Contents lists available at ScienceDirect

Materials Letters

Featured Letter

The effect of vitreous phase on mullite and mullite-based ceramic composites from kaolin wastes as by-products of mining, sericite clays and kaolinite

P.J. Sánchez-Soto [a], D. Eliche-Quesada [b], S. Martínez-Martínez [b], E. Garzón-Garzón [c], L. Pérez-Villarejo [b,*], J. Ma. Rincón [d,e]

[a] Institute of Materials Science of Sevilla (ICMS), Joint Center of the Spanish National Research Council (CSIC)-University of Sevilla, 41092 Sevilla, Spain
[b] Department of Chemical, Environmental and Materials Engineering, University of Jaén, 23071 Jaén, Spain
[c] Department of Engineering, University of Almería, 04120 Almería, Spain
[d] Department of Geology, MNCN-CSIC, Madrid, Spain
[e] Department of Agrochemistry and Environment, Miguel Hernández University (UMH) of Elche, 03202 Elche, Alicante, Spain

ARTICLE INFO

ABSTRACT

Mullite precursors were prepared using kaolin waste, sericite clay containing kaolinite and industrial kaolin with addition of alumina in a wet medium to synthesize mullite (72 wt% Al_2O_3 and 28 wt% SiO_2). Uniaxial pressed bars of the powdered mullite precursors were fired in the range 1400–1600 °C with soaking times 30–120 min. The resultant materials were studied by XRD and SEM-EDX. Bulk densities, apparent porosities and flexural strengths in four points were determined in the fired bars at 1500, 1550 and 1600 °C. It was concluded that the thermal behaviour of these mullite precursors was influenced by the presence of impurities in the raw materials. These impurities originate a liquid phase forming a glassy phase which produces a progressive and enhanced densification of the mullite materials by reaction sintering at 1500–1600 °C. The technical properties were also influenced by the relative proportion of vitreous phase. The microstructure of characteristic mullite crystals was revealed by SEM. It was emphasized the use of kaolin waste by-products of mining and sericite clays as valuable raw materials for mullite preparation.

1. Introduction

Mullite is one of the most common crystalline phases in ceramics having nominal composition $3Al_2O_3·2SiO_2$ (72 wt% Al_2O_3 and 28 wt% SiO_2) [1–12]. It is the only stable crystalline phase, at normal pressure, in the binary Al_2O_3-SiO_2 system. This material shows excellent properties: high-temperature strength, creep resistance, low thermal expansion coefficient, good chemical and thermal stability, with retention of mechanical properties to elevated temperature and stability in oxidative atmospheres. This ceramic material and their composites are important for high-temperature engineering applications as structural advanced materials, besides electronic and optic applications [2,4–9]. Mullite can be found only as scarce mineral at the Mull Island (Scotland), the origin of its name [2,9]. However, it can be produced by thermal decomposition of aluminosilicates (for instance, kyanite, kaolinite, pyrophyllite,

etc.) [1,2,4–11], raw clays containing mixtures of these silicates and clay minerals [1,4–7,9–12], and by thermal reaction of mixtures of SiO_2 and Al_2O_3 [8,9,13]. In the last case, a very high temperature (1700 °C) and long periods of heating are required for obtaining dense sintered mullite materials because the high activation energy for Aluminium and Silicon bulk diffusion in the mullite lattice [1,13]. The use of clays containing Silicon and Aluminium is the most attractive way for mullite preparation at relatively low cost. Kaolinite ($2SiO_2·Al_2O_3·2H_2O$) has a layered structure of ($Si_2O_5)^{2-}$ and $[Al_2(OH)_4]^{2+}$ molecular sheets and produces mullite by heating, being similar to that of silica-alumina diphasic precursors [1]. Mullite and cristobalite are produced by kaolinite thermal decomposition (>1200 °C), although leading to incomplete mullitization because there is not enough proportion of Al_2O_3. Amorphous silica segregated from kaolinite thermal decomposition originates cristobalite [1,5,7,10]. However, a complete mullitization can be produced at higher temperatures (>1300 °C) by reaction-sintering of mixtures of kaolinite and alumina in a $3Al_2O_3·2SiO_2$ proportion, i.e., 72 wt% Al_2O_3. Mullite and mullite-based

