JOURNAL OF MATERIALS SCIENCE 25 (1990) 2253–2258

Preparation and sintering of fine composite precursors of mullite–zirconia by chemical copolymerization of metal alkoxides

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Composite precursors of mullite–zirconia were prepared by mixing a mullite precursor prepared by the partial hydrolysis method and zirconium alkoxide. The mullite precursor was reacted with zirconium alkoxide in order to achieve a uniform dispersion of fine zirconia particles in the mullite matrix. The composite precursors were hydrolysed and heat-treated to examine the properties of the precursors. X-ray diffraction data showed that a large amount of tetragonal zirconia existed in the composite powders in spite of the high temperature calcination below 1600° C. These results suggested that transformation toughening of mullite-based ceramics prepared by firing the composite precursor compacts could be attained if the total densification occurred at low temperature.

1. Introduction

Recently, mullite has become a candidate for manufacturing high temperature structural materials because of its high strength and high creep resistance at high temperatures [1, 2]. However, the low fracture toughness of mullite ceramics hinders the application. Therefore, toughening of mullite ceramics is indispensable for its use as a structural material. The most promising method to toughen ceramics is to disperse fine tetragonal zirconia particles in the matrices, which transform into monoclinic symmetry by mechanical stress. But it is very difficult to achieve a uniform dispersion of fine particles in the composites, especially in ceramics. In this study, fine mullite–zirconia composite powders were successfully prepared through the alkoxide to obtain mullite-based composites containing up to 40 vol % uniformly dispersed fine zirconia particles.

2. Experimental procedure

Tetraethylorthosilicate (TEOS), $Si(OC_2H_5)_4$, aluminium i-propoxide, $Al(OC_3H_7)_3$, and zirconium n-propoxide, $Zr(OC_3H_7)_4$, were used as raw materials. A precursor solution with a stoichiometric mullite composition was prepared by partial hydrolysis [3, 4]. The mullite precursor solution was mixed with zirconium n-propoxide solution refluxed with i-butanol and then followed by sedimentation with excess amount of distilled water. The process is described elsewhere [5]. The concentration of zirconia varied from 10 to 40 vol %. The prepared precursor powders were calcined up to 1600° C and then analysed by infrared (IR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The percentage of tetragonal zirconia, $t\text{-}ZrO_2/(t\text{-}ZrO_2 + m\text{-}ZrO_2)$, was estimated by the following equation [6],

$$V_t = 1 - 1.311X_m/(1 + 1.311X_m)$$

where V_t is the vol % of zirconia and X_m is the integrated intensity ratio (I) defined by XRD as

$$X_m = [I_m(\bar{1}\,1\,1) + I_m(1\,1\,1)]/[I_m(\bar{1}\,1\,1) + I_m(1\,1\,1) + I_t(1\,0\,1)]$$

where subscripts m and t represent the monoclinic and tetragonal phases, respectively.

Sintering was carried out as follows. The composite precursor powders were calcined at 800° C for 12 h and then uniaxially pressed at 120 MPa followed by isostatic pressing at 300 MPa. The compacts were sintered at 1400, 1500 or 1600° C for 2 h, respectively. The densities of the sintered compacts were measured by the displacement method using distilled water. A four-point bending test was carried out using a polished specimen of 3 × 4 × 36 mm in size.

3. Results and discussion

3.1. Composite powders

3.1.1. IR spectra and crystalline phases

As-prepared composite powders were amorphous by X-ray diffraction but their IR spectra were different from that of the mullite precursor [4]. As shown in Fig. 1, absorption peaks of mullite precursor which appeared around 610, 780, 880 and 1060 cm^{-1} were shifted towards lower wavenumbers and were broad in the case of the composite precursors. These results may be caused by the coordination of zirconium alkoxide. That is, aluminium alkoxide reacts with zirconium alkoxide to form a double alkoxide [7]. Therefore, in the course of the preparation of composite precursors, mullite precursor reacted with zirconium alkoxide to form Zr–O–Al coordinate bond, resulting in the shifts and broadening of the IR peaks. However, zirconium silicate ($ZrSiO_4$) did not crystallize at elevated temperatures, suggesting the

