Research paper

Microstructure development in clays upon heat treatment: Kinetics and equilibrium

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ABSTRACT

Knowledge about the relationships between mineralogical and microstructural characteristics of clays and the transformations that occur during firing is of fundamental importance for various industries, enabling the manufacture of better quality products and widespread use of those raw materials. The aim of this study was to interpret phase development and morphological transformations in clays subjected to different heat treatments, with emphasis on the effect of impurities (iron and alkalis), temperature and heating rate. The experiments were carried out using conventional and microwave heating, with characterization by X–ray diffraction and scanning electron microscopy. The interpretation of the results based on the mullite–silica–leucite phase diagram showed that crystallization and grain growth are closely related to the amount and viscosity of the liquid phase present at the firing temperature, which vary with the composition and can be predicted by the phase diagram. Faster heating rates tend to slightly delay the establishment of equilibrium, which appears to have special bearing on the liquid phase viscosity, hence, on grain growth. As a consequence, the resulting microstructure contains mullite needles that are shorter and more uniform in size.

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1. Introduction

Clays, particularly those rich in kaolinite, smectite and illite, are natural raw materials involved in a variety of industrial applications, for which they are selected mostly based on chemical and mineralogical composition. It has been observed that structural defects and impurities can also be used as selection criteria, as they play determinant roles in the heat treatment needed to accomplish the desired phase formation at high temperature (Volzone and Garrido, 2012).

Applications that include high temperature processing stages also require the comprehension of the phase formation sequence during heat treatment. The mechanical strength of ceramic parts is generally of great concern and some works (Kamseu et al., 2007; Tucci et al., 2007) showed that it depended on the presence of mullite needles and particles embedded in the glassy matrix, which act as hard inclusions and cause crack path deflection. In other works, however, the increase in the grain size and the amount of glassy phase appears to hinder the mechanical properties (Deniel et al., 2010; Iqbal and Lee, 2000; Johnson and Pask, 1982; Lee and Iqbal, 2001; Lee and Yeh, 2008). Still other authors (Carbajal et al., 2007) associated the

mechanical strength to differences in thermal expansion coefficients between the glassy matrix and the embedded quartz particles, which resulted in compression stresses in the glass matrix.

Although the microstructure development in specific clays has been studied in recent years (Bennour et al., 2015; Bourret et al., 2015; Carbajal et al., 2007; García et al., 2009; Holtzer et al., 2011; Lecomte-Nana et al., 2011, 2013; Lee and Yeh, 2008; Tucci et al., 2007), there is still much controversy about the mechanisms that operate during heating, due to the presence of small quantities of different components (whether impurities or not), the variability of the crystallinity degree and the interactions that occur between the constituents.

Phase equilibrium relationships in the vast majority of silicate systems, relevant to the heat treatment of clays, became available in the early decades of last century. So, it is no wonder that this subject looks old and does not sound exciting. As a consequence, those working with clays often disregard the use of this powerful tool. However, its criterious use still provides valuable insights. Being alumino-silicates, usually containing alkali ions, mainly potassium and sodium, and accompanied almost always by quartz grains, the phases formed upon heat treatment of any clay would be those predicted by the phase equilibrium diagram of the Al_2O_3–SiO_2–K_2O system (Segadães, 2006). The alkaline impurities present in the clay, particularly K_2O and Na_2O oxides, favour the formation of liquid phase by decreasing the

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Table 1
Experimental heat treatment parameters.

Heat treatment	Maximum temperature (°C)	Heating rate (°C/min)	Dwell time at maximum temperature (min)
Conventional	900, 1000, 1100, 1200, 1300, 1400	10	60
Conventional	1400	10	60, 120, 180
Conventional	1150, 1200, 1250, 1300, 1400	20	60
Microwave	~1200	50	30

temperature of first melting from 1587 °C in the Al_2O_3–SiO_2 system, to 985 °C in the SiO_2–Al_2O_3–K_2O system (McConville and Lee, 2005; Segadães, 2006; Tomba et al., 1999).

Given the high viscosity of the siliceous liquid phase that forms at the beginning of the melting and the low solubility of quartz grains, it is not always possible to ensure that the equilibrium is actually established. Nevertheless, when clays are subjected to temperatures above 1000 °C (i.e. above the first melting temperature predicted by the phase diagram), the final microstructure usually contains different forms of mullite crystals and cristobalite dispersed in a glassy matrix. Upon cooling, the liquid phase formed at elevated temperature solidifies in the form of glass (effect of high viscosity) and residual quartz grains remain in the microstructure (effect of slow dissolution kinetics). Thus, the final microstructure is essentially that existing at high temperature and phase development may still be predicted based on the phase diagram and the heat treatment temperature.

