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NEW DATA ON THE THERMAL ANALYSIS OF DIPHASIC MULLITE GEL

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Abstract

A diphasic mullite gel has been synthesized by using Ludox and $Al(NO_3)_3 \cdot 9H_2O$ in ammoniacal solution. Both DTA and DDTA studies have been performed with a sensitive differential thermal analyzer system. Besides usual exotherm due to mullite formation, a pronounced exotherm between 800–1300°C has been noted. Considering previous XRD data, it is explained as due to formation of Si–Al spinel phase, which is subsequently transformed exothermally at ~1320°C to mullite.

Keywords: diphasic mullite gel, Si–Al spinel, mullite

Introduction

Diphasic Al_2O_3–SiO_2 xerogel is described as being consists of nanohomogeneous mixture of discrete silica and alumina phases. Hoffman *et al.* [1] first synthesized it by three different sets of component materials. DTA analysis of first set of it made by use of boehmite sol and TEOS showed an endotherm at 400°C and explained as due to decomposition of boehmite phase and then showed a broad exotherm associated with mullite formation occurred over the entire region from 700–1230°C. Ismail *et al.* [2] prepared second set of diphasic mullite gel by using γ-Al_2O_3 sol and colloidal silica sol and noted endotherms at 96 and 420°C represented with loss of moisture form the gel and dehydration of boehmite to form γ-Al_2O_3 and finally showed an exotherm at 1296°C due to crystallization of mullite. Subsequently, Li and Thomson [3] made diphasic gel as per first set of mixture and conformed the exhibition of endotherm at 500°C and exotherm at 1320°C. Hyatt *et al.* [4] prepared diphasic gel bz dispersing boehmite (AlOOH) powder and colloidal silica (Ludox As-40, DuPont), noted a small and broad exotherm over a wide temperature range at 1360°C besides two usual large endotherms. This exotherm was assigned by them as due to simultaneous crystallization of α-Al_2O_3, and cristobalite and the solid state reaction accounts for the formation of mullite. Subsequently various researchs [5–10] also synthesized different sets of gel and showed broad and

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less significant peak claimed as due to mullite crystallization. Instead of using boehmite sol and TEOS or Ludox as used by several earlier researchers, boehmite is being developed 'insitu' during gelification process itself. In the present communication, the resultant gel has been studied by DTA/TG analysis by using a highly sensitive apparatus along with derivative attachment to enable to trace even a low thermal effects.

Experimental

Inorder to make diphasic gel of 3:2 stoichiometry of mullite, 4.5 ml Ludox 'As' 2M in SiO_2: E. 1 du point de Nemours & Co., Inc., Wilmington, DE. (an aqueous silica sol) and 20.4 g $Al(NO_3)O_3 \cdot 9\ H_2O$ A. R. grade were separately measured out and then dissolved in 400 ml distilled water. Dilute ammonia solution (1:10) was added drop wise with vigorous stirring so that boehmite was precipitated along width gelification of silica sol. The gel mixture was filtered in a buchner funnel fitted with a flux and connected to a vacuum pump. The filtered gel was washed with 1.0% warm ammonium nitrate solution for several times. Finally, it was dried at ~80°C and labeled as G-49. The dried gel was analyzed by DTA in a Shimadzu Thermal Analyzer System with a derivative attachment. Conditions: Sample weight, 40 mg; Heating rate, 20°C min^{-1}; Reference material α-Al_2O_3: Sensitivity for DTA run, ±100 µv; Chart speed, 1.25 mm min^{-1}; Range for derivative run, 10 mv min^{-1}.

Results

Figure 1 shows the DTA trace of diphasic gel G-49. It exhibits two endothermic peaks. First one appears with the start of DTA experiment and exhibits its maximum, T_m at ~200°C. Second one occurs with T_m at ~450°C. These two peaks corroborate well with two steps of water loss noted in TG trace (Fig. 2) of G-49. First step accounts to loss of 14.39% and second is shown to loss of 11.74%. Within these two endotherms, one sharp exotherm exhibits with its T_m ~300°C. The cause of it is not known but the two endotherms are due to dehydration of silica gel and boehmite respectively which confirms the diphasicity of the gel G-49. On continued heating, the thermoanalytical curves show a broad exotherm between 800 to 1300°C (area mark as ABC) with its T_m at 1180°C. Lastly, at ~1320°C, the gel exhibits one sharp exotherm (area marked as CDE). All these four thermal effects have been complemented by the derivative DTA run as shown in Fig. 3, DDTA curve shows two peaks for each single DTA peak. Usually for endothermic peak, occur either at 200 or at 450°C in DTA, corresponding DDTA curve begins first with one peak below and continued with one peak above the base line for completion. Thus for exhibition of endotherm PQR in DTA, the corresponding endo-exo peak assembly is PQ'QQ''R endo in DDTA curve. For the occurrence of exothermic peak RST