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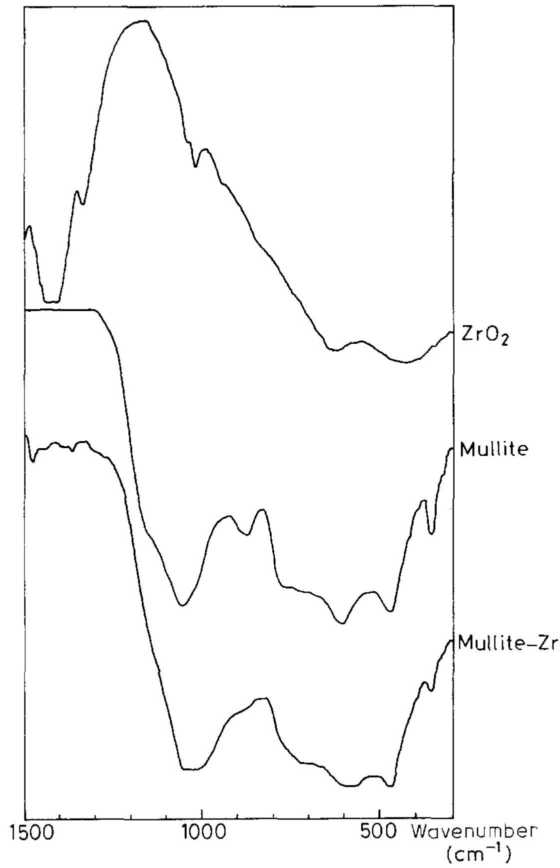

Figure 1 Infrared spectra of the precursor powders. ZrO$_2$ is zirconia gel powder prepared by the hydrolysis of zirconium alkoxide. Mullite is mullite precursor powder prepared by the copolymerization of silicon and aluminium alkoxides. Mullite–ZrO$_2$ is composite precursor powder with a composition of 20 vol % ZrO$_2$.

formation of Si–O–Al bond at preparative stage of the mullite precursors. The coordination of zirconium alkoxide would restrain the growth of zirconia particles to achieve the uniform dispersion of zirconia in the composites.

The composite precursors were amorphous below 400° C and tetragonal zirconia was identified above 500° C. At 900° C, faint Al, Si-spinel or γ-Al_2O_3 solid solution was identified by XRD, corresponding to the crystallization process of mullite precursor [4]. However, crystallization of the mullite phase took place at 1000° C in all compositions. It is considered that the mullitization temperature of the composite precursors determined by XRD is lowered, compared with that of the mullite precursor (1100° C) [4], by the accelerated nucleus formation due to the uniformly dispersed zirconia particles.

The crystallization process was also examined by differential thermal analysis (DTA). Fig. 2 shows the DTA–TG (thermo gravimetry) curve of the composite precursor with a composition of 30 vol % ZrO$_2$. The exothermic peaks in the temperature range from 250 to 400° C corresponded to the combustion of the residual alkoxyl groups derived from zirconium alkoxide because the DTA curve of the composite precursor was similar to that of the zirconium alkoxide hydrolysed with a small amount of water [8], except for the exothermic peak around 965° C which corresponded to the crystallization of mullite. However, the exothermic peak corresponding to the crystallization of zirconia was very broad and appeared at higher temperatures. (In the case of the crystallization of the zirconia gels prepared by the hydrolysis of zirconium alkoxide with ammoniated or distilled water, the exothermic peak appeared sharply at around 430° C [8, 9].) This suggested that the coordination of zirconium alkoxide would occur in the course of the preparative stage of the composite precursors, and the crystallization of zirconia gradually took place near or in the matrices of the mullite precursors.

