JOURNAL OF MATERIALS SCIENCE **34** (1999) 3577 – 3580

Characterization of the spinel phase in a diphasic mullite gel using dynamic X-ray diffraction

Y. WANG, W. J. THOMSON
Department of Chemical Engineering, Washington State University, Pullman, WA 99164-2710
E-mail: chedept@che.wsu.edu

Dynamic X-ray diffraction (DXRD) has been used in an effort to identify the specific phase changes which are responsible for observed thermal events at ∼980 °C in mullite gel precursors. Specifically, changes in the evolution of the common and strongest diffraction peak ($d = 0.139$ nm) corresponding to both transient alumina phases and the Al-Si spinel were followed in order to descriminate between these two phases. Results which compare the DXRD results for a diphasic mullite gel and a boehmite gel are presented and suggest that the Al-Si spinel phase forms at ∼980 °C in diphasic gels along with δ- and/or γ-Al_2O_3. These results are corroborated by separate TEM measurements which indicate the presence of both phases in samples quenched from 1000 °C. © *1999 Kluwer Academic Publishers*

1. Introduction

Sol-gel synthesis is a promising means to produce high purity mullite at relatively low temperatures. The general agreement is that the mixing scale in mullite sol-gel precursors actually controls both the phase transformation sequence and the temperature of mullite formation. Essentially, mullite sol-gel precursors can be characterized into two general categories, according to the scale of alumina-silica mixing: single phase gels [1–4] and diphasic gels [4, 5].

In single phase gels, alumina and silica are mixed in the molecular range and the phase evolution has well been documented. In these gels, tetragonal mullite always forms at ∼980 °C [1–4, 6–8] and is sometimes coupled with Al-Si spinel formation depending on sol-gel processing conditions used. The kinetics of mullite formation from the amorphous aluminosilicate matrix is a nucleation controlled mechanism [8] and the subsequent transformation to orthorhombic mullite at ∼1250 °C is sluggish.

On the other hand, the concept of diphasic gels is relatively new. Although orthorhombic mullite forms directly at ∼1250 °C, which is higher than tetragonal mullite formed from single phase gels (∼980 °C), diphasic gels are better suited for low temperature (1250 to 1500 °C) densification through viscous deformation of the amorphous matrix [4, 9]. The mixing scale in diphasic gels has been characterized to be in the nanometer range [5]. Phase development in diphasic gels has been hypothesized to follow a mechanism where δ-Al_2O_3 forms through the same phase transformation sequence as that in boehmite and then reacts with amorphous silica to form orthorhombic mullite at ∼1250 °C [5, 10–12]. This phase transformation scheme was proposed simply based on the fact that XRD measurements showed the disappearance of transient alumina (in θ or δ forms) simultaneously with the formation of orthorhombic mullite at 1250 °C [5, 12, 13]. However, as reported previously [14], XRD is unable to determine whether the Al-Si spinel also exists in addition to transient alumina since these phases not only have similar crystalline structure and close lattice parameters, but also have very faint and diffuse XRD peaks with considerable overlapping. Moreover, experimental observations indicate, that not only is silica crystallization hindered (cristobalite did not crystalize at all at 1200 °C prior to mullite formation) [15], but that the crystallization of alumina polymorphs is also retarded [10]. This implies that diphasic gels may not be composed of two discrete phases prior to mullite formation, but rather, some Al_2O_3 may be incorporated into the silica phase and some Si^{4+} replaces Al^{3+} in the tetrahedral sites.

In view of the above, we have attempted to re-characterize phase transformations in diphasic gels using dynamic X-ray diffraction (DXRD) with an emphasis on whether the Al-Si spinel exists or not. Although XRD is not able to distinguish between the transient alumina (γ, δ, and θ) and the spinel phase since their peaks are overlapping (Table I), our previous work with DXRD [14] has demonstrated that simply following *changes* in the strongest and the common reflection of both transient alumina and the spinel phase at ∼80° 2θ provides added insight into the specific phases which are the causes for the change of peak intensities. Transmission electron microscope (TEM) with energy dispersive X-ray spectroscopy (EDX) and differential thermal analysis (DTA) were also used to complement the DXRD experiments.

