Modification of YSZ fiber composites by Al₂TiO₅ fibers for high thermal shock resistance

Wei LIU, Yongshuai XIE, Zhezhe DENG, Ying PENG, Jianhong DONG, Ze ZHU, Dehua MA, Luyi ZHU*, Guanghui ZHANG, Xinqiang WANG

State Key Laboratory of Crystal Materials, School of Crystal Materials, Shandong University, Jinan 250100, China

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Abstract: Yttria-stabilized zirconia (YSZ) fiber composites are highly efficient thermal insulating materials; however, the poor thermal shock resistance limits their versatile applications. In the present study, YSZ fiber was mixed directly with Al₂TiO₅ fiber, which had an extremely low thermal expansion coefficient, to prepare YSZ–Al₂TiO₅ (ZAT) fiber composites by compression molding and heat treatment. The minimum thermal expansion coefficient of the prepared ZAT fiber composites was measured to be $7.74 \times 10^{-6}$ K$^{-1}$, which was 26% lower than that of the YSZ fiber composites (10.42 $\times 10^{-6}$ K$^{-1}$). It was shown that the prepared ZAT fiber composites maintain the integrity after undergoing 51 thermal shock cycles between 1100 °C and room temperature. Whereas, YSZ fiber composites burst immediately after only one thermal shock cycle under the same condition. In addition, the ZAT fiber composites also exhibit considerable mechanical and thermal insulating performance.

Keywords: Al₂TiO₅ fibers; YSZ–Al₂TiO₅ fiber composites; thermal expansion; thermal shock resistance; thermal insulating

1 Introduction

Yttria-stabilized zirconia (YSZ) ceramics are endowed with high melting point, low thermal conductivity, high chemical resistance, and considerable mechanical strength, making them promising thermal protection and energy-saving materials [1–4]. YSZ fibers not only exhibit the above advantages, but also are flexible and self-supporting compared to their bulk counterparts [5,6]. These fibers can be further processed into composites, such as bricks, papers, blankets, and felts, offering additional advantages of lightweight materials and improved thermal insulation performances [7–9]. As a result, they have broad applications in national defense, military industry, and other thermal insulation fields involving ultra-high temperature conditions [10–12]. However, YSZ has a relatively high thermal expansion coefficient of about $10 \times 10^{-6}$ K$^{-1}$. This results in the unsatisfactory thermal shock resistance of YSZ fiber composites [13–15], and these composites will easily crack and be destroyed under repeated thermal cycling.

Incorporating a second modifier with a low expansion coefficient into the matrix is expected to be an efficient way to improve the thermal shock resistance of YSZ fiber composites. During the past years, numerous materials with low thermal expansion coefficients have been extensively studied, including quartz glass,
cordierite, spodumene, zirconium ditungstenoxoide, etc. Quartz glass precipitates cristobalite and produces an abnormal volume expansion, resulting in a limited long-term operating temperature (about 1200 °C) [16]. Cordierite and spodumene have low melting points and are unstable above 1200 °C [17], while zirconium ditungstenoxoide easily decomposes into ZrO2 and WO3 at 780–1105 °C [18]. Therefore, these materials are unsuitable for improving the thermal shock resistance of YSZ fiber composites. Al2TiO5 exhibits a high melting point (about 1860 °C) [19,20], a negligibly low thermal expansion coefficient ((0.2–1)×10−6 K−1) [21–23], and the best thermal insulation performance among the known low expansion ceramic materials [29], making it a promising second phase for modifying YSZ fiber composites [30,31].

Granular Al2TiO5 has been used to improve the thermal shock resistance of matrix materials. Kucuk et al. [32] fabricated Al2TiO5-reinforced Mg2SiO4 ceramics via powder metallurgy, and the obtained Al2TiO5-reinforced Mg2SiO4 ceramic composites exhibited high resistance against thermal shock. Boyraz [33] demonstrated that the addition of Al2TiO5 powders could reduce the thermal expansion coefficient of La2O3-stabilized ZrO2. However, our preliminary work showed that it was too difficult to homogeneously distribute Al2TiO5 powders in YSZ fiber composites, due to the sedimentation of powders.

Theoretically, two fibers can be easily cross-linked together due to their large aspect ratios and self-supporting peculiarity, resulting in a homogeneous composite structure. Thus, YSZ–Al2TiO5 (ZAT) fiber composites with different Al2TiO5 contents were prepared by directly mixing YSZ fibers and Al2TiO5 fibers in the present study. The thermal expansion coefficient, thermal shock resistance, mechanical properties, and thermal insulation performance of the prepared composites were examined in detail. It was shown that Al2TiO5 fibers could effectively improve the comprehensive thermo-mechanical properties of the YSZ fiber composites.

