



Note

Mullite formation from bentonites containing kaolinite: Effect of composition and synthesis parameters



L.N.L. Santana ^{a,*}, J. Gomes ^a, G.A. Neves ^a, H.L. Lira ^a, R.R. Menezes ^a, A.M. Segadães ^b

^a Federal University of Campina Grande, Department of Materials Engineering (UFCC/DEMa), 58109-970 Campina Grande, PB, Brazil

^b University of Aveiro, Department of Materials and Ceramics Engineering (CICECO), 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form 13 November 2013

Accepted 14 November 2013

Available online 7 December 2013

Keywords:

Clay

Bentonite

Mullite

Phase diagrams

Microwave processing

ABSTRACT

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is rare in nature and not so easy to synthesize, but its unique ceramic properties explain the continuous search for alternative synthesis methods and precursors. Suggested precursors include other naturally occurring aluminosilicates, among which bentonites, and alternative methods include fast microwave heating, which might accelerate mullite nucleation kinetics and crystal growth. Thus, the aim of this work was to study the effect of bentonite composition and microwave exposure time (15–25 min) on the amount of formed phase and the morphology of mullite grains, which were characterized by X-ray diffraction and electron microscopy. Despite the short firing cycles, mullite formation and growth were found to closely follow the changes in fluxing oxide content and the estimates provided by the phase equilibrium diagram of the relevant system. The elongated grain morphology was promoted by impurities soluble in the mullite structure.

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1. Introduction

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only thermodynamically stable compound within the ceramic $\text{SiO}_2\text{--Al}_2\text{O}_3$ system and, although rare in nature, is one of the crystalline phases most frequently found in the final phase composition of both traditional and technical ceramics. Due to its excellent electrical, thermal and mechanical properties, and good stability in harsh chemical environments, mullite has become an important material, particularly in advanced ceramic applications such as catalyst supports, filters, optical devices, heat exchangers and electronic packaging (Carty and Senapati, 2005; Schneider et al., 2008; Somiya and Hirata, 1991). Existing natural deposits are not enough to supply a growing market interested in using this material and various methods and precursors have been used to produce synthetic mullite.

Mullite synthesis from the individual oxides by conventional solid state methods requires temperatures near 1600 °C, but alternative synthesis methods and precursors have been reported to favor synthesis at lower temperature. Suggested precursors include other naturally occurring aluminosilicates, given the presence of a molecular scale mixture of the Al and Si cations (Bagchi et al., 2010; Castelein et al., 2001; Chen et al., 2004; Deniel et al., 2010; Ebadzadeh, 2010; Ganesh and Ferreira, 2009; Gomes et al., 2010; Johnson and Pask, 1982; Lee et al., 2008; Li et al., 2009; McConville and Lee, 2005; Menezes et al., 2008; Nour and Awad, 2008; Stoyanova et al., 2005; Yamuna et al., 2002; Yang et al., 2011).

The great majority of naturally abundant aluminosilicates are kaolinite-based and microstructural development and phase formation during the mullitization of kaolinite has been thoroughly studied. However, the mullitization of other natural aluminosilicates, such as smectite minerals, has been much less investigated (Dellisanti et al., 2006; Gomes et al., 2010; McConville and Lee, 2005; Stoyanova et al., 2005).

Bentonites are rocks whose major components are clay minerals like montmorillonite, a member of the smectite group, formed by devitrification and subsequent chemical weathering of vitreous material of igneous origin. Smectites are 2:1 phyllosilicates, formed by regular stacking of two sheets of SiO_4 tetrahedra sandwiching a sheet of $\text{Al}(\text{OH})_3$ or $\text{Mg}(\text{OH})_2$ octahedra. Smectite particles can be exfoliated and fully separated into individual layer (Dennis et al., 2001; Gomes et al., 2010; Poli et al., 2008), typically 100 to 200 nm long and 1 nm thick, thus being rather attractive for the production of nanosized ceramic particles.

