

# Simultaneous fabrication of a composite with low thermal expansion and high strength in the eucryptite – yttria-stabilized PSZ system

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Low thermal expansion coefficient and high mechanical strength have been attained simultaneously in a composite with microstructures in which the low thermal expansion grains are surrounded by a continuous texture of the grains with high strength. Alloying eucryptite with yttria-stabilized PSZ (partially stabilized zirconia) simultaneously achieved the low thermal expansion coefficient,  $1.45 \times 10^{-6}$ , and the high bending strength, 220 MPa, by adjusting the composition and controlling the microstructures by changing the starting powders and the milling durations. Grain size and reactions between the coupled materials determined the critical processing conditions.

## 1. Introduction

Typical low thermal expansion ceramics with coefficients lower than  $2.0 \times 10^{-6} \text{ K}^{-1}$  [1], for example, cordierite [1], pseudo brookite-type oxides [2], lithium aluminosilicates such as eucryptite [3] and spodumene [4, 5], have low mechanical strength, less than 100 MPa, due to microcracks in the body caused by a thermal expansion anisotropy [6–8]. Industrial application, therefore, was limited. The ceramics with a thermal expansion coefficient less than  $2 \times 10^{-6} \text{ K}^{-1}$  and a bending strength more than 200 MPa could have potential for industrial application.

Roy [9] pointed out the theory based on the Megaw correlation between high bond strength and low expansion, and a corollary to the theory leading to a relationship between  $\alpha$  and  $T_m$  given by van Uitert and co-workers, but that such a theoretical approach sacrificed many target materials in the search for zero expansion material. He proposed that major families of low thermal expansion, such as silica–glass, zircon, cordierite and eucryptite–spodumene, should be modified to have materials of zero expansion by designing a new composite in nanoscale, despite several difficulties with the premise of the compatibility of the components. A nanocomposite is attractive for the simultaneous goals of zero expansion and the promotion of high strength [10]. Eucryptite, however, resists ionic substitution necessary to form the nanocomposite.

The studies on the simultaneous achievement of low thermal expansion and high bending strength in one composite are incomplete. Two ideas are combined to design such a composite. The first is to minimize the thermal expansion coefficient of the composite by averaging the negative thermal expansion coefficient of a dispersed component by alloying it with a component matrix with positive expansion coefficient in a suitable ratio, according to the descriptions given by Roy [9] and Matsumoto *et al.* [11]. The second is to strengthen the composite through the microstructure, by embedding grains of low thermal expansion in a continuous matrix of grains having high strength. The strength of the composites would be carried by the continuous texture of the high strength matrix component provided that the matrix is compatible with the dispersed component. A densified continuous matrix was effective for the strengthening of titanium aluminate composites [12–15]. Partially stabilized zirconia (PSZ) with yttria is one of the candidates for the matrix component. PSZ has a positive expansion coefficient and high strength and also forms fine grains which are capable of surrounding grains of the other component in a continuous texture. Eucryptite (YK) is a candidate for the material with a negative thermal expansion.

The purpose of the present work was to simultaneously produce low thermal expansion and high bending strength in YK–3Y–PSZ composites by adjusting the composition and controlling microstructure by changing the starting powders and milling durations as processing parameters.

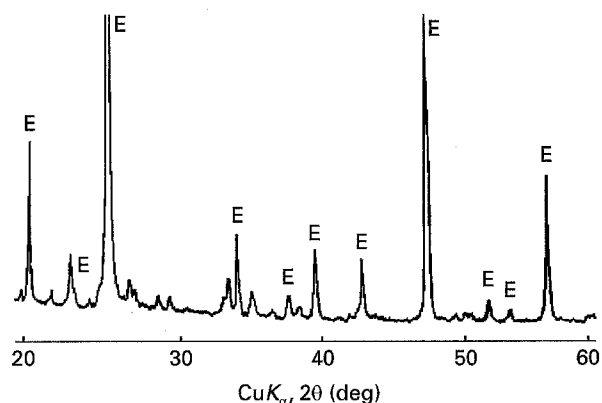


Figure 1 X-ray diffraction pattern of the as-received eucryptite powder. E, Peaks assigned for eucryptite.

