Journal of the European Ceramic Society 20 (2000) 413–421

Phase evolution in mechanically treated mixtures of kaolinite and alumina hydrates (gibbsite and boehmite)

J. Temuujin [a,*], K.J.D. MacKenzie [b], M. Schmücker [c], H. Schneider [c], J. McManus [d], S. Wimperis [d]

[a] *Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 51, Mongolia*
[b] *Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*
[c] *Institute for Materials Research, German Aerospace Center, 51140 Köln, Germany*
[d] *Physical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK*

Received 10 May 1999; received in revised form 20 June 1999; accepted 3 July 1999

Abstract

The phase evolution behaviour of kaolinite–gibbsite mixtures ground for 5 min and 4 h has been investigated by X-ray powder diffraction (XRD). Differential scanning calorimetry (DSC) and MAS NMR. The thermal behaviour of mixtures ground for 5 min was similar to that of kaolinite-α-alumina mixtures. After grinding for 4 h, the mixture is transformed into an amorphous state. Grinding caused the acceleration of thermal reactions in these mixtures, with a degree of mechanochemical reaction being found to occur between kaolinite and α-alumina. Grinding kaolinite-boehmite mixtures produced mullite precursors which were more homogeneous than those in which the kaolinite had been dehydroxylated, suggesting the participation of the structural water from the kaolinite. Secondary mullite is formed during thermal reaction of these mixtures by a solution-precipitation mechanism. The mullite initially formed was alumina-rich, but approached the stoichiometric composition with increasing firing temperature.

Keywords: Boehmite; Gibbsite; Kaolinite; Milling; Mullite

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1. Introduction

Mullite is an important material for both conventional and high-technology applications. The latter require high-purity mullite which is prepared by advanced processing techniques such as sol-gel synthesis, precipitation, hydrolysis, spray pyrolysis or chemical vapour deposition (CVD).[1] Mullite synthesised from mixtures of clay minerals with bauxite, aluminium hydroxide or alumina is used mainly for refractory purposes and furnace materials.[1] Kaolinite ($Al_2O_3.2SiO_2.2H_2O$) is a commonly-used clay mineral from which stoichiometric mullite can be prepared by heating with α-aluminium oxide[2] or gibbsite ($Al(OH)_3$).[3–5] The thermal decomposition of kaolinite above 980°C forms a mixture of primary mullite, silica and an impurity-containing silica-rich liquid. The latter two react with alumina to form secondary mullite upon further heating.[2,6] Several authors[2,6,7] have reported that during the heating of kaolinite-α-alumina mixtures, primary mullite is formed from the kaolinite above 980°C, with secondary mullite being formed at higher temperatures by a solution-precipitation mechanism via the transitory liquid phase. For complete mullitization of a kaolinite-α-alumina mixture, the firing temperature must be 1500–1700°C.

Kawai et al.[3] have reported that in mechanochemically treated kaolinite–gibbsite mixtures, exothermic mullite formation begins at 950°C, the mullite intensity increasing with increasing firing temperature without the formation of minor phases. Although these authors did not demonstrate a mechanochemical reaction between kaolinite and gibbsite, we believe that grinding should lead to the polymerization of Al-O-Si bonds for the following reasons: in mechanochemically amorphized gibbsite, the transformation temperature to α-alumina is lowered by more than 200°C, and the transformation is complete at about 1000–1100°C.[8] If mechanochemical reaction does not occur in kaolinite-gibbsite mixtures, this α-alumina should be detectable in

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* Corresponding author. Tel.: +976-1-364367; fax: +976-1-364367.
E-mail address: monchemi@majicnet.mn (J. Temuujin).

PII: S0955-2219(99)00188-0

the ground mixtures at about 1000–1100°C,[9] especially where high-purity kaolinite is used. The fact that Kawai et al.[3] did not observe α-alumina in this temperature range can be explained in terms of the stabilization of the transition alumina formed from the gibbsite by incorporation of a small amount of silica.[9,10]

Aluminium hydroxide exists in several modifications (gibbsite, bayerite, boehmite and diaspore).[11] Boehmite (γ-AlOOH) may have some advantages over gibbsite because of its lower water content which should result in less shrinkage during sintering. For the preparation of homogeneous mullite precursors by mechanochemical treatment of kaolinite-alumina mixtures, it is necessary to break the Si–O–Si bonds of the tetrahedral kaolinite sheet and form new Si–O–Al tetrahedral bonds. This may be facilitated by the use of dehydroxylated kaolinite (metakaolinite) which has a defect structure and may more readily form such bonds, lowering the temperature of mullite formation.

The amorphous mullite precursors formed by grinding kaolinite-hydrous alumina mixtures cannot be sufficiently well characterized by XRD to determine the details of the mechanochemical reaction occurring between the gibbsite and kaolinite. However, the local environment of Al and Si atoms has been studied by MAS NMR in ground mixtures of gibbsite and amorphous silica[9,10] and in the ground clay mineral pyrophyllite.[12] In the present work, solid state MAS NMR spectroscopy was used to study ground kaolinite–gibbsite and kaolinite–boehmite mixtures to determine the nature and extent of any mechanochemical reactions. The relative mechanochemical reactivity of boehmite with kaolinite and metakaolinite was also examined by comparing the mullite formation temperature and homogeneity of both mixtures ground under identical conditions.

