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Effect of mechanochemical treatment on the crystallization behaviour of diphasic mullite gel

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Abstract

The effect of mechanochemical treatment on the structure and crystallization behaviour of diphasic mullite gel was investigated. The structural differences caused by mechanochemical treatment in diphasic gel were characterized by ^{27}Al and ^{29}Si MAS-NMR, XRD, DTA-TG and FT-IR. These investigations show that the crystallization process in this system is affected by the structural changes caused by grinding. Grinding for 20 h changed a diphasic system containing discrete octahedral Al–O units (8 ppm) and silica units (−111 ppm) to a more homogeneous system containing tetrahedral, ''pentahedral'' (30 ppm) and octahedral alumina, and a strong ^{29}Si resonance at −83 ppm (≈70% of the total Si) associated with aluminosilicate units. The ground gel converts to mullite via the spinel-phase at 1150–1200°C. Mechanochemical treatment thus converts the diphasic type II gel precursor into a more homogeneous type III gel precursor, as reflected by its thermal behaviour.

Keywords: A. milling; D. mullite; solid-state MAS NMR

1. Introduction

Mullite is an important compound in material science and technology because of its excellent properties (high temperature strength, low thermal expansion, creep resistance and good chemical stability) [1,2]. Mullite can be synthesized from monophasic and diphasic gel obtained either by sol–gel or coprecipitation methods [3–15] leading to the different precursor types described by Schneider et al. [16] The main difference between monophasic and diphasic gels is their homogeneity; monophasic gels are homogeneous at the atomic level and mullite formation occurs by exothermic reaction around 980°C [3,4,12,14,15]. In diphasic gels, homogeneity is in the nanometer range (1 to 100 nm) and mullite formation occurs above 1200°C [3,5,6,8–10,12,14,15]. Diphasic gels consisting of discrete alumina and silica particles do not show an exothermic effect around 980°C, the silica and alumina components reacting independently to form mullite at temperatures >1300°C for complete crystallization [3,10,15].

In our previous experiments [17] we have shown that mechanochemical treatment of mixtures of gibbsite and amorphous silica promoted the formation of Al–O–Si bonds, enhancing the homogeneity of the system, and leading to crystallization of spinel-phase at about 980°C. A further consequence of mechanochemical processing was the lowering of the mullitization temperature. The presence of surface excess hydroxyl groups in the starting material leads to a decrease in the mullitization temperature at about 150–200°C after mechanochemical processing [18].

Since diphasic gel obtained via a liquid medium contains two discrete types of hydroxide particles with homogeneity on a nanometric scale, it is possible that mechanochemical treatment of such a system might produce a precursor with an increased mullitization rate and a reduced mullitization temperature by comparison with an untreated diphasic gel. The mechanochemical process should also be facilitated by starting with gibbsite and silica gel [17,18], which has better initial homogeneity and smaller particle size than hydroxide mixtures.

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The aim of this investigation was to experimentally verify the predicted effect of mechanochemical treatment of diphasic gel.

2. Experimental procedure

2.1. Preparation

The diphasic gel was prepared by dissolving aluminum nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$ (Wako Pure Chemical Industries Ltd) in deionized water and adding fumed silica (Aerosil 200, Aerosil Co. Ltd) during ultrasonic treatment. The dispersion was stirred vigorously and dilute NH_4OH was added to precipitate of the aluminium and silicon hydroxides. The pH of the solution was adjusted to about 8.2 and stirred continuously during the time of the precipitation (30 min). The precipitated gel was filtered, washed and dried at 60°C for 12 h. The composition of the powder was 73.1 wt% Al_2O_3 and 26.9 wt% SiO_2. After grinding in an agate mortar to pass a 145 mesh sieve, a portion of the powder was ground for 20 h in a laboratory pot mill (ITOH Co. Ltd, La-Po.1) at room temperature with rotation speed 400 rpm. Both the pot and milling media were silicon nitride. The weight ratio of balls to powder was 20:1. The ground and unground samples are denoted MC-20 and MC, respectively.

