Chem. Mater. **2003,** *15,* 2247−2252

Novel Microwave Method for the Synthesis and Sintering of Mullite from Kaolinite

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Received January 9, 2003. Revised Manuscript Received March 27, 2003

A novel and potentially economical microwave route has been developed for the synthesis and sintering of mullite from the naturally available minerals kaolinite and alumina. Mullite obtained by this route could be sintered to as high as 98% of theoretical density in under 60 min. A detailed structural investigation has been carried out using XRD, IR, and MAS NMR. It is clearly evident from the structural studies that there is a partial conversion of octahedral Al to tetrahedral Al with time during the formation of mullite. Also, it is evident that the exsolved SiO_2 reacts with the added Al_2O_3 to form secondary mullite over primary mullite which is nucleated from the decomposition of kaolinite. A detailed microstructural evolution of this conversion has been followed. A possible microwave−material interaction has been discussed for the rapid formation of mullite.

Introduction

Mullite is an aluminosilicate ceramic of great technological importance and several studies have been reported regarding its preparation, characterization, and sintering.[1−8] The standard method of preparation of mullite ($3Al_2O_3{\cdot}2SiO_2$) is to heat kaolinite to high temperatures with the required quantity of Al_2O_3.[9−16] This reaction occurs only above ∼1300 °C. The course of this reaction is very interesting for the following reasons. Kaolinite, $Al_2Si_2O_5(OH)_4$, is a layered aluminosilicate in which each layer in the structure in reality consists of two sublayers.[9] The Al sublayer consists of octahedrally coordinated Al and structural water in the form of hydroxyl groups. The other sublayer consists of tetrahedrally coordinated Si. Decomposition of kaolinite reveals that the first stage of decomposition occurs below 500 °C when water gets eliminated. This results in a collapse of the Al sublayer leading to the formation of metakaolinite. The second stage involves a reaction between the collapsed sublayer of Al_2O_3 and of SiO_2 at still higher temperature (∼1000 °C) which results in the formation of mullite and SiO_2. The exsolved SiO_2 is generally amorphous (a-SiO_2) and crystallizes to cristobalite at higher temperatures unless there is added Al_2O_3 available for further reaction.[9,14,17,18] The internally converted product mullite is referred to as primary mullite (p-mullite) and the product resulting from the reaction between exsolved SiO_2 and added Al_2O_3 is referred to as secondary mullite (s-mullite).[13,14] Metakaolinite can decompose via an alternate pathway which leads to the formation of either γ-Al_2O_3 or a highly disordered spinel structure of Al_2O_3.[14]

An important structural change that occurs during the formation of mullite is the partial conversion of octahedral Al (both in kaolinite and Al_2O_3) to tetrahedral Al, and this is an endothermic process.[18] During the formation of both p- and s-mullite Al^{3+} ions have to diffuse into SiO_2 sheets formed during the initial decomposition of kaolinite. This diffusive reaction, by its very nature, is slow and activated.[17,18] Therefore, it provides opportunity for the system to explore alternate reaction paths. This is the reason for the formation of spinel-like structure reported in the literature.

The involvement of ionic diffusion immediately suggests that it should be possible to exploit a microwave route for the preparation of mullite. Because of the presence of hydroxyl groups kaolinite is susceptible to microwaves particularly at higher temperature, but it reaches a maximum of 200 °C in the absence of a

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10.1021/cm0301423 CCC: $25.00

secondary heater (such as SiC). Metakaolinite and Al_2O_3 become reasonably microwave active above 500 °C. Therefore, by using a secondary heater like SiC and increasing the temperature of the reactants, it should be possible to carry out microwave synthesis of mullite. In this paper we describe a very efficient microwave route for the preparation of mullite. The fastness of the reaction appears to suppress alternate reaction pathways and lead to very rapid formation of s-mullite by the reaction between Al_2O_3 and a-SiO_2. During product formation there are unique morphological changes despite which the integrity of the pellet remains unaffected. In a single step mullite is not only formed but gets sintered to about 98% of theoretical density.