## 2. Experimental procedure

### 2.1. Starting materials

Eucryptite, type E-42, produced by Shibata Ceramic Raw Materials, had a 5  $\mu\text{m}$  average diameter. The X-ray diffraction pattern of the eucryptite is shown in Fig. 1 and the analytical data of the material obtained by X-ray fluorescence are given in Table I.

Two kinds of PSZ powders, 3YS-PSZ and 3Y-PSZ, were provided. A sintered body of these powders themselves could give a high strength of 1200 MPa owing to the fine grains developed from the fine crystallites of the starting powder. The 3YS-PSZ powder, used for slip casting, had a larger crystallite size and lower specific surface than those of 3Y-PSZ, the powder for ordinary use. The average agglomerate size was 0.3  $\mu\text{m}$  for both powders. The specific surface area and the crystallite size were 7 and 17  $\text{m}^2 \text{g}^{-1}$ , and 40 and 24 nm for 3YS-PSZ and 3Y-PSZ, respectively. Fig. 2 shows the XRD patterns of zirconia, (a) as-received powder, and (b) powder fired at 1300  $^{\circ}\text{C}$ . As-received powder retains the monoclinic form, but after firing, it is completely transformed into the tetragonal form.

### 2.2. Forming and firing

A fixed amount of alumina balls, water, dispersant (ammonium polycarbonate; 0.25 wt % in dry weight base (dwb) to powders) and starting powders were put together in an alumina pot in the described order and milled for 24 h. The slips were cast into a plaster mould under mechanical vibration to produce a rectangular piece, 0.5 cm  $\times$  1.0 cm  $\times$  7.0 cm. Dried samples were fired in an electric furnace with a Kanthal Super electric heater in an air atmosphere at various temperatures and for various times.

### 2.3. Measurement of mechanical properties and microstructural observation

Bending strength was determined using a TENSILON-III-Model 500 bending test machine in three-point bending mode. Dilatometric measurements were conducted using the dilatometer, Koeiseiki Model HD-21, in the temperature range 40–900  $^{\circ}\text{C}$ . Micro-

TABLE I Analytical data of the starting powders of the eucryptite (wt %) obtained by X-ray fluorescence

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
49.1	39.8	0.24	0.76	0.04	0.04	0.12	0.03

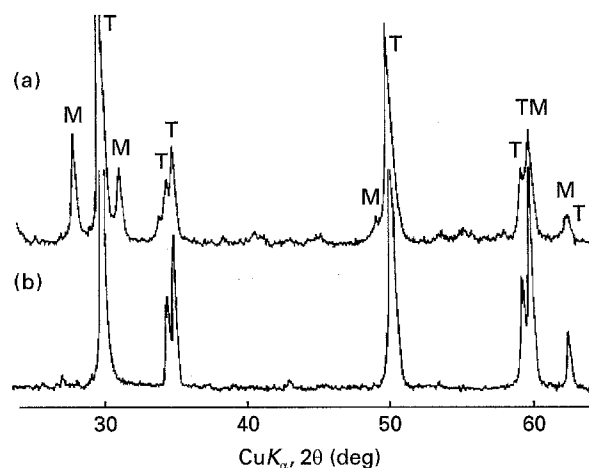


Figure 2 X-ray diffraction patterns of zirconia: (a) as-received 3Y-PSZ powder, (b) after firing at 1300  $^{\circ}\text{C}$  for 3 h.

structures were observed by scanning electron microscopy, AKASHI SIGMA, for fractured or polished and etched surfaces of the fired body.

### 2.4. Chemical analysis

The amount of lithium ions dissolved from eucryptite into solution during milling was determined by atomic absorption analysis with a Jarrel Ash atomic absorption flame emission spectrophotometer model A-8500 for the supernatant of the slip after centrifugation.

