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Fine Pure Mullite Powder by Homogeneous Precipitation

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Abstract

A fine pure mullite powder was prepared by homogeneous precipitation. A suspension consisting of fumed silica (Aerosil 200®) and a mixture of aqueous solutions of aluminium sulphate and ammonium bisulphite, was heated to decompose and eliminate sulphur dioxide. This homogeneous precipitation process produced an amorphous basic aluminium sulphate salt coating the surface of fumed silica. This precursor was transformed principally into Al–Si spinel immediately after the decomposition of sulphate at 950°C, at the same time, a trace of crystalline mullite was produced. The phase changed according to heating temperatures from 950° to 1350°C for 1 h. The single phase of mullite was obtained by calcining the precursor at temperatures higher than 1250°C, and the peak of the XRD and IR were sharpened with increasing temperature. The powder calcined at 1350°C was characterized by XRD, IR, SEM, and Klyachko–Gurvich technique. The final product was an agglomerate consisted of 100–200 nm mullite particles in size, and from which fine pure mullite particles were easily obtained by milling. The specific surface area of mullite powder was 27·5 $m^2 g^{-1}$. This process for preparing fine mullite powder was very simple and inexpensive. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) has many favourable characteristics that make it an excellent prospect for engineering applications.[1–5] Several different processes for preparing the mullite powder have been recently reported.[1,6–11] The ideal ceramic process would be based on extremely well characterized ceramic powders of tailored particle size, size distribution and surface chemistry, as well as high purity and high homogeneity.[12] The degree of mixing of both components affects the mullite-phase formation. When the scale of chemical homogeneity of the mullite precursors is at the molecular level, mullite crystallizes exothermally at $\approx$ 980°C. On the contrary, when the scale of homogeneity is in the nanometer range (1–100 nm, i.e. diphasic precursors), mullite formation is usually proceeded by the crystallization of transient alumina phases and occurs only at higher temperatures through a second exothermic reaction[13–15] at about 1250°C. High purity mullite precursors could also be obtained using fumed silica.[8–10] The advantage of using fumed silica as source of silicon is that the size of its primary particles is much smaller (i.e. typically in the range $\sim$ 40 nm), and it has much higher purity (i.e. $\geq$ 99·8 wt% SiO_2), than precipitated silica. Additionally, because of its non-porosity, it only has external surface, and thus more reactivity.

On the other hand, previous studies have shown the method for preparing basic aluminium sulphate and its applications.[16–18] An amorphous basic aluminium sulphate salt could also be prepared by homogeneous precipitation from a mixture of aqueous solutions of aluminium sulphate and ammonium bisulphite. In this paper, we discuss the method for preparing fine pure mullite powder by homogeneous precipitation.

2 Experimental

Figure 1 shows the flow sheet of the procedure used for the preparation of mullite powders. Reagent grade aluminium salt, $Al_2(SO_4)_3{\cdot}18H_2O$ (J.T. Baker S.A. De C.V., Xalostoc, Mexico) was

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*To whom correspondence should be addressed. Fax: 52 473 29312; e-mail: satoshi@quijote.ugto.mx dissolved in distilled water. The solution was filtered to eliminate the insoluble residues. On the other hand, an ammonium hydroxide solution (Merck-Mexico, S.A. De C.V., Edo De Mexico, Mexico) was neutralized by addition of SO_2 gas (Linde De Mexico, S.A. De C.V., Mexico, D.F.) to obtain the ammonium bisulphite solution. Furthermore, fumed silica (Aerosil® 200, Degussa AG, Frankfurt, Germany. The specific surface area is $200\,m^2\,g^{-1}$) was dispersed in distilled water. The three solutions were mixed, and heated to cause the precipitation of basic aluminium sulphate and the elimination of SO_2 gas. The precipitate was subsequently filtered, washed (to remove ammonium and sulphate), and dried. This precursor with a 3:2 mole ratio of Al_2O_3:SiO_2 was calcined at 950°C to eliminate sulphate ion, and then the sample was heated between 950–1350°C for 1 h. The product was milled in agate mortar. The powders obtained were characterised by X-ray diffractometry (XRD), using a Siemens 500 Diffractometer; solid-state infrared spectrophotometry (FTIR), by a Perkin–Elmer TFIR 1600; scanning electron microscopy (SEM), by a Jeol JMS356; and thermal analysis (DTA and TG), by a Metler 233 thermoanalyzer. The chemical analysis of final products was realised by an atomic absorption spectrophotometer Perkin–Elmer 503, and by a Siemens SRS 200 X-ray fluorescence spectrophotometer. The specific surface area of the products was determined by the Klyachko–Gurvich technique.[19] The lattice constants of mullite were determined using silicon powder as an internal standard.