Experimental

Kaolinite (BHEL, India) and α-Al_2O_3 (Aldrich) were used as starting materials. The chemical composition of kaolinite is as follows (all units are wt %): 43.7 SiO_2, 38.8 Al_2O_3, 1.4 Fe_2O_3, 1.0 TiO_2, 0.4 K_2O, 0.3 Na_2O, and 0.05 CaO. The reaction to be brought about was

$$Al_2Si_2O_5(OH)_4 + 2Al_2O_3 \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 2H_2O\uparrow$$

Kaolinite and Al_2O_3 were mixed in 1:2 stoichiometric ratio and ground together in an agate pestle and mortar while using acetone as grinding media. The powders were of 1800 mesh size. The powders were pressed into pellets of 10-mm diameter and 2-mm thickness using a load of 70 KN in a uniaxial press. Pellets were placed inside a thin-walled SiC crucible which was placed inside a well-insulated monomode microwave cavity (Micronde Energy Systems, France). The SiC crucible is used as a secondary heater in the microwave field. Pellets were irradiated with 2.45 GHz microwaves at a power level of 550 W for various durations of time after which they were allowed to cool in the microwave cavity. Temperature attained by the pellet was continuously monitored during microwave irradiation by using a sheathed Pt−10%Rh thermocouple kept in contact with the pellet. Positioning of the thermocouple was perpendicular to the direction of irradiation. Considering the thickness of the pellet was 2 mm, much lower than the penetration depth (3.9 cm), the temperature was assumed to be uniform inside the pellets. The accuracy of temperatures recorded by this method is generally ±5 °C taken over the whole range of heating. The products formed by the microwave reaction were characterized using X-ray diffraction (XRD, JEOL-JDX 8P, Japan), infrared spectroscopy (FTIR, Perkin-Elmer, Spectrum1000, UK), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR, Bruker DSX300, Germany), and scanning electron microscopy (SEM, JEOL-JSM-5600LV, Japan). Volume changes of the pellets after microwave exposure were also measured. Densities of the sintered pellets were measured using the Archimedes method.

Results and Discussion

Microwave reactions were found to be very rapid.[19−21] The most important observation made was that despite elimination of structural water from kaolinite, the structural integrity of the pellet was not lost even during this fast reaction. The XRD patterns of samples irradiated for 10, 20, 30, 45, and 60 min are shown in Figure 1. At the end of only 10 min formation of mullite is clearly in evidence. There are also strong peaks arising from the reactant Al_2O_3. A small hump in the region of $2\theta = 20°-30°$ is suggestive of the formation of a-SiO_2. The intensities of Al_2O_3 peaks have decreased and those of mullite have increased in the 20 and 45 min samples. Al_2O_3 peaks have vanished completely in the 60 min sample. At the end of 10 min, the observed mullitic peaks are probably due to p-mullite. The a-SiO_2−Al_2O_3 reaction giving rise to s-mullite contributes to the growth of mullitic peaks in the 20, 45, and 60 min samples. The temperature variation during the reaction, monitored by keeping the shielded Pt−Rh thermocouple in contact with the pellet, is shown in Figure 2. Temperature is nearly constant after 20 min (within a range of 30 °C). Thus, the formation of s-mullite to a first approximation may be considered as having formed, under isothermal conditions. The XRD pattern did not reveal any significant size variations in widths so that a first approximation particle size effects could be ignored. Therefore, the intensity of the (210) peak of mullite in the 60-min irradiated sample minus the intensity of the same peak at the end of 10 min (which represents approximately the quantity of p-mullite and beginning of the formation of s-mullite) as a measure of maximum s-mullite formed, and a kinetic plot of f vs ln t was generated as in Figure 3 where f is the fraction of s-mullite formed. The variation is quasi-linear suggesting that the unconverted fraction of the reactants, $(1 - f)$, can be considered as varying according to a linear law $(-(dC_r/dt) \propto KC_r)$ where $C_r = 1 - f$, and K is the rate constant. Because a stoichiometric mixture has been used, the probability of the reaction appears to be determined by the concentration of either of the components. Nevertheless, this conclusion is intended to be only a quantitative deduction.

