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Effect of Seeds on the Formation of Sol–Gel Mullite

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Abstract: Mullite precursor gels have been prepared from a mixture of particulate boehmite sol and tetraethoxysilane at a pH of 4. The sol has been seeded with submicron size α-Al_2O_3, γ-Al_2O_3 and mullite limited to two percent by weight of the mullite phase. These gels have been invesitgated with respect to phase formation, densification and microstructural development. Dilatometric studies on the seeded precursor gels indicate marked shrinkage in their profiles. Of the different seed nuclei, fine mullite particles have shown excellent influence in the early ceramic phase formation as well as densification. Further they induce complete transformation of the precursor gel to the high temperature phase as well as a uniform fine-grained microstructure. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Mullite ($3Al_20_32SiO_2$), the stable crystalline phase in the alumina–silica system has several attractive characteristics as an advanced structural material, such as chemical stability with oxygen at high temperature, low creep rate and reasonable thermal expansion coefficient.[1] Mullite is also a candidate ceramic substrate in multilayer packagings.[2] Specially processed mullite is identified as a window material in the mid IR range.[3,4] The synthesis route for mullite is often decided by the type of end use.[4,5] Various processing techniques such as solid-state mixing, coprecipitation from mixed salt solution[6,7] and sol–gel methods involving both particulate sols and alkoxides[8,9] are reported. The scale of chemical homogeneity of the precursor plays the major role in deciding the mechanism of mullite formation as well as the temperature of complete mullitization. Mullite phase is reported at 980°C[10] from monophasic precursors and at still higher temperatures of 1300°C[11] from diphasic ones. A promising way of obtaining low temperature mullite is by use of crystalline seeds as in the case of boehmite derived alumina.[12] Seeding by appropriate nuclei in precursor systems such as aluminium titanate and cordierite has yielded low temperature phases with enhanced densification.[13] Transformation in sol–gel ThO_2–SiO_2[14] and ZrO_2–SiO_2[15] systems is also influenced by seed nuclei. Addition of crystalline seeds to premullite sol, as well as the development of grain morphology,[16] has been reported in brief previously. The present work concentrates on mullite precursor sol seeded systematically with different seed nuclei such as mullite, γ-Al_2O_3 and α-Al_2O_3 in separate experiments. The effect of seeds on phase formation and microstructural development are studied. Boehmite sol and tetraethylorthosilane (TEOS) were used as the precursors for Al_2O_3 and SiO_2, respectively.

2 EXPERIMENTAL PROCEDURE

Stoichiometric mullite precursor gels were prepared by reacting boehmite sol and tetraethylorthosilane (Alfa Chemicals, USA). Boehmite sol was prepared by the method reported earlier.[17] In a typical experiment 19.622ml of TEOS was added dropwise to 855.12 ml of boehmite sol (1.68×10^{-2}g Al_2O_3/ml sol) during vigorous stirring, keeping the pH of the mixture at 4. The mix-

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ture was stirred for about 5 h to achieve maximum homogeneity, aged for 10 h and concentrated to half the volume. Fine-grained mullite seed suspensions and 2% by weight of α-Al_2O_3, γ-Al_2O_3 were added to the boehmite–TEOS mixture in separate experiments. All the mullite precursor gels were dried at 60°C and calcined for 2 h at 1200°C, 1225°C and 1300°C.

Thermal analysis of the mullite gel precursors was carried out in a Shimadzu TGA-50H and DTA-50H thermal analyser. XRD patterns of the samples were taken using a Rigaku X-ray diffractometer (Model Dmax/2C, Japan) with Ni filtered CuKα radiation. TMA analysis of the samples was done in a Shimadzu TMA-50H at a heating rate of 5°C/min up to 1450°C in nitrogen atmosphere. The scanning electron micrographs of the fractured surface of the samples sintered at 1550°C and of the TMA samples heated at 1450°C were taken in a Hitachi S-2400 (Japan) scanning electron microscope.