2.2. Characterisation of materials

DTA and TG measurements were carried out using a Rigaku (Thermoplus 8120) analyser at a heating rate of 10°C min^{-1} up to 1300°C. IR spectra of the powders were obtained using an FT-IR 8600 PC spectrometer (Shimadzu Corporation) with the samples suspended in KBr pellets. Powder XRD patterns were recorded using a Rigaku (Geigerflex) diffractometer with monochromated CuK_α radiation. The specific surface area was measured at −196°C by the BET method using nitrogen gas with a Quantachrome Autosorb-1 instrument. ^{29}Si and ^{27}Al MAS-NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and Doty probe spun at 10–12 kHz. The ^{29}Si spectra were acquired using a 90° pulse of 6 μs and recycle time of 100 s, and were referenced to tetramethylsilane (TMS). The ^{27}Al spectra were acquired using a 15° pulse of 1 μs and a recycle time of 1 s, and were referenced to $Al(H_2O)_6^{3+}$.

3. Results and discussion

Fig. 1 shows the DTA–TG traces of the unground and ground powders. Unground diphasic gel shows endothermic peaks at 83 and 468°C due to the dehydration of

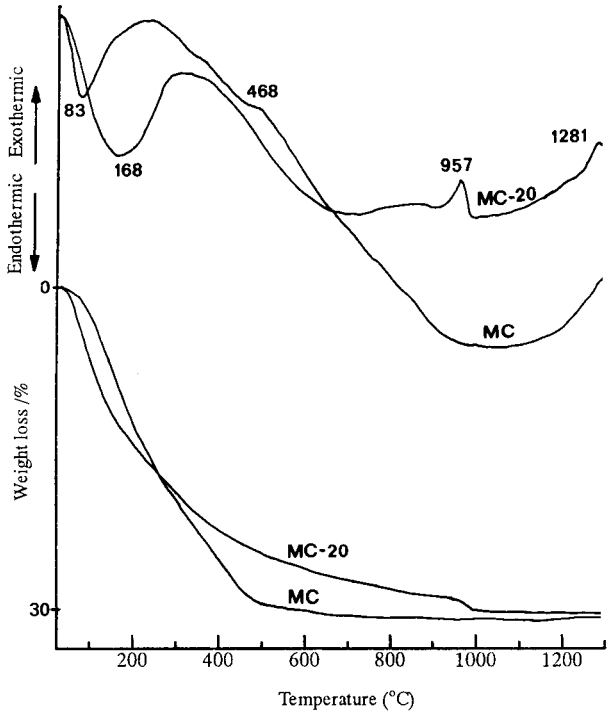

Fig. 1. DTA and TG curves of ground (MC-20) and unground (MC) diphaic gels.

adsorbed water and dehydroxylation of aluminum hydroxide, respectively. There is very little weight change above 600°C. The DTA and TG curve of ground diphasic gel is distinctly different; the DTA endothermic peak is shifted to 168°C and broadened, due to mechanochemical dehydration and increased adsorption of surface water. Mechanochemically-treated diphasic gel shows exothermic peaks at 957 and 1281°C, similar to previous findings [18]. Below 300°C the weight loss of the ground gel is greater than for unground gel, but becomes more gradual >300°C and reaches constant weight only above 1000°C. The 960°C exothermic effect in the ground gel is associated with a 0.75% weight loss. Similar behaviour was reported without explanation by Schneider et al. [19] in coprecipitated mullite gel and by Tsuchida and Ichikawa [20] in hydrous alumina (bayerite, gibbsite and boehmite) ground for 8 and 20 h. Tsuchida and Ichikawa suggest that this weight loss is due to the decomposition of carbonates formed mechanochemically by prolonged grinding [20]. The delayed weight loss in the ground gel may be due to the trapping of H_2O, NO and CO_2 in the small pores of densely-packed aggregates.

Fig. 2 shows the FT-IR spectra from 4400 to 400 cm^{-1} in unground and ground diphasic gel. Both gels show a sharp absorption band at 1384 cm^{-1} due to nitrate or ammonium [10]. The absorption band at about 3450 cm^{-1} is broadened by the presence of increased adsorbed water in the ground gel. Grinding also shifts the Si–O–Si vibration from 1109 cm^{-1} to 1050 cm^{-1}

