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Research paper

Effects of grain size on the reactivity of limestone temper in a kaolinitic clay

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ABSTRACT

Carbonates in clay based ceramics produces higher sintering at lower firing temperatures, but may cause lime spalling, affecting the physical and mechanical behaviour of the ceramic body. The present study investigated the mineralogical and microstructural changes that occur in a kaolinitic clay tempered with different contents of limestone sand with two skewed grain size distributions, after firing. The firing temperatures were set at 500, 750 and 1000 °C. The mineralogy of the fired bodies was analyzed by XRPD and quantitative phase analysis was performed using Rietveld method. SEM–EDS analyses were carried out to investigate the changes in microstructures and the clay/limestone reactivity. The use of sand-sized limestone temper and short firing times induced the formation of non-stoichiometric phases at the clay/limestone boundary, ruled by the lateral variation of CaO activity. The structure and composition of the spinel-type phase (e.g. γ-Al_2O_3), as typical firing product of kaolinite clays, were investigated. Different Ca-silicates and -aluminosilicates (gehlenite, rankinite and larnite) in ceramics fired at 1000 °C are found according to the limestone grain size. Lime spalling already occurs in ceramics fired at 750 °C; it is triggered by coarse calcined grains ($\sigma_{\text{spalling}} > \sigma_{\text{matrix failure}}$) and then fractures propagates through finer calcined limestone grains.

1. Introduction

Carbonates as temper in clay-based ceramics produces much complications in mineralogical and textural evolution during the firing process, making the physical and mechanical behaviour of the ceramic body less predictable. Despite the apparent danger of using limestone as a tempering material, it has been, and still is, extensively used.

During firing, most of the hydrated phases and carbonates in the clay body decompose and recrystallize through different reaction paths according to the existing microchemical domains, without attaining thermodynamical equilibrium and giving the coexistence of original and high temperature phases. Such mineralogical mixtures affect the physical and mechanical properties of ceramics.

Many previous researches have established the phase transformation sequence obtained by firing kaolinite or illite clays mixed with calcite are fired (e.g., Cultrone et al., 2001; Duminuco et al., 1998; Heimann, 1989; Jordan et al., 2008; Maggetti, 1982; Peters and Iberg, 1978; Riccardi et al., 1999; Traoré et al., 2003), but less attention has been paid to the effects of the type and grain size of temper on reactivity and microstructures.

The reactions which take place along grain boundaries between calcite and clay matrix are indeed also a function of the granulometry, other than paste composition and firing conditions (soaking temperature/time, heating rate, duration of firing and kiln redox atmosphere). Moreover, physical and mechanical properties of ceramic products are also related to the different variables occurring in the production process (i.e. shaping technique, type of kiln, etc) (Carretero et al., 2002; Delbrouck et al., 1993; Dondi et al., 2004; Gonzalez-Garcia et al., 1990; Parras et al., 1996). The influence of carbonates on the physical and mechanical properties of ceramics was frequently addressed in the literature (e.g. Allegretta et al., 2014, 2015; Carretero et al., 2002; Lassinantti Gualtieri et al., 2010; Traorè et al., 2007).

In this study, test pieces made with kaolinite clay and crushed limestone with known grain size distribution were investigated to understand the existing correlations between the mineralogical content and the microstructure. Since the reacting environment is ruled by disequilibrium conditions, where the presence of different reacting subsystems occur according to the different phases in contact one to another, the deliberate use of 1 h as soaking time to fire the ceramic tests allowed some insight into the dynamic aspects of the process by the coexistence of relic and new formed phases. Because of the analogy between the mineral assemblages obtained with such experimental conditions and those detected in archaeological ceramic artefacts, the results here presented are useful to determine some technological and functional attributes of historical ceramics. The results of this study are part of a

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wider research project aimed to investigate the effects of the nature, percentage and grain size of the temper and firing temperature, on the thermo-mechanical properties of pre-industrial ceramics, by using both an experimental and a numerical approach (Allegretta, 2014; Allegretta et al., 2014, 2015).

2. Materials and methods

2.1. Raw materials and sample preparation

For the preparation of the samples, a Ukrainian kaolinitic clay, distributed by Imerys Tiles Minerals Italia S.r.l. of Reggio Emilia (Italy) was used. A 1 mm-mode (mean 2.7, median 1.5, standard deviation 1.7 and skewness 0.7 in φ values) and a 0.125 mm-mode limestone sand (mean 0.3, median 1.5, standard deviation 1.7 and skewness −0.7 in φ values) were obtained from the grounding of a pelbiosparite limestone, coming from the Calcare di Bari formation and sampled along the coast between Molfetta and Giovinazzo (Bari — Italy). They were added to the clay in quantity of 5, 15 and 25 vol.%. An amount of 5 vol.% of water was added in each mix and twenty-one disks (70 mm of diameter and 10 mm of height) were prepared by uniaxial pressing using a pressure of 25 MPa. Finally, ceramic samples were fired at 500, 750 and 1000 °C using heating rate of 150 °C/h and a soaking time of 1 h. One month was waited (at 25 °C and 20% of relative humidity) before doing any analysis in order to allow the CaO hydration to occur fully. All the sample characteristics are summarized in Table 1.