2.1 Preparation of mullite seed suspension

Mullite seeds were prepared from phase pure mullite prepared by calcining at 1250°C for 5 h. The phase puritry was confirmed by XRD. Five grammes of mullite powder was dispersed in 200 ml of distilled water at pH 3, ultrasonically treated for 30 min and then ball milled in a poly vinyl chloride (PVC) container for 30–40 h. The fines from this lot were separated by suspension. The seed used had a concentration of 1.49 g/litre.

2.2 Preparation of α- and γ-alumina seed suspensions

α- and γ-alumina seed suspensions were prepared from powders obtained by calcining 5 g each of boehmite (Condea Chemicals, Germany) over a period of 5 h at 1200°C and 10 h at 750°C, respectively and subjected to a procedure similar to that described for the preparation of mullite seed. Concentrations of 1.65 g/litre for α-alumina and 1.45 g/litre for γ-alumina were used.

3 RESULTS AND DISCUSSION

The thermogravimetric curve [Fig. 1(a)] of the mullite seeded precursor, indicates a three step decomposition involving weight losses both due to absorbed water, the organics and the chemically bound gel water. The major decomposition peak is supported by an endothermic transition at about 250°C [Fig. 1(b)]. The weak endotherm above 300°C could be due to formation of precursor oxide phases along with the elimination of bonded water. The small exothermic peaks at higher temperature are due to mullite from particulate precursors, this usually being above 1250°C (Fig. 2). A partially amorphous precursor with prominent peaks for transition alumina phases could be seen on samples heated at 1200°C. The XRD patterns of the seeded and unseeded mullite samples heated at 1200°C for 2 h are presented in Fig. 3. The mullite phase in the seeded sample is indicated even at a temperature of 1200°C. A close look at these XRD patterns shows that the preferential formation of mullite phase has started in the seeded precursor sample [Fig. 3(b),(c) and (d)].Further, at a low temperature of 1225°C sharp crystalline mullite peaks were observed in the case of all the seeded mullite gels (Fig. 4), while this happens only at higher temperatures (around 1300°C) in the unseeded one with preferential phase formation in the mullite seeded precursor (Fig. 5).

Seeding of boehmite with fine α-Al_2O_3 has shown a reduction of phase formation temperature for α-Al_2O_3 up to 150°C.[18] Seeding introduces preferred nucleation sites in the form of low energy

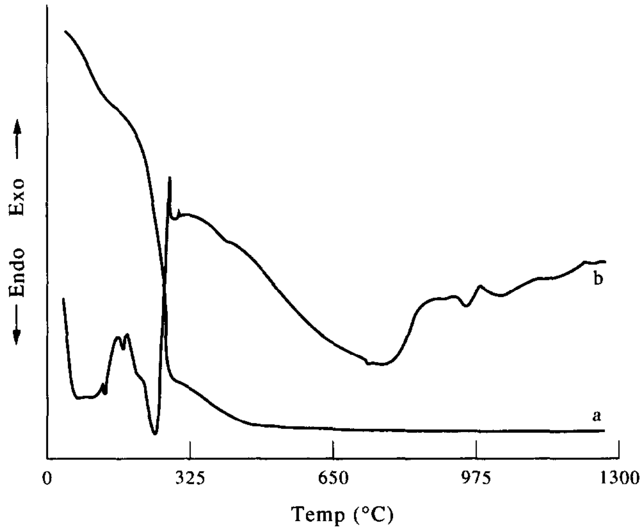

Fig. 1. (a) Thermogravimetric curve of mullite seeded precursor gel. (b) DTA of mullite seeded precursor gel.

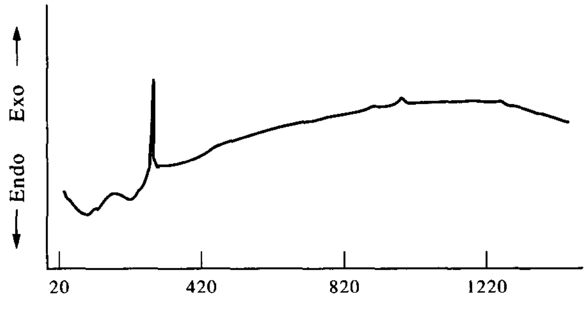

Fig. 2. DTA of mullite precursor gel without seed.