## 3. Results and discussion

### 3.1. Selection of starting materials

The dilatometric measurements were conducted on a body of the YK-3YS-PSZ system fired at 1300  $^{\circ}\text{C}$  with varied composition, and the curves are shown in Fig. 3. The curves for the body with a high YK ratio had a negative slope. With an increase in the ratio of 3Y-PSZ in the composites, the absolute value of the slope initially decreased and then increased, changing the sign of the slope from negative to positive, and gave a minimum thermal expansion coefficient at the composition of 55 wt % YK to 45 wt % 3Y-PSZ. Table II shows the thermal expansion coefficients for the body fired at 1275, 1300 and 1325  $^{\circ}\text{C}$ .

The minimum for the expansion coefficient at the composition ratio of 55 wt % YK to 45 wt % 3Y-PSZ did not move when the firing temperatures were changed from 1275–1325  $^{\circ}\text{C}$ . The first objective, to lower and minimize the thermal expansion coefficient, has been attained by alloying the material with the negative coefficient with the material with the positive coefficient, to average the coefficient. However, the bending strength of the composites was insufficient to

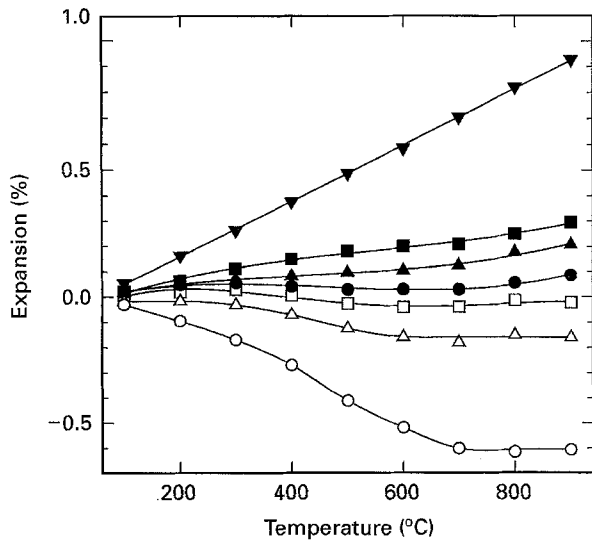


Figure 3 Thermal expansion curves of the YK-3YS-PSZ composites with various composition ratios. (▼) 0 wt % YK, (■) 35 wt % YK, (▲) 45 wt % YK, (●) 55 wt % YK, (□) 65 wt % YK, (△) 75 wt % YK, (○) 100 wt % YK.

TABLE II Thermal expansion coefficient of the composite

Composition		Thermal expansion coefficient [ $10^{-6} \text{ } ^\circ\text{C}^{-1}$ ]		
3YS-PSZ (wt %)	YK (wt %)	1275 °C	1300 °C	1325 °C
0	100	-6.3	-7.1	-7.5
25	75	-1.8	-1.8	-2.6
35	65	-0.34	-0.24	-1.0
45	55	+1.6	+0.98	+0.79
55	45	+3.7	+2.3	+2.2
65	35	+4.4	+3.2	+3.1
100	0	+11	+11	+11

achieve an objective strength of more than 200 MPa for the composites with 3YS-PSZ. The microstructures of the composites of YK-3YS-PSZ and YK-3Y-PSZ at the composition of 55 wt % YK and 45 wt % PSZ, respectively, are compared in Fig. 4a and b. Grain sizes of YK in the YK-3YS-PSZ system are  $\sim 5 \mu\text{m}$  on average, and are larger than that in the YK-3Y-PSZ system; large YK grains in the sintered body of eucryptite itself exhibit microcracks, as shown in Fig. 4c. Dispersion of zirconia, which should be a continuous matrix in the composite and should

