Solutions and Main Phase | Influence and Properties |
|---|---|---|---|
| $Mg^{2+}$ | 0.78 Å in B | $Mg_xAl_{2(1-x)}Ti_{(1+x)}O_5$ | [69]moderate stability, low grain growth,[53]accelerate formation temperature |
| $Fe^{3+}$, $Fe^{4+}$ | 0.67 Å in A (0.65 Å) in B | $Al_{2-y}Fe_YTi_{1-y}Ge_yO_5$, $(Mg_{0.5}Fe_{0.5})Ti_2O_5$ | [69]good stability, promote grain growth,[53]faster formation |
| $Cr^{3+}$ | 0.64 Å in A | $Al_{2-x}Cr_xTiO_5$ | [23]fine grain size, good thermal shock resistant,[15]good sinterability |
| $Ti^{3+}$, $(Ti^{4+})$ | 0.67 Å, in A (0.61 Å) in B | $Ti_3O_5$ | [16]thermodynamically unstable phase |
| $Ge^{4+}$ | 0.53 Å in B | $Al_2Ti_{1-y}Ge_yO_5$ | [16]reduced decomposition, y = 0,2 |
| $Ga^{3+}$ | 0.76 Å in A | $Al_{2-q}Ga_qTiO_5$, q : 0,0 – 0,3 | [16]significant stability only q > 0.15 |
| $Zr^{4+}$ | 0.87 Å in B | $Al_2Ti_{1-x}Zr_xO_5$ | [69]slow grain growth, delay formation,[15]improve mechanical strength, hysteresis effect |
| $Si^{4+}$ | 0.39 Å | $Al^{3+}_{6(2-x)/(6+x)})Si^{4+}_{6x/(6+x)} >$ $T_{6x/(6+x)}Ti^{4+}O_5$, smaller Si-solubility | [16]very good stability, controlled grain growth, low thermal conductivity,/high temperature formation |
| $Co^{2+}$ | 0.82 Å in A | distorted octahedral geometry | [53]slow grain growth, improve strength, fast formation |
| $La^{3+}$ | 1.12 Å | | [69]poor stability, very low thermal conductivity, moderate grain size, high strength |
| $Y^{3+}$ | 1.06 Å | | [69]bring about fine grain size,[70]good hysteresis effect with small grain size |

The largest increases in strength can occur with the synthesis of $Al_2TiO_5$ powder, particularly using $Al_2O_3$, MgO or $ZrO_2$. The increase in mechanical strength was correlated in microstructural terms to the observation of fine $Al_2O_3$, $MgAl_2O_4$, mullite, $ZrO_2$, or $ZrTiO_4$ particles at the grain boundaries (Fig. 7) [37]. Such distributions of fine particles at grain boundaries would prevent grain growth and reduce microcracking, thereby increasing strength [13, 29, 31].

The addition of $SiO_2$ improved the strength of reaction-sintered material by a limited amount of 3 %. This was attributed to the formation of a grain boundary liquid phase during sintering [7]. Pena *et al.* [131] examined the properties of an $Al_2TiO_5$-mullite-$ZrO_2$ mixture and found a strength of 30 MPa, representing a 10-fold improvement compared to that of pure $Al_2TiO_5$.

Yano *et al.* [132] reported a mechanical strength of approx. 100 MP for a material containing 25 vol% mullite; the increase in strength coincided with the control of decomposition. Morishima *et al.* [133] reported a strength of 70 MPa for an $Al_2TiO_5$-mullite composite material containing 91 vol% $Al_2TiO_5$, but this material did not retain its strength.