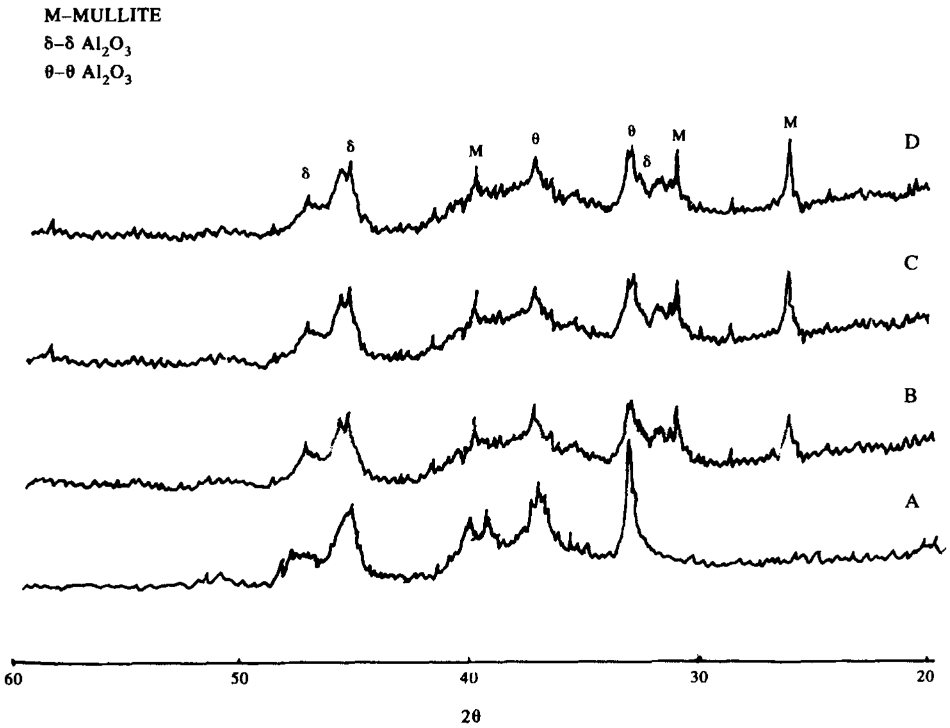

Fig. 3. XRD patterns of mullite precursor gels calcined at 1200°C. (A) Without seed. (B) With γ-alumina seed. (C) With α-alumina seed. (D) With mullite seed.