2 Experimental details

2.1 Preparation of the Al2TiO5 fibers

Titanium tetrachloride (TiCl4, Sinopharm Chemical Reagent Co., Ltd.), anhydrous aluminum chloride (AlCl3, Sinopharm Chemical Reagent Co., Ltd.), deionized water (H2O, resistivity ≥ 18.2 MΩ), acetylacetone (C5H8O2, Tianjin Damao Chemical Reagent Factory), and triethylamine (C6H15N, Tianjin Fuyu Fine Chemical Co., Ltd.) were used as the raw materials. The molar ratio for AlCl3 and TiCl4 was 2 : 1. According to our previous two-step method, a spinnable polyacetylacetonato-titaniun-aluminum (PAAT) precursor was synthesized [34].

Subsequently, we dissolved 5 g of PAAT precursor and 0.05 g of polyethylene oxide (PEO, Mw = 1,000,000, Shanghai Aladdin Chemical Reagent Co., Ltd.) in 10 mL of anhydrous ethanol (C2H5OH, Tianjin Fuyu Fine Chemical Co., Ltd.). The mixtures were magnetically stirred for 8 h to form the transparent golden-yellow PAAT spinning solution. Then, the PAAT precursor fibers were heat-treated at 1200–1500 °C for 2 h with a heating rate of 2 °C/min in air to obtain the Al2TiO5 fibers.

2.2 Preparation of YSZ–Al2TiO5 fiber composites

The YSZ fibers (Fig. S1 in the Electronic Supplementary Material (ESM)) were prepared from polyacetylacetonatozirconium (PAZ) and Y(NO3)3·6H2O, and the details of the preparation procedure can be found in Ref. [35]. The as-obtained Al2TiO5 and YSZ fibers were mixed with a high-speed agitator using a 2 wt% PEO aqueous solution as a low-temperature binder. The mass ratios of YSZ fibers/Al2TiO5 fibers were 100/0, 99/1, 98/2, 95/5, and 92/8 (Table S1 in the ESM). The mixed fibers were injection molded under a certain pressure, sintered at 800 °C with a heating rate of 5 °C/min, and then heated to 1500 °C for 2 h at 10 °C/min to obtain the ZAT fiber composites.

2.3 Characterization

2.3.1 Thermal decomposition

The molecular structure analysis of the PAAT precursor and preheated fibers was conducted with a Bruker ALPHA Fourier transform infrared (FT-IR) spectrometer in the range of 500–4000 cm−1. Thermogravimetry and differential scanning calorimetry (TG–DSC) of the
PAAT precursor fibers were performed in air with a Diamond TG–DSC Perkin Elmer thermal analyzer within the temperature range of room temperature to 1500 °C and the heating rate of 10 °C/min.

2.3.2 Crystallization process and phase analysis

The crystalline phase compositions of Al$_2$TiO$_5$ fibers and ZAT fiber composites were analyzed by X-ray diffraction (XRD) with a Panalytical X’pert3 powder diffractometer (40 kV, 40 mA), using Cu Kα radiation (wavelength $\lambda = 0.15418$ nm) within the 2θ range of 10°–90° and a step size of 0.02°. The thermal stability of Al$_2$TiO$_5$ fibers was studied in Ar atmosphere by cyclic in-situ high-temperature X-ray diffraction (HTXRD) with Panaco Empyrean X-ray diffractometer, the Netherlands. The test temperature range was 1000–1500 °C and the heating rate and cooling rate were 5 °C/min. The sample was scanned in the 2θ range of 10°–90°. The crystal face spacings were calculated by the Bragg equation:

\[
d_{hkI} \sin \theta = n\lambda
\]

(1)

The lattice constants of each crystal axis were calculated according to the spacing formula for the crystal planes of the orthorhombic crystal systems, as follows:

\[
d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}
\]

(2)

2.3.3 Microscopy characterization

The microstructure of the fibers and the cross-linked state between the fibers have an important influence on the properties of composites. For microstructural characterization investigations, the Hitachi S-4800 scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS) was carried out. In this process, the samples were placed on a carbon double-sided tape and coated with Au powder to make the surface electrically conductive.

2.3.4 Thermal expansion property

For analyzing the thermal expansion properties of the Al$_2$TiO$_5$ fibers and the ZAT fiber composites, the thermal expansion coefficients of samples were measured with an RPZ-03P automatic thermal expansion instrument (Sinosteel Luoyang Refractory Research Institute Co., Ltd.). The sample dimension is $\Phi$10 mm × 50 mm and the measurement condition is in the temperature range of 500–1200 °C and the heating rate of 5 °C/min.