2. Experimental procedure

The starting materials used in the investigation were kaolinite (Kaolin und Quarzsandwerke GmbH & Co., Germany), gibbsite (Merck, Germany) and boehmite (Dispersal, Condea Chemie, Germany). The kaolinite contained minor amounts of mica and quartz. Its chemical analysis is shown in Table 1.

Table 1
Chemical composition of the kaolinite[a]

Element	wt%	Element	wt%
Al_2O_3	36.5	SiO_2	47.5
K_2O	2.1	CaO	0.05
Fe_2O_3	0.58	TiO_2	0.35

[a] Loss on ignition 13%.

Metakaolinite was prepared from this kaolinite by heating at 700°C for 2 h.

Mixtures of kaolinite + gibbsite (K–G), kaolinite + boehmite (K–B) and metakaolinite + boehmite (M–B) with a stoichiometric mullite composition were dry ground in a planetary ball mill (Retsch PM4) at a rate of 250 rpm. The weight ratio of the milling media to powder was 100:1 and the grinding pot was Teflon. Although the ground samples contained slight contamination by debris from the milling media, the effect of this was assumed to be negligible for the present purpose. The effect of grinding time was investigated in the kaolinite-gibbsite mixtures by grinding for 5 min and 4 h. Since the longer grinding time was found to be necessary to induce mechanochemical effects, this longer grinding time was adopted in the subsequent experiments on the kaolinite–boehmite and metakaolinite–boehmite mixtures.

The ground samples were heated in air at a rate of 5°C min^{-1}, held at 900–1300°C for 2 h then cooled at 10°C min^{-1}. X-ray powder diffraction (XRD) was carried out using a computer-controlled Siemens D-5000 diffractometer with Cu K_α radiation. Differential scanning calorimetry (DSC) was carried out in air at a heating rate of 10°C min^{-1} to 1400°C using a Netzsch 404 thermoanalyser. The mullite lattice parameters were determined by a least-squares method using high purity Si powder as the internal standard. The ^{27}Al and ^{29}Si MAS NMR spectra were obtained at 9.4 T using a Bruker MSL 400 spectrometer operating at 104.3 MHz for Al and 79.5 MHz for Si and sample spinning speed of 9 kHz. The ^{27}Al spectra were acquired using a 1 μs 90° pulse with a 1 s recycle delay, and were referenced to $Al(H_2O)_6^{3+}$. The ^{29}Si spectra were acquired using a 1.5 μs 90° pulse with a 30 s recycle delay, and were referenced to tetramethylsilane (TMS).

3. Results and discussion

3.1. Mixtures containing gibbsite

Fig. 1 shows the XRD patterns of the starting materials and ground K–G samples. Grinding for 5 min caused a decrease in the intensity of the gibbsite and kaolinite peaks but without the destruction of their crystalline structure. The sample ground for 4 h is fully amorphous, but shows peaks due to Si_3N_4 contaminant introduced from the milling media. Although this will slightly increase the silica content above that for stoichiometric mullite, Liu et al.[7] have shown that slight differences in the starting composition of kaolinite-α-alumina mixtures produce little change in the phase evolution or the reaction kinetics.

The DSC trace for the sample ground for 5 min shows endothermic effects at 320 and 539°C due to the dehydration of gibbsite and of kaolinite respectively (Fig.

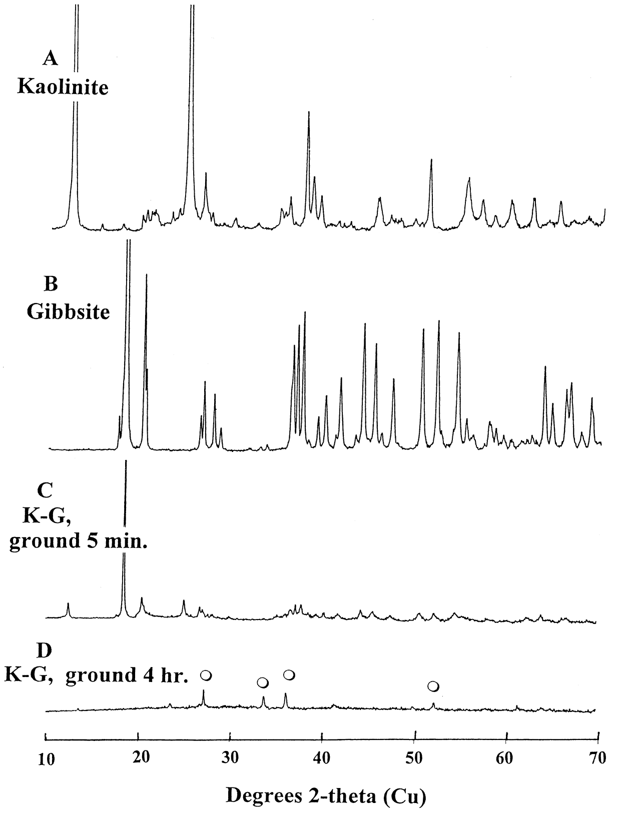

Fig. 1. XRD traces of the kaolinite and gibbsite starting materials and their mixtures ground for the indicated times. ○, silicon nitride from the milling media.