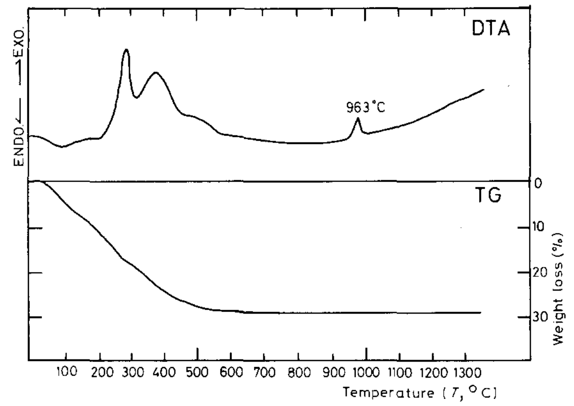

Figure 2 DTA–TG curves of the composite precursor with composition of 30 vol % ZrO$_2$.

As shown in Fig. 2, the weight loss continued up to 500° C and levelled off at elevated temperatures, indicating that the desorption of the water and combustion of the residual alcohol or alkoxyl groups was complete below 500° C. Moreover, the mullitization process was affected by the uniformly dispersed zirconia particles. Table I lists the crystallization temperature of mullite in the composite powders determined by DTA. The mullitization temperature decreased with concentration of zirconia, indicating that the uniformly dispersed fine zirconia supplied a large number of the sites for nucleus formation. The lower mullitization temperature may also be related to the composition of mullite.

3.1.2. Change in the tetragonal : monoclinic ratio in zirconia with heating

The change in the volume per cent of the tetragonal phase with heating was measured by XRD and shown in Fig. 3. The tetragonal : monoclinic ratio in the composite powders varied with the concentration of zirconia and the calcination temperature. In all compositions, more than 50% of tetragonal phase existed below 1400° C. Especially in the composition with 10% ZrO$_2$, the tetragonal to monoclinic transformation hardly occurred below 1500° C, indicating the possibility of a dense mullite–zirconia composite containing a large amount of tetragonal zirconia particles.

TABLE I Mullitization temperatures determined by DTA

Specimen	Mullitization temperature (° C)
Mullite + 10% ZrO$_2$	973
Mullite + 20% ZrO$_2$	965
Mullite + 30% ZrO$_2$	963
Mullite + 40% ZrO$_2$	961

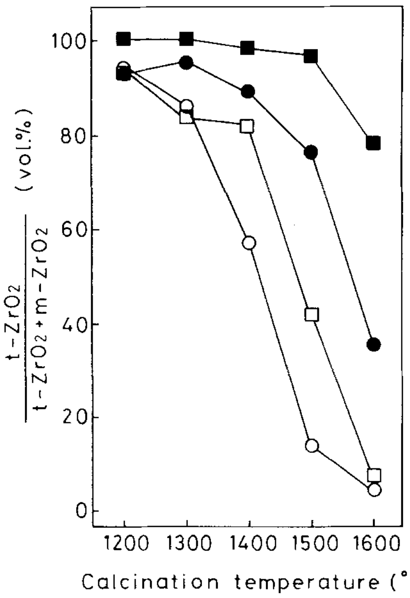

Figure 3 Change in the volume ratio of tetragonal zirconia in the composite precursors with calcination temperature. Precursor powders were calcined for 2 h. (■) 10 vol %, (●) 20 vol %, (□) 30 vol %, (○) 40 vol %.

It is considered that the stabilization of tetragonal zirconia in the composite powders is successfully accomplished by the uniform distribution of fine zirconia particles which crystallize *in situ* during heating.

The constraint force of the rigid mullite matrix may also be ascribed to the stabilization. For higher concentrations of zirconia, a grain growth occurred at elevated temperatures, resulting in a reduced amount of tetragonal phase. The metastable zirconia in the composite powders was sensitive to the mechanical stress, suggesting the transformation toughening of the ceramics prepared by sintering of the composite powders. Considering the sintering conditions, a large amount of metastable tetragonal phase should exist in the composites after high temperature calcination and the tetragonal zirconia particles should form monoclinic symmetry by the stimulus of the mechanical stress. Fig. 4 indicates the amount of transformable tetragonal zirconia in the composite powders calcined at 1500° C for 2 h. The amount of transformable zirconia was estimated by the differences in the volume per cent of the tetragonal phase before and after pulverizing the composite powders. As shown in Fig. 4, a fair amount of transformable zirconia existed at elevated temperatures, especially for low concentrations of zirconia.