2.3.5 Thermal shock behavior

To investigate the thermal shock resistance behavior, the ZAT samples with size of 30 mm × 30 mm × 8 mm were quenched in water and assessed. The samples were rapidly heated from room temperature to 1100 °C and held for 10 min to make it heat uniformly, and then immersed in cold water immediately for rapid cooling. When the sample was cooled to room temperature, it was reheated to 1100 °C rapidly, and the cycles were repeated. The maximum number of thermal shock cycles at sample cracking was taken as the measurement index of thermal shock resistance.

2.3.6 Mechanical property

The compressive strength and the three-point bending strength of the ZAT fiber composites were measured with a DDL10 microcomputer-controlled electronic universal testing machine (Changchun Institute of Mechanical Science Co., Ltd.) with a crosshead speed of 2 mm/min. The sample dimensions are 38 mm × 38 mm × 25 mm and 100 mm × 20 mm × 20 mm for compressive strength measurement and three-point bending strength measurement, respectively.

2.3.7 Thermal insulation performance

The high-temperature thermal insulation performances of the ZAT samples (thickness: 8 mm) exposed to a butane blowtorch flame were characterized. The surface near the butane blowtorch flame served as the hot surface, and the surface away from the flame served as the cold surface. When the temperature of the cold surface does not change, it is considered as thermal equilibrium. Both hot surface and cold surface temperatures were intuitively observed by using an FLIR T540 infrared camera observation. The thermal conductivities of the samples with dimension of $\Phi$12.6 mm × 1 mm were measured with the laser flash thermal conductivity instrument NETZSCH LFA 457 in the temperature range of 300–1000 °C.

3 Results and discussion

3.1 Thermal analysis, crystallization, and morphology of the Al$_2$TiO$_5$ fibers

Figure 1(a) shows the FT-IR spectra of the PAAT
precursor and Al_{2}TiO_{5} fibers which were obtained by heat-treating the PAAT precursor at different temperatures. The vibration peaks at 771 and 686 cm\(^{-1}\) corresponded to \(v(\text{Al}-\text{O}-\text{Al})\) [36], while those at 659 and 492 cm\(^{-1}\) corresponded to \(v(\text{Ti}-\text{O}-\text{Ti})\) [37]. In addition, the peaks around 583 and 439 cm\(^{-1}\) were assigned to the hetero metal–oxygen bonds of \(v(\text{Ti}-\text{O}-\text{Al})\) [38]. Therefore, it could be determined that the prepared precursor was an M-acetylacetone (M = Al, Ti) complex. The peaks located at 1200–1600 cm\(^{-1}\) in the PAAT precursor belonged to the characteristic vibration peaks of acetylacetone [39,40]. It is obvious that with the increase of heat-treatment temperature, the intensity of absorption peaks in the 1200–1600 cm\(^{-1}\) region decreases a lot, indicating the decomposition of the organics.

To further analyze the thermal decomposition process of the PAAT precursor fibers in air, the TG–DSC was characterized as shown in Fig. 1(b). From the TG curve, it could be seen that evaporation of solvent and removal of the uncoordinated ligands occurred below 150 °C, corresponding to an 8% weight loss [41]. A huge weight loss (43.5%) between 150 and 300 °C was caused by the decomposition of the ligands in the precursor [42]. The broad exothermic peaks in the DSC curve at 300–400 °C were due to the carbonization of organics and the oxidative removal of residual carbides, accompanied by a weight loss of about 17% at 300–600 °C in the TG curve [36,43]. When the temperature was over 600 °C, no apparent weight loss was found. However, two exothermic peaks around 710 °C appeared in the DSC curve were attributed to the crystallization of rutile and corundum, and an endothermic peak at 1300 °C indicated the beginning of the transformation of Al_{2}O_{3} and TiO_{2} to Al_{2}TiO_{5}, which was confirmed by the XRD spectra given in Fig. 1(c). In the XRD spectra, the Al_{2}TiO_{5} phase (PDF Card No. 26-0040) began to form at 1300 °C. As the temperature increased, the diffraction peaks of Al_{2}TiO_{5} became the main crystal phase. When the temperature reached 1500 °C, only the diffraction peaks of Al_{2}TiO_{5} were observed, and the peaks of Al_{2}O_{3} and TiO_{2} completely disappeared, suggesting that the single-phase Al_{2}TiO_{5} fibers were successfully obtained.