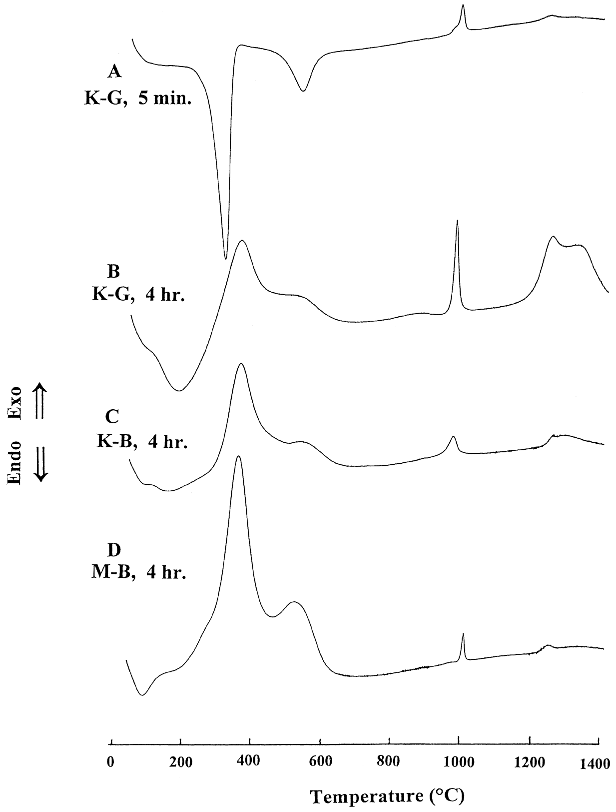

Fig. 2. DSC curves for ground mixtures. A and B, kaolinite + gibbsite. C, kaolinite + boehmite; D, metakaolinite + boehmite. Heating rate: 10°C min^{-1} in air.

2A). The two small exothermic events at 980 and 1249°C are due to the formation of the spinel phase and the acceleration of mullite growth, respectively. Thus, the DSC curve of this sample shows all the thermal effects expected in pure kaolinite and gibbsite. By contrast, the DSC trace of the sample ground for 4 h (Fig. 2B) contains a broad endotherm at about 100°C, consistent with the mechanochemical dehydration of kaolinite and gibbsite. Additional exothermic peaks also occur at 366, 539, 1241 and 1317°C. The latter two events are respectively due to the acceleration of mullite growth by liquid formation or by reaction of the spinel phase with excess silica, and cristobalite formation from amorphous silica.[13] The endothermic peaks at 366 and 539°C are due to the oxidation of Teflon debris from the pot. The intensity of all the exothermic peaks is greater than in the sample ground for 5 min, confirming that they are associated with mechanochemical changes in the sample.

The XRD and thermal analysis results for ground kaolinite–gibbsite mixtures are confirmed by the ^{27}Al and ^{29}Si MAS NMR spectra of these samples (Fig. 3).

Sample K–G ground for 5 min (Fig. 3E) retains the principal spectral characteristics common to both kaolinite and gibbsite starting materials (an octahedral resonance at about 3–9 ppm (Fig. 3A and C) and a sharp Si resonance at −92 ppm arising from the tetrahedral kaolinite sheet). Formation of aluminosilicate precursors of mullite would lead to the appearance of a new tetrahedral Al resonance at about 55–60 ppm, and another peak at about 30–33 ppm which is attributed to either pentahedral Al or to the distorted tetrahedral tricluster unit which occurs in mullite.[14]

Aluminosilicate precursors also show characteristic ^{29}Si resonances at about −83 to −87 ppm.[9]

Grinding the mixture K–G for 5 min produces no evidence of these features, which however occur in K–G ground for 4 h (Fig. 3F and J). Thus, the NMR results indicate that grinding K–G for up to 4 h is necessary to induce the formation of new Si–O–Al bonds which facilitate the thermal crystallization of mullite.

3.2. Mixtures containing boehmite

The XRD patterns of the starting materials and ground K–B and M–B mixtures are shown in Fig. 4. Grinding caused the kaolinite to become fully amorphous, by contrast with the boehmite, which retained broadened diffraction peaks of reduced intensity. Grinding for 4 h caused a greater degree of structural distortion in the kaolinite-containing mixture than in that containing metakaolinite. The greater stability of