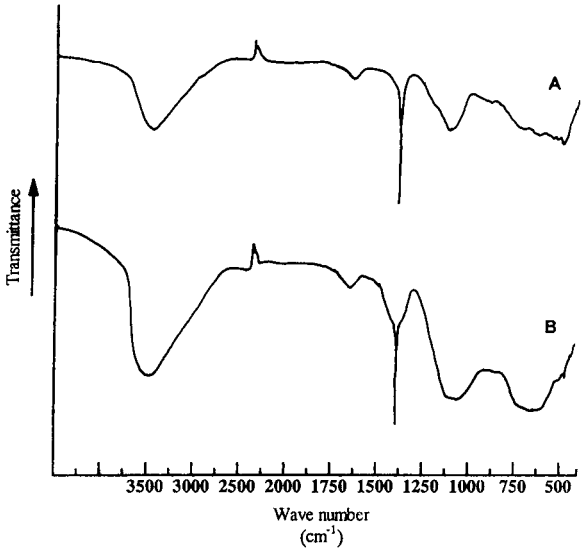

Fig. 2. FT-IR spectra of diphasic gel: (A)-MC; (B)-MC-20.

and broadens the band at 900–1150 cm^{-1}, reflecting the substitution of Si^{4+} by Al^{3+} in the amorphous solid [21,22]. The broadened absorption band at 500–800 cm^{-1} is also similar to those ascribed to four-coordinated aluminium oxide formed by chemical polymerization [23]. Apparently the formation of four coordinated alumina in diphasic gel occurs only with the incorporation of silica.

Fig. 3 shows the ^{27}Al and ^{29}Si solid-state MAS NMR spectra of unground and ground diphasic gel. Both the ^{27}Al and ^{29}Si spectra of the unground gel (Figs. 3(A) and (C), respectively) are typical of a diphasic system containing discrete octahedral Al–O units (8 ppm) and silica units (−111 ppm). Grinding produces some tetrahedral Al sites (61 ppm) and sites giving a resonance at 32 ppm (Fig. 3(B)) which are often ascribed to Al in five-fold coordination with oxygen, but may alternatively arise from distorted tetrahedral sites in the vicinity of an oxygen vacancy (tricluster sites) [24]. This ^{27}Al spectrum is typical of a gel in which the Al and Si are in intimate and homogeneous association. The appearance of a new resonance at −83 ppm in the ^{29}Si spectrum of the ground gel likewise reflects the presence of a significant proportion of the Si (≈70%) associated with aluminosilicate units.

The XRD patterns of unground and ground diphasic gel are shown in Figs. 4 and 5, which also includes the patterns of samples heated to various temperatures. Both the unheated ground and unground gels are essentially amorphous, but the latter shows slight indications of amorphous silica and pseudoboehmite (Fig. 4(A)) which are not present after grinding (Fig. 5(A)).

When heated at 850–1000°C, the unground gel shows evidence of the typically broad γ-Al_2O_3 reflections (Figs. 4(B) and (C)); a similar pattern attributable to a