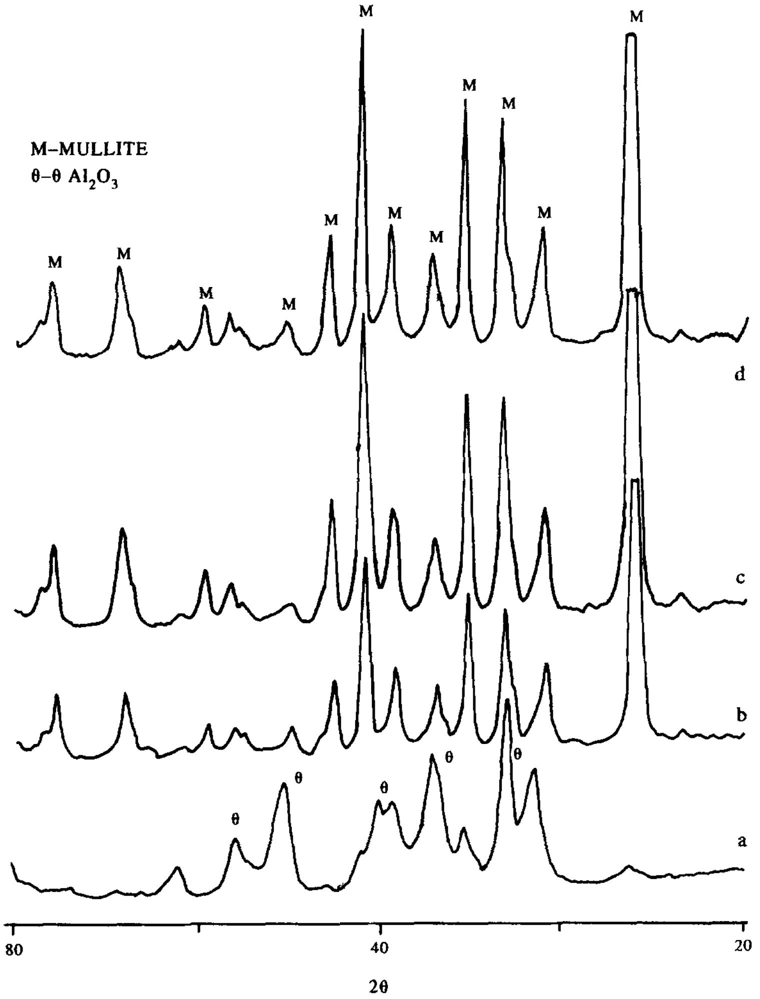

Fig. 4. XRD patterns of mullite precursor gels calcined at 1225°C. (a) Without seed. (b) With γ-alumina seed. (c) With α-alumina seed. (d) With mullite seed.

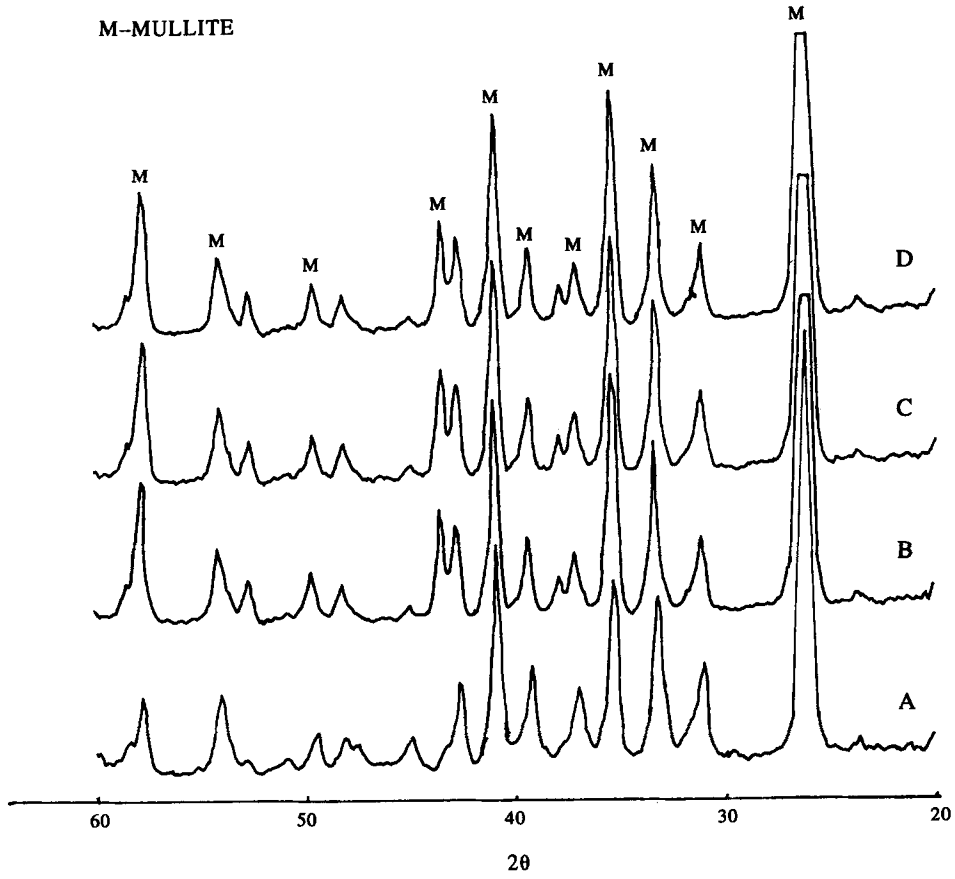

Fig. 5. XRD patterns of mullite precursor gels calcined at 1300°C. (A) Without seed. (B) With γ-alumina seed. (C) With α-alumina seed. (D) With mullite seed.