In order to investigate the phase stability of the Al_{2}TiO_{5} fibers, the cyclic in-situ HTXRD curve of Al_{2}TiO_{5} fibers after heat-treatment at 1500 °C was shown in Fig. 1(d). During the heating cycle process in the temperature range of 1000–1500 °C, phase change was not observed, which indicated that the Al_{2}TiO_{5} fibers had excellent phase stability at high temperatures. Furthermore, the unique low-thermal-expansion performance of Al_{2}TiO_{5} was attributed to the high thermal expansion anisotropy and the different expansion of each crystal axis [44]. The three most intense diffracted crystal planes (110), (023), and (020) were selected from the HRXRD spectrums at different temperatures in Fig. 1(d), and three crystal face spacings were calculated by Eq. (1). Because Al_{2}TiO_{5} is obtained as an orthorhombic crystal, the lattice constants of each crystal axis were calculated by Eq. (2), as shown in Fig. 1(e). The linear thermal expansion rates of the three axes of the Al_{2}TiO_{5} fibers were calculated according to \(\Delta L/L\) (Fig. 1(e)). As can be seen, the lattice constants of the b-axis and c-axis in the Al_{2}TiO_{5} fibers increased with increasing temperature and decreased with decreasing temperature. This is in line with the crystal thermal expansion theory, where the higher the temperature, the greater the adjacent particles’ average distance, increasing the lattice constant and linear thermal expansion rate [45]. This is mainly because in the Al_{2}TiO_{5} crystal, Al\(^{3+}\) and Ti\(^{4+}\) are randomly distributed in the lattice of M metal ions, forming an \([\text{MO}_{6}]\) (M = Al, Ti) octahedron with O\(^{2-}\), as shown in the inset in Fig. 1(e) [46,47]. The common-sided octahedrons formed a double-chain structure in the b and c directions, and three coaxial octahedrons formed a single-chain structure on a-axis (\(a = 3.591 \text{ Å}, b = 9.429 \text{ Å}, c = 9.636 \text{ Å}\)) [48–50].

Moreover, a fiber block was constructed to measure the thermal expansion coefficient of the Al_{2}TiO_{5} fibers. As shown in Fig. 1(f), the thermal expansion coefficient increased slightly with the increasing temperature. The average thermal expansion coefficient of the Al_{2}TiO_{5} sample was only 1.02×10\(^{-6}\) K\(^{-1}\) from 200 to 1100 °C, revealing that the prepared Al_{2}TiO_{5} fibers exhibited a low thermal expansion coefficient.

Figures 2(a)–2(c) are the macroscopic morphologies of the PAAT precursor fibers, with superior flexibility, which could unfold and recover after repeated folding. In addition, the PAAT precursor fibers had a large aspect ratio and a rather smooth surface, as suggested by the SEM images in Fig. 2(d). Figures 2(e)–2(h) display the SEM images of Al_{2}TiO_{5} fibers sintered at 1200, 1300, 1400, and 1500 °C, respectively. As shown in the inset in Figs. 2(e)–2(h), the grain size gradually increased with the increase of temperature. At 1500 °C, the fibers were formed by crystalline particles tightly connected.
Fig. 1  (a) FT-IR spectra of the PAAT precursor and Al₂TiO₅ fibers heat-treating at different temperatures. (b) TG curve of the PAAT precursor fibers below 600 °C (the inset: TG–DSC curves of the PAAT precursor fibers in RT–1500 °C). (c) XRD spectra of Al₂TiO₅ fibers. (d) Cyclic in-situ HTXRD curves of Al₂TiO₅ fibers in the range of 1000–1500 °C, testing a temperature point at intervals of 100 °C (1-heating process, 2-cooling process). (e) Lattice constants and linear thermal expansion rates of the three crystal axes of Al₂TiO₅ with the change of temperature in 1000–1500 °C (the inset: crystal structure of Al₂TiO₅). (f) Thermal expansion coefficient (CTE) and linear thermal expansion rate of Al₂TiO₅ fibers heat-treated at 1500 °C.