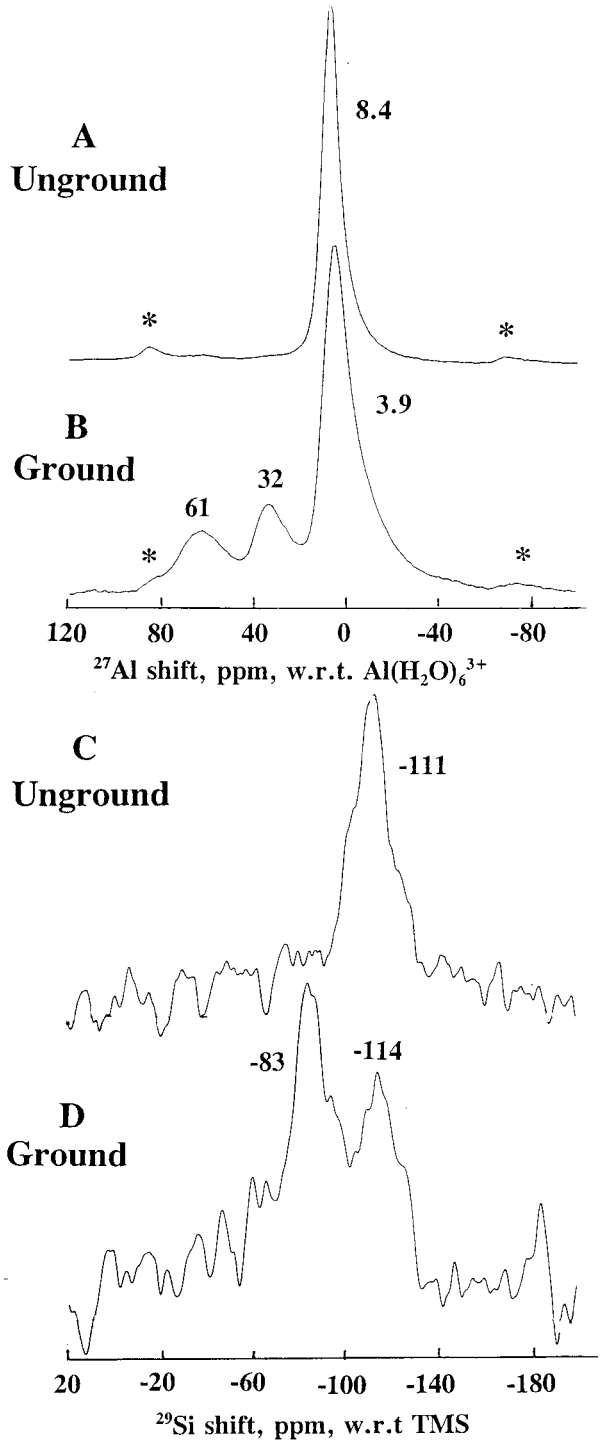

Fig. 3. ^{27}Al and ^{29}Si MAS NMR spectra of unground and ground diphasic gel: (A),(C)- ^{27}Al and ^{29}Si spectra of MC sample; (B),(D)- ^{27}Al and ^{29}Si spectra of MC-20 sample.

cubic spinel, is also found in the ground sample heated to 1000°C (Fig. 5(C)). Heating the unground gel to 1200°C produces the transition θ alumina, α-Al_2O_3, and a small amount of mullite, the latter two phases increasing in concentration at 1300–1400°C (Figs. 4(E) and (F)). This behaviour is similar to that of a type II

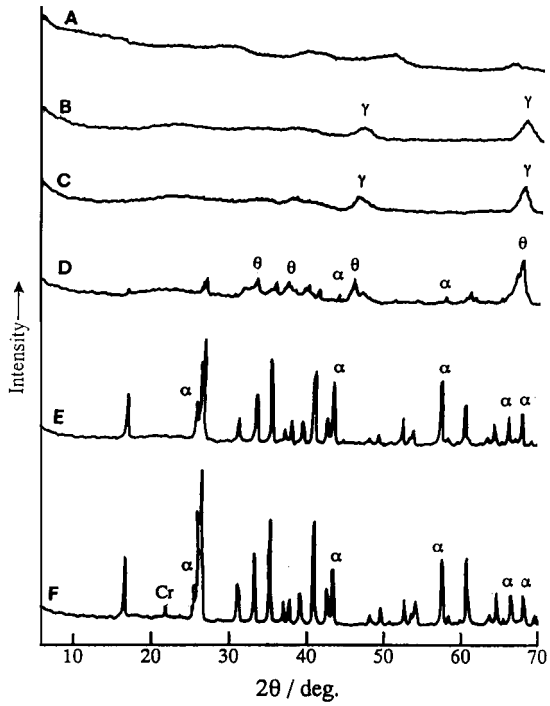

Fig. 4. XRD patterns of unground diphasic gel calcined at different temperatures: (A) uncalcined, (B),(C),(D),(E),(F) after calcining at 850, 1000, 1200, 1300 and 1400°C, α, γ, θ-Al_2O_3, Cr; cristobalite; unmarked peaks; mullite.