* Corresponding author.
   E-mail address: lperezvi@ujaen.es (L. Pérez-Villarejo).

composites have been prepared by this processing route [5,9]. High porosity mullite-corundum [11] and high porosity mullite ceramics, in that case using sericite, have been of recent interest [12]. The present paper is a part of a wide investigation on processing of mullite and mullite-based ceramics from silico-aluminous raw materials, wastes with high Aluminium content and by-products of mining with high kaolinite content. It is focused on the preparation of mullite and mullite-based ceramic composites from a kaolinitic waste as by-product of mining, a sericite clay containing kaolinite and an industrial kaolin with high content of kaolinite. It is examined and compared the effect of impurities from these raw materials because they will produce liquid phases, which will form glassy or vitreous phase by firing.

2. Experimental

2.1. Materials and procedures

Several samples as raw materials were considered. *Sample W*: A waste solid by-product of mining granitic tin-bearing alluvial sands by washing was used [14]. The kaolinite content was 60 wt %, with potassium mica 15 wt%, potassium feldspar 10 wt% and quartz 15 wt%. The chemical composition (in wt%) was 48.30 SiO_2, 32.00 Al_2O_3, 5.13 Fe_2O_3, 0.52 TiO_2, 0.42 CaO, 0.85 MgO, 0.10 Na_2O, 2.43 K_2O, and 10.30 wt% of weight loss after heating at 1000 °C (LOI). This sample shows a particle size < 2 μm, 74.75 wt % with <1.12 μm, 30.45 wt%. *Sample S*: A sericite clay (Garlitos, Badajoz, Spain) was also used. The sericite (potassium mica, illite) content was 35 wt%, with 45 wt% kaolinite, 10 wt% potassium feldspar (microcline) and 10 wt% quartz. The oxide chemical composition (in wt%) was 58.53 SiO_2, 29.46 Al_2O_3, 1.14 Fe_2O_3, 0.94 TiO_2, 0.11 CaO, 0.23 MgO, 0.60 Na_2O, 2.40 K_2O, and 6.70 wt% of LOI. The particle size was <2 μm of 45 wt%. *Sample P*: Kaolin powder, (Caobar S.A., Poveda, Guadalajara, Spain), with kaolinite content >90 wt% and quartz (~10 wt%) was also used. The chemical composition (in wt%) was 47.98 SiO_2, 38.10 Al_2O_3, 0.57 Fe_2O_3, 0.16 TiO_2, 0.05 CaO, 0.20 MgO, 0.04 Na_2O, 0.43 K_2O, and 12.26 wt% of LOI. This sample shows 45.4 wt% of particle size <2 μm. *Sample A*: Powdered alumina (corundum, α-Al_2O_3), with particle size <63 μm, used in the fabrication of commercial high-alumina refractories (from the Company Alfran, Sevilla, Spain) was selected for this study. The chemical composition (in wt%) was 98.9 Al_2O_3, with 0.08 Fe_2O_3, 0.25 TiO_2, 0.55 Na_2O and 0.16 of LOI. After ball milling, the powder shows 90 wt% of particle size <63 μm.

For the preparation of mullite precursors separate aqueous suspensions, using deionized water, of samples W and S were obtained and pH adjusted by addition of HCl (35 vol%). After vigorous mixing by mechanical stirring during 3 h with powdered alumina A in the stoichiometric molar ratio of mullite (Al_2O_3/SiO_2 = 1.5 M ratio), the wet solid products were dried at 110 °C. The resultant powders were the mullite precursors *sample WA and sample SA*, respectively. To compare all the results, kaolin powder, sample P, was also mixed with alumina A under the same conditions as above, yielding the mullite precursor *sample PA*. Other mullite precursors were processed by a chemical method but using the same kaolin sample P and wastes of Aluminium metal dissolved with HCl (35 wt%) and the hydroxide precipitated using basic chemical agents [15,16]. They were designed here as *sample PAD*, processed using hexamethylenediamine (HMDA), and *sample PAM*, processed using ammonia.