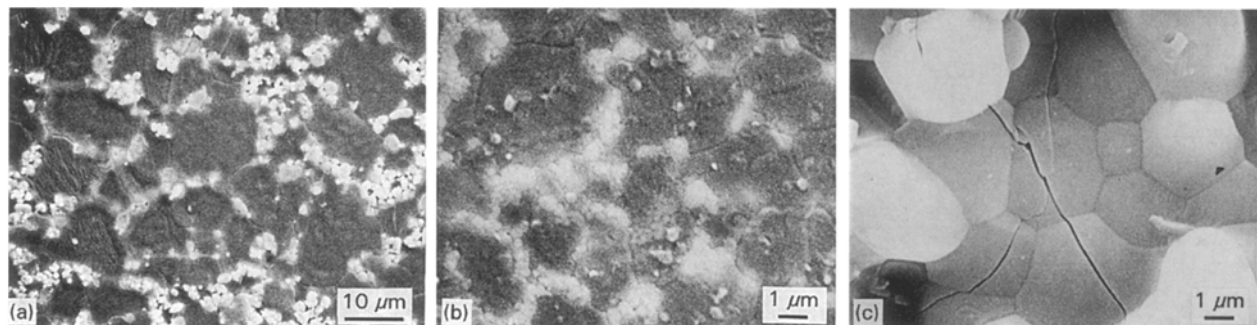


Figure 4 Microstructures of the composites with different zirconia sources. (a) YK:3YS-PSZ = 55:45, (b) YK:3Y-PSZ = 55:45 with ratios in wt %. Samples were milled for 115 h and then fired at 1325 °C for 3 h. (c) Microcracks observed in the sintered body of the eucryptite itself.

carry the strength, was poorer than that in the YK-3Y-PSZ system. The development of the texture of the continuous zirconia matrix in which to embed eucryptite grains was insufficient. In order to obtain the desired microstructure, it was necessary to grind the YK particles and to enhance the dispersion of 3YS-PSZ particles to produce the ideal matrix by further milling for long times. The use of 3Y-PSZ instead of 3YS-PSZ would also be helpful for this purpose owing to the finer crystallite size of 3Y-PSZ than that of 3YS-PSZ.

### 3.2. Grain-size reduction and the improvement of dispersion by optimization of the composition and milling time

Fig. 5 shows the thermal expansion curves of the YK-3Y-PSZ composites, and the expansion coefficients are shown in Fig. 6. For shorter milling times than 21 h, the curve gave a low thermal expansion coefficient under the effect of the YK component. The body after 115 h milling, however, gave a positive coefficient which increased with increase in the milling time in spite of the improvement of the dispersion and the

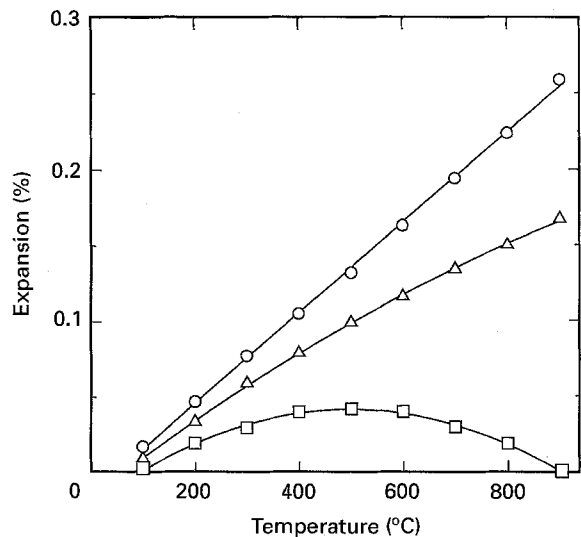


Figure 5 Thermal expansion curves of the composites of 55 wt % YK milled for different durations and fired at 1300 °C for 3 h. (□) 21 h, (△) 115 h, (○) 382 h.

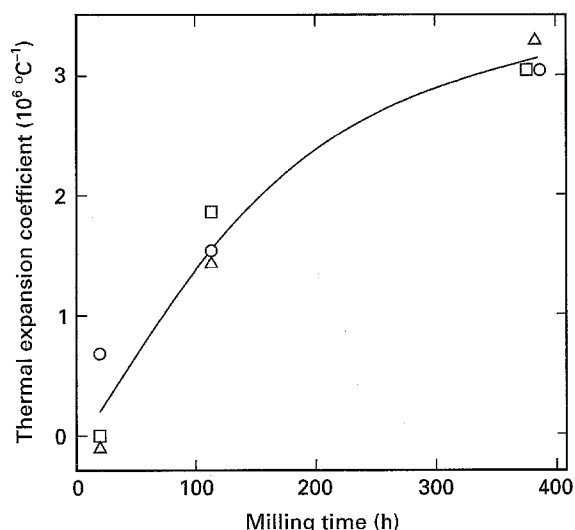


Figure 6 Changes in thermal expansion coefficient of the composite for various firing temperatures with milling durations: fired at ( $\Delta$ ) 1275 °C, ( $\square$ ) 1300 °C, ( $\circ$ ) 1325 °C.