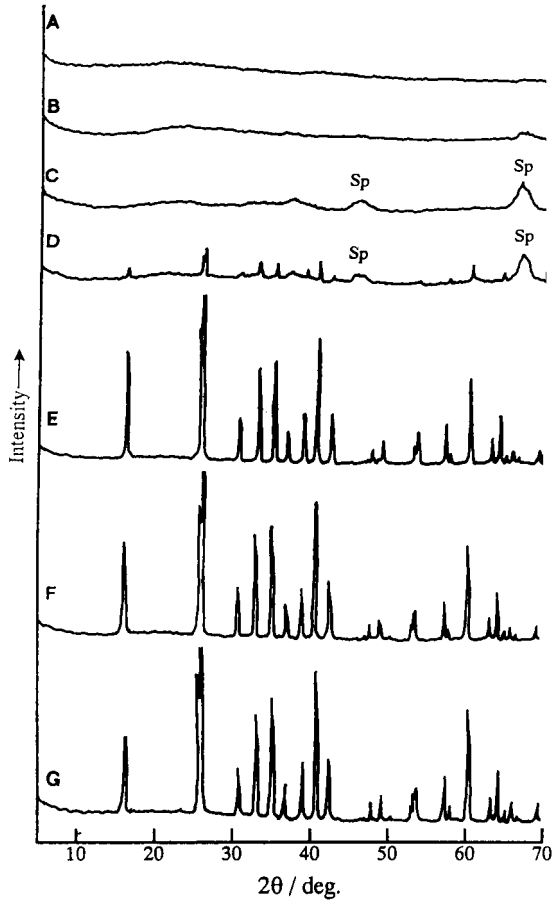

Fig. 5. XRD patterns of ground diphasic gel calcined at different temperatures: (A) uncalcined, sample; (B),(C),(D),(E),(F) and (G) after calcining at 850, 1000, 1150, 1200, 1300 and 1400°C; Sp, spinel-phase, unmarked peaks, mullite.

precursor gel as described by Schneider et al. [16]. By contrast, the ground gel converts, via the spinel-phase, to mullite at 1150–1200°C (Figs. 5(D) and (E)). Similar thermal behaviour has previously been described by Li and Thomson for a colloid gel [14], and also corresponds to the behaviour of a type III precursor as defined by Schneider et al. The exothermic inflexion at about 1280°C in the DTA curve of the ground gel (Fig. 1) may result from the crystallization of additional mullite from minor amounts of mechanochemically distorted amorphous alumina and silica which cannot be distinguished by XRD. These results suggest that the mechanochemical treatment converts the diphasic type II gel precursor into a more homogeneous type III gel precursor.

Fig. 6 shows the change in specific surface area of the unground and ground diphasic gel as a function of calcining temperature. The specific surface area (S_{BET}) and median size d_{50} of the unground diphasic gel is $200\,m^2\,g^{-1}$ and 7.58 μm, respectively. Grinding for 20 h reduces the specific surface area by ≈19 times and the median size to 3.7 μm, suggesting a change in the surface of the gel from a porous to a monolithic state. These data are in agreement with the weight loss curve for the MC-20 sample. The decrease in S_{BET} may cause an increase in the Al/Si contact area attributable to the stuffing of micropores in the aggregates of small particles by the mechanical stress introduced by grinding. When unground and ground powders are calcined at 500°C, the specific surface area increases due to the liberation of nitrate and water. At higher calcination temperatures the particles begin to sinter, with a decrease in surface area.

The formation mechanism of diphasic gel involves the precipitation of pseudoboehmite and silica gel under weakly basic conditions. The precipitation is too fast to allow chemical bonding to develop between the two dissimilar molecules and the compounds remain discrete. By contrast, the ground diphasic gel is not a mixture of colloidal pseudoboehmite and silica, but contains polycondensed and polymerized particles of Al–O–Si resulting from the mechanical treatment, which enhances the short range diffusion of Al^{3+} near the silica/alumina interface with consequent chemical interaction. The polymerization is not sufficiently complete for mullite to form directly at 980°C. As reported Huling and Messing [25], direct mullite formation at ≈1000°C requires not only molecular-scale alumina–silica mixing, but nearly complete molecular-scale mixing.

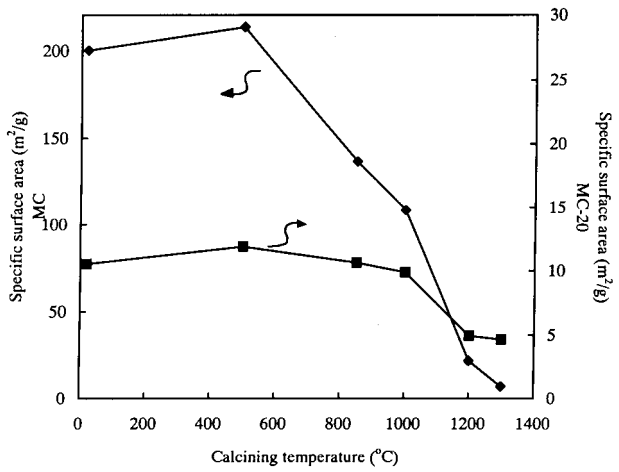

Fig. 6. Change of specific surface area of MC and MC-20 samples as a function of calcining temperature.