## (4) Thermal shock resistance

The thermal shock resistance of $Al_2TiO_5$ ceramics is influenced not only by their thermal expansion coefficient, thermal conductivity, strength, modulus of elasticity, Poisson's ratio, etc. but also by their macroscopic size and shape, heating and cooling states, and the heat transfer speed [134]. These effects and the particle size often govern the sensitivity of physical properties including the coefficients of thermal expansion, porosity, or pore size, and low firing temperature, which are undesirable in DPF manufacture. Properties desirable for DPF are difficult to achieve. $Al_2TiO_5$-based materials have phase stabilities and physical/mechanical properties that are difficult to control because of the complex microcracking behavior.

Thermal shock resistance is generally difficult to quantify, and it is usually expressed in terms of a number of empirical resistance parameters, which are dependent on the test conditions. However, an examination of strength retention after quenching is easily performed.
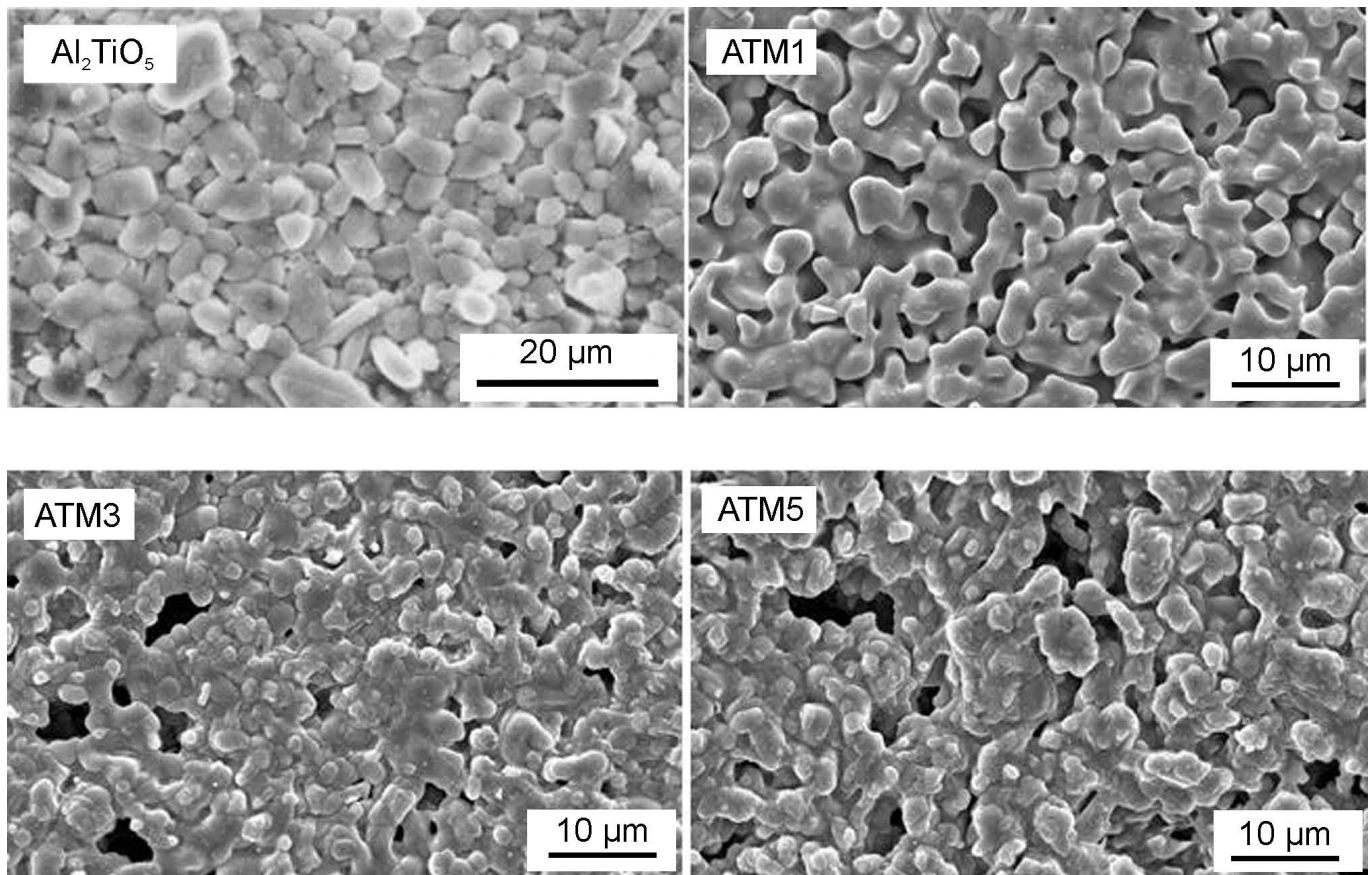
**Fig. 7:** Microstructure of $Al_2TiO_5$-mullite (ATM) ceramics with various mullite contents: 10 vol%, 30 vol% and 50 vol%.