Fig. 2  Macroscopic morphologies of PAAT precursor fibers: (a) folding in half, (b) unfolding, (c) refolding. (d) SEM images of PAAT precursor fibers. SEM images of Al₂TiO₅ fibers after heat-treatment at: (e) 1200 °C, (f) 1300 °C, (g) 1400 °C, (h) 1500 °C (the inset: macroscopic morphologies and high-magnification SEM images of the corresponding temperature). (i) SEM image of Al₂TiO₅ fibers heat-treated at 1500 °C (the inset: EDS spectrum of element content distribution of Al₂TiO₅ fibers). Mapping images of Al₂TiO₅ fibers heat-treated at 1500 °C: (j) O map, (k) Al map, (l) Ti map.
and appeared the obvious sintering necks, but still maintained the one-dimensional fiber morphology. Therefore, Al₂TiO₅ fibers offered good flexibility after heat-treatment at 1200 °C and became brittle after calcination at 1500 °C, due to the obvious growth of grains in the fibers. The selected area EDS mapping results of the Al₂TiO₅ fibers heat-treated at 1500 °C were displayed in Figs. 2(i)–2(l), showing that Al, Ti, and O elements of the fibers were detected. All the adopted elements were homogeneously distributed without segregation, implying that Al and Ti elements in the fibers were uniformly dispersed [51]. The Al:Ti atomic ratio was close to 2:1, which was consistent with the stoichiometric ratio of Al₂TiO₅.

### 3.2 Modification of the YSZ–Al₂TiO₅ fiber composites

YSZ–Al₂TiO₅ (ZAT) fiber composites were prepared by mixing the YSZ fibers and Al₂TiO₅ fibers and injection molding followed by sintering at 1500 °C (Fig. 3(a)). Figure 3(b) shows the optical images of the prepared ZAT fiber composites, and Table S1 in the ESM lists the mass, volume, density, and shrinkage rate of the ZAT fiber composites. As suggested, after heat treatment, the density and shrinkage rate of the ZAT fiber composites increased as the Al₂TiO₅ fiber content increased. Figures 3(c)–3(l) present the SEM images of the fracture surfaces of the ZAT fiber composites, indicating that the bond between fibers was more tightly with an increasing amount of Al₂TiO₅ fiber content, which can be attributed to the obvious sintering of the Al₂TiO₅ fibers at high temperatures (Fig. 2(h)). According to the research by Zu et al. [52], Ti⁴⁺ weakened the ionicity of the Zr–O bond, allowing Zr⁴⁺ to move easily. During the sintering process, densification enhancement was attributed to the viscous flowability of the liquid phase, strong cation diffusion, and cavity elimination ability. Additionally, the diameter of the Al₂TiO₅ fibers was only 1–2 μm.

![Fig. 3](image-url)
(Fig. 2(h)) and the diameter of the YSZ fibers was at least 5 μm (Fig. S1 in the ESM). The smaller the fiber diameter, the easier it sintered. Therefore, the ZAT fiber composites after heat-treatment at 1500 °C occurred the interfibrous sintering phenomenon.

Figures 3(m)–3(q) present the elemental mappings of ZAT-8 fiber composites, showing that the fiber composites contained O, Zr, Y, Ti, and Al elements. In the selected area, the Zr and Y elements were uniformly distributed in the coarser fibers, while Ti and Al elements were enriched in the finer fibers, indicating that the two fibers were YSZ fiber and Al2TiO5 fiber. The boundary of the elemental distribution region between Zr–Y and Ti–Al was clear, demonstrating that there was no interdiffusion of multiple elements between the individual fibers, which provided strong evidence for distinguishing the Al2TiO5 fibers in the YSZ fibers.

In order to further explore the phase compositions of the ZAT fiber composites, we analyzed the XRD patterns shown in Fig. 4(a), showing that the ZAT fiber composites were composed of a ZrO2 phase (PDF Card No. 89-9069) and an Al2TiO5 phase (PDF Card No. 26-0040). As the Al2TiO5 fiber content increased, the diffraction peak intensity of the Al2TiO5 phase became higher, which could be explained by the absence of chemical bonding between the YSZ fibers and the Al2TiO5 fibers.

The low thermal expansion coefficient of the Al2TiO5 fibers could be partially offset the thermal expansion coefficient of ZAT fiber composites. The measurement results showed that the thermal expansion coefficients of ZAT fiber composites were found to be negatively correlated with Al2TiO5 fiber content (Fig. 4(b)). Among them, the average thermal expansion coefficient of the ZAT-0 fiber composites exceeded 10×10^-6 K^-1 at 500–1200 °C. In comparison, when the Al2TiO5 fiber content was 8 wt%, the ZAT fiber composites had a minimum thermal expansion coefficient of 7.74×10^-6 K^-1, which was about 26% lower than that of the ZAT-0 fiber composites (Fig. 4(d)). In addition, the linear thermal expansion rate of ZAT samples showed a downward trend with an increase of Al2TiO5 fiber content as shown in Fig. 4(c). The average linear

![Fig. 4](https://www.springer.com/journal/40145)
expansion rate of the ZAT-0 fiber composites was measured to be 0.83%, while that of the ZAT-8 fiber composites was reduced to 0.60% (Fig. 4(d)). Therefore, the above results confirmed that the Al$_2$TiO$_5$ fibers could effectively reduce the thermal expansion coefficient of the YSZ fiber composites, resulting in a superior low thermal expansion property of the ZAT fiber composites.