Full polymerization may not be achieved during the dry grinding, because of agglomeration of part of the sample on the bottom of the grinding vessel resulting in these portions remaining inhomogeneous.

The mullite which develops during calcining was characterized by FT-IR spectroscopy (Fig. 7). Cameron [26] and Okada et al. [27] have reported a relationship between the chemical composition of mullite and its absorption bands at 1130 and 1170 cm^{-1}. The 1130 cm^{-1} band is stronger than that at 1170 cm^{-1} when the chemical composition of mullite is richer in Al_2O_3, but the 1170 cm^{-1} band becomes much stronger as the composition approaches 60 mol% Al_2O_3. In the present sample heated to 1300°C, the intensity of the 1130 and 1170 cm^{-1} bands is almost identical, but at higher temperatures (1400 and 1500°C) the 1170 cm^{-1} band predominates, suggesting a progressive decrease in Al_2O_3 content as heating proceeds and the composition approaches that of 3:2 mullite.

4. Conclusions

Mechanochemical treatment of diphasic gel is found to promote Al–O–Si polymerization between the silica and alumina gel components. Mullite formation in ground diphasic gel begins at a lower temperature (1150°C) than in the unground diphasic gel. The crystallization behaviour of mechanochemically-treated diphasic gel is similar to that of type III mullite precursors. Initially, the mullite is alumina-rich in composition, but gradually approaches the stoichiometric composition at higher temperatures. Mechanochemical treatment could provide a useful technique for synthesizing mullite from diphasic gel which can be obtained from cheap raw materials.

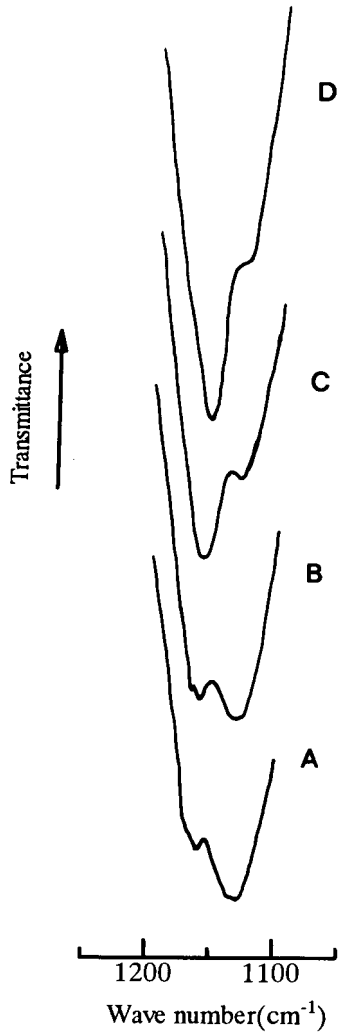

Fig. 7. Portion of the FT-IR spectra of MC-20 samples calcined at different temperatures: (A) 1200, (B) 1300, (C) 1400 and (D) 1500°C.

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References

[1] I.A. Aksay, D.M. Dabbs, M. Sarikaya, Mullite for structural, electronics, and optical applications, J. Am. Ceram. Soc. 74 (1991) 2343–2357.
[2] S. Somiya, R. F. Davis, J. A. Pask, (Eds.) Ceramic Transactions, Vol. 6, Mullite and Mullite Matrix Composites, American Ceramic Society, Westerville, OH, 1990.
[3] D.W. Hoffman, R. Roy, S. Komarneni, Diphasic xerogels, a new class of materials: phases in the system Al_2O_3–SiO_2, J. Am. Ceram. Soc. 67 (1984) 468–471.
[4] B.E. Yoldas, Effect of ultrastructure on crystallization of mullite, J. Mater. Sci. 27 (1992) 6667–6672.
[5] K. Hamano, T. Sato, Z. Nakagawa, Properties of mullite powder prepared by coprecipitation and microstructure of fired bodies, Yogyo-Kyokai-Shi 94 (1986) 818–822.