3 Results and discussion

3.1 Precipitation process of precursor

The following sequence of formation of basic aluminium sulphate during the homogeneous precipitation process can be proposed as:

$$2NH_4HSO_3 \xrightarrow{\Delta} (NH_4)_2SO_3 + H_2O + SO_2$$

$$\begin{aligned} &Al_2(SO_4)_3 + x(NH_4)_2SO_3 \\ &+ xH_2O \xrightarrow{\Delta} 2Al(OH)_x(SO_4)_{(3-x)/2} \\ &+ (NH_4)_2SO_4 + SO_2 \end{aligned}$$

These reactions occur almost simultaneously. The x value varied with precipitation conditions (i.e. concentration of solutions, temperature, etc.), generally x varied from 2 to 2·6. An amorphous basic aluminium sulphate (typical x value was 2·6) could be obtained, where the precipitation was realised in a low concentration of aluminium and with an excess quantity of added ammonium bisulphite. On the other hand, the x value decreased, when the initial concentration of aluminium was high and a deficiency of ammonium bisulphite was added. This precipitated amorphous basic aluminium sulphate could be filtered easily and both ions of ammonium and sulphite could also be eliminated completely by consecutive washing with water. This process could precipitate the total aluminium quantities in solution.

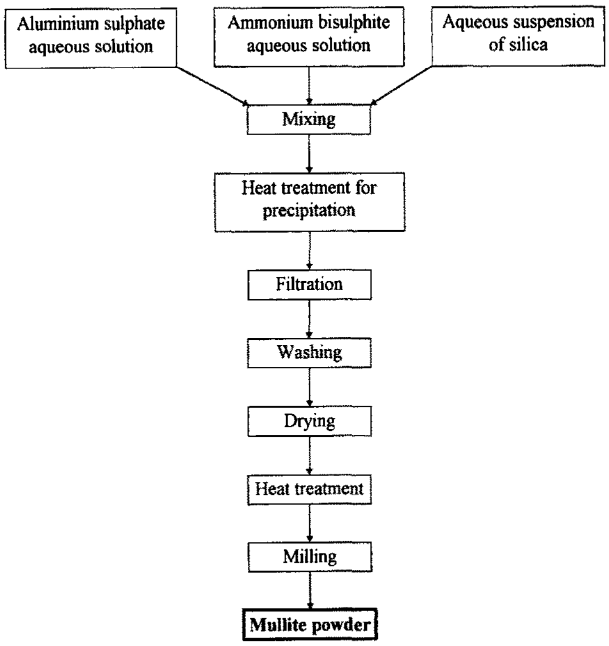


Fig. 1. Processing of mullite powder.

3.2 Heat treatment of precursor

The following sequence of dehydration and decomposition of basic aluminium sulphate is proposed as:

$$2Al(OH)_x(SO_4)_{(3-x)/2} \xrightarrow{280°C} Al_2(SO_4)_3 +_x H_2O$$

$$Al_2(SO_4)_3 \xrightarrow{900°C} \gamma - Al_2O_3 + 3SO_3$$

DTA and TG curves in Fig. 2 of the precursor of mullite formed by homogeneous precipitation show a large endothermic peak around 280°C, corresponding to the dehydration (OH^- ion) of basic aluminium sulphate. The second endothermic peak around 900°C corresponds to the decomposition of aluminium sulphate to spinel (γ-alumina type). The samples prepared with and without fumed silica produced identical thermograms, not showing thermal effects, which corresponded, to the reaction between alumina and silica. The thermal analysis of this precursor did not exhibit the

