

## **Mullite Matrix Composites Reinforced by SiC Plus Yttria-Stabilized ZrO<sub>2</sub> Particulates**

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### **Abstract**

Mullite is a good structural material when properly processed. However, this paper will report that its high temperature strength, fracture toughness as well as its thermal shock resistance can be substantially improved by double reinforcements with SiC and yttria-stabilized zirconia particulates. Such mullite matrix composite material can almost hold its flexural strength at a level of 600 MPa from room temperature to 1000°C. Its fracture toughness has a value of 6.7 MPa·m<sup>1/2</sup> and a thermal shock resistance of 500°C when quenched to water. Its enhanced fracture behaviour has been preliminarily analyzed. This composite material has been fabricated into piston caps for adiabatic engine and successfully tested for well over hundred hours.

### **1. Introduction**

In recent years, the research on structural materials for ceramic heat engines has focused on developing ceramic matrix composites. The advanced ceramic materials for heat engines should have long-term thermal stability to achieve the required engine life. The operation temperature of these materials is as high as 1200°C or above and appreciable property deterioration or catastrophic failure must not take place. Mullite(M) is a potential candidate for heat engine technology because of its low thermal conductivity, low thermal expansion coefficient and high creep resistance. Its strength is not degraded that much with temperature. However, mullite shows relatively low strength and fracture toughness, which impede its successful application in practice. The fracture toughness and strength must be improved if it is to be used in heat engines or broaden its application in other areas.

The incorporation of SiC whisker or a transformation toughened ZrO<sub>2</sub> phase to improve the properties of ceramics has been reported<sup>(1-2)</sup>. Either of them can improve the mechanical properties of mullite to some extent. Recently, some findings indicated that the combination of multiple toughening and strengthening routes can result in ceramic composites with better properties than that achieved by either mechanism alone. This is, thus, one of the leading trends for strengthening and toughening of ceramics. Some encouraging results have been reported lately with combined whisker plus transformation toughening<sup>(3-5)</sup>.

Particle-reinforced composites have the potential of possessing isotropic

properties, which will be advantageous for various applications. The properties of ceramics can be improved by a second phase dispersion, e.g., by SiC particles(P) in Y-TZP<sup>(6)</sup>, TiC particles in Al<sub>2</sub>O<sub>3</sub><sup>(7)</sup> and SiC<sup>(8)</sup>. The strength and fracture toughness of mullite can also be improved by particle reinforcement, furthermore, the strength and toughness of mullite have been shown to be enhanced further by both particle reinforcement and ZrO<sub>2</sub> toughening<sup>(9)</sup>. In the present investigation, SiC and Y-TZP particles were selected as two reinforcing agents for mullite matrix.

## 2. Experimental Procedure

Commercial mullite powder having an average grain size of 2  $\mu\text{m}$  was used as the matrix material. This powder contains 75.92 wt% Al<sub>2</sub>O<sub>3</sub>, 23.34 wt% SiO<sub>2</sub>, and 0.74 wt% of other oxide impurities(CaO, Fe<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O etc.). SiC particles used were commercially available in  $\alpha$ -type with an average diameter of 0.93  $\mu\text{m}$  and a specific surface of 7.53 m<sup>2</sup>/g. The compositions of SiC particles are as follows: total C: 27.0 wt%, free C: 0.41 wt%, total Si: 68.50 wt%, free Si: 1.08 wt%, O: 2.15 wt%, Al<sub>2</sub>O<sub>3</sub>: 0.13 wt%, Fe<sub>2</sub>O<sub>3</sub>: 0.18 wt%, and CaO: 0.02 wt%. Y-TZP powder(containing 2.8 mol% Y<sub>2</sub>O<sub>3</sub>) was prepared by coprecipitation method in the laboratory.

The mullite, SiC and Y-TZP powders were mixed with the desired volume ratio by wet milling with distilled water using Al<sub>2</sub>O<sub>3</sub> balls in a polyethylene container for 6 h, and followed by drying. The mixed powders were sieved to pass 120 mesh, and were molded in a BN-coated graphite die for sintering. Hot-pressing was carried out at 1600°C for 40 min under a pressure of 25 MPa for all composites.

The hot-pressed samples were cut and ground into 2.5 by 5 by 28 mm rectangular bars with a diamond wheel. A three-point bend test was carried out at a crosshead speed of 0.5 mm/min with a span of 20 mm. Test bars of dimensions 5 by 2.5 by 28 mm were prepared for single edge notched beam(SENB) fracture toughness measurements. The notches used were 0.22-0.25 mm wide and 2.5 mm depth. The SENB specimens were fractured by three-point bending at a crosshead speed of 0.005 mm/min with a span of 20 mm.