Theoretical thermal shock resistance is calculated from the thermal stress parameters, $R_1$ and $R_2$ (pertaining to severe and mild quenching, respectively). Thus,

$$R_1 = [\sigma_{br}(1 - \vartheta\nu)]/\alpha E \qquad (21)$$

$$R_2 = R_1 \times \lambda \qquad (22)$$

where $R_1$ and $R_2$ are constants that can be described as a material's resistance factor against thermal stresses. $\sigma_{br}$ is the flexural strength, $E$ is Young's modulus and $\alpha$ the thermal expansion coefficient. Poisson's ratio ($\vartheta = 0.24$); and the thermal conductivity ($\lambda = 1.5$ WmK⁻¹) were assumed to be constant [135, 136]. Once the material's resistance to crack initiation has been exceeded, its resistance to damage (from crack propagation) becomes the decisive element of the thermal cycling behavior. This resistance is described by the thermal stress parameter, $R_7$ [137].

$$R_7 = \gamma_{eff}E/[\sigma_{br}^2(1 - \vartheta\nu)] \qquad (26)$$

where $\gamma_{eff}$ is the specific fracture-surface energy [138, 139]. The above discussion of the dependence of $\sigma_{br}$, $E$, and $\tau$ on the mineral phase content indicates that the resistance to damage described by Eq. (6) is not uniquely dependent in the same sense. The fracture-surface energy (not investigated in the present study) should have been determined primarily on the basis of microcracks, depending on the type and extent of the second phase, as indicated by the temperature dependence of stress.

For high-temperature applications (1000 – 1300 °C), long-annealing thermal durability, thermal cycling sta-

bility and residual mechanical properties are very important. Attempts to improve the thermal durability of $Al_2TiO_5$ between 750 and 1400 °C are in progress. In particular, $Al_2TiO_5$-mullite (ATM) ceramics have very high volumetric heat capacities (approx. 3.9 – 4.0 J cm⁻³ °C⁻¹ for fully dense ATM at 800 K) in combination with low CTE [125].

However, in the manufacture of ATM ceramics involving sintering at above 1600 °C, the high temperatures increase manufacturing costs and therefore also the final product costs. The production of $Al_2TiO_5$-based ceramics often requires the use of pre-reacted $Al_2TiO_5$ or mullite powders, which also increases manufacturing costs. Moreover, properties desirable for DPFs are difficult to achieve.

Approaches have been employed to reduce sintering temperatures, including the addition of, for example, inorganic micro-balloons (1450 – 1600 °C) [119], an amorphous phase (1375 – 1450 °C) [126], $SE_2Ti_2$ (1400 – 1650 °C) [125], anatase and boehmite (1375 – 1500 °C) [57, 111, 113, 126, 140]. In general, raw materials, such as alkali feldspar, SrO feldspar, kaolin, silicate, aluminosilicate, magnesium silicate, hematite, rutile, $SE_2O_3$, and inorganic micro-balloons are added to form solid solutions of $Al_2TiO_5$-mullite or glass-phase-based ceramics by means of reaction sintering.