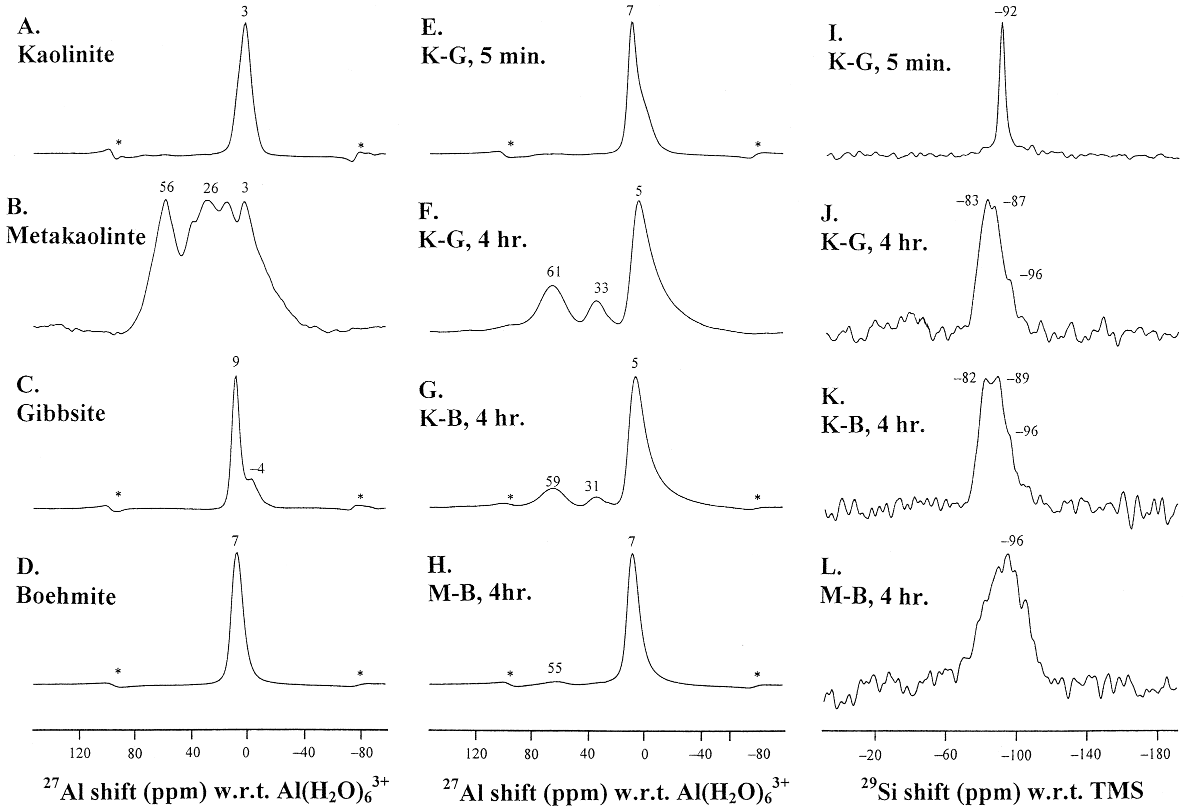

Fig. 3. Room-temperature 9.7 T MAS NMR spectra of the starting materials and ground mixtures as indicated. Asterisks denote spinning side bands.

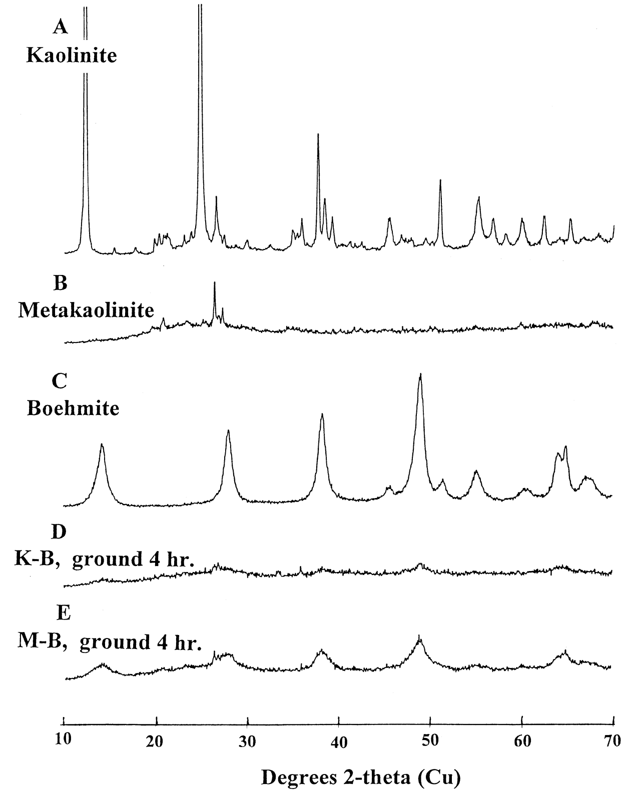

Fig. 4. XRD traces of kaolinite, metakaolinite and boehmite starting materials and their mixtures ground for 4 h.

boehmite towards mechanochemical treatment is indicated by the fact that it is not fully amorphized under conditions which cause the kaolinite to be amorphized; this stability of the boehmite lattice towards grinding is in contrast to gibbsite and bayerite.[8] A small amount of Si_3N_4 from the milling media is again seen by XRD, and the samples also contain Teflon debris from the milling pot.