epitaxial interfaces, thereby increasing nucleation frequency in the thermally activated nucleation process.[19] Thus, use of seeds isostructural with the final ceramic phase should result in low temperature formation by enhancing the nucleation and growth process. Seeding mullite precursor gel with γ-Al_2O_3 and α-Al_2O_3 would preferentially promote the low temperature α-Al_2O_3 phase which should then influence formation of mullite. On the other hand, mullite seeds added to the precursor gel in the fine form, directly, should influence the early formation of the mullite phase. The linear thermal expansion measurement indicates that there is a small shrinkage at about 175°C. Further, there is a two step shrinkage corresponding to 952°C and 1200°C [Fig. 6(a)] in the unseeded sample, which should be due to the transition alumina phase and the pre-mullite formation as generally reported. When 2% α-Al_2O_3 is used as the seed, a sharp shrinkage is recorded at 975°C. This is according to the reported value for the α-Al_2O_3 seed in boehmite. Since the α-Al_2O_3 phase formation is the preferred transformation, further formation of mullite is delayed and takes place only above 1250°C [Fig. 6(b)].

Use of γ-Al_2O_3 seed [Fig. 6(c)] appears to promote the transition to the alumina phase first at

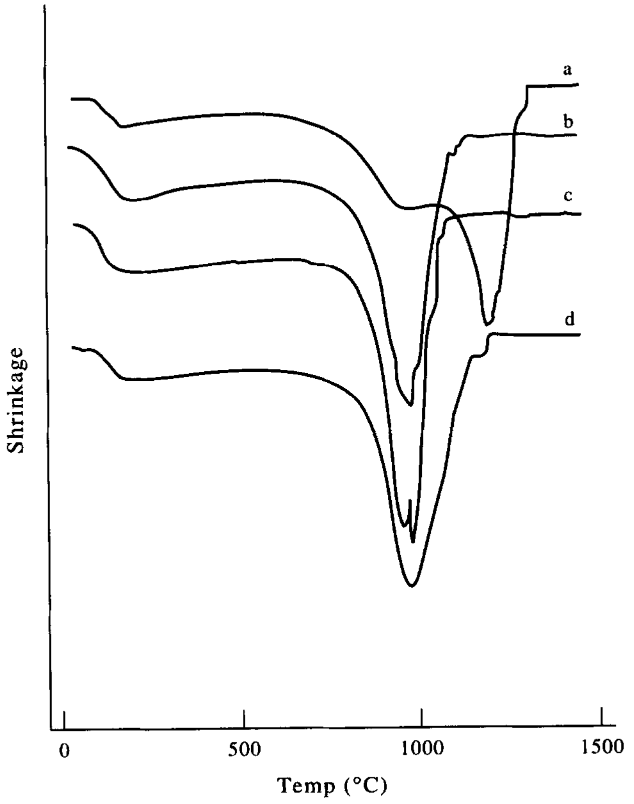

Fig. 6. Derivative of dilatometric curves of mullite precursor gels heated to 1450°C. (a) Without seed. (b) With α-alumina seed. (c) With γ-alumina seed. (d) With mullite seed.

