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Research paper

Anisotropy of thermal conductivity and elastic properties of extruded clay-based materials: Evolution with thermal treatment

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ABSTRACT

Kaolinite and muscovite are major clay mineral phases found in the raw materials used for tile and brick production. As phyllosilicates, the crystal structures are layered yielding anisotropic properties. The thermo-physical properties of an extruded clay material, essentially composed of kaolinite, quartz and muscovite have been investigated in the parallel and perpendicular directions to the extrusion axis. Texture is characterized by scanning electron microscopy observations and X-ray diffraction measurements. Values of effective thermal conductivity measured by the laser flash technique and Young's modulus measured with an ultrasonic pulse-echo method reveal an anisotropy factor of 2 for the material in the green body at the macroscopic scale. The thermal conductivity of the solid phases of the material without the quartz fraction was then estimated using an analysis based on the Maxwell–Eucken and Landauer relations. This yields an anisotropy ratio = 3.5 for the clay phase, explained by the alignment of kaolinite and muscovite particles with the extrusion process. The elastic and thermal properties evolve as a function of the heat treatment temperature for the clay, resulting in isotropic behavior after treatment at 1300 °C. These evolutions are concomitant with mineralogical transformations of kaolinite including the formation of mullite above 1000 °C.

1. Introduction

Ceramic materials exhibiting anisotropic properties present both scientific interest and technological importance. Though the crystallographic structure must lie at the root of the behavior, the measured properties at the macroscopic scale are modulated by the microstructure and in particular related to the crystallite orientation. As a relevant example, industrial clays typically contain large proportions of clay minerals such as kaolinite, illite and muscovite in the form of fine particles <2 μm across. These clay mineral phases have layered crystal structures yielding anisotropic properties in terms of thermal expansion, thermal conductivity and elastic moduli. Particle orientation in the ceramic body can be promoted in a given direction by the chosen shaping method such as pressing (Shui et al., 2002; Kenfaui et al., 2011; Romagnoli et al., 2013), slip casting (Takao et al., 2002; Boussois et al., 2013) or extrusion (Habelitz et al., 2001; Taruta et al., 2006; Krakowiak et al., 2011). Thus in clay based materials, extracted and processed for the construction industry, controlled texturing of micron scale particles in the form of stacked platelets can be used to optimize thermal and mechanical properties. More explicitly for a clay brick, alignment of the particles with their $\vec{c}$-axes in the direction of the thermal gradient across a wall should advantageously decrease the thermal conductivity. Furthermore mechanical resistance to compression could be enhanced in the perpendicular load bearing direction. However, beyond some macroscopic values, there are few detailed studies on anisotropy in the thermal and elastic properties for textured clay based materials. This is the topic of the present work.

Large cleaved crystals of mica can be obtained naturally. With respect to the cleavage plane, Gray and Uher evaluated the anisotropy in thermal conductivity at 300 K to be a factor of 10, varying from a cross-plane value of 0.46 $W \cdot m^{-1} \cdot K^{-1}$ to an in-plane value of 4 $W \cdot m^{-1} \cdot K^{-1}$ (Gray and Uher, 1977). The relation of these values to the elastic constants and crystal symmetry was confirmed in a study where the cross-plane conductivity was increased to >6 $W \cdot m^{-1} \cdot K^{-1}$ by the application of 24 GPa along the $\vec{c}$-axis direction which presumably artificially decreases the bond length (Hsieh et al., 2009). In natural clays containing kaolinite, illite or montmorillonite, reports by geologists reveal anisotropy ratios which are much lower in the range 1.2 to 2.5 (Brigaud and Vasseur, 1989; Djéran-Maigre et al., 1998). However, the analysis is obscured by the complexity of the clay material involving factors such as a mixture of several solid phases, porosity, water content

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and stratification. For example an increased fraction of more conducting quartz particles tends to reduce the anisotropy ratio in the macroscopic conductivity values (Jougnot and Revil, 2010). Fired clay products such as bricks or tiles have also been the object of thermal conductivity studies but the aspect of anisotropy is generally neglected (Dondi et al., 2004; Ten et al., 2010). This can be reasonably attributed to the action of the mineralogical transformations such as dehydroxylation and formation of mullite which modify physical properties at the macroscopic scale towards an isotropic character. Consequently, the effect of thermal treatment on anisotropy merits more detailed investigation, especially in view of optimizing processing of clay based materials for thermal insulation (Gualtieri et al., 2010).

In a similar vein, the elastic and mechanical properties of clay materials, which are relevant to the performance of structural products, should also exhibit an anisotropy ratio which evolves with thermal treatment. In-situ measurements of the longitudinal ultrasonic velocity by the pulse-echo technique in the long bar mode can be made as a function of temperature giving access to effective values of Young's modulus for a ceramic material. Earlier work on the ceramic superconductor $YBa_2Cu_3O_{7-\delta}$ has shown that the technique is very sensitive to structural and microstructural changes. Measurements made on a partially sintered bar sample, subjected to a heating cycle up to 1000 °C, revealed characteristic signatures in the evolution of effective Young's modulus for the orthorhombic to tetragonal phase transition, the appearance of a liquid phase, densification and on cooling the opening of microcracks (Suasmoro et al., 1992). For a natural clay containing kaolinite, illite and quartz, Pialy et al. have observed a very strong increase in elastic modulus above 1100 °C due to the formation of mullite crystals which join up to constitute a connected phase (Pialy et al., 2009). This was also studied by Stubna and co-workers who identified in addition the role of the $\alpha \rightarrow \beta$ quartz transition and dehydroxylation (Trník et al., 2009). However, anisotropy was again not explicitly taken into account.