The DSC traces of K–B and M–B (Fig. 2C and D) show exothermic effects at 360°C due to oxidation of the Teflon debris, at 972 and 1004°C respectively (formation of the spinel phase) and at 1245 and 1257°C respectively (mullite formation). The endothermic dehydroxylation peak of kaolinite is absent due to the effect of amorphization. Moreover, both samples show an exothermic peak at about 516°C which may be due to the conversion of boehmite to γ-alumina. Although no exothermic reaction has been reported at 500–600°C in either ground or unground boehmite,[8] the XRD traces of samples fired at 500 and 600°C (not shown here) contain peaks of γ-alumina (JCPDS card 10-0425). The general features of the DSC traces of K–B and M–B are comparable.

The conclusion that mixture K–B is more reactive to grinding than mixture M–B is also confirmed by the MAS NMR results (Fig. 3). The ^{27}Al spectra of both boehmite-containing mixtures ground for 4 h show evidence of Si–O–Al formation [i.e. the resonances at 59 and 31 ppm in K–B (Fig. 3G)], but these are less highly developed in M–B, in which the 55 ppm peak is only just discernable and the 30 ppm peak is not detected (Fig. 3H). Interestingly, the principal effect of grinding M–B is to destroy the characteristic tetrahedral/pentahedral features of metakaolinite at about 20–56 ppm (Fig. 3B) without evidence of significant formation of a mullite precursor. The ^{29}Si MAS NMR spectrum of K–B ground for 4 h (Fig. 3K) also contains a characteristic aluminosilicate resonance at -82 ppm, but the situation is less clear in M–B, in which the sharp kaolinite resonance at -92 ppm has been broadened and shifted to about -96 ppm during the formation of metakaolinite by dehydroxylation prior to grinding. The envelope of the broad ^{29}Si spectrum of M–B ground for 4 h (Fig. 3L) could contain a contribution at about -86 ppm from an aluminosilicate, in addition to the metakaolinite features above about -100 ppm. The combined evidence of the ^{27}Al and ^{29}Si NMR spectroscopy is that mechanochemical treatment has produced a more homogeneous and highly polymerized mullite precursor from the mixture containing kaolinite than from metakaolinite.

3.3. Heat treatment of the ground mixtures

Fig. 5 shows the XRD patterns of K–G samples ground for 5 min then heated at different temperatures. These traces show evidence of poor homogeneity, since the expected reaction products of the individual kaolinite and gibbsite constituents are detectable up to high temperatures. The reaction sequence of unground gibbsite has previously been shown[8,11] to be $Al(OH)_3 \rightarrow \chi \rightarrow \kappa \rightarrow \alpha\text{-}Al_2O_3$, the transformation being complete at about 1200–1300°C. In the present sample ground for 5 min and heated at 1000°C (Fig. 5B), a small amount of corundum was detected, with mullite starting to form from the kaolinite at 1100°C. At this temperature the samples contain mullite, a significant amount of crystalline corundum and an impurity-containing silica-rich liquid phase resulting from the presence of the K_2O which produces a ternary eutectic at 985°C.[15] After firing at 1400°C (not shown here), the intensities of the corundum peaks decrease and have almost disappeared by 1600°C. The phases formed in this sample are similar to those reported in kaolinite-α-alumina mixtures, consistent with a lack of mechanochemical reaction. The mullite XRD peak area increases continuously up to 1600°C as the mullite content increases. As reported previously[2,6,7] for the kaolinite-α-alumina system, primary mullite forms first from the kaolinite, with secondary mullite crystallizing >1400°C by solution of α-alumina in a liquid phase, followed by mullite precipitation from this liquid. The reaction between the newly-formed α-alumina and the constituents of kaolinite is detectable between 1300 and 1400°C by a decrease in the intensity of the corundum peaks and an increase in the mullite peaks. The onset temperature for extensive reaction between α-alumina and the kaolinite constituents is lower than those reported by Liu et al.[7] and Rezaie et al.,[2] due either to the greater reactivity of the newly-formed α-alumina in our system compared with their corundum, or to the higher alkali content of our kaolinite, or both.

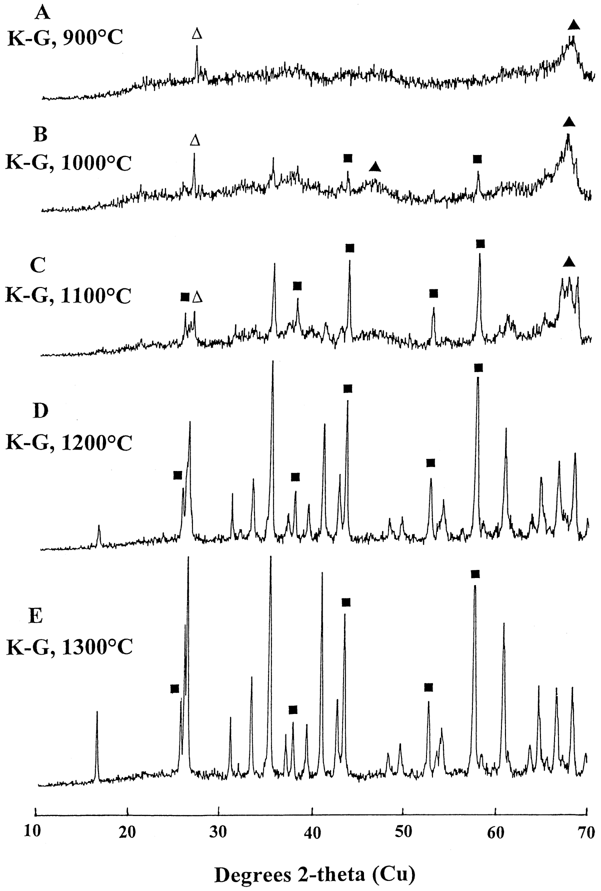

Fig. 5. XRD traces of kaolinite–gibbsite mixtures ground for 5 min then heated in air at the indicated temperatures. Key: △, quartz; ▲, spinel phase; ■, α-alumina; unmarked peaks: mullite.