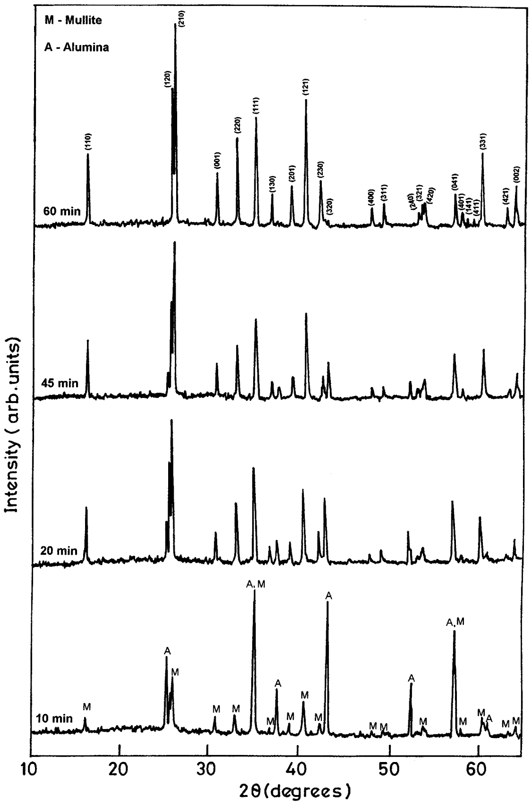

Figure 1. XRD patterns of kaolinite and Al_2O_3 mixture at different intervals of microwave irradiation.

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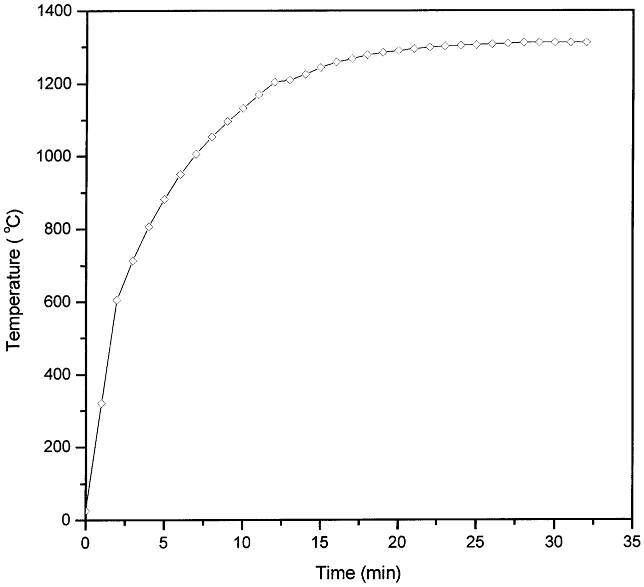

Figure 2. Temperature vs time profile of kaolinite and Al_2O_3 mixture under microwave irradiation.

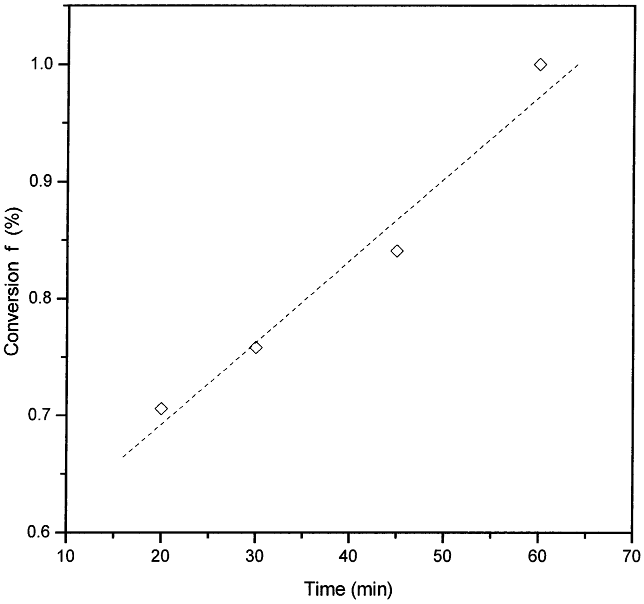

Figure 3. Fractional conversion of kaolinite and Al_2O_3 to s-mullite with time.

