

Low-Temperature Mullitization in Boehmite-Tetraethoxysilane Gel Precursor Containing γ -Alumina and Mullite Nucleating Seeds

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Received March 9, 1998. Revised Manuscript Received June 4, 1998

The formation of mullite from diphasic mullite gels of stoichiometric composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ through a mixture of seed nuclei has been studied. The precursor gels are prepared from boehmite (AlOOH) sol and tetraethoxysilane (TEOS) seeded with mullite (2 wt %) and γ - Al_2O_3 (2 wt %) individually and as a mixture consisting of γ - Al_2O_3 (1 wt %) and mullite (1 wt %). The phase formation in such gels has been compared with sample containing no seeds. The presence of mullite is observed as early as 1150 °C in the mixed seeded sample, while in the unseeded one, this is observed only at 1250 °C, as reported generally. On the otherhand, the mullitization reaction has been initiated at a temperature of 1200 °C in gels seeded separately with 2 wt % γ - Al_2O_3 and 2 wt % mullite. The results suggest that the mechanism of mullite formation in seeded gel is similar to that of diphasic gels in which the transitional alumina–amorphous silica reaction predominates to form mullite. Mixed seeding appears to be appreciably favorable in reducing the transformation temperature of mullite compared to the individually seeded counterparts and also results in a finely grained dense microstructure.

Introduction

Mullite, $\text{Al}_6\text{Si}_2\text{O}_{13}$, has received much attraction during the past decade as a potential matrix material for high-temperature structural applications.^{1–3} Different approaches have been adopted to synthesize phase-pure mullite, such as solid-state mixing of fine oxides of alumina and silica, coprecipitation from mixed salt solutions, and sol–gel methods involving both particulate sols and alkoxides.^{4–8} The sol–gel method is found to be one of the best for its preparation, especially in view of the excellent homogeneity of the precursor phases.⁹ The formation characteristics of mullite depend largely on the nature of precursors. Molecular level mixing of the aluminum and silicon species and low-temperature crystallization of mullite at around 980 °C by an exothermic reaction are reported in precursors involving an aluminum salt and TEOS.¹⁰ On the other hand, in diphasic colloidal gels obtained by mixing sols of boehmite and silica, the crystallization takes place in the range 1250–1350 °C.¹¹ The nucleation process

of formation of spinel is believed to be diffusion-controlled on one hand but also limited by alumina solubility, nevertheless being rapid in colloidal gels. Microcomposite particles which consist of an α -alumina core and amorphous silica coating form mullite phase only above 1500 °C, through an endothermic reaction, even though full densification is achieved at as low as 1300 °C.^{12,13}

A nucleation and growth process is known to be associated with transformation from particulate gel precursors to mullite, and introduction of extremely fine ceramic particles of isostructural/isotypic nature (also known as nucleating seeds) enhances the possibility of crystallization of the ceramic phase. α -Alumina particles were first shown to act as nuclei by Messing¹⁴ in the transformation of boehmite to α -alumina by lowering the transformation temperature by as much as 170 °C. Suwa et al. investigated the effect of different types of seeds in the structurally diphasic Al_2O_3 –MgO xerogels and found that only isostructural seeds contribute in lowering the crystallization temperature.¹⁵ In addition to the reduction in transformation temperature and enhanced transformation kinetics, low-temperature densification also was reported in the presence of nucleating seeds in boehmite gel by Messing et al.^{16,17} A 10% increase in apparent density compared to the unseeded one has been observed by Komarneni et al.¹⁸ for a 93%