To further verify that the reduction in thermal expansion coefficient was beneficial to improve the thermal shock resistance of the ZAT fiber composites, the thermal shock behaviors of the ZAT fiber composites under repeating thermal cycling were studied using the water-quenching method. The ZAT fiber composites with size of 30 mm × 30 mm × 8 mm were rapidly heat-treated to 1100 °C and then immersed in cold water immediately for rapid cooling (Fig. 5(a)). The morphological characteristics of the ZAT samples after multiple thermal shock cycles were summarized in Table S2 in the ESM. As shown in Fig. 5(b), the ZAT-0 fiber composites burst and broke instantaneously after only one thermal shock cycle. By contrast, the thermal shock resistance of the ZAT fiber composites improved significantly (Figs. 5(c)–5(f)), and the higher Al$_2$TiO$_5$ fiber content led to better thermal shock resistance of the ZAT fiber composites. In particular, the ZAT-8 sample only cracked slightly after undergoing 51 thermal shock cycles, exhibiting outstanding thermal shock resistance (Fig. 5(f)). It can be concluded that the addition of Al$_2$TiO$_5$ fibers could effectively enhance the thermal shock resistance of the YSZ fiber composites. The reason is that according to the thermal shock fracture initiation and crack propagation theory proposed by Hasselman, the stability factor of the thermal stress increases as the thermal expansion coefficient decreases, making it more difficult for the crack to propagate, resulting in an improvement in the thermal shock resistance of the material [53,54].

The mutual connections between the YSZ fibers and Al$_2$TiO$_5$ fibers were expected to increase the mechanical properties of the ZAT fiber composites. Thus, the mechanical properties of the ZAT fiber composites were investigated (Fig. 6). As expected, the compressive strengths of the prepared ZAT fiber composites improved with the increase of Al$_2$TiO$_5$ fiber content can be clearly observed in Figs. 6(a) and 6(b). Among them, the maximum compressive strength of the ZAT-8 fiber composites was measured to be 20.35 MPa, which was about 18 times larger than that of the ZAT-0 fiber composites (1.14 MPa). The crack propagation paths during fracture of the ZAT fiber composites determined a ductile fracture mode, according to the compressive stress–strain curves of the ZAT fiber composites in Fig. 6(c). Furthermore, Young’s modulus of the ZAT fiber composites increased with increasing Al$_2$TiO$_5$ fiber content (Fig. 6(b)). Of note, Young’s modulus of the ZAT-8 fiber composites reached 13.92 MPa, which was much higher than that of the ZAT-0 fiber composites. To comprehensively analyze the mechanical properties of the ZAT composites, the three-point bending tests were also carried out as shown in Figs. 6(d) and 6(e). Similarly, the three-point bending strength of the ZAT-8 fiber composites was 56.52% higher than that of ZAT-0 fiber composites. As suggested, the bending stress increased almost linearly with the displacement under the bending loads as shown in Fig. 6(f). In addition, the