A preliminary characterization of the clay by means of granulometric and mineralogical investigations was performed before the preparation of fired samples. Clay granulometry was studied coupling both water-assisted sieving and fractional sedimentation according to Dell'Anna and Laviano (1987).

2.2. Mineralogical analysis

The mineralogy of the clay was investigated by means of X-ray powder diffraction (XRPD) using both a qualitative and a quantitative approach. Laboratory X-ray powder diffraction patterns were recorded at room temperature with a PANalytical X'Pert pro MPD diffractometer using CuKα radiation and a graphite monochromator on diffracted beam. Initial qualitative analyses of the clay were performed on untreated, calcined (550 °C) and glycerol-treated oriented samples (Azaroff and Buerger, 1958). XRPD data were collected in a Bragg–Brentano (θ/2θ) vertical geometry (flat reflection mode) between 2° and 65° (2θ) in steps of 0.02° 2θ and step-counting time of 1 s. The X-ray tube operated at 40 kV and 40 mA. A 1/2° divergence slit, a soller slit (0.04 rad) and a 10 mm fixed mask were mounted in the incident beam pathway. The diffracted beam pathway included a soller slit (0.04 rad) and a 1/2° fixed anti-scatter slit.

Quantitative phase analyses (QPA) of the clay were conducted in two different ways: 1. with the method developed by Shaw and coworkers (Griffin, 1971) and modified by Laviano (1987); 2. using the Rietveld method. Besides, QPA by the Rietveld method were also performed on fired test ceramic samples.

X-ray powder data for QPA quantitative phase analyses were collected from carefully ground powders, sideloaded in Plexiglas sample holders. X-ray data were collected with the same PANalytical diffractometer described above. Analytical conditions were: angular range 2°–70°, step scan 0.02° 2θ, step counting time 11 s. The Rietveld refinements for QPA were performed by means of the fundamental parameters based Rietveld program BGMN Version 1.8.6b (Bergmann et al., 1998). For fired samples, the quantitative phase analysis method using the Rietveld technique was combined with the internal standard method in order to quantify the amorphous phase (Bellotto and Cristiani, 1991; Gualtieri, 1996, 2000; Gualtieri and Artioli, 1995; Gualtieri and Zanni, 1998) formed after the dehydroxylation of clay minerals. Corundum was thus added to the samples (10 wt.%) as internal standard and included in the refinements. The refined weight fraction of each crystalline phase (X_{ic}) was rescaled with respect to the known weight fraction of the added standard (X_s) in order to obtain the real crystalline phase weight fraction (X_i) according to the following equation:

$$Xi = \frac{1}{1-X_s}\left[\left(\frac{X_s}{X_{sc}}\right)X_{ic}\right]$$

where X_{sc} is the refined weight fraction of the internal standard. After calculating the real weight fraction of the crystalline phases, the amorphous content (X_a) was calculated by the following equation:

$$X_a = 1-\Sigma_i \quad X_i.$$

The following generalized refinement models were applied for the analyzed samples: background was modeled by a 5-parameter polynomial for the clay sample and by a 12-parameter polynomial for test-samples at 1000 °C; zero point (limits ± 0.02°) and sample displacement (±0.03 mm) were always refined.

Lattice parameters were refined for all phases with 'reasonable' interval restraints, with the exception of the β parameter of the monoclinic structure of the 2:1 layers of smectites which was fixed because of disordering; all atomic coordinates and displacement parameters were kept fixed; a number of occupancy parameters was refined, within predefined limits, e.g. interlayer K in mica was limited to 0.6–1, interlayer complex (cation and water) in smectites was limited to 0.1–0.3, in dioctahedral smectites Fe was substituted for Al in the octahedral sheet and cis-trans distribution was refined.

Isotropic size-related line broadening was assumed for all non-clay minerals and mica. Spherical harmonics models were used to correct preferred orientation, which was observed especially for layer silicates.

All the structures used for the Rietveld refinement were taken from the BGMN database; kaolinite and smectites were refined according to a disordered kaolinite and a Na-smectite structure model, respectively. After testing several existing structural model, the spinel-type phase was refined by using a γ-alumina structure (Zhou and Snyder, 1991) and applying both a size-related and microstrain-related line broadening with limits 0–0.1 and 0–0.0001, respectively. As in samples fired at 1000 °C the refinement gave a small but significant misfit (intensity calculated too high) at about 32° 2θ, pattern simulations were performed by means the program Powder Cell in order to check the dependence between intensities and structural parameters of the γ-alumina

Table 1
Sample list and specifications about their preparation.

Sample	Limestone temper		Firing temperature (°C)
	Quantity (vol.%)	Grain size (mm)	
NT500			500
NT750			750
NT1000			1000
5CL500	5	1.000	500
15CL500	15	1.000	500
25CL500	25	1.000	500
5FL500	5	0.125	500
15FL500	15	0.125	500
25FL500	25	0.125	500
5CL750	5	1.000	750
15CL750	15	1.000	750
25CL750	25	1.000	750
5FL750	5	0.125	750
15FL750	15	0.125	750
25FL750	25	0.125	750
5CL1000	5	1.000	1000
15CL1000	15	1.000	1000
25CL1000	25	1.000	1000
5FL1000	5	0.125	1000
15FL1000	15	0.125	1000
25FL1000	25	0.125	1000