2. Experimental

The diphasic gel was prepared by dispersing boehmite powder (γ-AlOOH, CATAPALD, Vista Chemical Company, Ponca City, OK) in a diluted HNO_3 solution.

TABLE I Major XRD peaks of the related compounds

Compound	Peak positions, ° 2θ ($\mathrm{Co}K_\alpha$)	Peak at ~80° 2θ ?
Spinel	~80, ~54	Yes
γ-Al_2O_3	79.8^{100}, 53.8^{100}, 44.0^{80}, 46.2^{50}, 22.6^{40}, 72.1^{30}	Yes
δ-Al_2O_3	79.7^{100}, 53.5^{75}, 42.6^{60}, 78.95^{50}, 54.5^{40}, 46.2^{40}, 38.3^{30}	Yes
θ-Al_2O_3	80.2^{100}, 36.8^{80}, 38.3^{65}, 42.9^{60}, 45.5^{45}, 52.6^{45}, 46.7^{35}	Yes
α-Al_2O_3	50.8^{100}, 41.0^{90}, 67.9^{80}, 29.8^{75}, 81.2^{50}, 61.9^{45}, 44.2^{40}	
Boehmite	16.8^{100}, 32.8^{65}, 44.8^{55}, 57.5^{30}	

A suitable amount of TEOS together with an equal volume of ethanol was mixed in with the Al_2O_3 dispersion to give stoichiometric mullite. After gelation (within 12 h in a 60 °C oven), the sample was ground to fine powder for further experimentation.

Non-isothermal DXRD experiments were carried out *in situ* with a Siemens D500 diffractometer ($\mathrm{Co}K_\alpha$ radiation) equipped with a position sensitive detector and a hot stage. The details of the DXRD technique have been previously described by Thomson [16]. For both diphasic and boehmite gels, both the 120 reflection of boehmite at 32.8° 2θ and the reflection at ~80° 2θ were normalized by comparing the ratio of their integrated intensities to the integrated intensity of the 120 peak of boehmite at room temperature. In order to provide a comparison with the DXRD results, DTA measurements were also performed in a Perkin-Elmer DTA 1700 differential thermal analyzer at a heating rate of 10 °C/min. In the DTA experiments, the quantities of the diphasic and boehmite gels were chosen so that they both contained the same quantity of boehmite. TEM observations were conducted using a Hitachi H600 with a Kevex 7000 energy dispersive X-ray spectroscopy and the specimens were prepared by first firing at 1000 °C for 10 min and then treating by boiling in ~10 wt % NaOH solution for 40 min to extract amorphous silica.

3. Results and discussion

For both diphasic and boehmite gels, the peak at ~80° 2θ was followed using DXRD at a heating rate of 10 °C/min and Fig. 1 shows the selected DXRD patterns at four different temperatures (400, 700, 1105, and 1390 °C). The relations between this peak's normalized intensity versus temperature are compared in Fig. 2. Although XRD is incapable of differentiating between the transient alumina (γ, δ, and θ) and the spinel phase, DXRD provides additional information because it is able to follow the *changes* in the common and strongest reflection of both the transient alumina and the spinel at ~80° 2θ. If it is a valid hypothesis [10–12] that alumina transformations follow the same sequence as they do in a boehmite gel, then similar changes in the normalized peak intensities at ~80° 2θ versus temperature should be expected for both samples. However, as Fig. 2 obviously shows, peak evolution at ~80° 2θ in the diphasic and boehmite gels are different. When the boehmite was heated to 300 °C, the appearance of the peak at ~80° 2θ indicates the decomposition of boehmite and the formation of γ-Al_2O_3. The gradual increase in the peak intensity between 850 and 1150 °C is due to the transformation of γ-Al_2O_3 to δ- or θ-Al_2O_3, while the decrease in the peak intensity at temperatures > ~1150 °C is an indication of α-Al_2O_3 formation (Fig. 1). All of these observations are consistent with the work of Wei *et al.* [10, 11] and Li *et al.* [12] on boehmite decomposition. On the other hand, when the diphasic gel was heated, γ-Al_2O_3 formed at a higher temperature (~400 °C) compared to 300 °C in boehmite gel as shown in Fig. 2. While the growth of the peak at ~80° 2θ was delayed in the diphasic gel, the decrease in the 120 peak of boehmite was identical in both gels, as can be seen in Fig. 3. In fact, even the rates