XRD patterns in Figure 1 provide further insight regarding the nature of the microwave synthesis. First, because crystalline SiO_2 (cristobalite) is not seen, collapse of the layer structure of metakaolinite at the end of 10 min is also associated with the destruction of the order in the SiO_2 layers. A part of SiO_2 in the layer is involved in the formation of p-mullite.[14] Second, the microwave reaction is very rapid and it blocks the chances for the formation of ordered defect phases such as spinel during the reaction. At the end of 60 min the product obtained is pure mullite, and the relative intensities of the peaks of mullite match well with those in the literature reports.[22,23] *These features clearly reveal the superiority of the microwave reaction in comparison to all other conventional methods presently known.*

Variations of the local structures have been followed using MAS NMR as shown in Figure 4 . MAS NMR of ^{29}Si is shown in Figure 4a. In the 10-min product, silica is present only as a-SiO_2. The −109 ppm peak is quite characteristic of Si connected to four other Si through Si−O−Si bridges (referred to as Q_4).[24] It also confirms the formation of p-mullite through the ^{29}Si peak at −88.9 ppm which is due to ^{29}Si present in Si−O−Al linkages and is in agreement with the XRD results.[10,18] The rapid increase of the mullitic peak at −88.9 ppm with time in the 20-, 30-, and 45-min samples is also associated with an amorphous vanishing −109 ppm peak due to a-SiO_2. The ^{27}Al MAS NMR shown in Figure 4b fully complements the ^{29}Si NMR results. The ^{27}Al MAS NMR of the 10-min sample is dominated by the signal due to octahedral Al signal at −1 ppm because of the large quantity of the reactant Al_2O_3 present in the mixture. This suppresses the signal due to tetrahedral ^{27}Al, which is in a smaller concentration. But in the 20-min product there is a clear emergence of a mullitic tetrahedral ^{27}Al peak at ∼50 ppm. The 30-min sample also reveals the possibility that some of the tetrahedral Al atoms are associated with vacancies in their coordination tetrahedra, because the tetrahedral ^{27}Al resonance peak is split with the new feature at 47 ppm. Nevertheless, in 45- and 60-min products, the splitting feature becomes less pronounced, suggesting gradual elimination of the vacancies as sintering progresses (see below). Therefore, the NMR results are in complete agreement with XRD results which suggest direct microwave-induced reaction between a-SiO_2 and added Al_2O_3.

IR spectra of the reacted samples are shown in Figure 5. The dotted lines correspond to the peak positions expected from theoretical calculations of Mackenzie et al.[25] Three groups of IR features can be distinguished in the spectra. S_1, S_2, and S_3 are vibrations arising from $[SiO_{4/2}]^0$ tetrahedral units (S_1, S_2, and S_3 are asymmetric stretching, symmetric stretching, and Si−O−Si bending modes, respectively).[4] As expected, the intensity of 1100 cm^{-1} mode exhibits a pronounced increase up to 10 min during the formation of a-SiO_2. Afterward the peak shifts toward higher frequencies because of the formation of Si−O−Al connections characteristic of mullite. The 920 cm^{-1} mode, however, remains insensitive to mullite formation and this is quite expected because it is the symmetric stretching mode of SiO_4 units. The intensities of the 450 cm^{-1} (theoretical value being 490 cm^{-1}) peak due to Si−O−Si bending mode follows a trend similar to that of the 1100 cm^{-1} asymmetric stretching mode, and it decreases gradually when substituted by Si−O−Al bending. The modes arising from tetrahedral $[AlO_{4/2}]^-$ units (which are not present in the initial reaction mixture) increase in intensity with time as revealed by the 1180 cm^{-1} band. A similar trend is exhibited by the 720 cm^{-1} band also which is attributed to $[AlO_{4/2}]^-$ units. The 830 cm^{-1} band is less sensitive, although in the 15-min sample it exhibits a relative increase in intensity. This is perhaps an indication of the formation of primarily mullite, which marks the beginning of the formation of tetrahedral Al. How-