The microstructural characterization and crack propagation of the specimens were observed by scanning electron microscopy(SEM) and transmission electron microscopy(TEM), and the crystal structure of the hot-pressed composites was analyzed by X-ray diffractometry(XRD). The TEM specimens were finally coated with amorphous carbon.

## 3. Results and Discussion

### (1) Sintering and mechanical properties of mullite

It is well known that mullite is difficult to densify because of its relatively low lattice diffusion coefficient. In the present investigation, sintering was performed by hot-pressing. Figure 1 illustrates densification dependence on sintering temperature for mullite samples. As shown, the density increased with increasing temperature and levelled off above 1650°C at which samples became near the theoretical density(~98% of theoretical).

To improve the sintering of mullite, sintering aid was used. Table 1 summarized the effects of Y<sub>2</sub>O<sub>3</sub> addition on densification of mullite. As shown in table 1, with no sintering aid, and hot-pressed at 1550°C and 1600°C for 1 h, the relative densities

are 91.7% and 96.4% of theoretical, respectively. However, with the addition of 0.5 wt%  $Y_2O_3$ , >99% of theoretical density is easily obtained. It indicates that  $Y_2O_3$  can greatly improve the sintering for mullite samples. According to the  $Al_2O_3$ - $SiO_2$ - $Y_2O_3$  ternary phase diagram<sup>(10)</sup>, the ternary eutectic is easily formed through the addition of  $Y_2O_3$  to  $SiO_2$ - $Al_2O_3$  system. EDS(energy dispersive spectroscopy) analysis revealed that the liquid phases contained  $Y_2O_3$  in the fired specimens. But the optimization of the sintering aid content has not been established at the present time. As the result of the addition of  $Y_2O_3$ , the strength and fracture toughness of mullite ceramics are also improved due to the densification being promoted.

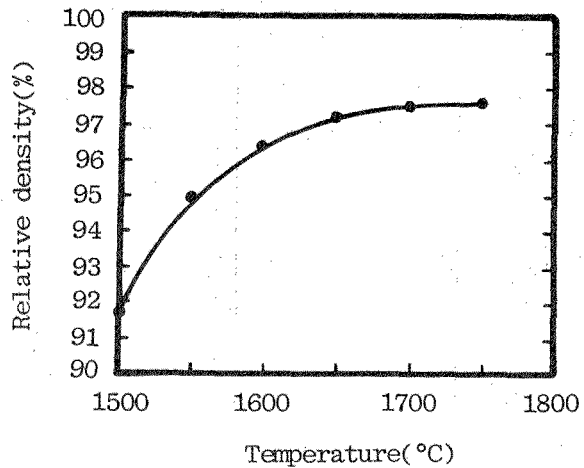


Fig.1 Relative density of mullite as a function of hot-pressing temperature (Soaking time: 1h)

Table 1 Effects of sintering aid addition on densification and properties

Sintering condition*	$Y_2O_3$ content (wt%)	Relative density(%)	Flexural strength(MPa)	Fracture toughness ( $MPa \cdot m^{1/2}$ )
1550°C, 1h	0	91.7	$190 \pm 2.1$	$2.2 \pm 0.1$
	0.5	99.2	$255 \pm 15.9$	$2.9 \pm 0.1$
1600°C, 1h	0	96.4	$210 \pm 8.9$	$2.8 \pm 0.1$
	0.5	99.8	$268 \pm 32.9$	$2.9 \pm 0.1$
1600°C, 0.5h	0	92.7	$191 \pm 4.5$	$2.5 \pm 0.1$
	0.5	97.8	$246 \pm 8.8$	$2.9 \pm 0.1$

\* Pressure: 20 MPa

Figure 2 shows the scanning electron micrograph of fracture surface of mullite samples (a) with no additive, and (b) with 0.5 wt% addition of  $Y_2O_3$  under identical sintering conditions. It is seen that the grain size of the mullite with addition of  $Y_2O_3$  is apparently smaller. This indicates that  $Y_2O_3$  additive can inhibit rapid growth of mullite grains, which improves the microstructure.