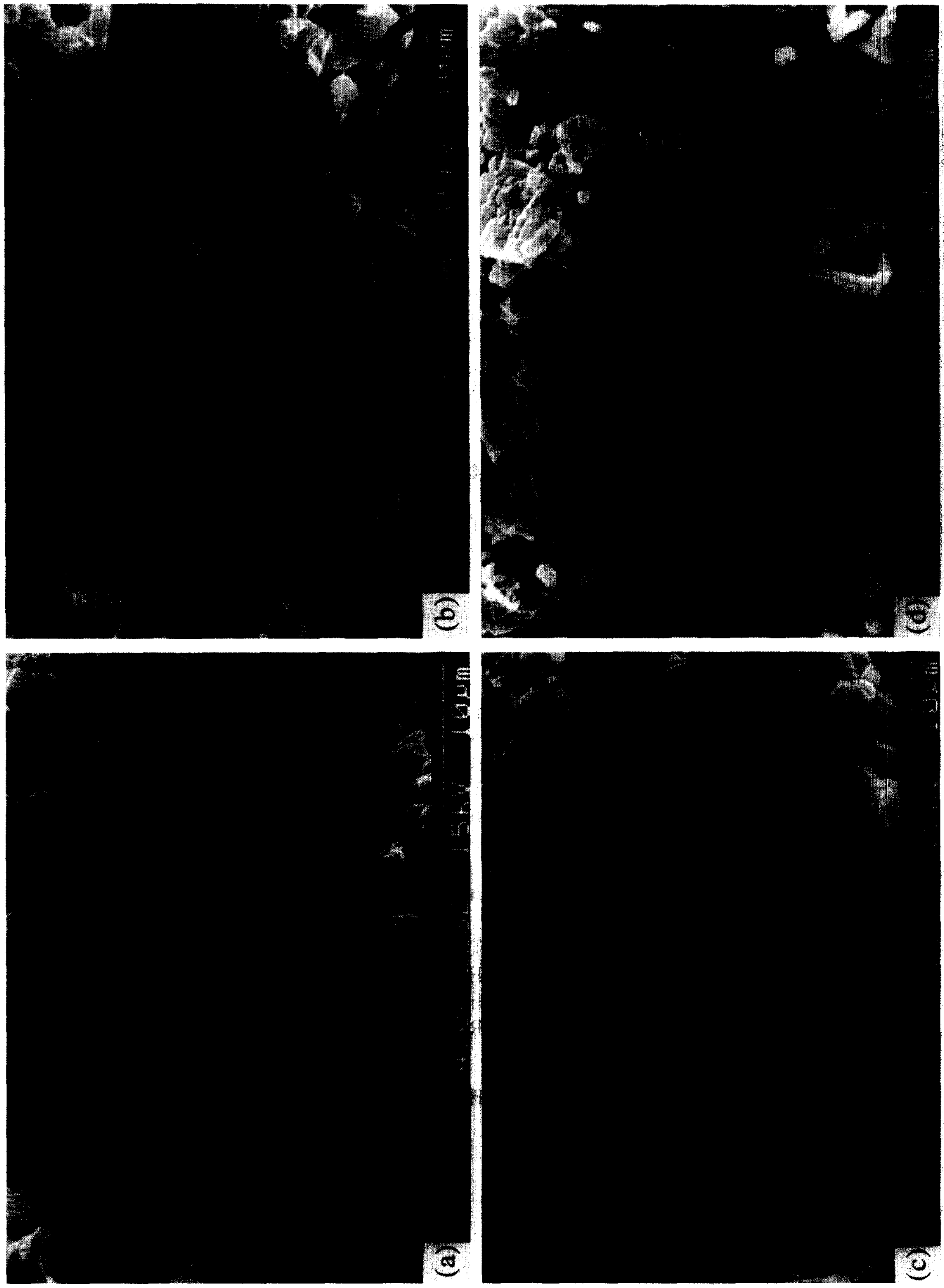

Fig. 7. SEM fractographs of sintered mullite (1550°C). (a) Without seed. (b) With α-alumina seed. (c) With γ-alumina seed. (d) With mullite seed.