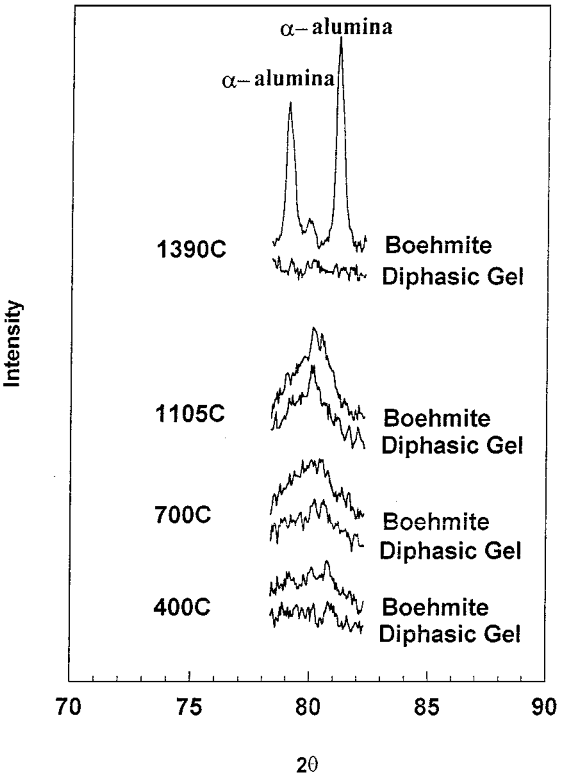

Figure 1 Selected DXRD patterns at various temperatures for both diphasic and boehmite gels (heating rate of 10 °C/min).

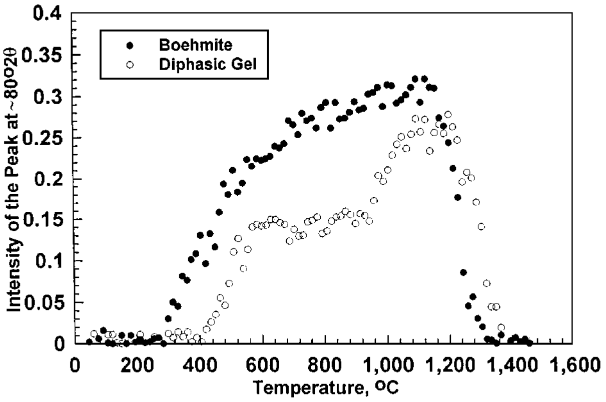

Figure 2 Comparison of normalized peak at ~80° 2θ versus temperature for both diphasic and boehmite gels (heating rate of 10 °C/min).

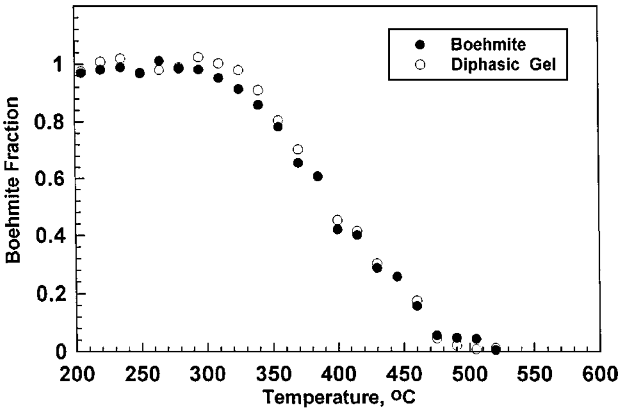

Figure 3 Comparison of normalized boehmite peak versus temperature for both diphasic and boehmite gels (heating rate of 10 °C/min).