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Al₂O₃-7% MgO triphasic xerogel composition seeded with α -alumina or a mixture of α -Al₂O₃ and MgAl₂O₄ at 1200 °C. McArdle et al.¹⁹ showed earlier that the presence of γ -Al₂O₃ seed particles in boehmite gel enhanced formation and densification of transitional alumina. Huling and Messing proposed hybrid gels, derived from a mixture of polymerically and colloiddally derived sols, for microstructure control as well as small reduction in mullite crystallization temperature. The polymeric gel crystallizes in situ to form mullite, which acts as seed crystals for the homoepitactic nucleation for the colloidal components of the gels.²⁰ A reduction of 30 °C in crystallization temperature was observed in DTA by the use of 5 wt % mullite crystalline seeds.²¹ A variety of microstructures were observed by Morz and Laughner with different mullite seed concentration ranging from whiskerlike grains to an equiaxed grain microstructure for low to high volume concentration.²² Sacks et al. introduced 2 wt % mullite seeds to the microcomposite particles, and a reduction of about 200 °C was achieved in the formation temperature.²³ Recently Hong et al. reported a decrease of ~30 °C in mullite formation with 10 wt % mullite seeds.²⁴ Most of the workers have used 2–10 wt % mullite seeds in the mullite precursor system to study the phase development and densification behavior. Hence it appears that in the presence of an enhanced transition alumina phase, the mullite transformation can be done more effectively with mullite seeds. Both these aspects can be achieved by introducing a mixture of suitable seed nuclei, which is being reported for the first time. Therefore this novel work concentrates on the preparation of mullite phase from boehmite-TEOS precursor seeded with a mixture of γ -alumina and mullite. The effect of such a combination of seeds on phase formation and microstructure development are reported.

Experimental Procedure

In the present work boehmite and TEOS were used as the precursors for Al₂O₃ and silica, respectively. Boehmite (Al(OH)₃) sol was prepared from aluminum nitrate (Qualigens) by a process reported earlier.²⁵ Seeded diphasic mullite precursor gel was prepared by dropwise addition of 19.62 mL of TEOS into 855.12 mL of boehmite sol (1.62 × 10⁻² g of Al₂O₃/mL) under stirring to get a stoichiometric composition of 3Al₂O₃·2SiO₂. To this mixture, which was kept at pH 4, were added mullite seed (2 wt %), γ -alumina (2 wt %), and a combination of γ -alumina (1 wt %) and mullite (1 wt %) seed suspension in separate experiments. The mixture was ball milled for 10 h and concentrated to half the volume. The concentrated sol was then dried at 45 °C and 65% relative humidity and calcined in the range 1150–1400 °C. Thermal analysis of the precursor

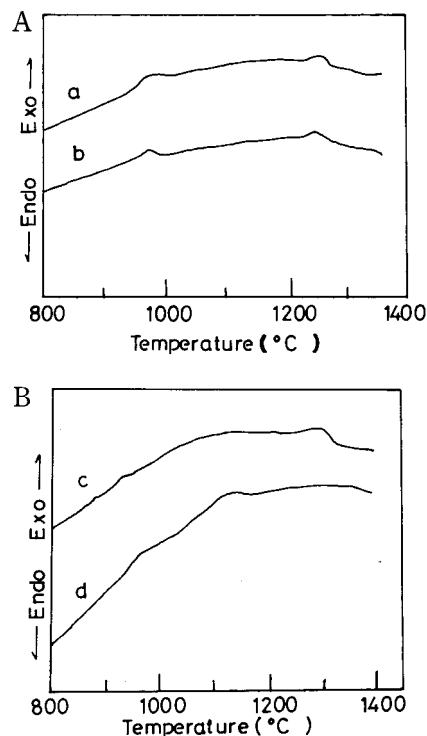


Figure 1. (A) DTA patterns of mullite precursor gel having (a) 2 wt % γ -alumina seed or (b) 2 wt % mullite seed. (B) DTA patterns of mullite precursor gel (c) without seed, (d) with γ -alumina (1 wt %) + mullite (1 wt %) seed.

gels was done in a Shimadzu DTA 50 H thermal analyzer in a flowing nitrogen atmosphere at a heating rate of 10 °C/min. Phase analysis of the calcined gels was done using an X-ray diffractometer (Philips 1710) with Ni-filtered Cu K α radiation. The samples calcined at 850 °C were made into pellets of 10 mm diameter and 2 mm thickness by uniaxial pressing at a pressure of 250 MPa and sintered to 1350 °C/4 h at a heating rate of 15 °C/min. The sintered densities were measured using Archimedes' principle. The fractographs of the sintered samples were taken using a Hitachi S-2400 scanning electron microscope.

Preparation of Mullite Seed Suspension. Mullite seed suspension was prepared from the powder obtained by calcining the mullite precursor gel at 1300 °C for 5 h. A 5 g portion of mullite powder was ultrasonically dispersed in 200 mL of distilled water at pH 3.5 for 30 min, followed by ball milling in a poly(vinyl chloride) (PVC) container using mullite balls for 15 h. The fines from this lot were separated by sedimentation. The seed used had a concentration of 1.49 g/L.