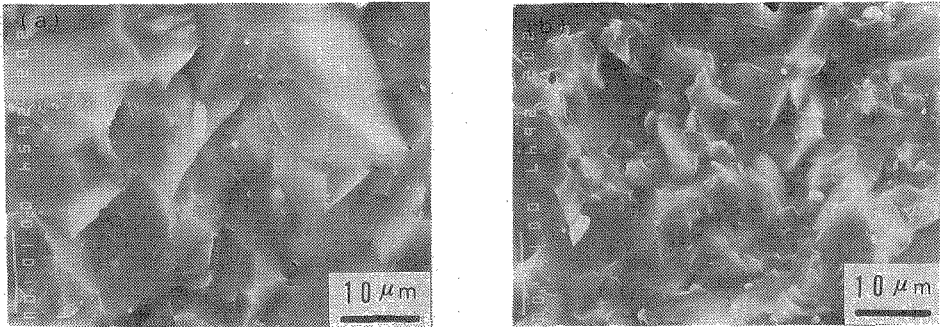


Fig.2 SEM micrographs of fracture surface of mullite ceramics. (a) without  $Y_2O_3$  additive, (b) with 0.5 wt%  $Y_2O_3$  additive

## (2) SiC(P)/M composites

Figure 3 shows the effects of SiC particle content on the flexural strength and fracture toughness of the mullite composites reinforced only by SiC particles. The

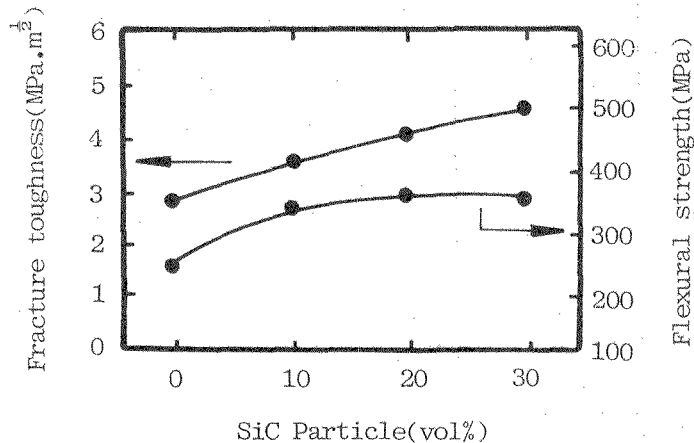


Fig.3 Flexural strength and fracture toughness of SiC(P)/M composites vs SiC particle content

flexural strength of the composite was improved by the addition of 10 vol% SiC particles. However, it levels off with increasing addition of 20 to 30 vol%. The fracture toughness values increased monotonously with increasing the SiC particle content. For 30 vol% SiC particle addition, the average toughness of the composites is  $4.6 \text{ MPa} \cdot \text{m}^{1/2}$  whereas for pure mullite, the average toughness is  $2.9 \text{ MPa} \cdot \text{m}^{1/2}$ . The scanning electron micrograph of the fractured surface of SiC(P)/M composite is shown in Fig.4. A

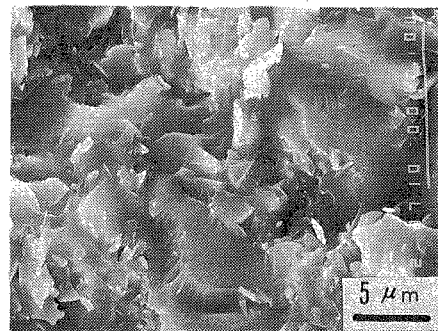


Fig.4 SEM micrograph of fracture surface of 20 vol% SiC(P)/M composite

very rough surface could be observed, compared with that of monolithic mullite, suggesting that the interaction of crack front with the dispersed SiC particles caused the composites to behave differently from monolithic mullite. Figure 5 shows the results of vickers indentation and radial crack propagation for monolithic mullite and SiC(P)/M composites. The paths of crack propagation in monolithic mullite were smooth whereas in SiC(P)/M composites the paths were tortuous due to crack deflection, bowing, and bifurcation by SiC particles. All of these are considered to be the reinforcing mechanisms for improving the fracture toughness and strength of this type of composites. Sometimes the propagating crack passed through SiC particles.