This paper is devoted to a study of anisotropy in the effective values of thermal conductivity and Young's modulus for a commercial extruded clay material subjected to different thermal treatments. The starting clay contains kaolinite, muscovite and quartz. The anisotropy was revealed by cutting samples for characterization in different directions with respect to the extrusion axis. The approach, in terms of parallel studies of heat conduction and ultrasonic wave propagation through the textured samples, is of interest because the vibrational nature of the clay material is probed at very different frequencies by the experimental techniques. Preferential orientation of kaolinite particles in the different cuts was studied by X-ray diffraction.

2. Materials and methods

2.1. Choice of raw materials and sample preparation

The clay material denoted GT100P and supplied by the Ceradel company (Saint Amand en Puisaye, France) is an extruded clay mixture used for the manufacture of stoneware. To ensure a good homogeneity, raw materials were first mixed in water (about 50 wt.%), screened to remove the coarsest agglomerates (>420 μm) and filter-pressed between a fine screen cloth for 2 h to eliminate the excess of water. Finally, the clay body was extruded in the forming square cross section (150×150 mm^2) of a die at a velocity of 25 mm·s^{-1}. At the end of the industrial process, the greenware products were then covered by two layers of plastic film to ensure a constant humidity of 25% in the bulk material.

When the material is pushed across the die by the screw, the profile of the moving paste presents a parabolic front in a plane cut parallel to the extrusion axis (Fadeeva, 1960). As the green body is constituted of small particles of clay mineral in the form of stacks of thin layers, it can be assumed that the extrusion process imposes a preferential orientation to particles and more particularly that their basal faces ($\vec{a}$, $\vec{b}$) are parallel to the extrusion direction (Fig. 1a). Two cuts are thus considered with the extrusion direction as the reference: one is parallel to this axis and the other is perpendicular to it (Fig. 1b). Manipulations of the product during transport and the memory of the propeller passage can slightly modify this orientation. That is why specimens are not sampled from the edges or the core but from the material inbetween, along the diagonals of the cuts. Prior to physical characterization, the clay samples were dried in an oven at 70 °C for 24 h.

2.2. Experimental technique

The chemical composition of the paste was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). First the dried powder was crushed and dissolved in an acid mixture ($57\%_{vol}$ of HF, $14\%_{vol}$ of HNO_3, $29\%_{vol}$ of HCl) and then placed in a microwave oven (180 °C, 30 bars, 600 W, 60 min) to ensure the complete dissolution.

The pore volume fraction v_p was evaluated from the true density d_{true}, measured by helium pycnometry, and the bulk density d_{bulk}, which is the ratio of the mass divided by the volume of the sample, using the relation:

$$v_p = 1 - \frac{d_{bulk}}{d_{true}}. \quad (1)$$

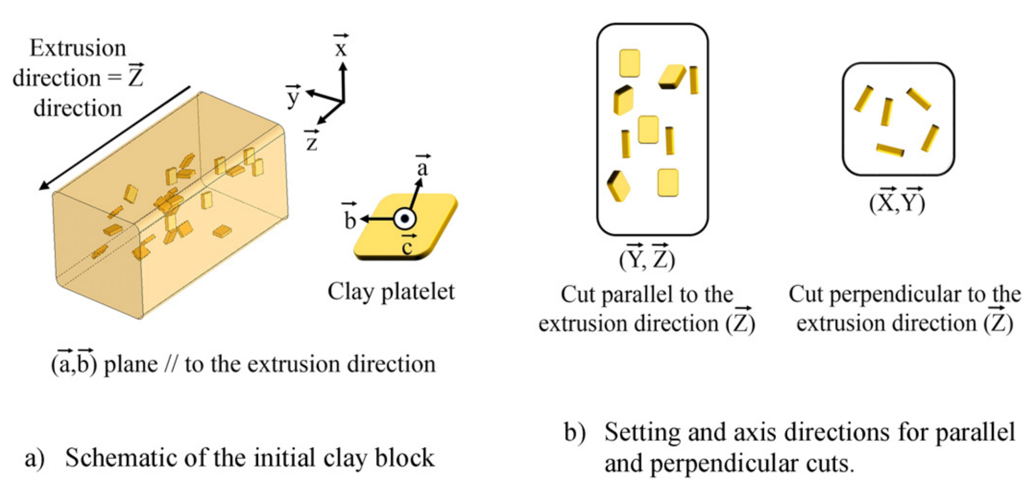

Fig. 1. Expected orientation of the platelets.