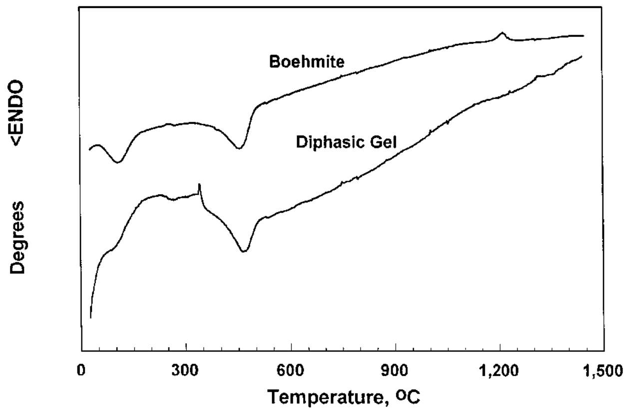

Figure 4 DTA scans of diphasic and boehmite gels (heating rate of 10 °C/min).

of decomposition are identical. Therefore, the presence of SiO_2 apparently does not affect boehmite decomposition but does retard the crystallization of γ-Al_2O_3. A possible explanation for this phenomena could be due to the fact that a solid state reaction between the amorphous SiO_2 and Al_2O_3 derived from the boehmite decomposition in the diphasic gel has taken place to form an amorphous aluminosilicate phase. Further evidence for this hypothesis is provided by the fact that the extent of γ-Al_2O_3 formed as indicated by the peak at ~80° 2θ is significantly lower in the diphasic gel than it is in the boehmite gel at ~600 °C. That is, some of the alumina has probably formed an amorphous aluminosilicate phase. Another difference between the two gels is the dramatic increase in the peak at ~80° 2θ at about 950 °C in the diphasic gel (Fig. 2). If this crystallization is solely attributed to the transformation of γ-Al_2O_3 to δ-Al_2O_3 [10–12], a gradual increase in the peak at ~80° 2θ would be expected as in the boehmite gel, instead of the sharp increase actually observed. Since Chakravorty and Ghosh [17] have reported that, at ~80° 2θ, the intensities of the Al-Si spinel peak are greater than that of γ-Al_2O_3, it is likely that the Al-Si spinel has also crystallized in addition to δ-Al_2O_3. The other difference in the two gels is that the maximum intensities of the peak at ~80° 2θ in the diphasic gel is less than that in the boehmite gel at ~1150 °C (Figs 1 and 2). It is likely that this is due to the incorporation of some of the alumina into the silica rich matrix as opposed to an alumina-free silica as proposed by some researchers [10–12]. This also explains the fact that cristobalite did not crystallize in the diphasic gel at 1200 °C as it does in a silica sol, for example [11]. The decrease in the peak intensity at ~80° 2θ starting at ~1200 °C in diphasic gel is due to the formation of orthorhombic mullite from a combination of the silica rich matrix, transient alumina and/or the Al-Si spinel. In boehmite gel, this decrease is due to the formation of α-Al_2O_3.

DTA curves for both the diphasic and boehmite gels are compared In Fig. 4. In both samples, the endothermic peaks at ~100 °C represent the desorption of physically adsorbed water and the endothermic peaks at ~460 °C are due to the decomposition of boehmite, as proven by the DXRD measurements (Fig. 3). The exothermic peak at ~350 °C in the diphasic gel corresponds to the burnout of the organics associated with the silica precursor. The exothermic peak at ~1200 °C in the boehmite gel is the result of α-Al_2O_3 formation while the broad exothermic peak in the diphasic gel at ~1300 °C is due to orthorhombic mullite formation. These were also corroborated with the DXRD measurements. There are no observable thermal events associated with γ-Al_2O_3 formation in either gel, which is consistent with the work of Hoffman *et al.* [5] and Li *et al.* [12] in the case of diphasic gels. Interestingly, a very diffuse and broad exothermic peak from 1000 to 1200 °C can be found in the diphasic gel and this could be attributed to Al-Si spinel formation. It should be noted that this exothermic peak is broader and more diffused than the exothermic peak at ~980 °C which has been observed in single phase gels when the Al-Si spinel formed [18]. This might be expected in view of the fact that SiO_2 incorporation into Al_2O_3 in the more discrete diphasic gel is probably much slower than would occur in single phase gels, where the alumina and silica are mixed on a molecular scale.