![Fig. 5](a) Thermal shock resistance of ZAT fiber composites (ZAT fiber composites were rapidly heat-treated from room temperature to 1100 °C and then immersed in cold water). Optical images of ZAT fiber composites subjected to different thermal shock times: (b) ZAT-0, (c) ZAT-1, (d) ZAT-2, (e) ZAT-5, (f) ZAT-8.
compressive strength and three-point bending strength of the ZAT fiber composites were higher than those of ZAT-0 fiber composites at the same density displayed in Figs. 6(a) and 6(c). Investigations revealed that the Al₂TiO₅ fibers could notably modify the mechanical properties of the YSZ fiber composites, which is due to the sintering and crosslinking between the intersection of the YSZ fibers and Al₂TiO₅ fibers at high temperatures. Because ZAT fiber composites have been primarily applied to thermal insulation industries, the thermal insulation performance at high temperature was measured by subjecting the ZAT samples to a butane blowtorch flame. A detailed schematic of the device is depicted in Fig. 7(a), and the sample size is 30 mm × 30 mm × 8 mm (Fig. 7(b)). Figure 7(c) shows that the maximum temperature of the hot surface could reach 1300 °C, while the cold surface temperature of the ZAT-0 fiber composites was stable at 552 °C after 300 s (Fig. 7(d)). In Figs. 7(d)–7(g), when the Al₂TiO₅ fiber content was less than 5 wt%, the cold surface temperature of the ZAT fiber composites exhibited an obvious decreasing trend with increasing Al₂TiO₅ fiber content. In particular, ZAT-5 fiber composites stabilized at 464 °C as shown in Fig. 7(g), indicating excellent thermal insulation performance. Nevertheless, the comparisons showed that when the Al₂TiO₅ fiber content increased to 8 wt%, the cold surface temperature increased to 480 °C given in Fig. 7(h). The cold surface temperatures of the ZAT fiber composites first decreased and then increased with increasing Al₂TiO₅ fiber content, as shown in Fig. 7(i). Furthermore, Fig. 7(j) displays the thermal conductivity of the ZAT fiber composites as a function of temperature. Similarly, with the increase of the Al₂TiO₅ fiber content, the thermal conductivity of the ZAT fiber composites first decreased and then increased, and the ZAT-5 fiber composites had the lowest thermal conductivity of 0.555 W·m⁻¹·K⁻¹ at 1000 °C. These results indicated that at similar densities, the thermal insulation performance of the ZAT fiber composites improved with increasing Al₂TiO₅ fiber content. However, when the density increased to a certain value, the thermal conductivity increased as the
density increased [55]. Thus, the thermal insulation performance of the ZAT-8 fiber composites was slightly decreased due to the higher density. In addition, the thermal conductivities of the YSZ and Al$_2$TiO$_5$ fibers with similar densities were tested (Fig. 7(k)). At the same temperature, the thermal conductivity of the Al$_2$TiO$_5$ fibers was noticeably lower than that of the YSZ fibers, which demonstrated the superior thermal insulation of the Al$_2$TiO$_5$ fibers.

As a result, the addition of Al$_2$TiO$_5$ fibers enhanced the thermal shock resistance and mechanical properties of the YSZ fiber composites, as well as ensured thermal insulation performance. Appropriate Al$_2$TiO$_5$ fiber content (≤ 5 wt%) reduced the thermal conductivity of the ZAT fiber composites, while excessive Al$_2$TiO$_5$ fiber content (8 wt%) greatly increased the density of the fiber composites, resulting in a decline in thermal insulation performance. With higher Al$_2$TiO$_5$ fiber content, such as 12 wt% (denoted as ZAT-12) and 16 wt% (denoted as ZAT-16), the thermal shock resistance continued to increase slightly (Fig. S3 in the ESM) due to the reduced thermal expansion coefficient of the
ZAT fiber composites (Fig. S2 in the ESM). Both these materials had higher densities than the composites with low Al₂TiO₅ fiber content (Table S1 in the ESM), resulting in increased mechanical strength (Fig. S4 in the ESM). As expected, the thermal insulation performances of ZAT-12 and ZAT-16 fiber composites were inferior to that of ZAT-8 fiber composites with increasing densities (Fig. S5 in the ESM). Comprehensive consideration of the mechanical and thermal properties, the content of Al₂TiO₅ fibers as 8 wt% was the optimum proportion.

4 Conclusions

In this work, YSZ–Al₂TiO₅ fiber composites were fabricated for the purpose of enhancing the thermal shock resistance of YSZ fiber composites. The Al₂TiO₅ fibers were incorporated into YSZ fiber composites by directly mixing the two fibers followed by compression molding and heat treatment. With the addition of 8 wt% of Al₂TiO₅ fibers, the thermal expansion coefficient of the sample was as low as 7.74×10⁻⁶ K⁻¹, which was 26% lower than that of the YSZ fiber composites. The modified YSZ fiber composites underwent 51 thermal shock cycles between 1100 °C and room temperature, compared to only one thermal shock for the pure YSZ fiber composites. The mechanical properties of the composites increased remarkably with increasing Al₂TiO₅ fiber content, and the compressive strength was as high as 20.35 MPa. The modified fiber composites were capable of isolating a hot surface temperature of 1300 °C and stabilizing the cold surface temperature at 464 °C with a thickness of 8 mm. Our findings may provide new opportunities for expanding the application fields of YSZ fiber composites as well as provide novel guidance for the rational structural design of fiber composites.

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Electronic Supplementary Material

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Declaration of competing interest

The authors declare no competing financial interests or personal relationships.

