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Research paper

The effect of mineralogy, microstructure and firing temperature on the effective thermal conductivity of traditional hot processing ceramics

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ABSTRACT

The present work analyses the effect of mineralogy, microstructure and firing temperature on the effective thermal conductivity of traditional hot processing ceramics. Samples prepared with two quartz-rich kaolinitic clays (BAR1 and BAR2), a fine kaolinitic clay (ARG) and a glaucophane-rich clay (SIF), were fired in the range between 950 and 1350 °C. The effective thermal conductivity is principally affected by the porosity of the body. Mullite further improves the thermal conductivity of BAR1 and BAR2 ceramics, while in ARG samples cristobalite is correlated with the increase in thermal conductivity. In SIF ceramics, the higher densification and the formation of spinel, pyroxene and hematite results in a higher conductivity compared to the other samples. The amorphous phase improves the ceramics' thermal conductivity since it seals voids between particles. In samples in which quartz exceeds 50 wt%, the ceramics' thermal conductivity decreases because of fissures and detachment zones formed after the α-β quartz phase transition. Finally, functional conclusions are drawn on traditional cooking pot and Medieval glass crucibles.

1. Introduction

The production of ceramics by using natural clays was one of the most important steps for the human civilization. Due to its characteristics and properties, ceramics played a key role in the ancient society and were used for a large variety of applications such as transport and storage vessels, bricks, tiles, cooking pots, decorative objects, technical tools, metal or glass crucibles, pipes, etc. Their technological evolution was influenced by the use of the most suitable raw materials, clay processing and firing technology in order to achieve the desired thermo-mechanical properties, which eventually determined the functionality of a ceramic artefact.

According to Rice (2005), three different use categories can be distinguished in traditional ceramic vessels: storage (e.g. jar), transport (e.g. amphorae), and processing (e.g. crucibles or cooking pots, with heat; mortars, without heat). In the last two cases, the required physical and mechanical properties are more restrictive in terms of functionality.

For example, transport amphorae should have a high tensile strength and toughening in order to provide a steady containment for their content. Otherwise their failure could have caused the loss of the content and endanger of the entire cargo of a merchant ship (Hein and Kilikoglou, 2014; Kilikoglou and Vekinis, 2002; Kilikoglou et al., 1998; Tite, 2008). In the case of hot processing ceramics which were exposed to a heating source, the thermal conductivity is one of the most important physical properties to be considered because it affects the heat transfer in a medium and it is strictly connected to the thermal shock resistance (Kingery et al., 1976; Tite et al., 2001; Velde and Druc, 1999). According to the context of use, the heating source could be set outside the container (i.e. cooking pots, glass crucibles) or inside (i.e. furnaces or early metal crucibles). In the first case, the ceramic should have a high thermal conductivity in order to allow the heat transfer through the container walls and heating of its content; in the second case, the container should have low thermal conductivity in order to reduce heat losses (Allegretta et al., 2014). This is also required in the production of building ceramics in order to reduce energy consumption (Gensel, 2015; Muñoz et al., 2014; Suctu, 2015).

In the last two decades, a lot of studies were published on the effect of raw materials on the thermo-mechanical properties of ceramics (Allegretta et al., 2014, 2015; Dondi et al., 2004; García-Ten et al., 2010a, 2010b; Hein et al., 2008, 2013; Hoard et al., 1995; Jordan et al., 2008; Kilikoglou et al., 1995, 1998; Lassinantti Gualtieri et al., 2010; Müller et al., 2010, 2016; Vekinis and Kilikoglou, 1998; Warfe, 2015). Porosity is one of the main parameters which affect the thermal properties of the material. At temperatures below 1200 °C the presence of

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pores in the ceramic body lowers its thermal conductivity, whilst at higher temperatures the relevant contributions of the radiation and convection in heat transfer can improve the thermal conductivity (Kingery et al., 1976; Kohl, 1964; Litovsky and Shapiro, 1992; Litovsky et al., 1996; Fedina et al., 1997). Several studies demonstrated that the shape and the orientation of pores should be considered because elongated pores perpendicular to the heat flux reduce, more than spherical ones, the heat diffusion in the body (Cernuschi et al., 2004; Hasselman and Johnson, 1987; Hein and Kilikoglou, 2007). However, the consideration of either porosity or bulk density is insufficient for the study of thermal conductivity of a clay-based ceramic, as demonstrated by Dondi et al. (2004) and Lassinantti Gualtieri et al. (2010). In particular, Lassinantti Gualtieri et al. (2010) found a correlation between the effective thermal conductivity and some components of the natural clay used for the preparation of ceramics such as organic material, feldspar and clay content. They also noted that the fine size of the clay contributes to improving thermal conductivity, probably due to a better sintering level. Furthermore, the addition of some additives to the clay mixture can affect the thermal conductivity of the body. Tempering materials such as quartz or granite improve the thermal conductivity of the fired body up to certain content (10–15%), but when they exceed this limit, they produce the opposite result because both the mismatch in thermal expansion and the α-β quartz phase transition create a detachment zone around temper grains (rim porosity) and cracks in the body (Allegretta et al., 2014; Hein et al., 2008). The addition of limestone temper decreases the thermal conductivity of the ceramic in particular when the firing temperature is set above the carbonate decomposition temperature (Allegretta et al., 2014; García-Ten et al., 2010b). The presence of organic materials had a positive effect on the thermal insulation of ceramics (Lassinantti Gualtieri et al., 2010) even if different effects have been observed according to the type of organic material used (straw, seeds, etc.) because they produce pores with different shapes (Hein et al., 2013).