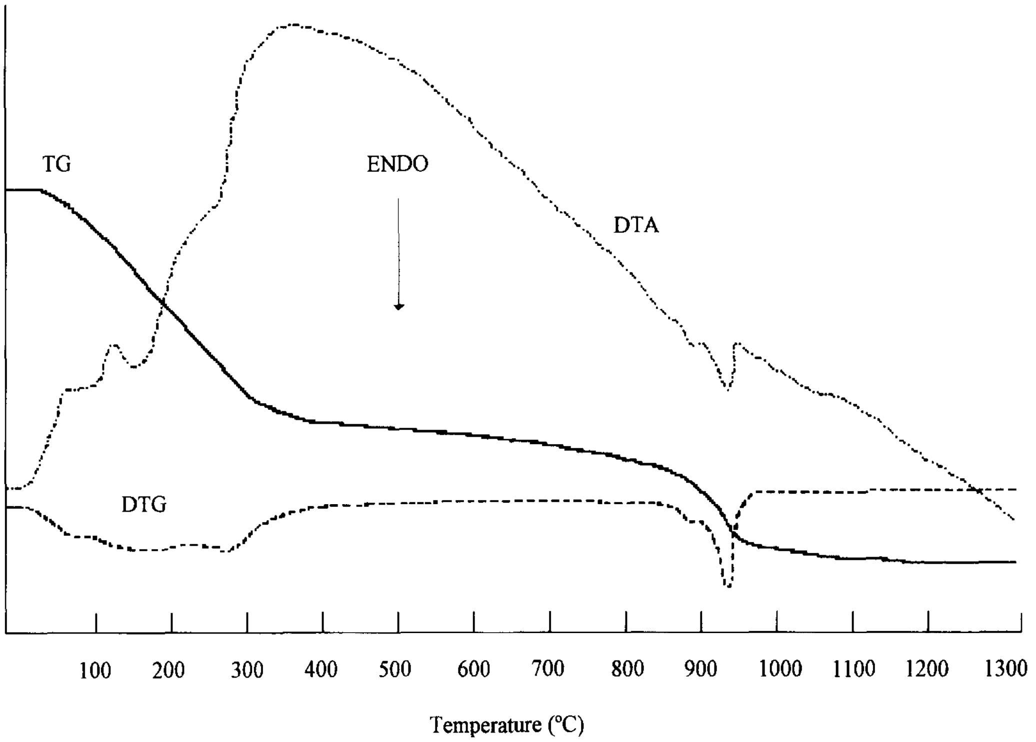


Fig. 2. DTA, TG and DTG curves of powder prepared by homogeneous precipitation.

exothermic effect, which was attributed to the transformation from spinel phase to crystalline mullite (around 1250°C).

3.3 Mullite transformation

According to the extensive reviews of mullite formation process realised by Schneider *et al.*,[20] Okada and Otsuka,[21] and Pask and Tomsia,[22] there are three routes of phase transformation sequence depending on mixture homogeneity of mullite precursors. As shown Fig. 3(1), when the intimate mixture was achieved (molecular level or type I of Schneider *et al.*,[20]) the amorphous precursor was transformed into primary mullite (solid solution of alumina in mullite) at 600–1950°C, and then it was evolved to crystalline mullite at temperatures ≥ 1200°C. On the other hand, in the diphasic mixtures (Types II and III of Schneider *et al.*,[20]) the spinel phase formation was observed in the precursors calcined at about temperatures ≥ 900°C, and it was transformed into crystalline mullite at temperatures ≥ 1200°C [Fig. 3(2)]. However, when the starting materials were poorly mixed (mixtures of sols and/or oxides in Okada[21]), there occurred preferentially a segregation phase process [Fig. 3(3)]. In this case, the γ-alumina, α-alumina and cristobalite phases were formed before the mullite crystallisation. And only above