Fig. 6 shows the XRD phase evolution behaviour of the sample ground for 4 h. At 900°C the peaks of Si_3N_4 and small amounts of transition alumina were still detectable by XRD. By 1000°C the intensities of the 46 and 67° 2θ CuK_α peaks have increased, reflecting the formation of the spinel phase from kaolinite and possibly also from mechanochemically polymerized aluminosilicate. By contrast with the results of Kawai et al.[3] for ground kaolinite–gibbsite mixtures, and Sanchez-Soto et al.[12] for ground pyrophyllite, we did not observe mullite formation after the strong 980°C exotherm, suggesting that this thermal feature is not due to the formation of mullite. Sanz et al.[16] have suggested that the 980°C exotherm in kaolinite is most likely to be due to the release of energy associated with the transformation of the Al ions to a more stable sixfold coordination. Such an explanation may also apply to the present system, since this temperature corresponds to the abrupt disappearance of the ^{27}Al NMR peak at 30 ppm which is sometimes attributed to Al in fivefold coordination. This peak has also been observed in ground clay minerals such as pyrophyllite[12] and ground gibbsite-silica gel mixtures;[10] the feature disappears at about 980°C in all these mechanochemically-produced mullite precursors. Mullite is formed in the present system as the heating temperature is increased to 1100°C. The Si_3N_4 peaks decrease with increasing temperature due to oxidation, and have completely disappeared by 1300°C, at which temperature a small peak attributable to cristobalite has appeared. Thus, the sharp exotherm at about 1315°C appears to be due to the transformation of the Si_3N_4 oxidation product to cristobalite. Kawai et al.[3] did not observe strong exothermic effects around 1200–1300°C; the present exotherms at these temperatures probably arise from a greater degree of grinding contamination rather than from mechanochemical effects in the mixtures. The presence of a small amount of transition alumina at 900°C suggests that this precursor has not become fully homogeneous, but contains alumina-rich regions. As was observed by Kawai et al.[3] and in the present mechanically ground kaolinite–boehmite mixtures (see below), no α-alumina was detected at any temperature within the present range, possibly due to stabilization of the transition alumina by a small amount of silica, since the transition alumina readily dissolved in the silica-rich liquid phase. However, the samples ground for only 5 min show abundant formation of α-alumina on firing >1000°C, consistent with the concepts outlined above regarding the mechanochemical formation of an aluminosilicate precursor and the stabilization of the transition alumina by the formation of a spinel phase.

Between 1300 and 1500°C the mullite XRD intensity of the K–G samples ground for 4 h remains constant, then decreases at 1600°C. This behaviour may be explained as follows: the formation of both primary and secondary mullite is almost complete at 1300–1400°C and no further secondary mullite is precipitated because of the changed stoichiometry of the system due to the additional silica from the Si_3N_4 contaminant. At higher firing temperatures the mullite begins to dissolve in the liquid phase.

Fig. 7 shows typical XRD patterns of K–B and M–B samples ground for 4 h and fired at different temperatures. At 900°C a transition alumina phase (γ-alumina) is observed. In both K–B and M–B the intensities of the transition alumina peaks at 46 and 67° 2θ increase on firing at 1000°C, at which temperature the formation of a Si-substituted spinel phase may occur. This spinel may also be formed exothermically as a result of mechanochemical

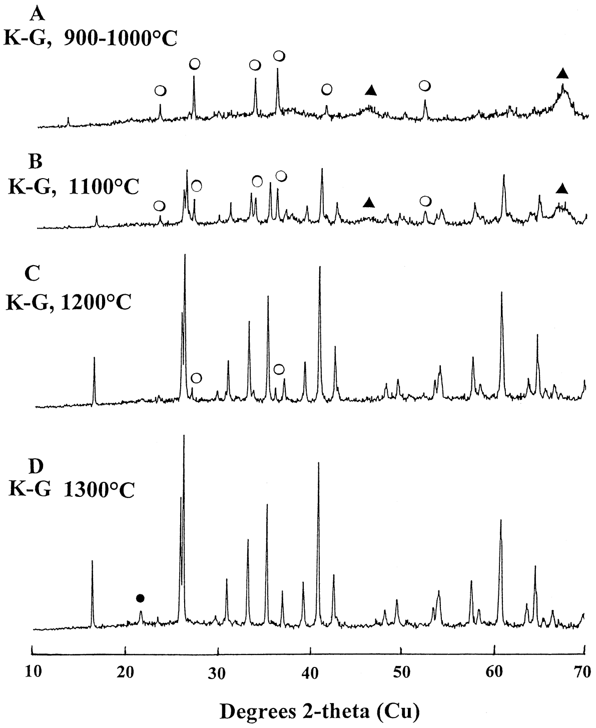

Fig. 6. XRD traces of kaolinite-gibbsite mixtures ground for 4 h then heated in air at the indicated temperatures. Key: ○, Si_3N_4; ▲, spinel phase and transition alumina; ●, cristobalite; unmarked peaks: mullite.