[6] S. Rajendran, H.J. Rossell, J.V. Sanders, Crystallization of a coprecipitated mullite precursor during heat treatment, J. Mater. Sci. 25 (1990) 4462–4471.
[7] M. Zhou, J.M.E. Ferreira, A.T. Fonseca, J.L. Baptista, Coprecipitation and processing of mullite precursor phases, J. Am. Ceram. Soc. 79 (1996) 1756–1760.
[8] J.S. Ha, K.K. Chawla, The effect of precursor characteristics on the crystallization and densification of diphasic mullite gels, Ceram. Int. 19 (1993) 299–305.
[9] A.K. Chakraborty, Role of hydrolysis water–alcohol mixture on mullitization of Al_2O_3–SiO_2 monophasic gels, J. Mater. Sci. 29 (1994) 6131–6138.
[10] J.S. Lee, S.C. Yu, Characteristics of mullite prepared from coprecipitated $3Al_2O_3{\cdot}2SiO_2$ powders, J. Mater. Sci. 27 (1992) 5203–5208.
[11] A.K. Chakraborty, Effect of pH on 980°C spinel phase-mullite formation of Al_2O_3–SiO_2 gels, J. Mater. Sci. 29 (1994) 1558–1568.
[12] I. Jaymes, A. Douy, D. Massiot, J.P. Coutures, Characterization of mono- and diphasic mullite precursor powders prepared by aqueous routes. ^{27}Al and ^{29}Si MAS-NMR spectroscopy investigations, J. Mater. Sci. 31 (1996) 4581–4589.
[13] S.K. Saha, P. Pramanik, Aqueous sol–gel synthesis of mullite powder by using aluminium oxalate and tetraethoxysilane, J. Mater. Sci. 29 (1994) 3425–3429.
[14] D.X. Li, W.J. Thomson, Effects of hydrolysis on the kinetics of high-temperature transformations in aluminosilicate gels, J. Am. Ceram. Soc. 74 (1991) 574–578.
[15] J.S. Hong, X.X. Huang, J.K. Guo, Synthesis and sintered properties of mullite powder from seeded diphasic Al_2O_3–SiO_2 gel, Mater. Lett. 24 (1995) 327–331.
[16] H. Schneider, B. Saruhan, D. Voll, I. Merwin, A. Sebald, Mullite precursor phases, J. Eur. Ceram. Soc. 11 (1993) 87–94.
[17] J. Temuujin, K. Okada, K.J.D. MacKenzie, Characterization of aluminosilicate (mullite) precursors prepared by a mechanochemical process, J. Mater. Res., in press.
[18] J. Temuujin, K. Okada, K.J.D. MacKenzie, Formation of mullite from mechanochemically activated oxides and hydroxides, J. Eur. Ceram. Soc., in press.
[19] H. Schneider, L. Merwin, A. Sebald, Mullite formation from non-crystalline precursors, J. Mater. Sci. 27 (1992) 805–812.
[20] T. Tsuchida, N. Ichikawa, Mechanochemical phenomena of gibbsite, bayerite and boehmite by grinding, Reactivity of Solids 7 (1989) 207–217.
[21] A.K. Chakraborty, D.K. Ghosh, Synthesis and 980°C phase development of some mullite gels, J. Am. Ceram. Soc. 71 (1988) 978–987.
[22] K. Okada, N. Otsuka, Characterization of the spinel phase from SiO_2–Al_2O_3 xerogels and the formation process of mullite, J. Am. Ceram. Soc. 69 (1986) 652–656.
[23] B. Yoldas, Formation and modification of oxide networks by chemical polymerization, Mat. Res. Soc. Symp. Pros. 24 (1984) 291–297.
[24] M. Schmucker, H. Schneider, A New approach to the coordination of Al in non crystalline gels and glasses of the system Al_2O_3–SiO_2, Ber. Bunsenges. Phys. Chem. 100 (1996) 1550–1553.
[25] J.C. Huling, G.L. Messing, Epitactic nucleation of spinel in aluminosilicate gels and its effect on mullite crystallization, J. Am. Ceram. Soc. 74 (1991) 2374–2381.
[26] W.W. Cameron, Composition and cell dimensions of mullite, Ceram. Bull. 56 (1977) 1003–1011.
[27] K. Okada, Y. Hoshi, N. Otsuka, Formation reaction of mullite from SiO_2–Al_2O_3 xerogels, J. Mater. Sci. Let. 5 (1986) 1315–1318.