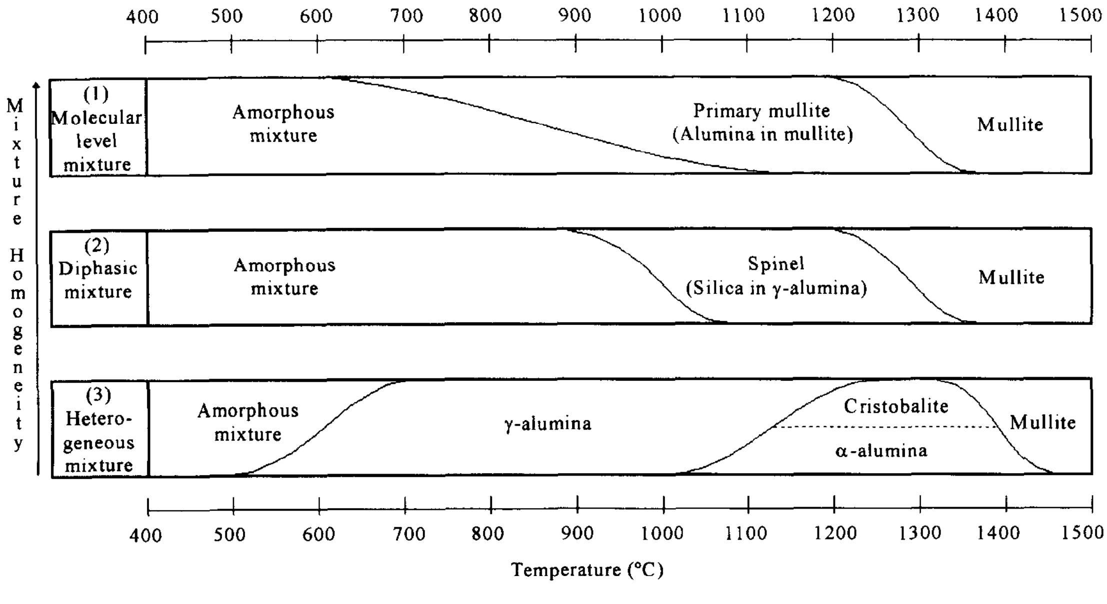


Fig. 3. Phase transformation sequences of mullite precursors (starting by amorphous materials), depending on the mixture homogeneity.

temperatures ≥ 1350°C (close to the fusion temperatures of SiO_2–Al_2O_3 system), the final crystalline phase was observed.

As shown in the X-ray diffractograms of Fig. 4, before heat treatment of precursor at 900°C (before elimination of SO_3), solids remained amorphous. However, at 950°C, solids were principally transformed into spinel (γ-alumina type). At the same time, this sample exhibited small peaks corresponding to trace of crystalline mullite.

In the XRD study, the mullite peaks become sharper after heat treatment at 1250°C, and only small peaks corresponding to spinel were detected. However, these last peaks disappeared at 1350°C. As shown in Fig. 5, where the change of phase composition was plotted versus heating temperature, mullite crystallisation required higher temperatures than 1250°C. According to Huling *et al.*,[23] mullite crystallization requiring temperatures ≥ 1200°C could be attributed to prior formation of the spinel, and thus, the nucleation and crystal growth required long distance migration of diffusion species.[20]

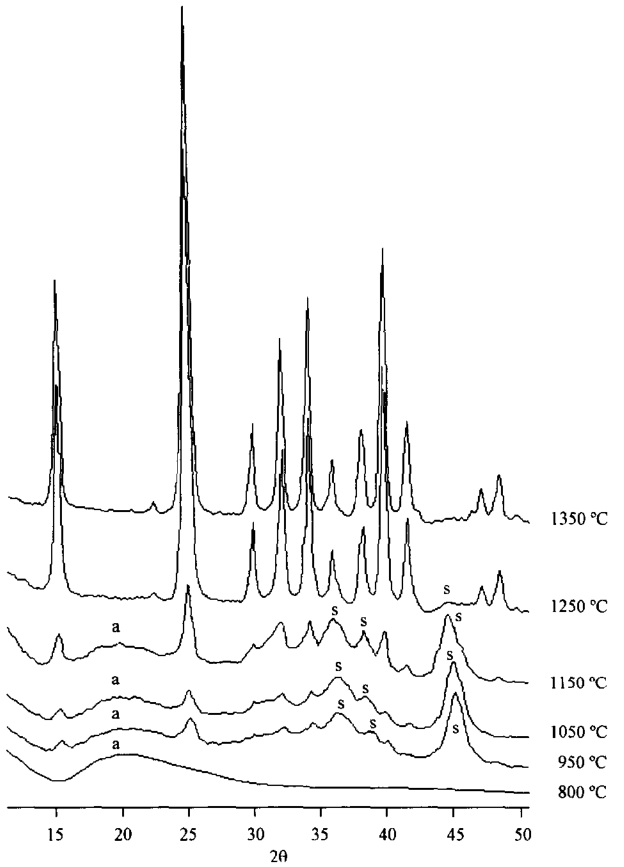


Fig. 4. X-ray powder diffraction patterns of products after heat treatment. (Peaks with an 'a' belong to amorphous silica, with an 's' belong to spinel, and the other peaks belong to mullite).

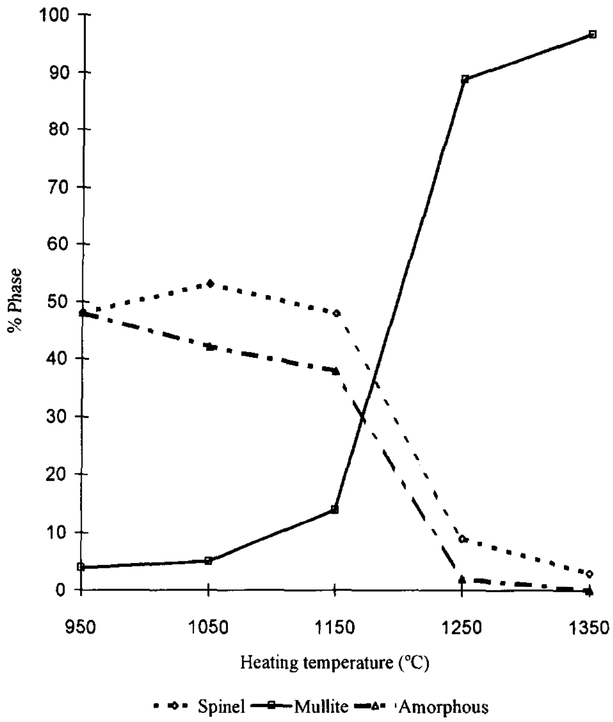


Fig. 5. Change of phase composition versus heating temperature.