3.1.3. Lattice parameters

Mullite has a solid solution region for the composition range from 72% to 75% Al_2O_3 at 1600° C, changing to 74% to 76% at 1800° C [10] and the lattice parameters of the mullite changes with its composition. Cameron [11] reported the relation between the lattice parameters and the compositions of the mullite or $Al_2O_3 : SiO_2$ ratio. In this study, the compositions of the mullite were deduced from the lattice parameters (Fig. 5).

The phase relationship in the vicinity of mullite reveals that a stoichiometric mullite, $3Al_2O_3 \cdot 2SiO_2$,

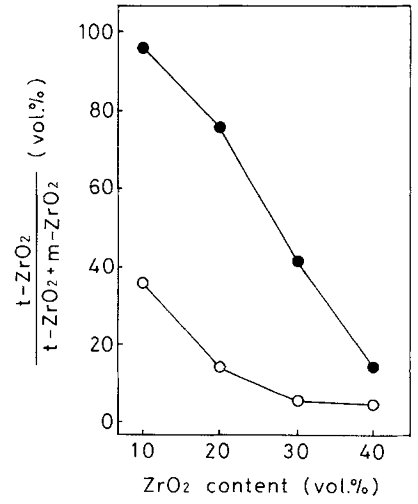

Figure 4 The amount of transformable zirconia due to mechanical stress, (●) before pulverizing, (○) after pulverizing.

described by Bowen and Greig [12] lies in the single phase region below 1600° C. As shown in Fig. 5, the c_0 axis of the mullite was independent of the temperature regardless of the composition. However, the a_0 and b_0 axes of the mullite phase in the composite varied with the calcination temperature. The a_0 axis tends to decrease with increasing temperature while the b_0 axis is apt to increase with calcination temperature, independently of the composition. This suggested that the composition of the mullite formed during heating changed with the temperature. This tendency is particularly obvious in the composition of 40 vol % ZrO_2. These results suggested the formation of SiO_2-rich mullite at high temperatures. However, the $Al_2O_3 : SiO_2$ ratio of the batch compositions was 3 : 2, i.e. the stoichiometric composition in the single phase region contained no liquid phase. No other phases except mullite and zirconia were identified by XRD, even though the

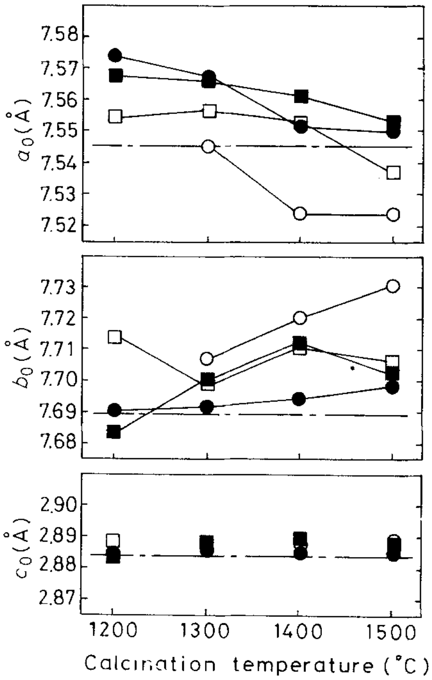

Figure 5 Change in the lattice parameters of mullite in the composite powders with calcination temperatures. Precursor powders were calcined for 2 h. --- shows the values reported in JCPDS 15-776. (■) 10 vol %, (●) 20 vol %, (□) 30 vol %, (○) 40 vol %.

composite powders were heated at temperatures as high as 1700° C. Therefore, the change in the lattice parameters relates not only to the alumina : silica ratio of the mullite formed. One of the probable reasons for the change in the lattice parameters is the formation of mullite–zirconia solid solution, but this has not been confirmed.