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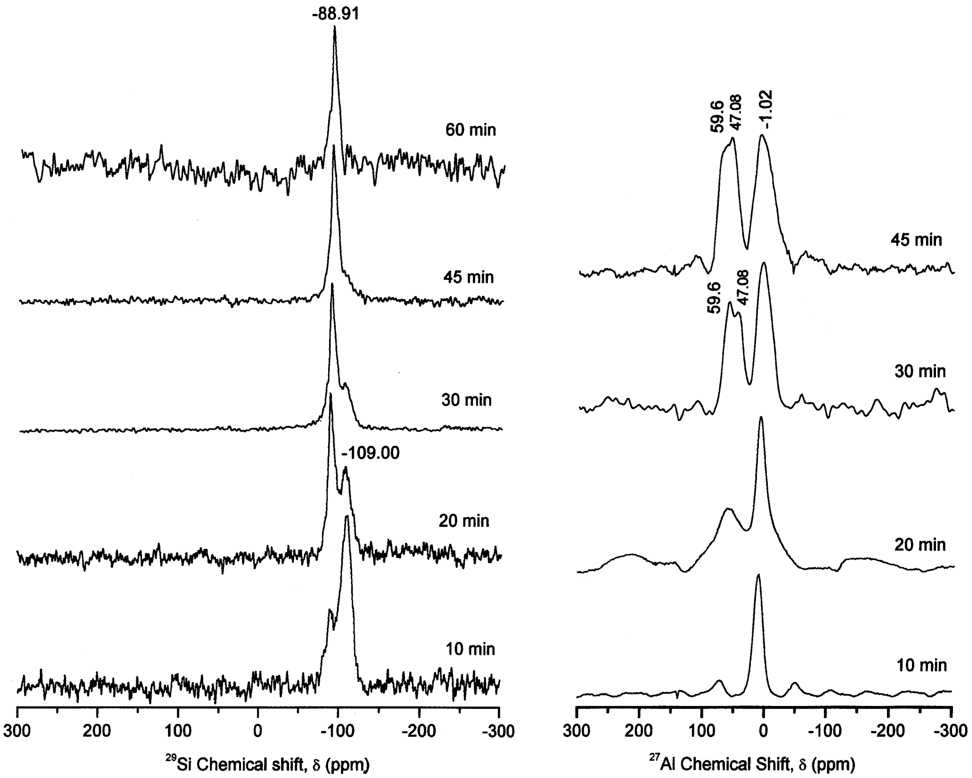

Figure 4. (a) ^{29}Si- and (b) ^{27}Al-MAS NMR spectra of kaolinite and Al_2O_3 mixture at different intervals of microwave irradiation.

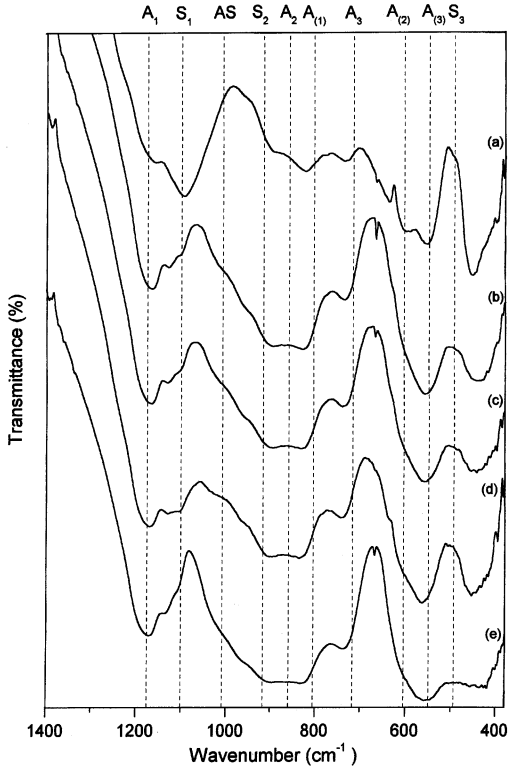

Figure 5. IR spectra of kaolinite and Al_2O_3 mixture at different intervals of microwave irradiation: (a) 10 min, (b) 20 min, (c) 30 min, (d) 45 min, and (e) 60 min. S_1, S_2, S_3; A_1, A_2, A_3; and $A_{(1)}$, $A_{(2)}$, $A_{(3)}$ are the theoretical values of the peaks arising from $[SiO_{4/2}]^0$, $[AlO_{4/2}]^-$, and $[AlO_{6/2}]^{3-}$ units, respectively. AS is due to Si$-$O$-$Al bending.

ever, the peaks arising from $[AlO_{6/2}]^{3-}$ and $[AlO_{4/2}]^-$ units are very close to each other in this region and difficult to delineate. The octahedral Al has a characteristic peak in the region of 550$-$600 cm^{-1}. These peaks are distinguishable in the 10- and 15-min samples, more so because they originate both from Al_2O_3 and p-mullite. But as the reaction progresses, these peaks merge into one broad band as observed in the 45- and 60-min samples. Therefore, the evolution of p- and s-mullite in the microwave reaction monitored using IR spectra are in complete agreement with the results from XRD and MAS NMR studies. Together the results confirm that the reaction between Al_2O_3 and exsolved *a*-SiO_2 after initial 10 min of heating is a direct one-step process in microwaves.