Owing to existing small amounts of crystalline mullite in samples calcined at 950°C, molecular level mixing of precursors (atomic interactions, type I of Schneider *et al.*,[20]) could also be achieved, at least in trace quantities, by this homogeneous precipitation. We suggest that the precipitation of basic aluminium sulphate occurs preferentially on suspended silica surface, and therefore, by coating the silica surface with alumina layer (coated precursor, Fig. 6). Initially, this interaction between silica core and alumina layer in precipitation stage, could be weak (Van der Waals type). However, during the drying and sulphate elimination process (≤ 950°C), the Si–O–Al linkage could be formed in this interface. Thus, the mullite crystallization could be evolved more easily. According to Okada *et al.*, Si–O–Al linkages were an important factor to decide the crystallising phase.[21] Furthermore, the extent of ≈ 1000°C mullite formation had been assumed to vary proportionally with the extent of Si–O–Al bonding in the precursor.[23]

In an additional experiment, the coated precursor was treated with aqueous ammonium solution in order to transform basic aluminium sulphate layer into pseudoboehmite and then peptized by nitric acid. This showed that no crystalline mullite was obtained after the treatment at 950°C and only negligible amount of mullite was formed at heating temperatures ≥ 1350°C. We suppose that during the peptization process, the weak interactions between silica core and alumina layer are broken and alumina–silica segregation occur. In this case, the system is similar to fumed silica–aluminium sulphate solution as reported by Mizuno *et al.*[8] This result is consistent with that reported by Okada *et al.*[20] The presence of Si–O–Al linkages in precursor produces crystalline mullite at low temperature (≈ 950°C), and this crystalline phase acts as mullite seed particles (nucleus). This is the reason why the precursor prepared by homogeneous precipitation differs from that prepared by Misno *et al.*[8] in mullite crystallisation. They obtained crystalline mullite by calcining the precursor only above 1100°C. They also used fumed silica mixing it with aqueous aluminium sulphate solution. However, in this process (mixing and drying), Si–O–Al linkages could not be formed, and therefore, crystalline mullite was not produced at the same time as sulphate ion was decomposed.

Starting material crystallinity and silica–alumina layer conformation in the precursor can affect the mullitization process. Sacks *et al.*[24] obtained coated precursor, using fine α-alumina particles as core material and coating it with silica layer after hydrolysis of TEOS. Extensive mullitization occurred by 1500°C, although a somewhat higher temperature was required for complete reaction. They showed that mullite initially formed in this microcomposite by nucleation and growth within the siliceous phase, but also that chemical interdiffusion within mullite grains is required to complete the reaction, and they proposed that the first stage of the reaction is controlled by the dissolution of alumina in the siliceous phase, and that for the second stage the alumina diffused more rapidly through mullite than silica. On the contrary, precursor prepared by homogeneous precipitation in this work consists of more fine silica core ($\approx$ 40 nm) coating it with alumina layer, instead of, alumina core and silica layer. Furthermore, alumina layer is amorphous phase, thus it has more reactivity than crystalline alumina (α-alumina). Therefore, microcomposite with silica core coated with alumina layer, and 'seeded with mullite' can be transformed into crystalline mullite at much lower temperature.

Changes in the infrared (FTIR) spectra of the powders on heating are shown in Fig. 7. The IR spectra of sample calcined at 950–1150°C is similar to that of an Al,Si-spinel phase. The IR spectra of powders calcined above 1250°C coincide with that of ideal mullite.[25] The two peaks between 1100 and 1200 cm^{-1} were observed in the samples calcined