The microstructural evolution on firing of clay minerals, namely the size and shape of mullite crystals, depends on the temperature reached and the starting composition (Lee and Iqbal, 2001) and is complicated by the presence of impurities. The presence of alkalis promotes low viscosity of the liquid phase formed at high temperature and affects species diffusion and, hence, nucleation and crystal growth (Deniel et al., 2010; Li et al., 2009; McConville and Lee, 2005; Yamuna et al., 2002). Also, impurities soluble in crystalline mullite, namely iron, seem to affect the morphology of crystals, lowering the surface energy in particular crystal directions and leading to preferential growth of elongated acicular grains. The higher the solubility, the less equiaxial is the crystal morphology (Johnson and Pask, 1982). It has been observed (Deniel et al., 2010; Lee et al., 2008; Schneider et al., 1994) that Na_2O , K_2O ,

* Corresponding author. Tel.: +55 8321011182; fax: +55 8321011178.
E-mail address: lisiane@dema.ufcg.edu.br (L.N.L. Santana).

and CaO in concentrations below 1 mass%, and the addition of titania and iron oxide, enhanced the transformation of clay minerals to mullite, by changing the liquid composition, influencing recrystallization mechanisms, and/or decreasing the reaction temperatures. Thus, the presence of iron in the clay, the isomorphous substitution and interlayer cations influence the characteristics of the microstructure that develops at high temperatures.

The use of microwave technology as a source of energy is attracting interest as an alternative to the conventional thermal processing of ceramic materials (Agrawal, 1998; Akpınar et al., 2012; Clark and Sutton, 1996; Ebadzadeh, 2010; Ebadzadeh et al., 2009; Gomes et al., 2010; Huang et al., 2009; Sutton, 1989). Unlike what occurs when heating is accomplished by convection, in which the energy is slowly transferred to the sample and the material heats from the surface inwards, in the reactions carried out in microwave ovens the reactants directly absorb the microwave energy, which results in a volumetric heating of the material, i.e. there are no temperature gradients within the sample. Also, microwave heating promotes densification and suppresses grain growth, which results in apparent lower temperature firings, while enabling much faster heating (and cooling) rates (Roy et al., 2002; Souto et al., 2011).

If microstructural evolution on firing of natural clay minerals, although now reasonably well understood, is still the subject of some controversy, the effect that microwave heating might have on phase transformations is mostly unknown. Based on the above, and because bentonites are abundant raw materials in the north-eastern Brazil, whereas kaolins are scarce, the aim of this work is to explore mullite formation from clays under microwave fast heating, with emphasis on the effect of composition and synthesis parameters in the phase transformation reactions.

2. Experimental procedure

The raw materials used in this work were two natural bentonites (A and B) and a third commercial bentonite, denoted as C. The three clays were dried at 60 °C, deagglomerated and sieved through 200 mesh. Samples were characterized in terms of chemical and mineralogical composition, respectively by X-ray fluorescence (XRF, Shimadzu XRF-720) and powder diffraction (XRD, Shimadzu XRD-6000, using Cu K α radiation, fixed time mode with 0.02 step and 0.6 s reading time, in the 2 θ range of 5 to 60°). Particle size distributions were determined by laser diffraction (Cilas, 1064LD).

To improve the fine fraction (below 0.2 μ m), samples were subjected to an exfoliation (hydration, freezing, thawing and ball mill deagglomeration) followed by gravity separation by centrifugation (Nova Técnica NT 820 centrifuge, at 1500 rpm for 6 min). The overlaying liquid containing most of the clay particles was then dried and the powder manually deagglomerated.

Samples of these powders were then heat treated in an adapted domestic Panasonic microwave oven (NN-GD587SRU, equipped with a low temperature high dielectric loss susceptor material, to assist the initial heating process) set at 900 W for 15, 20 and 25 min.