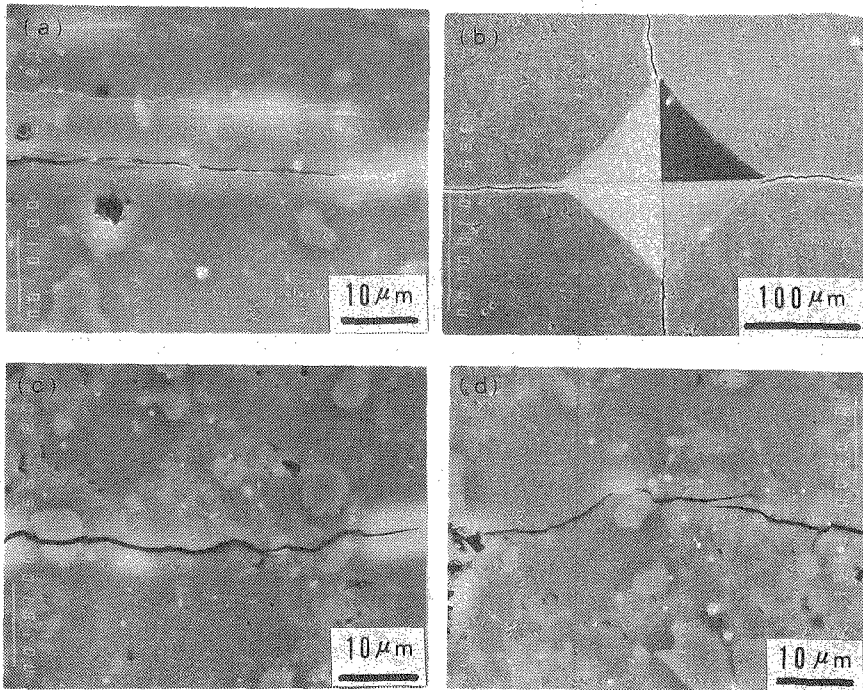


Fig.5 Indentation and crack propagation of monolithic mullite and SiC(P)/M composite with 20 vol% SiC. (a) Indentation crack propagation of mullite, (b) indentation of SiC(P)/M composite, (c) and (d) indentation crack propagation of SiC(P)/M composite

### (3) Y-TZP/M composites

The effects of Y-TZP content on fracture toughness and flexural strength of the mullite composites reinforced by only Y-TZP are shown in Fig.6. The fracture toughness increased with increasing the Y-TZP content. For 30 vol% Y-TZP, the fracture toughness of the composite is  $6.7 \text{ MPa} \cdot \text{m}^{1/2}$ . The flexural strength of the composites increased with increasing Y-TZP content up to 20 vol%. On the basis of the result, a constant Y-TZP content of 20 vol% was selected for late investigation.

XRD analysis showed that a large amount of monoclinic  $\text{ZrO}_2$  existed in the Y-TZP/M composite samples. This indicates that a great part of the tetragonal  $\text{ZrO}_2$

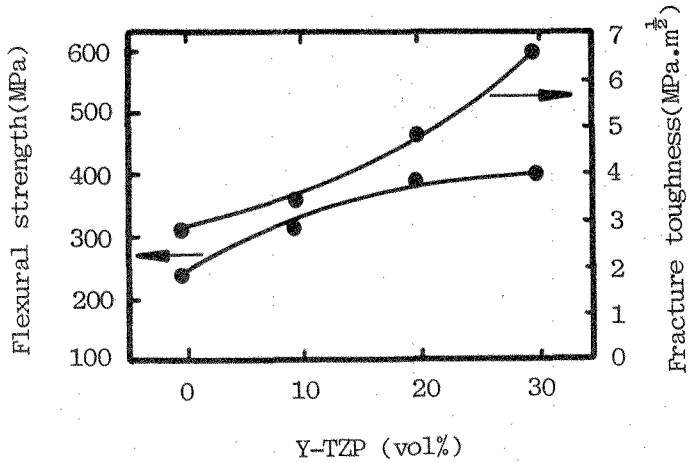


Fig.6 Flexural strength and fracture toughness of Y-TZP/M composites vs Y-TZP content

transformed to monoclinic symmetry during cooling. Expansion of  $ZrO_2$  during transformation would generate microcracks around the transformed  $ZrO_2$  grains. The microcrack nucleation, and the mechanisms of crack deflection, bowing and branching caused by the interaction of main crack tip with the microcracks, would improve the fracture toughness and strength of the composites. The microcracks would shield the main crack tip and lower the effect of stress concentration. The density of microcracks increases with increasing numbers of  $ZrO_2$  particles, therefore, the toughness increases. However, extensive microcracks occurred would join up to decrease the strength, and even the toughness. The XRD analysis also revealed that the amount of  $ZrO_2$  phase transformation occurred during the fracture process was relatively little. Transformation toughening is, therefore, not a dominant mechanism in the present case.