References

[1] Liu BX, Zhu LY, Xu D, et al. Tailoring the grain size of zirconia polycrystalline fibers by cetyltrimethyl ammonium bromide. Ceram Int 2017, 43: 10743–10749.
[2] Schlichting KW, Padture NP, Klemens PG. Thermal conductivity of dense and porous yttria-stabilized zirconia. J Mater Sci 2001, 36: 3003–3010.
[3] Hoch M, Nakata M, Johnston HL. Vapor pressures of inorganic substances. XII. Zirconium dioxide. J Am Chem Soc 1954, 76: 2651–2652.
[4] Yu ZC, Xu CH, Yuan KK, et al. Characterization and adsorption mechanism of ZrO₂ mesoporous fibers for health-hazardous fluoride removal. J Hazard Mater 2018, 346: 82–92.
[5] Si Y, Wang XQ, Dou LY, et al. Ultralight and fire-resistant ceramic nanofibrous aerogels with temperature-invariant superelasticity. Sci Adv 2018, 4: eaas8925.
[6] Abdullah M, Ahmad J, Mehmood M. Effect of sintering temperature on properties of Al₂O₃ whisker reinforced 3 mol% Y₂O₃ stabilized tetragonal ZrO₂ (TZ-3Y) nanocomposites. Compos B Eng 2012, 43: 1785–1790.
[7] Espitia-Cabrera I, Orozco-Hernández H, Torres-Sánchez R, et al. Synthesis of nanostructured zirconia electrodeposited films on AISI 316L stainless steel and its behaviour in corrosion resistance assessment. Mater Lett 2004, 58: 191–195.
[8] Xu GF, Olorunyolemi T, Carmel Y, et al. Design and construction of insulation configuration for ultra-high-temperature microwave processing of ceramics. J Am Ceram Soc 2003, 86: 2082–2086.
[9] Gan XZ, Yu ZC, Yuan KK, et al. Effects of cerium addition on the microstructure, mechanical properties and thermal conductivity of YSZ fibers. Ceram Int 2018, 44: 7077–7083.
[10] Chandradass J, Balasubramanian M. Effect of magnesium oxide on sol-gel spin alumina and alumina-zirconia fibres. J Eur Ceram Soc 2006, 26: 2611–2617.
[11] Ma Z, Zhang Q, Liu L, et al. Preparation and heat insulating capacity of Sm₂Zr₂O₇–SiC composites based on photon thermal transport. J Adv Ceram 2020, 9: 454–461.
[12] Pang X, Wang TC, Kong J. Fabrication of lightweight ZrO₂ fiberboards using hollow ZrO₂ fibers. Ceram Int 2020, 46: 9103–9108.

www.springer.com/journal/40145
[44] Li SJ, Queyroux F, Boch P. Particulate composites in the Al₂O₃–SiO₂–TiO₂ system by infiltration processing. *J Eur Ceram Soc* 1994, **13**: 3–9.

[45] Wang CZ. *Material Properties*. Beijing: Beijing University of Technology Press, 2007.

[46] Kornaus K, Lach R, Szumera M, *et al.* Synthesis of aluminium titanate by means of isostructural heterogeneous nucleation. *J Eur Ceram Soc* 2019, **39**: 2535–2544.

[47] Wang XQ, Liu CB, Li JJ, *et al.* Porous aluminum titanate-strontium feldspar-mullite fiber composite ceramics with enhanced pore structures and mechanical properties. *Ceram Int* 2018, **44**: 22686–22691.

[48] Low IM, Lawrence D, Smith RI. Factors controlling the thermal stability of aluminum titanate ceramics in vacuum. *J Am Ceram Soc* 2005, **88**: 2957–2961.

[49] Ilatovskaia M, Savinykh G, Fabrichnaya O. Thermodynamic description of the ZrO₂–TiO₂–Al₂O₃ system based on experimental data. *J Eur Ceram Soc* 2017, **37**: 3461–3469.

[50] Skala RD, Li D, Low IM. Diffraction, structure and phase stability studies on aluminium titanate. *J Eur Ceram Soc* 2009, **29**: 67–75.

[51] Peng Y, Xie YS, Wang L, *et al.* High-temperature flexible, strength and hydrophobic YSZ/SiO₂ nanofibrous membranes with excellent thermal insulation. *J Eur Ceram Soc* 2021, **41**: 1471–1480.

[52] Zu YF, Chen GQ, Fu XS, *et al.* Effects of liquid phases on densification of TiO₂-doped Al₂O₃–ZrO₂ composite ceramics. *Ceram Int* 2014, **40**: 3989–3993.

[53] Hasselman DPH. Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics. *J Am Ceram Soc* 1969, **52**: 600–604.

[54] Ni DW, Cheng Y, Zhang JP, *et al.* Advances in ultra-high temperature ceramics, composites, and coatings. *J Adv Ceram* 2022, **11**: 1–56.

[55] Hayashi K. Thermal conductivity of ceramic fibrous insulators at high temperatures. *Int J Thermophys* 1984, **5**: 229–238.

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