2.2. Methods

Thermal treatments of uniaxial cold-pressed prismatic bars (100 × 10 × 10 mm), prepared using the powders with 5 wt%

humidity, at 150 MPa, were performed in air using a furnace at 10 °C/min, from 1400 to 1600 °C, with 120–30 min of soaking time and natural cooling. X-ray powder diffraction (XRD) diagrams of fired ground samples were obtained with a Siemens D-501 diffractometer using Ni-filtered CuKα radiation and graphite monochromator.

Bulk density and apparent porosity were measured by Archimedes' method using deionized water. Flexural strength was performed by a four-point bending test using an Instron machine, Model 8501. Scanning electron microscopy (SEM) observations of the fired samples were carried out using a JEOL JSM-5400 microscope equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer Oxford Link system. Chemical treatment with HF aqueous solution (20 wt%) revealed the mullite crystals.

3. Results and discussion

3.1. Phase evolution

XRD was used to follow the formation and development of mullite by firing the precursors WA, SA and PA. Fig. 1 shows, as an example, the thermal sequence of the mullite precursor WA studied from 1425 °C to 1600 °C. It is evidenced the disappearance of α-alumina and quartz and the development of well-developed mullite crystals formed at temperature lower than 1400 °C. Further heating produced the disappearance of quartz and cristobalite, a decrease of α-alumina by reaction and an increase of mullite formation, as deduced from XRD peak intensities. Table 1a shows a summary of the phase composition of all the samples from 1500 to 1600 °C, as deduced from the XRD study. Mullite, quartz and unreacted α-alumina are observed in all the samples at 1500 °C for 120 min. Quartz appears in samples WA and PA because was originally present. In samples WA and PA sintered at 1600 °C for 30 min, single-phase mullite was obtained. A mixture of mullite and unreacted α-alumina was found in sample SA. On the other hand, amorphous silica from kaolinite thermal decomposition produced cristobalite after heating from 1300 °C, being only observed in sample PA, the sample with higher content of kaolinite (see Experimental section). These results can be compared with those previous obtained using two mullite precursors (PAD and PAM), prepared by chemical methods but using the same kaolin sample P [15,16], where mullite and a large relative proportion of α-alumina were found at 1500 °C. At 1600 °C mullite is a single phase in all the samples with relics of α-alumina in sample SA (Table 1a).

The reaction of mullite formation from kaolinite and α-alumina mixtures during the sintering of the precursors is:

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O + 2Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2H_2O \qquad (Reaction1)$$
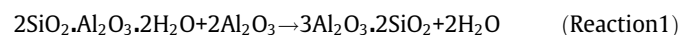
First of all, the thermal decomposition of kaolinite produces mullite and a segregation of amorphous silica:

$$3(2SiO_2 \cdot Al_2O_3 \cdot 2H_2O) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O \qquad (Reaction2)$$
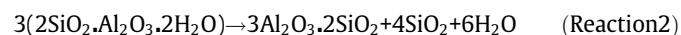
The formation of this primary mullite, from kaolinite thermal decomposition, can be observed by XRD after heating the precursors and further heating produces additional mullite, i.e., a secondary mullite, by reaction between segregated silica and alumina:

$$3Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3 \cdot 2SiO_2 \qquad (Reaction3)$$
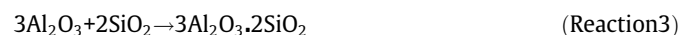
The evidence of liquid phase sintering, the rapid kinetics of secondary mullite formation according the literature [5], and the characteristics of the coexisting glassy phase, strongly suggests that a solution-precipitation via a transitory liquid phase is the major mechanism for secondary mullite formation: solution of alumina particles and precipitation of mullite grains. It is assumed that a similar reaction pathway, as previously observed [5], accounts in