TABLE III Dissolution of lithium ions into solution from the eucryptite powder during milling and the effect of alcohol on the dissolution

Amount of alcohol added to water in the slip (wt %)	Fraction of the amount of dissolved lithium ions to the theoretical amount in eucryptite
0	0.45
10	0.16
30	0.12
50	0.10
100	0.025

attainment of a fine grain size. YK does not work to reduce the thermal expansion coefficient in the composite milled for long durations. The instability of the YK to prolonged milling might be the cause of the decrease in the effect of YK. Table III shows the amount of lithium ions in solution for various milling times. Half the theoretical amount of lithium ions in the YK can be dissolved into solution during 24 h milling and this might be a cause of the instability of the YK, thus bringing about the interruption of the lowering effect of YK on the thermal expansion of the

composite. The addition of 10% alcohol to the water in the preparation of slips was helpful in suppressing the dissolution to below 20% theoretical lithium ions. However, dissolution of a considerable amount of lithium ions was unavoidable, even in the presence of alcohol during milling.

### 3.3. Achievement of high strength

The bending strength of the composites is plotted for various milling times in Fig. 7. The strength showed a maximum for the milling durations. A maximum of 220 MPa, which exceeded the objective strength of the composite by more than 200 MPa, has been attained for the composite with the ratio YK:3Y-PSZ = 55:45, after milling for 115 h and firing at 1275–1325 °C. As shown in Fig. 8, dispersion of YK and 3Y-PSZ particles in the composites was greatly improved by the 115 h milling and the fine grains of YK were embedded in the 3Y-PSZ matrix. The second objective, to achieve maximum strength of the composite through a microstructure in which grains of low thermal expansion are embedded in a continuous matrix of high strength grains, has been attained.

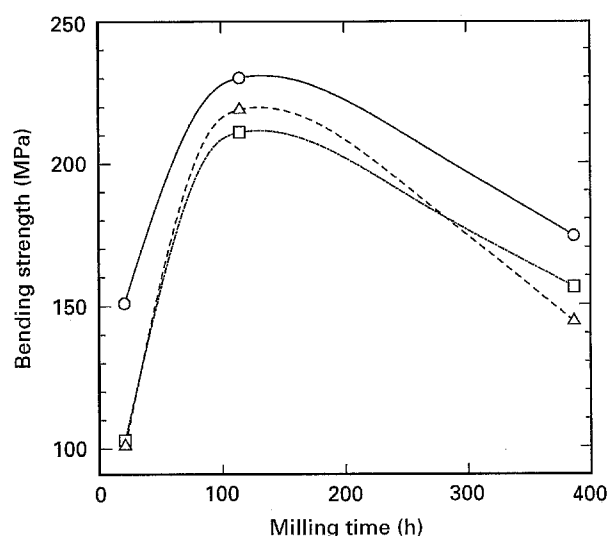


Figure 7 Changes in bending strength of the composites of 55 wt % YK for various firing temperatures with milling durations: fired at ( $\Delta$ ) 1275 °C, ( $\square$ ) 1300 °C, ( $\circ$ ) 1325 °C.