The presence of alkali metals as isomorphic substitution and interlayer cations affects the liquid composition and viscosity, and were said to influence mullite recrystallization and decrease the reaction temperatures (Kim et al., 2009). The effect on the liquid phase formation is also predicted by the phase diagram, which shows that the presence of K_2O and Na_2O (or other impurity oxides, namely alkaline earth oxides) causes the development of a more abundant liquid phase at any temperature. The lower viscosity favours a faster reaction with other phases in liquid/solid interfaces and promotes crystal growth (Lee and Iqbal, 2001). Obviously, the interactions between minerals can be affected by any change in heat treatment and may be hindered when the heating rate increases (Castelein et al., 2001). In some cases, changes on heating or cooling rates can even lead thermal transformations to a path different from that predicted by the phase diagram. In any case, transformation of clay minerals to mullite is also affected, with changes in the characteristics of the microstructure (namely, morphology and size of mullite crystals) that develops at high temperature.

One of the practical ways to change the heat treatment is to alter the heating rate, and microwave heating is particularly suitable for producing higher heating rates. This partly explains why the use of microwave technology as source of energy has been attracting interest as an alternative to the conventional thermal processing of ceramic materials (Akpinar et al., 2012; Ebadzadeh, 2010; Ebadzadeh et al., 2009; Menezes et al., 2012; Santana et al., 2014). When heating is accomplished by convection, the energy is slowly transferred to the sample and the material heats from the surface inwards. On the contrary, in microwave heating the reactants directly absorb the microwave energy, which results in a volumetric heating of the material. Moreover, when microwave heating is combined with an external heating source (susceptor hybrid heating), as is generally the case, temperature gradients in the furnace chamber and across the sample are minimized. While enabling much faster heating (and cooling) rates, microwave heating promotes densification without grain growth, which results in apparent lower firing temperature (Gómez et al., 2004; Menezes et al., 2012; Roy et al., 2002; Souto et al., 2011).

In this context, the aim of this study was to investigate the microstructure changes of clays subjected to different heat treatments (heating rate, sintering temperature and dwell time), seeking a more straightforward relationship between phase transformations (and mullitization kinetics) and the influence of impurities (iron and alkalis) on the establishment of the equilibrium state.

2. Experimental

In this work two local clays were used (A and B), from deposits located in the city of Cubati-PB, which are representative of the two major types of smectite clays used in Brazil. As such, it is expected that behavioural changes due to differences in the minor components contents will be easily noticed and, hence, these clays can be regarded as "model systems". The two clays were dried at 60 °C, manually deagglomerated and sieved through 200 mesh (74 μm). Samples were characterized in terms of chemical and mineralogical composition, respectively by X–ray fluorescence (XRF, Shimadzu XRF–720) and diffraction (XRD, Rigaku Geigerflex D/max Series, using Cu Kα radiation at 1.5418 Å, fixed time mode with 0.02° scanning step and 1.0 s acquisition time, in the 5–60° 2θ range). Particle size distributions were determined by laser diffraction (Cilas, 1064LD).

As listed in Table 1, samples (~6 g) of each clay were subjected to different heat treatments in alumina crucibles in a muffle furnace (Termolab) between 900 and 1400 °C, with heating rates of 10 and 20 °C/min, dwell time at the maximum temperature from 60 to 180 min and furnace cooling. Clay A was also heat treated in a domestic microwave oven (Teka) in a hybrid heating configuration (using a SiC susceptor as auxiliary heating source, and adapted with an external controller and a thermocouple), at approximately 1200 °C with 50 °C/min heating rate and 30 min dwell time at the maximum temperature. The sample was also contained in an alumina crucible placed at the oven main hot spot.

After heat treatment, the powders were again deagglomerated and sieved through 200 mesh. Crystalline phases developed upon heat treatment were identified by XRD and microstructure was observed by scanning electron microscopy (SEM, Hitachi SU-70 and S4100 at 15 kV in secondary electrons mode, coupled with EDS). The presence of a glassy phase tends to result in a smeared microstructure, as illustrated in Fig. 1(a). To improve the characterization by SEM, some heat-treated powders were washed with 40 vol.% hydrofluoric acid (HF) for 10 min, to remove the glassy phase. The powder was then suspended in ethanol and a suspension droplet deposited on the SEM sample holder. After drying, the sample was coated with carbon. Fig.
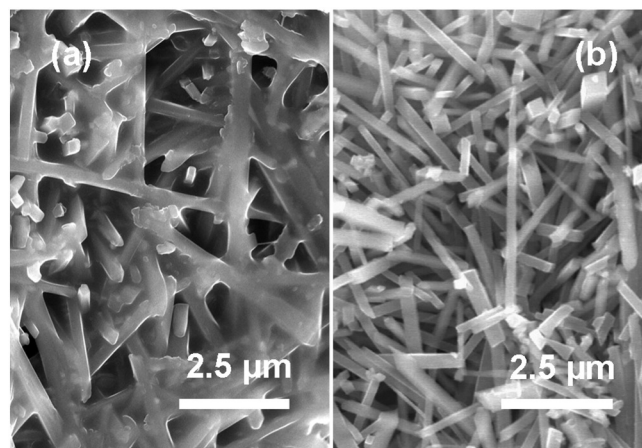

Fig. 1. Typical SEM microstructure of heat-treated powder samples: (a) without HF washing, and (b) with HF washing.