#### (4) SiC(P)/Y-TZP/M composites

Mullite matrix composites with the incorporation of both SiC and Y-TZP particles together as two reinforcing phases were further investigated. The compositions of the composites were x vol% SiC + 20 vol% Y-TZP + (100-

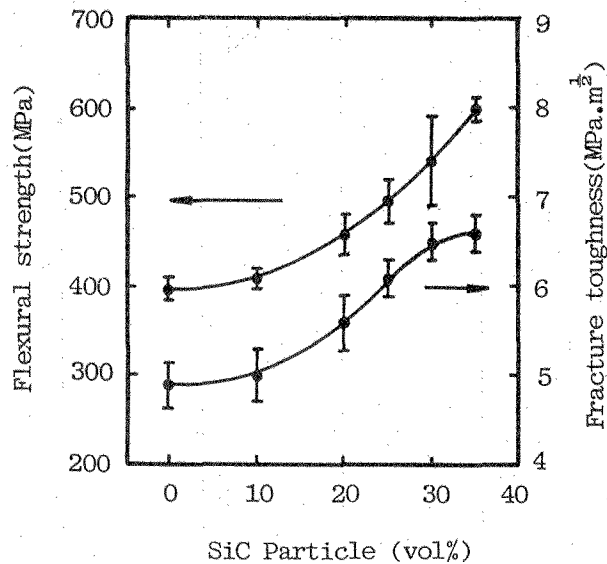


Fig.7 Flexural strength and fracture toughness of SiC(P)/Y-TZP/M composites vs SiC particle content

x-20) vol% mullite. Figure 7 shows the effects of the content of added SiC particles on fracture toughness and strength of the composites. The fracture toughness and strength of the composites were found to increase with additions of SiC particles, showing a high fracture toughness of  $6.7 \text{ MPa} \cdot \text{m}^{1/2}$  and strength of 600 MPa at 35 vol% of SiC particle addition. Comparing with the effect of reinforcement with SiC particle dispersion alone in SiC(P)/M system (See Fig.3), the addition of SiC particles beyond 10 vol% along with Y-TZP particles in the SiC(P)/Y-TZP/M composite system showed much more enhanced strengthening and toughening effect. The mechanism is not yet clearly understood although the concurrent actions in this complicated composite system may be in some way synergistic. It is encouraging anyhow that the fracture toughness and strength of the mullite matrix composites reinforced by SiC and Y-TZP particles together were dramatically improved, in comparison to that of the mullite matrix composites reinforced by SiC particles or Y-TZP alone.

#### (5) Microstructural characterization of the SiC(P)/Y-TZP/M composites

The typical TEM microstructures of the SiC(P)/TZP/M composites are given in Figs.8(a)-(c). Microcracks were observed at the  $\text{ZrO}_2$ /mullite interface(a),  $\text{ZrO}_2$ /SiC interface(b) and  $\text{ZrO}_2$ / $\text{ZrO}_2$  interface(c). The experimental results show that a large amount of monoclinic  $\text{ZrO}_2$  grains has existed in the fired samples. Apparently, they formed during cooling through transformation.