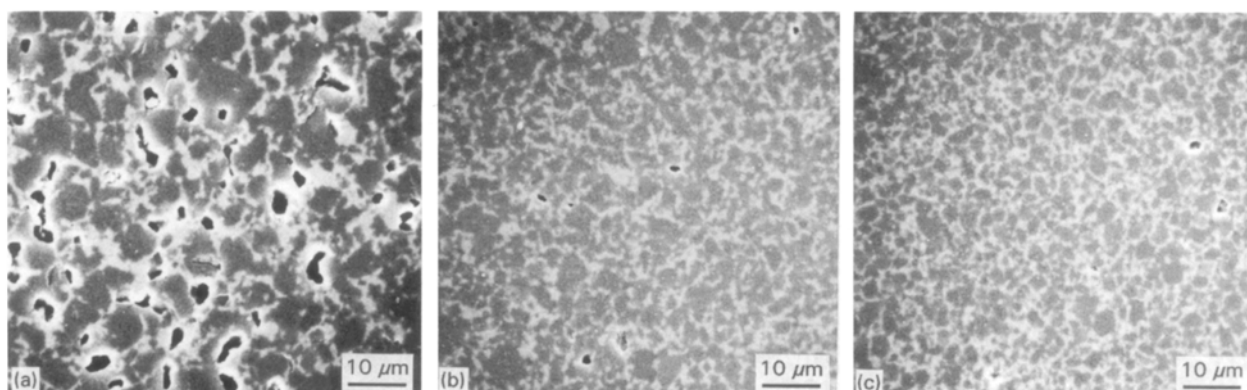


Figure 8 Comparison of the microstructure for the composites of 55 wt % YK fired at 1325 °C for 3 h with different milling durations: (a) 21 h, (b) 115 h, (c) 382 h.

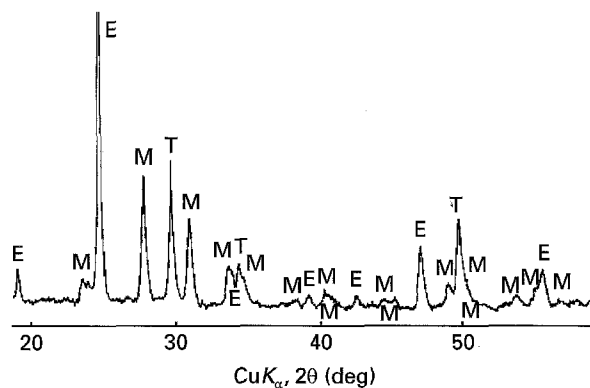


Figure 9 X-ray diffraction patterns of the composites of 55 wt % YK fired at 1300 °C for 3 h after 115 h milling. Peaks were assigned for T, tetragonal zirconia, M, monoclinic zirconia and E, eucryptite.

Long milling times, exceeding 115 h, however, lowered the strength against expectations, in spite of promotion of dispersion. Monoclinic zirconia was found in the composite, as seen in Fig. 9 showing the X-ray diffraction of the composite at YK:3Y-PSZ = 55:45 milled for 115 h. Monoclinic forms were already found in the composite after 21 h milling. The body of 3Y-PSZ itself shows only the tetragonal form after firing, and is not unstable, as shown in Fig. 2. The great reduction in strength at 382 h milling could be due to the instability of zirconia during milling. The instability of the partially stabilized zirconia in the composites must have occurred due to the good contact with YK particles and the subsequent firing. There must be some interaction between YK and  $ZrO_2$ , or between the stabilizer  $Y_2O_3$  in  $ZrO_2$ . The longer milling times for better dispersion need adjusting because shorter milling times are required to avoid the instability of  $ZrO_2$  and YK to achieve low expansion. Milling for 115 h was found to be the optimum matching point. Prevention of the instability of YK and tetragonal zirconia was the key for the increase in strength of more than 200 MPa and the lowering of the thermal expansion coefficient.

#### 4. Conclusion

Eucryptite was alloyed with 3Y-PSZ in the composition ratio YK:3Y-PSZ = 55:45, processed by milling for 115 h and subsequently fired at 1275–1325 °C. The

composite achieved a low thermal expansion coefficient,  $1.45 \times 10^{-6}$  and a high bending strength, 220 MPa, simultaneously.

The instability of eucryptite, brought about by dissolution of lithium ions into solution during milling, interrupted the lowering of the thermal expansion coefficient; instability of the partially stabilized zirconia also occurred during prolonged milling and also interrupted the increase in strength.

Composites with high strength and low thermal expansion coefficient could however, be produced by adjusting the composition and also milling duration in the processing.

#### Acknowledgements

One of the authors thanks Dr Taizo Hibino and Dr Iwao Yamai for their comments and discussions.

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Received 8 August

and accepted 21 December 1995