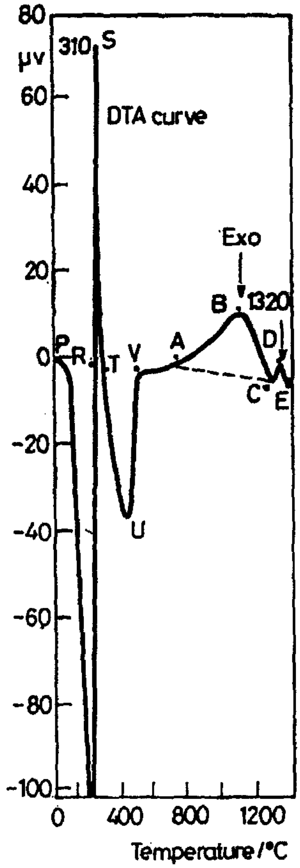

Fig. 1 DTA curve of diphasic Al_2O_3–SiO_2 mullite gel(G-49)

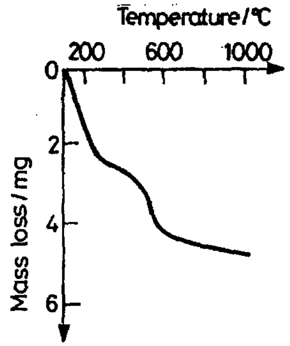

Fig. 2 TG curve of G-49

in DTA at 310°C the corresponding exo-endotherm peak assembly is RS'SS''T in DDTA curve. Likely, for the endotherm at TUV in DTA, the corresponding

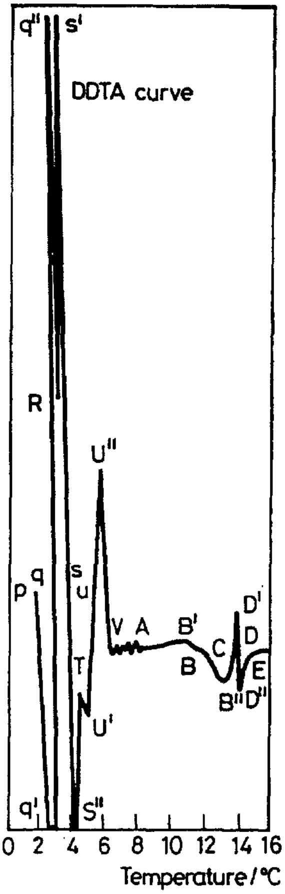

Fig. 3 Derivative DTA curve of G-49

endo-exotherms peak assembly to TU' UU''V in DDTA curve. The exhibition of new broad exotherm between 800–1300°C in DTA (ABC) characteristically shows two other broad peaks AB' B (exo) and BB''C (endo) in DDTA curve. Lastly, the comparably sharp exotherm at ~1320°C in DTA is in concurrence to the two peaks named, CD'D and DD''E in differential DTA curve. Thus the occurrence of broad exotherm at ~1180°C prior to sharp exotherm at 1320°C in DTA is also well noticed in DDTA analysis as done in the Shimadzu Thermal Analyzer system. The real cause of the occurrence of this peak has been the subject of present discussion.

Discussion

Hoffman *et al.* [1] conjectured that during heating two discrete phases transformed independently up to 1000°C to form β-cristobalite and γ-alumina spinel which subsequently reacted to form mullite. Okada *et al.* [11] and thereafter Chakravortty and Ghosh [12] analyzed the XRD pattern of diphasic gel heated to 1010°C and interpreted that amorphous halo observed at 22° 2θ CuK$_\alpha$ in X-ray diffractogram tracing of Hoffman *et al.* [1] was due to amorphous SiO_2 and not due to β-cristobalite as stated. Later authors [12] further showed by QXRD study that diphasic gel prepared out of aqueous silica sol and aluminium salt, mullitized very rapidly between 1150 to 1250°C and suggested the so-called spinel phase as Si–Al spinel other than simple γ-Al_2O_3 as believed [1]. That the two components of the gel did not transform independently upto 1200°C may not hold good. Because, both β-cristobalite and α-Al_2O_3 did not crystallize. It may be due to incorporation of Al_2O_3 into amorphous silica phase and thus hinders silica crystallization [13]. The following evidences indicate that the intermediate spinel phase contains silica.