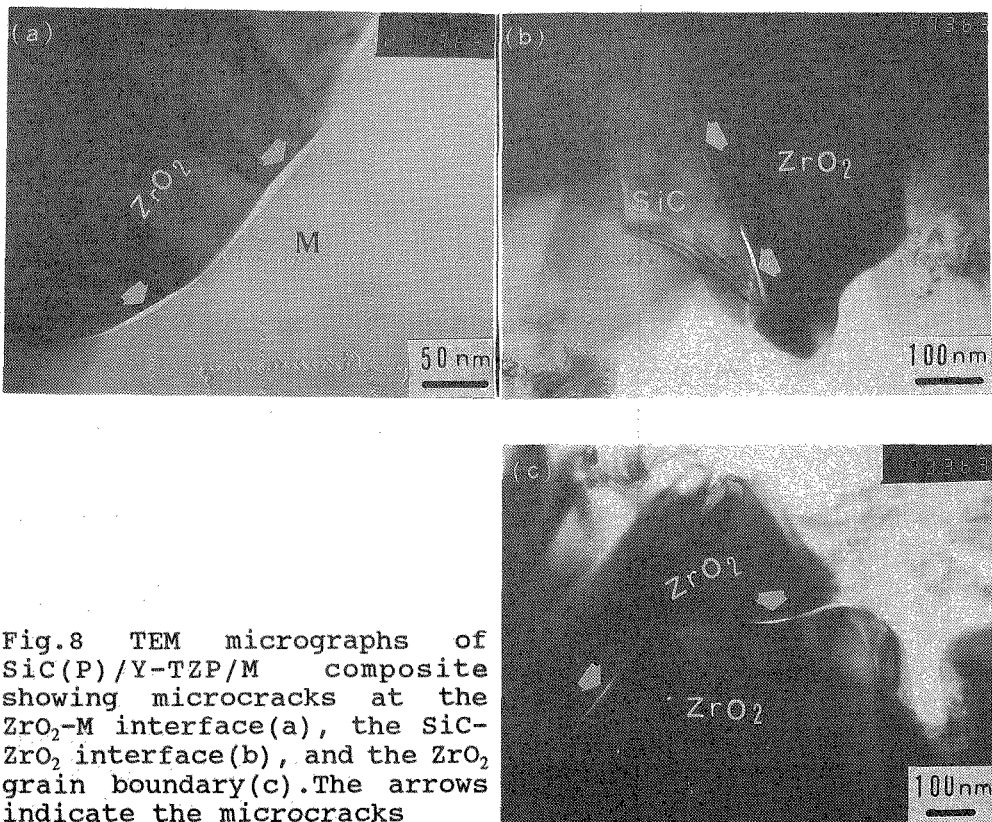


Fig.8 TEM micrographs of SiC(P)/Y-TZP/M composite showing microcracks at the  $\text{ZrO}_2$ -M interface(a), the SiC- $\text{ZrO}_2$  interface(b), and the  $\text{ZrO}_2$  grain boundary(c). The arrows indicate the microcracks

Figure 9 shows the TEM micrograph of SiC(P)/Y-TZP/M composites. As shown, the propagating crack was also deflected by SiC particle at the SiC/mullite interface.

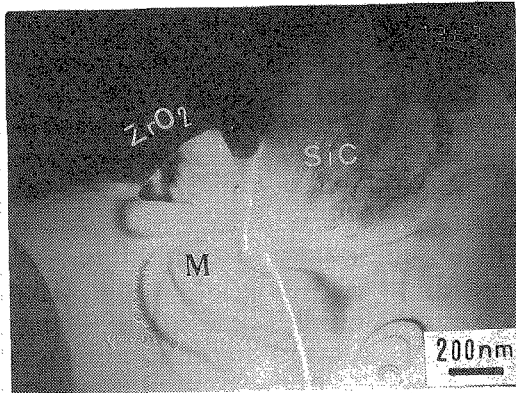


Fig.9 TEM micrograph of SiC(P)/Y-TZP/M composite

(6) High temperature strength of the SiC(P)/Y-TZP/M composites

The temperature dependence of flexural strength was investigated for the SiC(P)/Y-TZP/M composite with a composition of 20 vol% Y-TZP and 35% SiC and the results are shown in Fig.10. The data for monolithic mullite is also presented for comparison. The flexural strength of the composite was almost constant from room temperature to 1000°C. Above 1000°C, the strength decreased somewhat. But at 1200°C, the strength of the composite remains at a rather high value.

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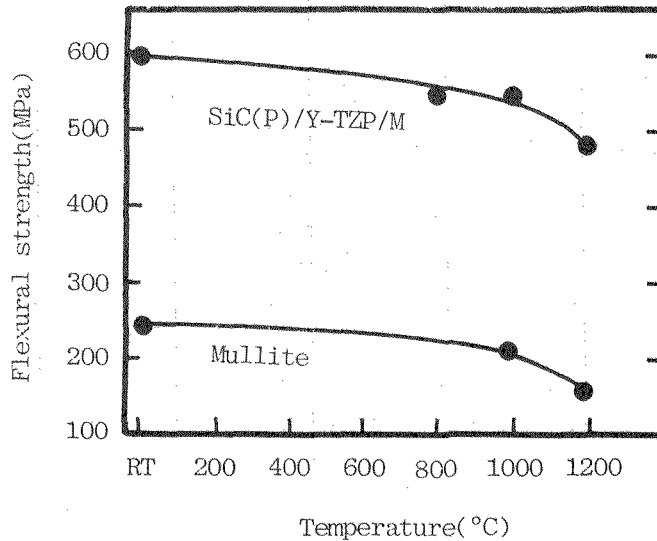


Fig.10 Flexural strength of mullite and SiC(P)/Y-TZP/M composite vs temperature

The tendency of the dependence of strength versus temperature of the composites is similar to that of monolithic mullite except the strength value of the composite were pushed up by almost two folds. This indicates that the strengthening effect of the SiC particles was not weakened in the range from room temperature to 1000°C and the transformation toughening of tetragonal zirconia is not significant. Conversely microcrack toughening is another responsible mechanism concurrently occurring. The fact that many microcracks occurred at the interface around  $ZrO_2$  grains in the composites is an additional support for this proposition.



And microcrack toughening is temperature-independent. The strength degradation above 1000°C is evidently caused by the mullite matrix itself. The glassy phase formed during sintering is responsible for such decreased. By increasing the purity of the mullite powder, further improvement in the high temperature strength of the composites can be expected.