3.2. Sintering

As already described, the composite precursors prepared by the chemical copolymerization of metal alkoxides have splendid potential for obtaining mullite–zirconia ceramic composites with superior mechanical properties. It is considered that the composite precursors have excess free energy [13] which can be utilized for sintering. For example, a cordierite precursor prepared by the copolymerization of partially hydrolysed TEOS and magnesium–aluminium double alkoxide can be sintered into a dense compact followed by homogeneous crystallization at temperatures as low as 1200° C to obtain a dense cordierite ceramic [14, 15]. Therefore, the composite precursors were calcined at 800° C for 2 h to remove the organic residue and water (surface silanol groups), and then

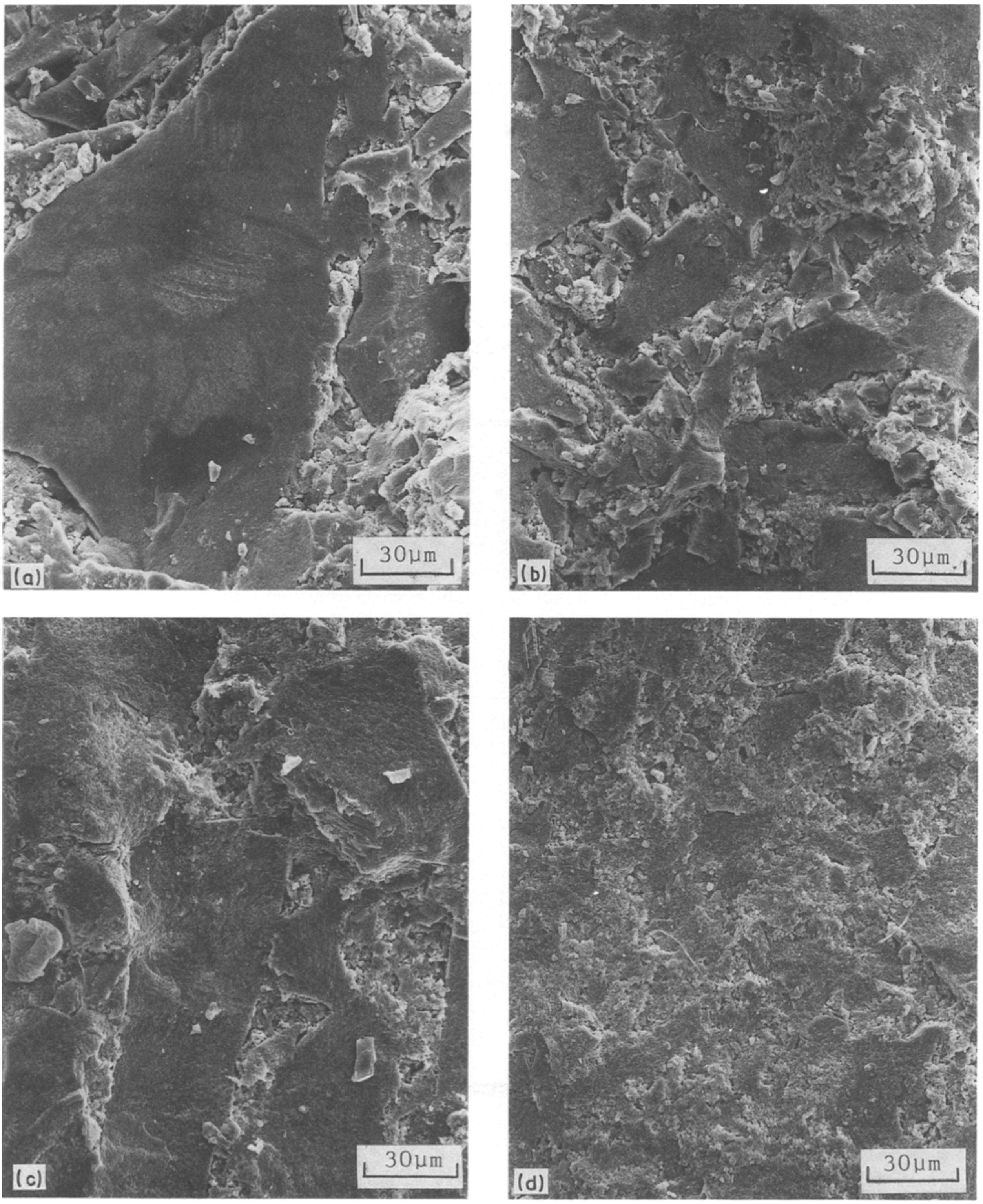

Figure 6 Fractured surfaces of the sintered compacts. (a) 10% ZrO_2, sintered at 1400° C, (b) 20% ZrO_2, sintered at 1400° C, (c) 40% ZrO_2, sintered at 1400° C, (d) 40% ZrO_2, sintered at 1500° C, (e) 40% ZrO_2, sintered at 1600° C.

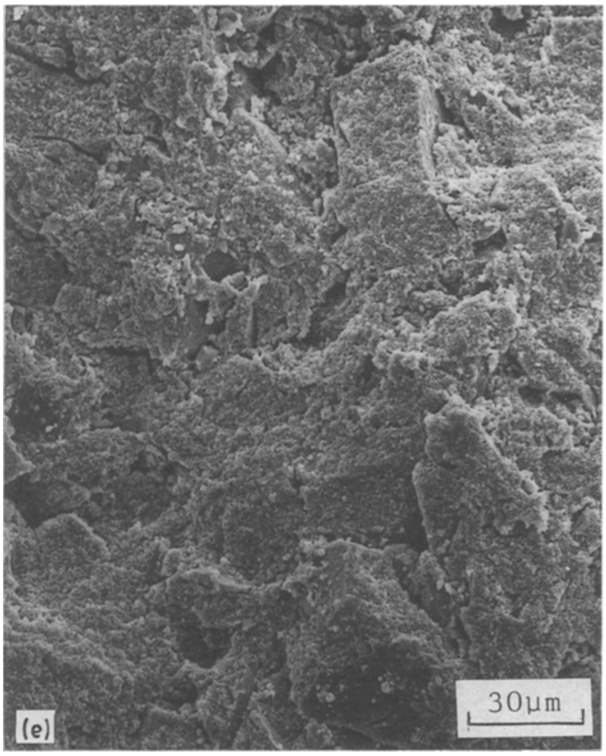

Figure 6 Continued.

sintered. However, tetragonal zirconia crystallized during the calcination.

The relative densities and flexural strengths of the sintered compacts are listed in Table II. As a result, full density was not attained in all compositions. The lower density of the sintered compacts was ascribed to a lower green density of the precursor compact of about 40%. It is considered that the large agglomerates caused by finer primary particle size less than 20 nm result in the low green density. Crystallization of the tetragonal zirconia and mullite at relatively low temperatures is also considered to hinder the densification of the compacts. The addition of zirconia did not accelerate the densification of the precursor compacts. Whether complete densification was attained or not depended upon the density of the green compacts. Early densification of the large agglomerates suppressed further densification and resulted in the low density of the sintered compacts. Especially in the composition of 10 vol % ZrO_2, crystallization and transformation of the zirconia in the mullite grains at low temperature restrained the densification of the compacts. However, for zirconia content greater than 20 vol %, fine zirconia particles uniformly dispersed in the mullite matrices prohibited crack propagation by the transformation, resulting in increased strength. As shown in Table II, about 30% of the increase in strength was attained by adding 40 vol % ZrO_2.