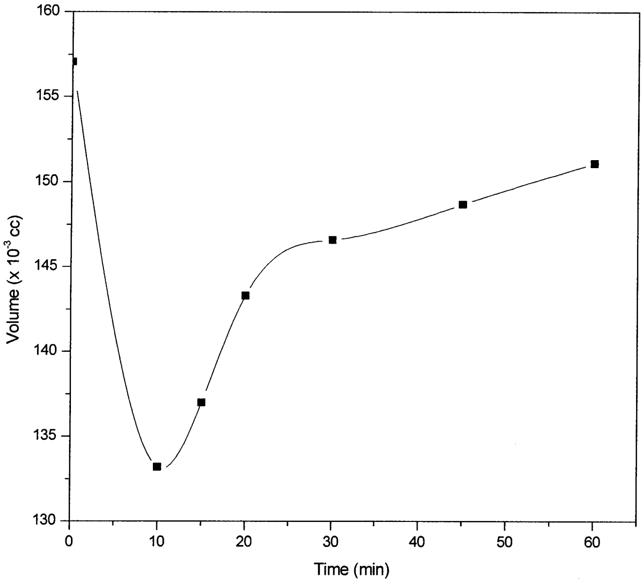

Figure 6. Volume change observed during microwave irradiation of kaolinite + Al_2O_3 pellet.

Another fascinating and industrially important feature noted in this work is the physical integrity of the pellet throughout the reaction and evolution of the