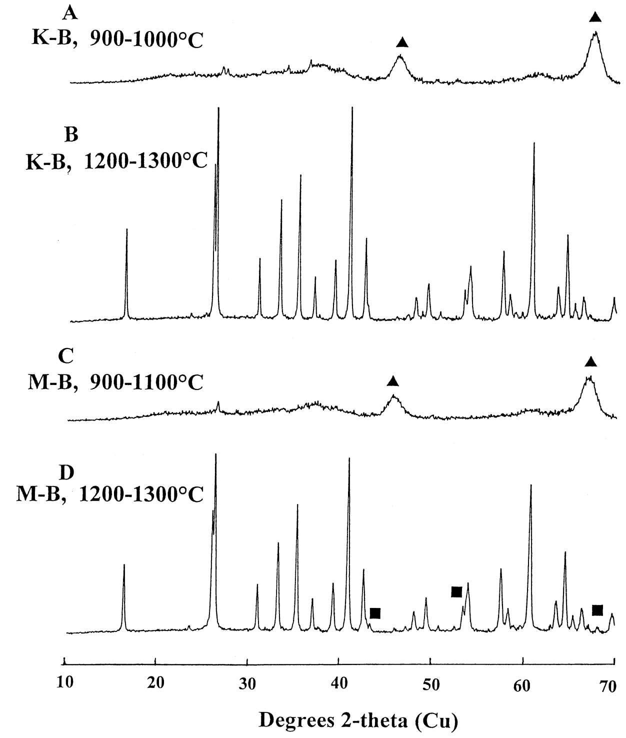

Fig. 7. XRD traces of kaolinite–boehmite and metakaolinite–boehmite, ground for 4 h then heated at the indicated temperatures. Key: ▲, spinel phase and transition alumina; ■, α-alumina, unmarked peaks: mullite.

reaction between boehmite and the silica component of the kaolinite. However, the low intensity of the exothermic peak at about 980°C suggests that such a reaction occurs slowly, if at all. At 1100°C the intensity of the spinel peaks in M–B decreases and weak mullite peaks appear. M–B samples fired at 1200°C contain crystalline mullite and a minor amount of α-alumina which decreases to almost zero at 1400°C with a corresponding increase in the intensity of the mullite peaks. By contrast, the K–B samples fired at 1200°C show only mullite XRD peaks which increase in intensity with increasing firing temperature. At all temperatures, the intensity of the mullite peaks is greater in K–B than in the M–B samples. This suggests a slightly different crystallization behaviour in K–B and M–B. It is possible that grinding the K–B samples initiates the polymerization of Al–O–Si, but the rate of this reaction is slow.

A small amount of α-alumina is observed in M–B fired to higher temperatures. Boehmite thermally transforms to α-alumina via γ, δ and θ-alumina; it has been shown that the transformation temperature of mechanically amorphized hydrous alumina is lowered by >200°C.[8] By contrast with this observation, the present K–B samples contain no α-alumina within the temperature range of these experiments. It is possible that the mechanochemical reaction of boehmite with other compounds may cause it to become stabilized as a Si-containing spinel during heating, or by dissolution of the transition alumina in the impurity-containing silica-rich ternary eutectic liquid, or both. However, the presence of minor amounts of α-alumina in M–B at >1200°C supports the possibility of mechanochemical bond formation in K–B. Previous work[8] shows that mechanochemically treated boehmite crystallizes to α-alumina in this temperature range, as observed in the M–B samples. As reported previously[2] the major reaction product of heated kaolinite-α-alumina is primary mullite formed from the kaolinite, and secondary mullite formed by solution-precipitation and interdiffusion processes. Secondary mullite formation is accelerated >1400°C due to increasing dissolution rates. This mechanism seems to be applicable to any kaolinite-alumina mixture, especially where the kaolinite contains impurities which form a low-temperature eutectic. Secondary mullite formation via interdiffusion is reported to play only a minor role in the kaolinite-α-alumina reaction. This suggests that the low temperature formation of secondary mullite in K–B occurs by a solution–precipitation mechanism. Above 1200°C, the lack of an observed transition alumina or α-alumina phase is explained by its solution in the liquid phase at higher temperatures. On the other hand, the intensity of the mullite peak increases with increasing firing temperature. This contradiction may be explained in terms of changes in the mullite composition at higher temperatures. Previous work[17,18] has shown a relationship between the lattice constant of mullite and its Al_2O_3 content, from which it has been deduced that mullite formed at about 1000°C always contains a high alumina content, but as the firing temperature increases, the Al_2O_3 content gradually approaches 60 mol%, the value for stoichiometric 3:2 mullite.[19] Fig. 8 shows the change in mullite composition of both series of ground samples, deduced from the measured lattice parameter[17] as a function of the heating temperature.