Although the Al-Si spinel contains fairly small quantities of silica (<10 wt % of silica as suggested by most researchers [7, 18–20]), an attempt was also made here to use TEM with an EDX-type analyzer to qualitatively evaluate the spinel phase in the diphasic gel sample. Fig. 5 shows a micrograph of a diphasic gel sample heated at 1000 °C for 10 min and treated with NaOH. The small rounded dark particles as shown in Fig. 5 were detected to be an alumina-rich, Al-Si phase while the other particles are pure alumina (primarily δ-Al_2O_3 as confirmed by separate XRD experiments). Therefore, the TEM measurements also suggest that the Al-Si spinel exists in addition to transient alumina.

4. Conclusions

Phase transformations in both diphasic and boehmite gels were characterized using DXRD as well as DTA and TEM. The DXRD experimental results suggest that a pronounced crystallization of the Al-Si spinel occurred at ~980 °C in addition to the formation of δ- and/ or γ-Al_2O_3 in the diphasic gel. A separate TEM measurement also confirmed the existence of the alumina-rich Al-Si spinel phase at 1000 °C.

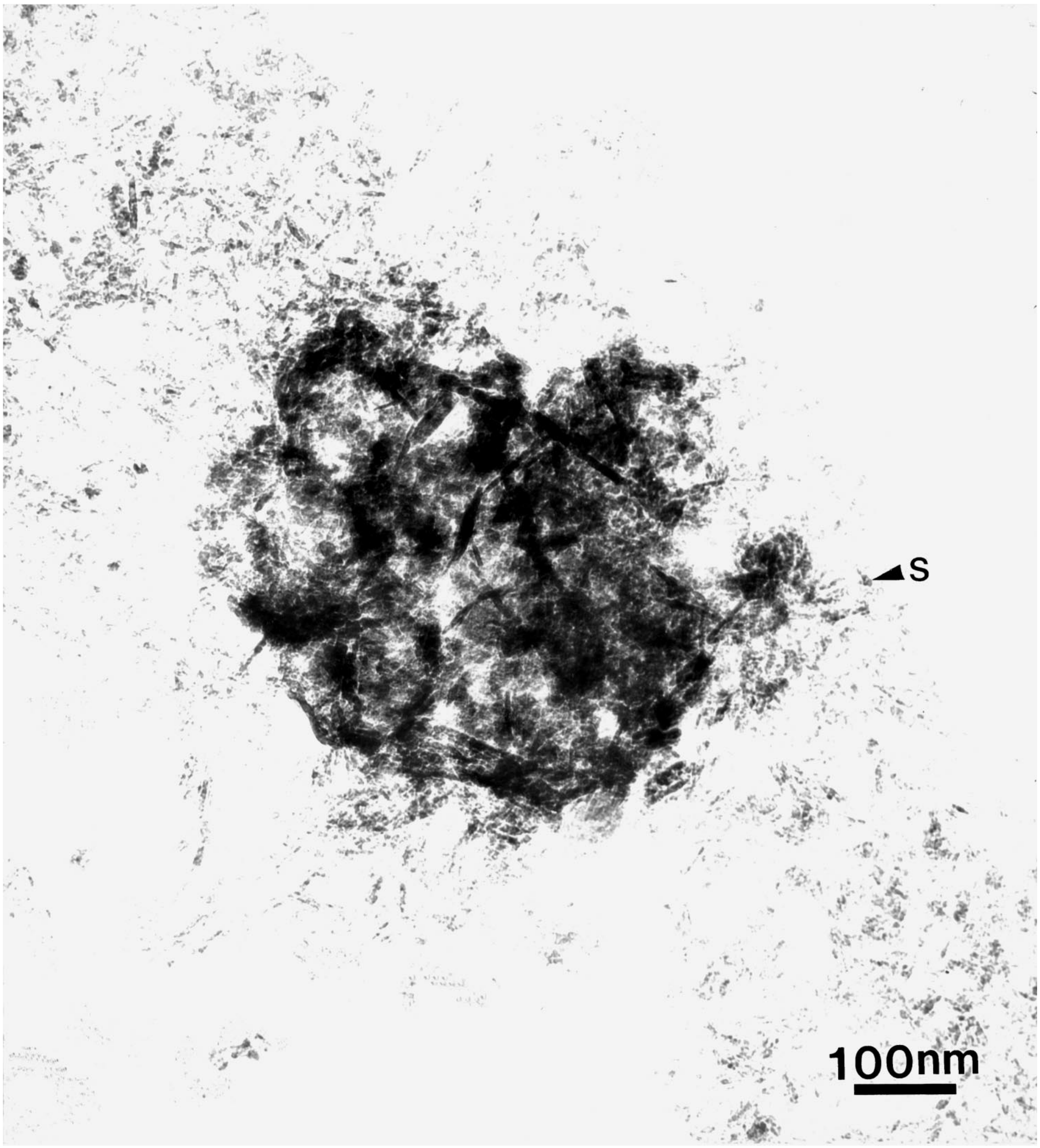

Figure 5 TEM micrograph of diphasic gel (heat-treated at 1000 °C for 10 min). S is spinel.

References

1. B. E. YOLDAS, *J. Mater. Sci.* **12** (1977) 1203.
2. R. ROY, *J. Amer. Ceram. Soc.* **39** (1956) 145.