1) Retardation of the crystallization of alumina polymorphs [5];

2) Inhibition of nucleations of the kappa and alpha alumina [14];

3) Change in the crystallization temperature of corundum in some cases [15];

4) Alkali leaching study showed the absence of free silica in diphasic Al_2O_3–SiO_2 gel heat treated to 1000°C [16] and lastly;

5) Semiquantitative XRD data [14] indicated the formation of ~80 wt% Si–Al spinel phase which was more than that of the percent Al_2O_3 content (Al_2O_3-71.8 wt%) taken during batch preparation. Later by EDX study, Suzuki *et al.* [17] conformed the conjecture of Chakravortty [16] as Si–Al spinal of composition analogous to 3:2 composition of mullite. Okada *et al.* [18] on the other hand by their AEM study showed the composition as containing 8–10 wt% SiO_2. Low and Mcpherson [19] suggested Si–Al spinel of composition corresponds to 2:1 composition of mullite. Recently, Schneider *et al.* [20] by EDX study showed the composition of spinel containing 18 mole% spinel.

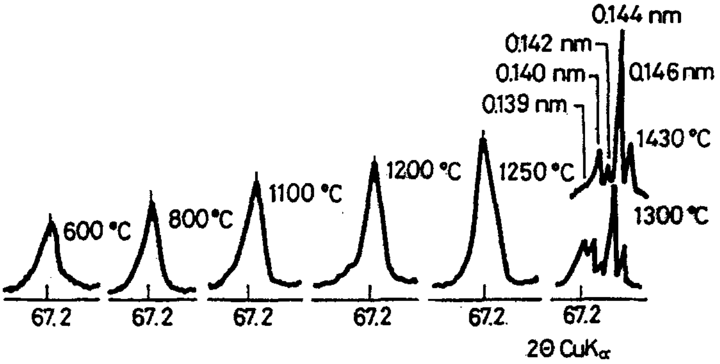

Fig. 4 A portion of X-ray diffractogram at the vicinity of 0.139 nm peak of Si–Al spinel phase

Thus, the formation of Si bearing spinel phase is gradually gaining ground except some dispute existing in its composition. Now the question is: whether Si–Al spinel formation is associated with an exothermic effect? Sequence of crystallization of diphasic gels made by three set procedures were studied by XRD technique [1, 2, 4, 5, 7 and 8]. Those were compared with reaction sequence of 'in situ' diphasic gel heat treated to various temperatures and shown elaborately by present author earlier [21]. For this reason a portion of X-ray diffractogram for one broad peak of Si–Al spinel is cited here (Fig. 4). It shows that the intensily of 0.139 nm peak of Si–Al spinel phase at 67.2° 2θ CuK_α increased with increase of temperature upto 1250°C. Thereafter, mullite formation ensued as noted by the appearances of several peaks of it namely 0.146 nm, 0.144 nm, 0.142 nm and 0.140 nm with simultaneous decrease of 0.139 nm, peak of Si–Al spinel. At 1300°C Si–Al spinel phase and mullite were found to coexist. Thereafter, mullite is the only crystalline phase to occur. This result substantiated the fact that after dehydration of boehmite, the two amorphous oxide phases namely SiO_2 and Al_2O_3 interact and gradually crystallize to Si–Al spinel phase with increase of temperature of heating. The course of crystallization process in between 800–1300°C is with the concurrence of the exotherm at the same temperature range in DTA analysis. Therefore, it is concluded that this peak is likely due to Si–Al spinel crystallization. Secondly, the onward transformation of this Si–Al spinel phase to orthorhombic mullite accounts for the last exotherm at ~1320°C which is in good agreement with both XRD and DTA results. The derivative of the differential thermal analysis curve (DDTA) as shown here also complements both the two consecutive exotherms. In comparison to earlier DTA curves shown [1, 2, 7], the exhibition of the above pronounced broad exotherm before the occurrence of most accepted mullite exotherm at 1320°C is significantly new one. Moreover, the present DTA trace is more smooth in comparison to large base line drifts shown earlier by Hsi *et al.* [7] and Hyatt *et al.* [4]. Klaussen [8] reported the exhibition of two sharp exothermic peaks before exotherm at ~1328°C due to mullitization. These peaks however vanished when rate of heating was raised form 5°C min^{-1} to 15°C min^{-1}. But the DTA curve still showed a broad peak before usual exotherm at 1345°C. Similar nature of broad peak was also observed by Hsi *et al.* [7] and more markedly by Huling and Messing [10] in their colloidal mullite gel and hybrid gels. With the corroboration of XRD studies with DTA in the present result, this broad peak as shown by previous researchers [1, 7, 8, 10] is explained as due to Si–Al spinel formation.

Conclusion

Therefore, the 'in situ' diphasic Al_2O_3–SiO_2 gel decomposes first into amorphous phases followed by endotherms as noted in DTA and weight losses occurred in TG analysis. Solid state reaction between newly liberated amorphous oxides start with rise of temperature and crystallize to intermediate Si–Al spinel phase with the exhibition of a broad exotherm between 800–1300°C. Further, phase transformation of this Si–Al spinel occurs at ~1320°C exotherm with the formation of orthorhombic mullite.

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