With increasing firing temperature up to 1400°C, the mullite composition in K–G ground for 4 h (Fig. 8A) approaches that of stoichiometric 3:2 mullite. By contrast, the mullite in the less homogeneous sample ground for 5 min has not become stoichiometric at 1400°C, possibly because even at this temperature the sample is continuing to form mullite by reaction of α-alumina with the siliceous constituent derived from the kaolinite. Both K–B and M–B show a decrease in the Al_2O_3 content with increasing firing temperature (Fig. 8B), but even at 1400°C the composition is more alumina-rich than 3:2 mullite.

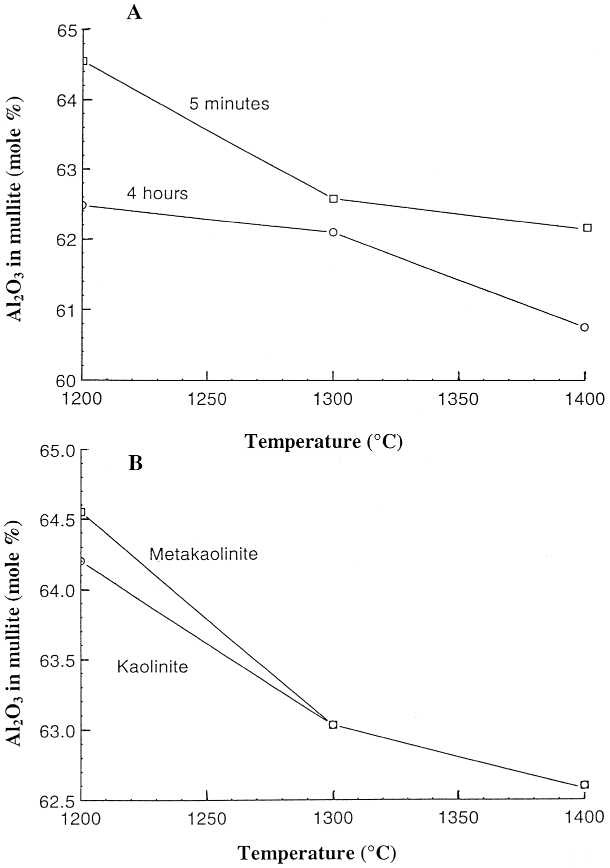

Fig. 8. Composition of mullites formed from ground mixtures as a function of heating temperature. A, kaolinite + gibbsite, ground as indicated; B, kaolinite + boehmite and metakaolinite + boehmite, ground for 4 h.

The foregoing results reveal differences in the mullitization behaviour of mechanochemically treated mixtures of boehmite with kaolinite and metakaolinite. Some degree of Al-O-Si bond formation may occur in the mixtures with kaolinite, resulting in a greater degree of mullitization (based on the intensity of the mullite XRD peaks) than in the mixtures containing metakaolinite, but less mullitization than in kaolinite–gibbsite mixtures.[3] This suggests that boehmite is a less suitable starting material than gibbsite for mechanochemical reaction with kaolinite. The ease with which new Al–O–Si bonds are formed during grinding is greater for kaolinite than for metakaolinite. This suggests that the formation of new bonds is facilitated more by the presence of structural water in the kaolinite than by the structural defects present in metakaolinite; the influence of the structural water suggests the operation of a "soft" mechanochemical reaction mechanism.[20] The mechanism of bond formation between two dissimilar oxide particles with a subsequent improvement in the homogeneity of the system has been explained in terms of an acid-base reaction[20,21] in which the surface acidity or basicity resulting from the presence of structural water in the kaolinite exerts a beneficial effect on the mechanochemical reaction.[9,20,21] On this basis we conclude that the difference in the surface acidity or basicity of kaolinite–boehmite is greater than in metakaolinite–boehmite mixtures. Even though metakaolinite is known to contain about 12% residual hydroxyl groups,[19] these appear to be insufficient to influence the mechanochemical reaction.

4. Conclusions

1. Grinding mixtures of kaolinite and gibbsite for 5 min produces a poorly homogeneous mullite precursor which behaves on thermal treatment more like a mixture of kaolinite and α-alumina. Grinding for 4 h increases the homogeneity, with NMR evidence for the formation of Al–O–Si bonds between the kaolinite and gibbsite. On heating, these homogeneous precursors form secondary mullite of 3:2 composition by a solution-precipitation mechanism.
2. Mechanochemical treatment of kaolinite–boehmite mixtures produces a more homogeneous mullite precursor than metakaolinite–boehmite mixtures treated similarly, suggesting that the lattice water of the kaolinite is more beneficial to the reaction than the influence of the defects present in the metakaolinite. The presence of structural water in the alumina hydrate also influences the mechanochemical reaction, which is more efficient in kaolinite–gibbsite mixtures than in kaolinite–boehmite treated identically.

Acknowledgements

J.T. thanks DAAD for providing a fellowship grant, and K.J.D.M. is indebted to the Royal Society of New Zealand for a James Cook Research Fellowship under which part of this work was carried out. JM is grateful to the EPSRC (grant no. GR/M12209) for support.

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