3. J. D. CROFTS and W. W. MARSHALL, *Trans. Brit. Ceram. Soc.* **66** (1964) 121.
4. S. KOMARNENI, Y. SUWA and R. ROY, *J. Amer. Ceram. Soc.* **69** (1986) C155.
5. D. W. HOFFMAN, R. ROY and S. KOMARNENI, *ibid.* **67** (1984) 468.
6. J. OSSAKA, *Nature* (London) **191** (1961) 1000.
7. K. OKADA and N. OTSUKA, *J. Amer. Ceram. Soc.* **69** (1986) 652.
8. D. X. LI and W. J. THOMSON, *ibid.* **73** (1990) 964.
9. I. A. AKSAY, D. M. DABBS and M. SARIKAYA, *ibid.* **74** (1991) 2343.
10. W. WEI and J. W. HALLORAN, *ibid.* **71** (1988) 166.
11. *Idem.*, *ibid.* **71** (1988) 581.
12. D. X. LI and W. J. THOMSON, *J. Mater. Res.* **5** (1990) 1963.
13. B. E. YOLDAS, *J. Mater. Sci.* **27** (1992) 6667.
14. Y. WANG, D. X. LI and W. J. THOMSON, *J. Mater. Res.* **8** (1993) 195.
15. M. W. TAMELE, *Disc. Faraday Soc.* **9** (1950) 270.
16. W. J. THOMSON, in “Ceramic Transactions,” Vol. 5, Advanced Characterization Techniques of Ceramics, edited by W. S. Young, G. L. McVay and G. E. Pike (American Ceramic Society, Vesterville, OH, 1989) p. 131.
17. A. K. CHAKRAVORTY and D. K. GHOSH, *J. Amer. Ceram. Soc.* **70** (1987) C46.
18. Y. WANG and W. J. THOMSON, *J. Mater. Res.* (1994), submitted.
19. K. OKADA, N. OTSUKA and J. OSSAKA, *J. Amer. Ceram. Soc.* **69** (1986) C251.
20. B. SONUPALAK, M. SARIKAYA and I. A. AKSAY, *ibid.* **70** (1987) 837.

Received 30 December 1998
and accepted 27 January 1999