Preparation of γ -Alumina Seed Suspension. γ -Alumina seed suspension was prepared from γ -alumina powder obtained by calcining 7 g of boehmite (Condea Chemicals) over a period of 10 h at 750 °C. A 5 g sample of the calcined powder was dispersed by sonication for 30 min in 200 mL of distilled water at pH 3.5, followed by ball milling for 15 h in a PVC container using alumina balls. The fines from this lot were separated by sedimentation. The seed suspension used had a concentration 1.45 g/L.

Results and Discussion

In the sol-gel transformation to the final phase by nucleation-growth process, it is generally observed that addition of certain seed particles to the ceramic precursor reduces the transformation temperature and also helps to control the sintered grain size.¹⁷ The differential thermal analysis curves of precursor gel with and without seed are presented in Figure 1A,B. The gel without seed transforms to mullite at about 1250

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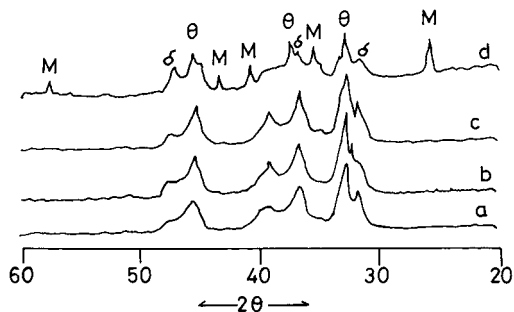


Figure 2. XRD patterns of mullite precursor gel heated at 1150 °C (a) without seed, (b) with 2 wt % mullite seed, (c) with 2 wt % γ -alumina seed, and (d) with γ -alumina + mullite seed (M, mullite; θ , θ -alumina; δ , δ -alumina).

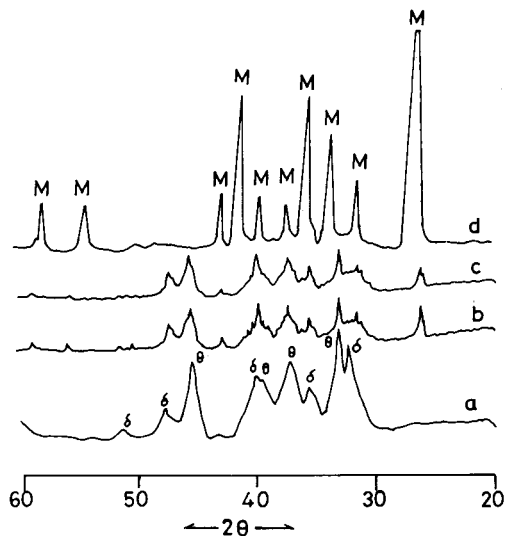


Figure 3. XRD patterns of mullite precursor gel heated at 1200 °C (a) without seed, (b) with 2 wt % mullite seed, (c) with 2 wt % γ -alumina seed, and (d) with γ -alumina + mullite seed (M, mullite; θ , θ -alumina; δ , δ -alumina).

°C, indicated by a small broad exotherm in the DTA curve through a small one at ~ 980 °C. A similar trend is observed in the seeded sample also. However, the exotherm temperature indicating the formation of mullite is reduced due to the seed addition. For the sample with 2 wt % γ - Al_2O_3 and 2 wt % mullite, the mullitization temperature is around 1200–1225 °C, while when a mixture of seeds is employed, this has been further reduced to 1150–1200 °C.

The XRD pattern of the gel heated at 1150 °C/2 h is presented in Figure 2. The unseeded sample indicates the presence of transitional alumina consisting of θ - and δ -alumina phases, while the precursor seeded by γ - Al_2O_3 and mullite separately also follow the same trend. There is no indication of formation of the mullite phase at 1150 °C. On the other hand, mullite phase along with transitional alumina is found in the precursor containing a mixture of γ - Al_2O_3 -mullite seeds, which is quite novel. At 1200 °C, the sample containing a mixture of seeds completely transforms to mullite (Figure 3). Samples seeded with 2 wt % mullite and 2 wt % γ -alumina show only transitional alumina at 1150 °C and indicate formation of traces of mullite along with a transitional alumina-rich composition at 1200 °C, with nearly full mullitization occurring at 1225 °C.²⁶ Meanwhile, the unseeded one shows only transitional alumina phase and no mullite at all (Figure 4). Possibly