TABLE II Relative densities and flexural strengths of the sintered compacts on sintering for 2 h at various temperatures

Specimen	Sintering temperature (°C)	Theoretical density (%)	4-point bending strength (MPa)
Mullite + 10% ZrO_2	1400	88	82
	1600	82	62
Mullite + 20% ZrO_2	1400	83	98
	1500	92	155
Mullite + 40% ZrO_2	1400	89	153
	1500	92	167
	1600	92	142
Mullite	1400	79	91
	1500	89	110
	1600	90	116
	1700	92	126

Fig. 6 shows the fractured surfaces of the sintered compacts. The flaw size of the composites also decreased with increasing zirconia content (Figs 6a to c), which was caused by the uniform dispersion of zirconia. In the composition with 40% ZrO_2, maximum strength was obtained by firing the compact at 1500° C, because of the higher density (Figs 6c and d) and a large amount of transformable zirconia. The decrease in strength on firing at 1600° C was due to the increase in the amount of monoclinic zirconia, to which the tetragonal phase was transformed by grain growth, resulting in the large flaw size of the sintered compact (Fig. 6e). These results indicated that if the total densification of the composite precursor compacts was accomplished at low temperatures (below 1500° C), mullite–zirconia composite ceramics with superior mechanical properties were obtainable. Further research of the packing behaviour of ultrafine powders is indispensable to overcome this problem.

4. Conclusions

Fine composite precursors of mullite–zirconia were prepared by the chemical copolymerization of metal alkoxides. The mullite precursor was reacted with zirconium alkoxide in a precursor solution and then hydrolysed. As a result, intimate mixing of the mullite and zirconia precursors on a molecular scale was achieved by the method, from which to prepare nanometer scale composite powders of mullite and zirconia by further heating. A large amount of tetragonal zirconia existed in the composite powders after high temperature calcination because of the small particle size and the constraint forces of the rigid mullite matrix. Furthermore, the tetragonal zirconia in the composite was sensitive to mechanical stress, suggesting transformation toughening of the sintered composites. However, total densification of the precursor compacts was not attained because of the low green density due to agglomeration.

References

1. R. RUH, K. S. MAZDIYASNI and M. G. MENDIRATTA, *J. Amer. Ceram. Soc.* **71** (1988) 503.
2. S. KANZAKI, T. KUMAZAWA, J. ASAUMI, O. ABE and H. TABATA, *Yogyo-Kyokai-Shi* **93**[7] (1985) 407–8.
3. H. SUZUKI and H. SAITO, *ibid.* **95**[7] (1987) 697–702.
4. H. SUZUKI, Y. TOMOKIYO, Y. SUYAMA and H. SAITO, *Nippon-Seramikkusu-Gakujutsuronbun-Shi* **96** (1988) 67–73.
5. H. SUZUKI, H. NAGATA, Y. SUYAMA and H. SAITO, *J. Jpn Soc. Powder and Powder Metall.* **35** (1988) 211.
6. H. TORAYA, M. YOSHIMURA and S. SOMIYA, *J. Amer. Ceram. Soc.* **67** (1984) C-119.
7. D. C. BRADLEY, R. C. MEHROTRA and D. P. GAUR, "Metal Alkoxides" (Academic Press, London, New York, San Francisco, 1978) p. 306.

8. H. SAITO, H. SUZUKI and H. HAYASHI, *J. Chem. Soc. Jpn* [9] (1988) 1571–7.
9. T. IKEMOTO, N. MIZUTANI, M. KATO and Y. MITARAI, *Yogyo-Kyokai-Shi* **93**[9] (1985) 585–6.
10. S. PROCHAZKA and F. J. KG, *J. Amer. Ceram. Soc.* **66**[12] (1983) 874–80.
11. W. E. CAMERON, *Amer. Ceram. Soc. Bull.* **56**[11] (1977) 1003–11.
12. N. L. BOWEN and J. W. GREIG, *J. Amer. Ceram. Soc.* 7[4] (1924) 238–54.
13. R. ROY, *ibid.* **52** (1969) 344.
14. H. SUZKUKI, K. OTA and H. SAITO, *Yogyo-Kyokai-Shi* **95**[2] (1987) 170–5.
15. *Idem, J. Mater. Sci.* **23** (1988) 1534–8.

Received 20 October 1988
and accepted 14 April 1989