(7) Thermal properties of the SiC(P)/Y-TZP/M composites

The thermal properties of the SiC(P)/Y-TZP/M composite were investigated. Figure 11 shows that temperature dependence of thermal expansion coefficient for the composite with a composition of 20 vol% SiC + 20 vol% Y-TZP + 60 vol% mullite. In the range room temperature to 1000°C, the average expansion coefficient of the composite is  $5.35 \times 10^{-6}/^{\circ}\text{C}$ , similar to that of monolithic mullite. At 400°C to 700°C, the thermal expansion coefficient shows a slight decrease. This phenomena can be explained by fact that monoclinic  $\text{ZrO}_2$  in the composite transformed to tetragonal form within the range of temperature. The effect of temperature on thermal conductivity of the composite is shown in Fig.12. The thermal conductivity of the composite is relatively low.

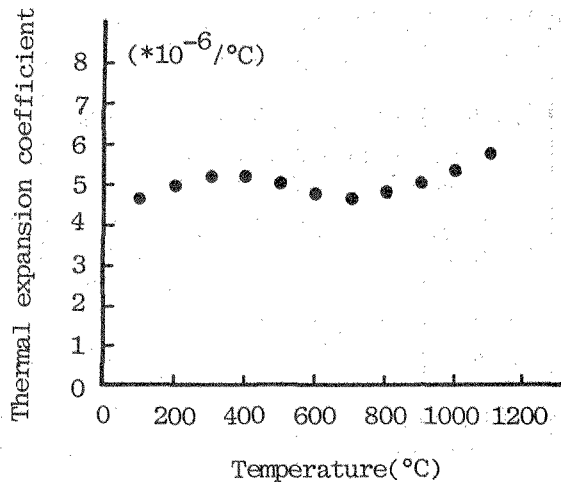


Fig.11 Temperature dependence of thermal expansion coefficient of SiC(P)/Y-TZP/M composite

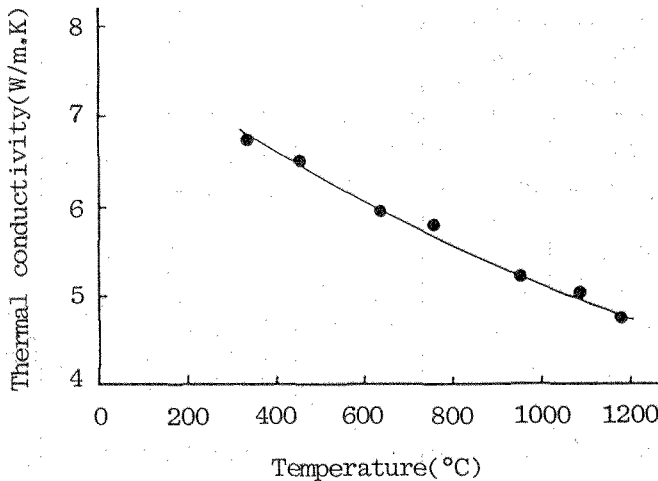


Fig.12 Temperature dependence of the thermal conductivity of SiC(P)/Y-TZP/M composite

### (8) Thermal shock resistance of the SiC(P)/Y-TZP/M composites

For high temperature structural applications of ceramic materials, thermal shock resistance is an important property. The thermal shock resistance of the SiC(P)/Y-TZP/M composites was evaluated by quenching with water. The results are listed in table 2. It is shown that monolithic mullite has retained 29.0% of its initial (unshocked) flexural strength after a thermal shock treatment from 525°C to 25°C, indicating that the thermal shock resistance,  $\Delta T_{\max}$  of mullite is less than 500°C. According to the literature<sup>(11)</sup>,  $\Delta T_{\max}$  of mullite is 350°C. However, the flexural strength of the composite decreased only slightly (from 456MPa to 422MPa) after quenching in water from 525°C to 25°C, indicating that the  $\Delta T_{\max}$  of the composite is at least 500°C. The thermal shock resistance of mullite matrix composites was significantly improved by adding both SiC and Y-TZP particles.

Table 2 Comparison between the initial strength and the retained strength after quenching in water from 525°C to 25°C for monolithic mullite and SiC(P)/Y-TZP/M composite

Materials	Initial strength (MPa)	Retained strength (MPa)
Mullite	246	71.8
SiC(P)/Y-TZP/M	456	422

### (9) Oxidation of the SiC(P)/Y-TZP/M composites

Oxidation study was conducted at 1000°C for SiC(P)/Y-TZP/M composite containing 20vol% SiC and 20vol% Y-TZP. The weight gains per unit surface area versus holding time of the sample treated at 1000°C is plotted in Fig.13. As show, the weight gain dependence against time follows basically to the parabolic law. The weight gain values per unit surface area reach asymptotically after about 60 h.