### (5) Raw materials for mixed stability

The raw materials for the formation of $Al_2TiO_5$ are oxide sources that react to form mullite or $ZrTiO_4$ and Mg- or

Fe-stabilized $Al_2TiO_5$ phases [141], and/or partially or completely pre-reacted mullite or $ZrTiO_4$ and Mg- or Fe-stabilized $Al_2TiO_5$ powders. The alumina source is a powder which, when heated to a sufficiently high temperature in the absence of other raw materials, yields largely pure aluminum oxide, which includes alpha-alumina, transition alumina ($\gamma$-alumina or $\delta$-alumina), boehmite, aluminum hydroxide, and mixtures thereof. The morphology of alumina has to be tabular with the particle sizes sufficiently large ($10-25 \mu m$) for microcracking to be induced in the final structure. Hematite is recommended as a source of an iron oxide. Suitable titania sources are rutile and anatase with particles of approx. $7-15 \mu m$. Silica sources can include amorphous $SiO_2$, such as cristobalite, kaolin ($SiO_2$ 46 %, $Al_2O_3$ 39 %, $Fe_2O_3$ 0.8 %, etc.), and inorganic micro-balloons, and $ZrO_2$ sources can include tetragonal and cubic forms stabilized by the addition of small amounts of CaO, $Y_2O_3$, or MgO. $ZrSiO_4$ (zircon) can be used as a silica and zirconia source; it contains 45.02 wt% Zr and 17.67 wt% Si. Material compositions are protected intellectual property and should not be inappropriately appropriated for DPF products based on $Al_2TiO_5$ and mullite. Therefore a thorough survey of the patent literature should be performed.

In particular, the survey should examine the most important requirements related to $Al_2TiO_5$ceramics with different inorganic materials for diesel exhaust filtration applications: low thermal expansion, high thermal shock resistance ($\Delta T = > 1000\,°C$), suitable porosity, and a narrow pore size distribution. Other considerations include maximum operation temperature ($1100-1200\,°C$), durability of microstructure, CTE : $< 1.5 *10^{-6}K^{-1}$, good mechanical strength ($50-70$ MPa), and excellent chemical resistance.

## III. Conclusions

The development of high-performance advanced ceramics for high-temperature applications has been limited owing to problems related to thermal stress induced by anisotropic thermal expansion. To avoid this, materials with low or zero thermal expansion should be developed. Such materials could be used to fabricate, for example, diesel particulate filters (DPFs) that require the materials to retain their original dimensions, without being affected by thermal shock at high temperature.

Because reduced thermal expansion in anisotropic $Al_2TiO_5$ materials minimizes thermal stress, considerable effort has been made to develop low-expansion materials for severe thermal shock applications. Pure $Al_2TiO_5$ tends to decompose reversibly into $Al_2O_3$ and $TiO_2$ at $800-1300\,°C$ on cooling below the equilibrium temperature of $1280\,°C$. After decomposition, it no longer exhibits a low thermal expansion coefficient or favorable thermal shock behavior. A literature survey was performed to explore low-thermal expansion $Al_2TiO_5$-mullite and $Al_2TiO_5$-$ZrTiO_4$ ceramics with good thermal shock resistance, suitable porosity, and a narrow pore size distribution for diesel exhaust filtration applications.

Silicon carbide (SiC) has been used as an alternative to cordierite in the fabrication of diesel particulate filters. However, it is expensive and must be segmented owing to its high coefficient of thermal expansion (CTE) and poor thermal shock resistance. Therefore, there is a need for a ceramic suitable for high-temperature applications that boasts the advantages of cordierite, but does not share its disadvantages. Furthermore, new materials based on $Al_2TiO_5$-$ZrTiO_4$-mullite (ATZM) or $Al_2TiO_5$-$ZrTiO_4$-$ZrO_2$ (ATZZ) compositions for DPFs must not infringe existing patents.

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