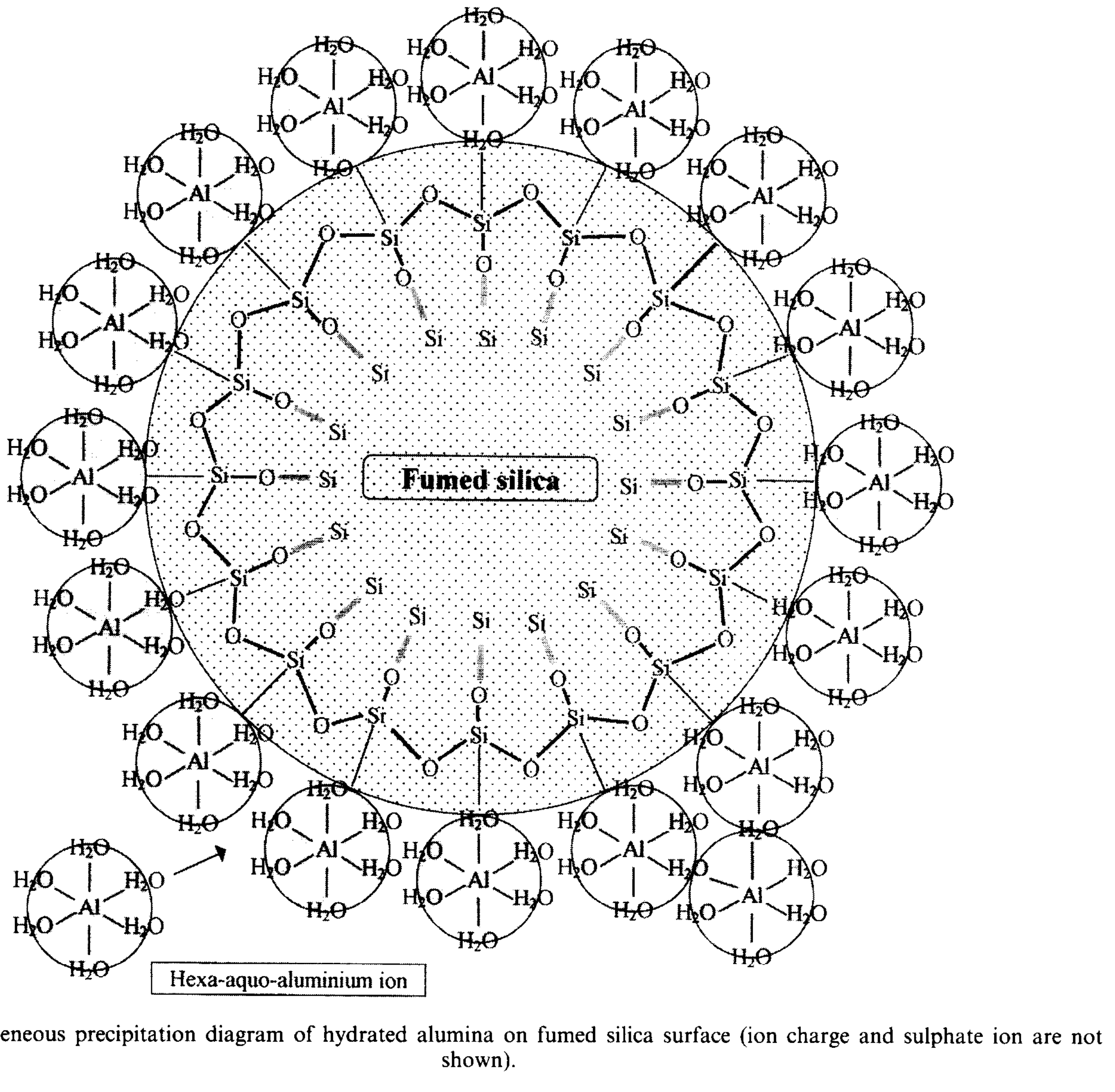


Fig. 6. Homogeneous precipitation diagram of hydrated alumina on fumed silica surface (ion charge and sulphate ion are not shown).

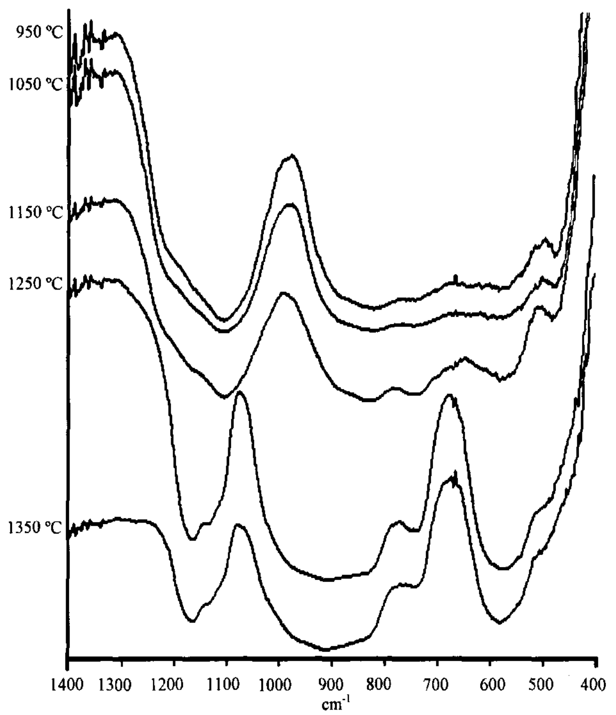


Fig. 7. IR absorption spectra of products after heat treatment.