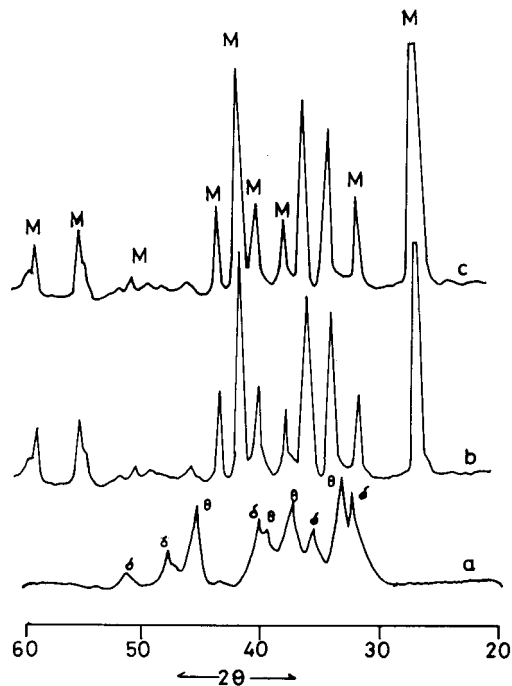


Figure 4. XRD patterns of mullite precursor gel (a) without seed (1225 °C), (b) with 2 wt % mullite seed (1225 °C), and (c) without seed (1250 °C) (M, mullite; θ , θ -alumina; δ , δ -alumina).

the reaction with amorphous silica to form mullite takes place only at a temperature of 1250 °C. Enhanced phase formation was earlier reported²⁷ for the samples prepared from γ - Al_2O_3 -TEOS mixture compared to the precursor gel prepared from boehmite sol and TEOS. However, the former one results in the formation of traces of α - Al_2O_3 phase also along with mullite, while the latter one directly transforms to phase-pure mullite. In diphasic precursors, the mullitization occurs mainly by the reaction between transitional alumina and silica²⁸ or some times by transformation from Al-rich spinel to mullite. Another study has reported the possibility of transitional alumina β -crystobalite reaction.²⁸ However, in the present study no β -crystobalite is observed, even at a high temperature, and the reaction to form mullite is observed to be between transitional alumina and amorphous silica. In the absence of seed particles, the transitional alumina is observed only at 1200 °C, and therefore the mullitization is delayed up to 1250 °C. The introduction of 2 wt % γ -alumina or 2 wt % mullite alone into the precursor gel indicates traces of mullite along with transitional alumina at 1200 °C. In boehmite the γ -alumina seed particles may provide active nucleation sites for the dehydroxylation.²⁹ According to Messing,¹⁹ the addition of γ -alumina seed particles into boehmite matrix could cause lattice strains across the incoherent interface between the matrix and the seed particles, thus enhancing the water vapor diffusion. Therefore, the γ -alumina seed addition should finally result in an active transitional alumina phase at a lower temperature, which

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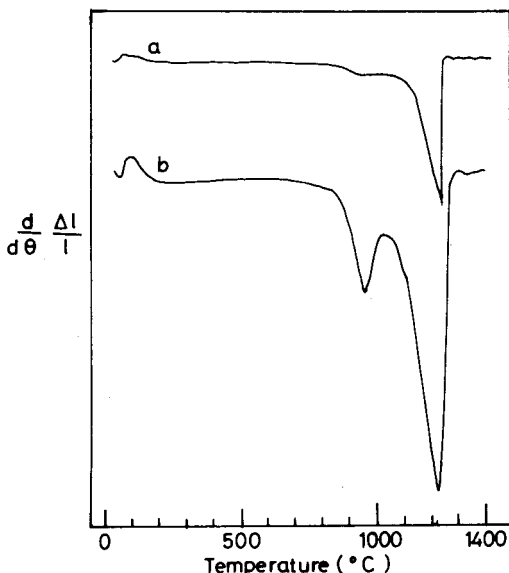