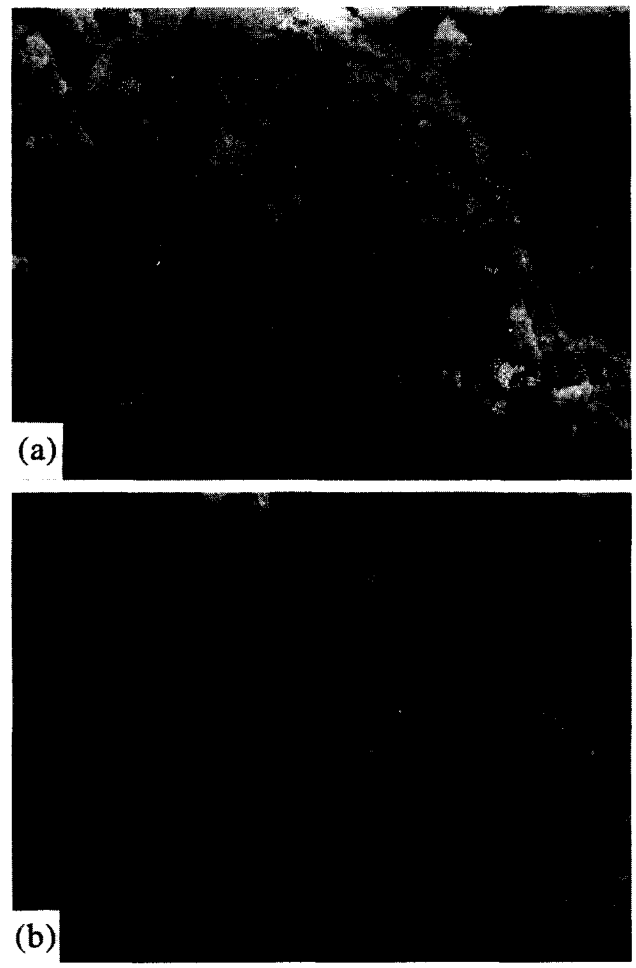

Fig. 8. SEM fractographs of mullite precursor heated to 1450°C. (a) With mullite seed. (b) Without seed.

about 940°C, followed at about 960°C. The mullite formation is in line with that of α-Al_2O_3 addition except that the reactivity is higher. Mullite seeds further enhance the high temperature formation of phases in view of its isostructural features with the final phase, and hence only one major shrinkage is found at about 973°C and the peak width is also larger, indicating the completion of the reaction. However, the further shrinkage at < 1300°C possibly indicates early mullite phase as well as sintering [Fig. 6(d)]. Comparing the shrinkage features in general, the value for mullite without seed at 1350°C is comparable with those at 1200°C in other compositions. The microstructural examination of the fractured surface of mullite without seed sintered at 1550°C indicates localised areas of high density and also a morphology with occasional large grain growth [Fig. 7(a)]. In presence of α-Al_2O_3 seed, the morphology appears to have finer grain size [Fig. 7(b)]. The addition of α-Al_2O_3 seed enhances the conversion of α-Al_2O_3 phase and the mullite is formed due to reaction between *in situ* nucleated fine α-Al_2O_3 and silica, resulting in finer grain size. On the other hand, the γ-Al_2O_3 seeds assist in formation of α-Al_2O_3 and later mullite phase. Because of the better consolidation, it has been possible to identify small, uniform grain size in the fractograph [Fig. 7(c)].

Mullite seed appears to have definitely resulted in enhanced density, low grain size and uniform grain pattern in the final ceramic because of its isostructural nature. The average grain size is of < 1 μm [Fig. 7(d)] with sintered localised areas consisting of cracks formed during the dehydroxylation. The precursor gel piece, with and without mullite seed, sintered at 1450°C with no soaking period presented in Fig. 8 indicates this difference more clearly. The complete mullitization has not taken place in samples without seed nuclei at low temperatures, resulting in localised minor silica rich phases promoting densification. The mullite seeded sample is more homogeneous in morphology and has relatively uniform grain structure.

4 CONCLUSION

The present study indicates the possibility of obtaining sintered pure mullite having uniform grain structure at relatively lower temperatures by appropriately seeding the mullite precursor gels. Out of the various seeds attempted, mullite seeds, isostructural with the final ceramic phase have been found to be most effective. However, the γ-Al_2O_3 seed addition also brings down the temperature of formation of mullite, but appears to be resulting in grain growth in the sintered ceramic. The possibility of the use of a mixture of seeds in such ceramic systems should yield excellent results.

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