The various microwave-heated powders were characterized by XRD and powder morphology was investigated, after 10 min etching with hydrofluoric acid (40 vol.% dilution) to remove the Si-rich vitreous phase, by scanning electron microscopy (SEM, Shimadzu SSx-550) and transmission electron microscopy (TEM, Hitachi H-9000, using copper grids) with EDX, after carbon coating.

3. Results and discussion

Table 1 shows the semi-quantitative chemical composition of the three bentonites. Mass losses ranging from 6.8% (sample C) to 12.0% (sample A) were observed and related to free and adsorbed water release and organic matter burn out. In all three clays, the (Al₂O₃ + SiO₂) content accounts for ~90 mass% of the total oxides. They contain

Table 1
Chemical composition (mass%) of bentonite samples (XRF, expressed as oxides).

Samples	LoI ^a	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	CaO	TiO ₂	Minor oxides
A	12.0	51.3	27.8	4.1	2.5	–	0.7	0.5	1.0	0.1
B	10.5	54.1	25.5	3.5	3.5	0.7	0.6	0.6	0.8	0.2
C	6.8	60.1	24.1	4.1	2.0	2.4	–	0.4	–	0.1

^a Loss on Ignition of samples dried at 110 °C.

increasing amounts of alkaline oxides but comparable amounts of other oxides, particularly iron oxide (~4.0 mass%). The contents of oxides other than alumina and silica were also found to be similar to those generally reported for South American bentonites (Amorim et al., 2004). It is interesting to note that bentonite A not only presents the lowest alkali content, but also does not contain sodium, whereas the high sodium content of bentonite C (2.4 mass% Na₂O), which might have been introduced during industrial beneficiation, is expected to have a strong fluxing effect during the synthesis process.

The particle size analysis of the untreated samples showed that particles with equivalent diameter below 0.2 μ m accounted for 1.1, 0.4 and 2.5 vol.% in bentonites A, B and C, respectively. After exfoliation, the corresponding contents increased to 77.4, 46.6 and 17.6 vol.%, respectively.

The purification process contributed to a reduction in the quartz contents but did not otherwise affect the mineralogy of the samples (major crystalline phases identified were smectite, kaolinite and quartz, with minor feldspar contents), as shown by the XRD patterns presented in Fig. 1. From the chemical composition and the XRD results, it can be concluded that bentonites A and B contain kaolinite and smectite (nontronite), with kaolinite dominating in bentonite A and smectite dominating in bentonite B. No kaolinite was detected in bentonite C and the only clay mineral present was montmorillonite. The diffraction patterns suggest that the Fe₂O₃ detected in the chemical composition of the samples likely refers to iron in the crystalline structure of smectite

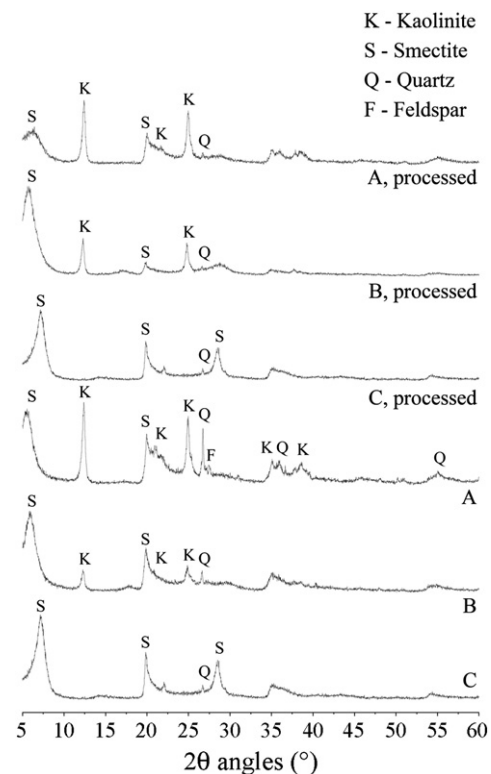


Fig. 1. X-ray diffraction patterns of the as-received and processed bentonite clays.

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