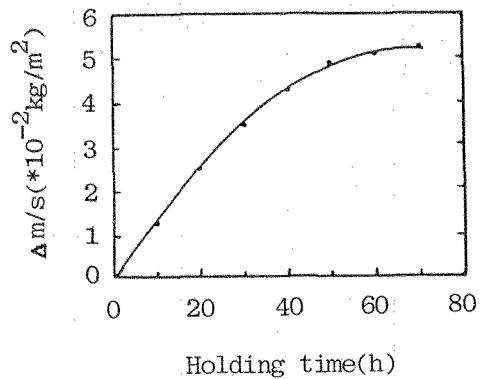


Fig.13 Weight grain per unit surface area versus holding time for SiC(P)/Y-TZP/M sample at 1000°C

## 4. Test for SiC(P)/Y-TZP/M composite material in heat engine

Fig. 14 shows a piston cap made of hot-pressed SiC(P)/Y-TZP/M composite. The bench test was conducted in Wuhan University of Water Transportation Engineering. The conditions are as follows: without cooling water, rotational speed of 1500(r.p.m), 90% of rated load and about 700°C of exhaust temperature. After

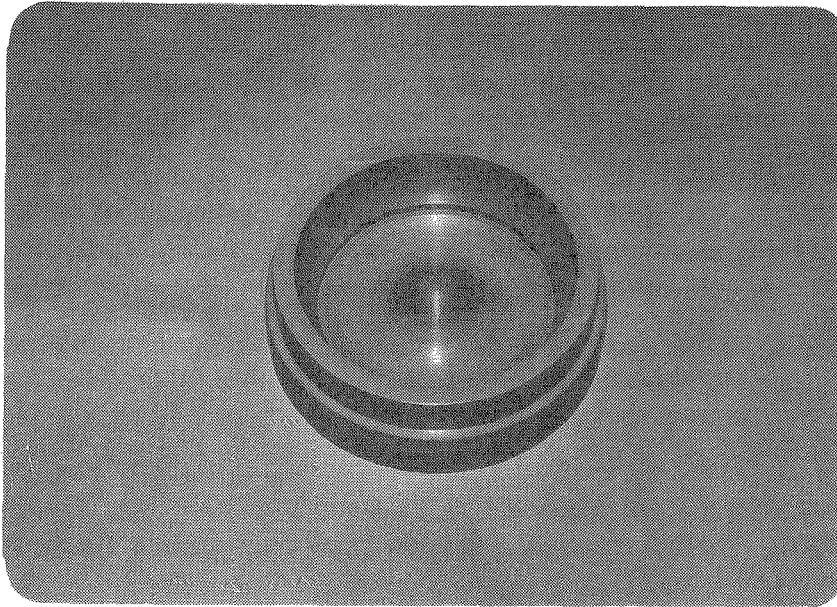


Fig.14 Photograph of B135 adiabatic engine piston cap made of SiC(P)/Y-TZP/M composite

100h, the piston caps were found intact, and can be tested further. Its thermal insulating effect was better than that of  $\text{Si}_3\text{N}_4$  materials. It is shown that the SiC(P)/Y-TZP/M composite is a potential candidate material as the thermal insulating structural components for heat engines.

### 5. Conclusions

- (1) A small amount of  $\text{Y}_2\text{O}_3$  additive can promote the densification and inhibit the abnormal grain growth of mullite material thus improving the microstructure.
- (2) The flexural strength and fracture toughness of the mullite matrix composites were significantly improved by introducing SiC and Y-TZP particles together. The maximum flexural strength of the composite was 600 MPa and the fracture toughness was  $6.7 \text{ MPa} \cdot \text{m}^{1/2}$  for addition of 20 vol% of Y-TZP and 35 vol% of SiC particles. The strength was kept almost constant to temperature around  $1000^\circ\text{C}$ .
- (3) Reinforcing mechanisms observed in the composites are mainly crack deflection and crack branching by the SiC particles, and microcrack toughening caused by Y-TZP. Such mechanisms seem to function together synergistically.
- (4) The SiC(P)/Y-TZP/M composite material remains to have low thermal expansion coefficient ( $5.35 \times 10^{-6}/^\circ\text{C}$ , at room temperature to  $1000^\circ\text{C}$ ), low thermal conductivity and good oxidation resistance. The thermal shock resistance when tested by a water quench has a  $\Delta T_{\text{max}}$  of about  $500^\circ\text{C}$ , which is much improved than pure mullite.
- (5) Piston caps were made from this SiC(P)/Y-TZP/M composite material and was successfully bench tested in a B135 adiabatic engine for over 100 hrs. It is shown that mullite matrix composite is a potential candidate material as the thermal insulating structural components for heat engines.

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