Figure 5. Shrinkage vs temperature curves of mullite precursor gel (a) without seed and (b) with γ -alumina + mullite seed.

reacts with amorphous silica, resulting in mullite at 1200 °C. When mullite seed alone is used, the transitional alumina–silica reaction is enhanced, resulting in an earlier crystallization of mullite (at 1200 °C), since it effectively eliminates the nucleation barrier for mullitization. When a seed composition containing both is introduced into the system, the active transitional alumina formed due to the presence of γ -alumina seed nuclei reacts with silica in the presence of mullite seed, thus resulting in an earlier mullite phase. This has also been further confirmed by repeated experiments. The shrinkage vs temperature curve of mullite precursor samples is presented in Figure 5. The gel without seed shows very little shrinkage around 950 °C. Another shrinkage around 1250 °C indicates the formation of mullite. On the other hand, the gel having mixed seeds shows two definite steps of shrinkage, and the mullitization reaction is indicated by the sharp shrinkage at 1200 °C; the larger peak width also indicates the completion of the mullitization reaction. The fractographs of sintered (at 1350 °C) seeded and unseeded mullite prepared from gel calcined at 850 °C are presented in Figure 6. Enhanced sintering has been observed for the sample seeded with a mixture of γ - Al_2O_3 and mullite with an average grain size less than 1 μm . On the other hand, in the unseeded sample densification occurs with much larger grain size.

Conclusion

The present study clearly indicates that seeding in diphasic mullite precursor gel reduces the transforma-

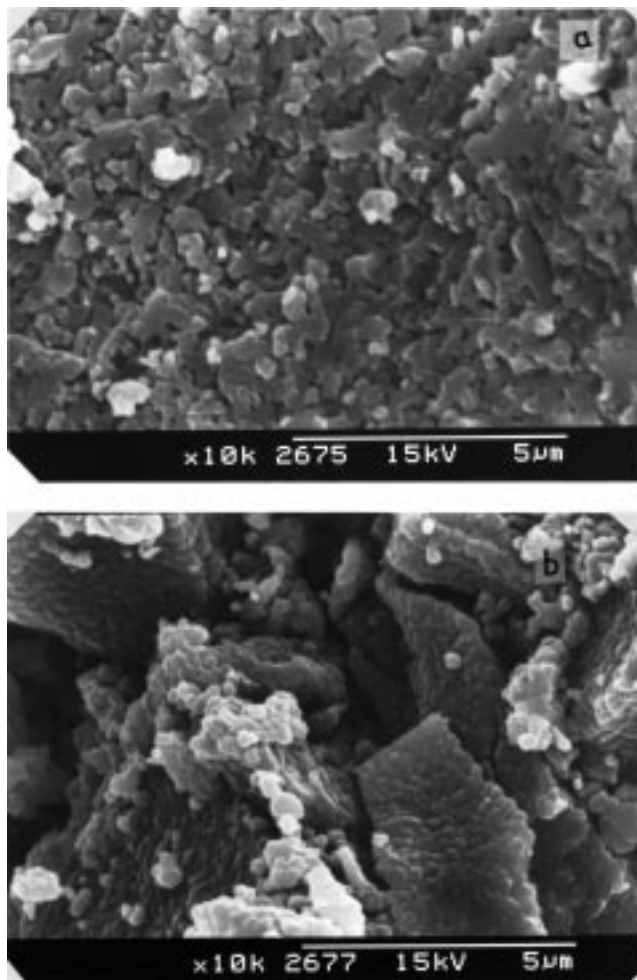


Figure 6. SEM fractographs of mullite samples (1350 °C) (a) without seed and (b) with γ -alumina + mullite seed.

tion temperature compared to the unseeded sample. Further, a novel concept of using a mixture of γ - Al_2O_3 and mullite nucleating seeds for early phase formation at <1250 °C, as well as finely grained sintered mullite at as low as 1350 °C, has been presented. The transitional alumina formation appears to be enhanced by γ - Al_2O_3 seeds, followed by reaction with silica in the presence of crystalline mullite seeds, resulting in early mullite at as low as 1150 °C, while this happens only at 1250 °C in the unseeded sample.

Acknowledgment. One of the authors (G.M.A.) acknowledges the Council of Scientific and Industrial Research (India) for a Senior Research Fellowship.

CM980149Y