above 1250°C, and the peak at 1165 cm^{-1} of these samples had higher intensity compared with the second one, thus suggesting the powders were of stoichiometric composition, as discussed by Suzuki *et al.*[26]

On the other hand, as observed by Suzuki *et al.*,[26] lattice parameters of the 'a' axis are also sensitive to the composition. As shown in Fig. 8, the 'a' axis length decreases with increase of firing temperature, and then remains constant above 1250°C. Since the peaks of crystalline mullite in the samples calcined at 950 and 1050°C, observed by XRD, were too small, few and very broad to be measured, therefore, the values of lattice parameters calculated at this temperature may be uncertain (high standard deviations, up to 4%). On the other side, lattice parameters of 'b' and 'c' axes are almost constant and coincide with the value reported in JCPDS 15-776 above 1150°C. According to the Cameron,[27] the mullite obtained by firing at low temperature (1150°C) appears to have a composition of $\approx$ 78 wt% Al_2O_3. This composition is very close to that of the metastable solubility limit of mullite in the system Al_2O_3–SiO_2.[28–31] As heating temperature increases, the alumina content in crystalline mullite phase decreases, changing its composition up to become stoichiometric mullite.

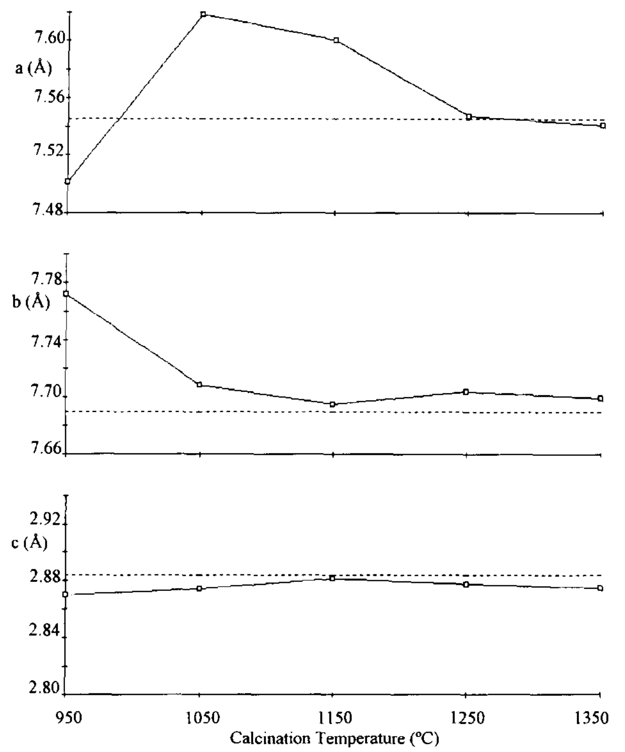


Fig. 8. Lattice parameters of mullite calcined at different temperatures. The dashed lines correspond to theoretical values of stoichiometric mullite.

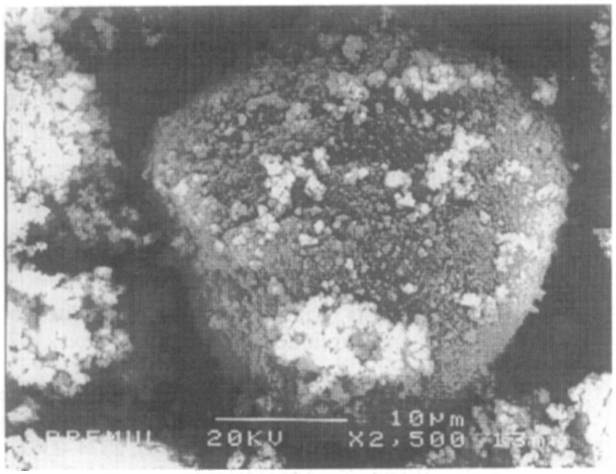
As described above, in precipitation reaction an alumina layer coating the silica surface was formed. Initially, by heat treatment of precursor, the elimination of SO_3 ion occurred, and in the interface between silica and alumina, crystalline mullite (alumina rich) and spinel (γ-alumina type) were formed. In order to complete reaction, temperatures $\geq$ 1250°C were necessary, for increasing dissolution of Al_2O_3 in the siliceous phase. Thus, we suppose that this homogeneous precipitation process can achieve an intermediate homogeneous mixture. This mixture homogeneity falls into both categories (1) and (2) (Fig. 3).