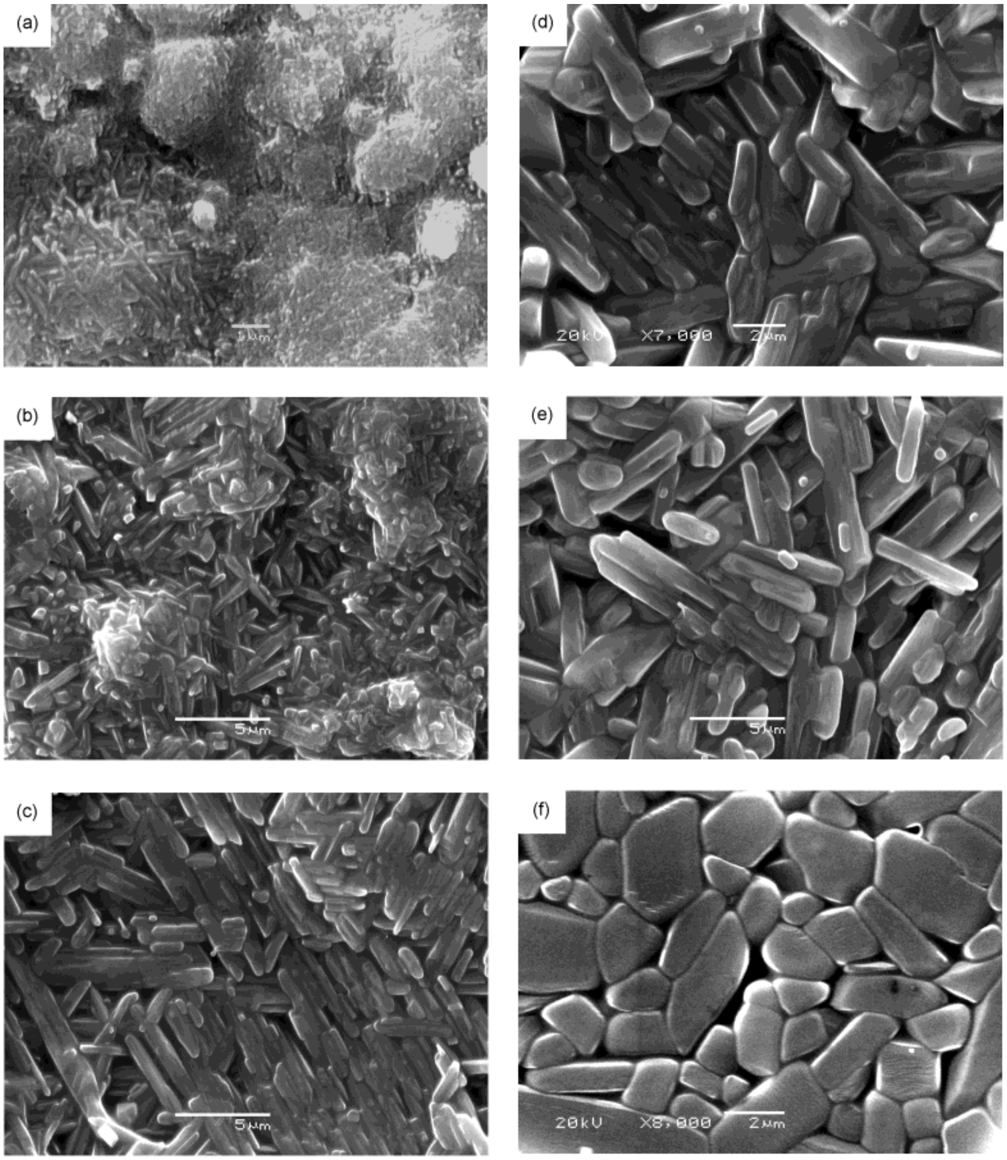

Figure 7. SEM images revealing the microstructural evolution of kaolinite and Al_2O_3 pellet under microwave irradiation at the end of (a) 10 min, (b) 15 min, (c) 20 min, (d) 30 min, (e) 45 min, and (f) 60 min.

microstructure. The elimination of water from the kaolinite structure appears to be smooth despite very rapid heating and associated collapse of the layered structure. This is perhaps a feature of layered clays as far as elimination of water is concerned. Correspondingly, there is an initial isotropic shrinkage of about ∼ 8% (kaolinite grains are randomly oriented). As pointed out earlier, the onset of the reaction between *a*-SiO_2 and Al_2O_3 (formation of s-mullite) marks the beginning of the conversion of part of the octahedral Al in Al_2O_3 to tetrahedral Al. This results in the gradual expansion and hence reverses the volume shrinkage process. The volume increases as shown in Figure 6. This results in a gradual recovery of the volume of the pellet and a decrease in its density. However, the range of variation of density through the entire process is not very high, varying between 3.05 and 3.15 g/cm^3. The final density of 3.10 g/cm^3 (60-min sample) corresponds to 98% of the theoretical density of mullite. The microstructural evolution in microwaves observed in SEM is shown in Figure 7. The 10-min sample appears as a collage of just-collapsed particles with the formation of tiny rodlike features attributable to p-mullite clearly seen. The 15- and 20-min samples indicate the growth of these tiny rods which is evidently due to the formation of s-mullite to which the p-mullite rods act as seeds. The 30- and 45-min samples show that this process continues. There is no evidence of a second distinguishable phase attributable to either glassy SiO_2 or to grainy Al_2O_3. We therefore speculate that Al_2O_3 and *a*-SiO_2 first form an amorphous aluminosilicate phase which simply surrounds these rodlike mullite particles. The processes of $Al_2O_3-SiO_2$ reaction and growth of mullite perhaps occur simultaneously until the completion of the reaction. The 60-min sample reveals a significant degree of recrystallization and a reduction in the aspect ratio of these rods. It also reveals some amount of uneliminated porosity which accounts for the 2% deficit in the observed density. However, the proportion of Al_2O_3 is very high compared to that of SiO_2 in the reaction mixture, and formation of homogeneous melt or a glass is very difficult.

Another interesting feature of the microwave reaction is that the maximum temperature of the reaction recorded is only 1312 °C, which is well below (up to 300−400 °C) the temperature reported in conventional reactions. This again focuses on the possibility of a genuine microwave effect. It is now well established that microwave fields are very intense at interfaces, surfaces, and cavities during irradiation. The microwave field gives rise to pondermotive forces which reduce the reaction barriers very effectively.[26−29] During the formation of s-mullite, in particular, pondermotive effect may be responsible for rapid diffusion of Al^{3+} ions into SiO_2 layers. This may also be responsible for the observed I-order type kinetics. When the reaction is over and only particles of mullite are present at the end of 45 min, the pondermotive force acts at the interfaces and cavities bringing about a rapid growth of the grains and a systematic elimination of porosity.[30−33]

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