However, all these results are related to clay mixtures fired at temperatures (from 500 to 1000 °C) lower than those used for firing technical ceramics like glass crucibles (Eramo, 2006a). At higher temperatures (1200–1400 °C), new phases form revealing different thermal properties. Also the porosity and the shape of the pores could change according to the viscosity of the melted part. High firing temperatures are reached in a few experimental studies (Michot et al., 2008) but in such cases the results are related to ceramic made with pure standard clay and not with natural clay.

The present work aims to analyse the thermal conductivity of ceramics prepared with different clay mixtures fired in the range between 950 and 1350 °C. Some of these clays were used in the preparation of ancient technical ceramics. In particular, two coarse kaolinitc clays from Switzerland were used in the manufacture of Medieval glass crucibles (Eramo, 2006b), whereas a glaucophane-rich clay from the Greek island of Sifnos is used for the production of cooking pots since the 17th century (Kyriakopoulos, 2015). In addition, a fine kaolinitic clay, already used by us in some previous works on thermo-mechanical properties of ceramics (Allegretta et al., 2014, 2015), was also tested in the present work in order to study the effect of clay particle size and composition on the thermal conductivity of the fired body. The thermal conductivity of these ceramics is discussed on the base of mineralogy, porosity and microstructures in order to consider all the possible variables changing during firing.

2. Materials and methods

2.1. Raw materials and ceramic preparation

Four different clays were used for the preparation of the samples: two clays (BAR1 and BAR2) were sampled in Switzerland (Court, Ct. Bern), SIF was sampled on the Aegean island of Sifnos (Greece) and ARG is an Ukrainian clay distributed by Imerys Tiles Minerals Italia S.r.l. of Reggio Emilia - Italy. The clays were water sieved and the fraction with particle size >2 mm was removed. After drying the powdered clays, 5 wt.% of water was added and disks of 30 mm of diameter and 7 mm of height were prepared using uniaxial pressing (25 MPa). This uniform pressure was applied in order to eliminate primary porosity and to avoid effects due to pore shape which could affect the thermal conductivity of the ceramic bodies (García-Ten et al., 2010a). The disks were left drying for 24 h at 100 °C and fired at 950, 1050, 1150, 1250 and 1350 °C using a rate of 150 °C/h and a soaking time of 1 h. As disks made from the SIF clay melted at temperatures above 1150 °C they were not considered in the paper.

2.2. Analytical techniques

Both clays and ceramics were analyzed via X-ray powder diffraction technique. Initial qualitative analyses of the clay fraction of each sample were performed on as-prepared, calcined (550 °C) and glycerol-treated oriented samples (Brindley and Brown, 1980), using a θ/2θ PANalytical X'Pert pro MPD diffractometer and X'Pert Highscore (PANalytical, version 3.0) with a PDF2 reference database implemented in the software. XRPD data for quantitative phase analyses (QPA) were collected using a θ/θ PANalytical Empyrean diffractometer, equipped with a time multiple strip (RTMS) *PIXcel*^{3D} detector. A 0.125° divergence slit, a 0.25° anti-scattering slit and a soller slit (0.02 rad) were mounted in the incident beam pathway. The diffracted beam pathway included a Ni filter, a soller slit (0.02 rad) and an antiscatter blade (7.5 mm). A virtual step scan of the RTMS detector of 0.026°2θ was used. The data were invariably collected with high counting statistics (360 s/step) from carefully ground powders, using sideloaded sample holders. The QPA were performed using Rietveld refinements which were carried out 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 dehydroxilation of clay minerals. Corundum was thus added to the samples (10 wt.%) as internal standard and included in the refinements.

The following generalized refinement models were applied for the analyzed samples: background was modelled by a polynomial function with a different number of coefficients depending of the sample, i.e. low degree of background polynomial in clay sample and high degree of background polynomial in fired samples; 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 and 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 with the exception of that of glaucophane (Papike and Clark, 1968); kaolinite and smectites were refined according to a disordered kaolinite and a Na-smectite structure model, respectively.

The particle size distribution of the four clays was studied by water sieving for the fraction between 2000 and 32 μm, and sedimentation applying Stoke's law for particles size <32 μm (Tickell, 1965).

In order to study the ceramic microstructures, backscattered electron (BSE) micrographs were acquired on graphite-coated samples using a ZEISS LEO 50XVP scanning electron microscope (SEM), operating at 15 kV. X-ray maps were obtained with a X-MaxN 80 mm^2 SDD detector and Aztec software (Oxford Instruments).

The open porosity was estimated by water immersion (EN 993-1, 1995).

Chemical analysis was conducted using a Rigaku Supermini 200 WDXRF equipped with a Pd-anode working at 50 kV and 4 mA. The WDXRF was calibrated using geological standards by SARN (Service

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