3.4 Characterisation of mullite powder

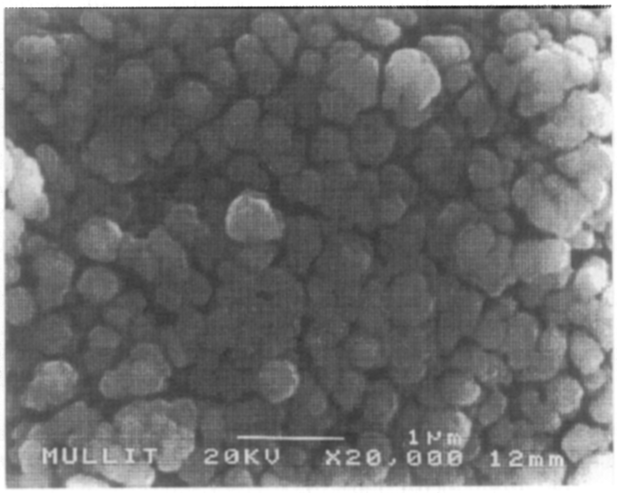
Chemical analysis of the powder calcined at 1350°C, determined by flame atomic absorption spectroscopy and X-ray fluorescence spectroscopy (XRF), confirmed that the final product was stoichiometric mullite (71·8 wt% Al_2O_3 and 28·2 wt% SiO_2), with very low level of impurities (i.e. total amounts of: Na_2O, K_2O, MgO, CaO, Fe_2O_3, and $SO_3 \leq 0{\cdot}01$ wt%).

The microstructure of the precursor calcined at 1350°C for 1 h, reveals that powder contains agglomerates with relatively large ($\approx$ 20 μm) particles [(Fig. 9(1)]. The precursors' morphology before and after calcined was not modified. The agglomerates after calcining could be milled effortlessly, and thus the large aggregates could be broken down rapidly into only primary particles. These primary particles had sizes in the range ($\approx$ 100–200 nm [(Fig. 9(2)].

The specific surface area of the milled sample is 27·5 m^2 g^{-1}, and the particle diameter, calculated by surface area data, is $\approx$70 nm coinciding with SEM data. On the other hand, this value is almost equal to that obtained by Suzuki *et al.*,[26] who



(1) General view of an agglomerate



(2) Primary particles

Fig. 9. Scanning electron micrographs of calcined powder.

produced the powder through alkoxide route (sol–gel method) by heating the precursor at 1200–1300°C. This result indicates that the homogeneous precipitation method is as efficient as sol–gel process to prepare fine pure mullite powder. However, the first method is more simple and inexpensive than the other.

4 Conclusions

1. By means of homogeneous precipitation, a mullite precursor was prepared, which could be filtered easily and both ions of ammonium and sulphite could also be eliminated completely by consecutive washing with water. This process could precipitate the total aluminium quantities in solution.
2. The precursor obtained was composed of agglomerates ($\approx 20\,\mu$m) with spherical primary particles of $\approx$ 100–200 nm in size. These particles consist of a silica core coated with basic aluminium sulphate.
3. By heating at 950°C for 1 h, precursor was transformed principally into spinel and a trace of crystalline mullite. In order to complete crystallisation, temperatures $\geq$ 1250°C was required. During heating treatment, the particles' morphology was not modified.
4. The powder calcined could be milled effortlessly, and thus the large aggregates could be broken down rapidly into only primary particles.
5. The final product was stoichiometric mullite (71·8 wt% Al_2O_3 and 28·2 wt% SiO_2), with very low level of impurities (i.e. total amounts of: Na_2O, K_2O, MgO, CaO, Fe_2O_3, and SO_3 $\leq$ 0·01 wt%).
6. The specific surface area of the milled product was 27·5 $m^2 g^{-1}$, and the diameter of particles was $\approx$ 100–200 nm.
7. The crystallisation path of mullite in the homogeneous precipitation system was: amorphous precursor → espinela/primary mullite → crystalline mullite. This crystallization path corresponding to an admixture of atomic and molecular level precursor type (Schneider *et al.*,[20]).
8. This homogeneous precipitation method is a new sort of inexpensive and efficient way to prepare the fine pure mullite powder.

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