

FEATURES OF MICROWAVE FIRED UTILITARIAN STONEWARE

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Abstract

Both high temperature phases and microstructure transformations of stoneware products microwave and conventionally (gas and electric) fired are investigated aiming at a better understanding of factors affecting their mechanical and aesthetic properties. The microstructure of microwave fired stoneware has similar characteristics to those of conventionally fired samples, microwave firing requiring lower temperatures to achieve a similar structure. X-Ray diffraction and scanning electron micrographs show that the most relevant transformations are complete for lower temperatures when using microwave heating. Microwave radiation is presented as an alternative heating technology for stoneware firing, leading to similar, or even better, mechanical properties and similar microstructural characteristics, requiring lower firing temperatures and shorter processing times.

Introduction

Stoneware, such as porcelain and other clay-based materials, is a composite material consisting of a glass matrix that embraces two main crystalline phases, quartz and mullite. It is a ceramic material, usually produced through a single firing stage at temperatures close to 1200 °C [1,2]. Like porcelain, it can be double fired, through a first firing stage at 1000 °C followed by the firing of the glazed body at 1325 °C [3]. The firing temperatures depend on the constituent raw materials, which can have significant variations: 30 – 40% of clay, 5 – 20% of quartz and 45 – 55% of feldspars. Secondary minerals such as flint, talc and zircon may be added to lower the melting temperature and to increase the whiteness of the finished product [1,2,4]. It is a product normally colored, presenting some impurities like hematite, goethite, maghemite, lepidocrocite, the purity of the raw materials being not so crucial as for porcelain [4,5].

The stoneware industry is highly hydrocarbons dependent, natural gas being the most used primary energy source for products drying and firing. Searching for a more decarbonized industry, microwave radiation is presented as an alternative heating technology, which shows to be a more environmentally friendly firing method for a wide variety of ceramic materials [6,7].

Experimental methodology- Firing

Samples were fired in both microwave and electric furnaces at temperatures of 500, 800, 1000, 1050 1100, 1140, 1180, 1225 and 1300 °C. The heating cycles, from room to maximum temperature, were processed from 40 up to 75 minutes. The cooling phase depends on the thermal inertia of each furnace. Results were compared with a reference, corresponding to the average of a set of 10 mugs fired in the tunnel kiln of Grestel Company at ~ 1200 °C in 200 minutes. One test was carried out in the microwave furnace using a firing cycle of 115 minutes.

Microwave furnace: Samples were fired in a 6 magnetrons multimode furnace, each one operating with a nominal power of 900 W at a frequency of 2.45 GHz. A pyrometer and a thermocouple were installed in the microwave furnace for temperature measurement, monitoring and control. Calibration of the pyrometer was made in an electric furnace for more accurate temperature measurements. The thermocouple used in the microwave furnace was temporarily installed in the electric furnace, presenting a temperature difference of the order of 2 to 5 °C when comparing with that indicated by the electric furnace thermocouple. The microwave firing process was automated through the development of a Labview program searching for homogeneous heating, by creating a sequence of combined permutations of the magnetrons operating at a given moment of the heating process. The system operates in a Microwave Hybrid Heating (MHH) mode [8], as it uses a SiC plate acting as the base for the stoneware mugs and as a microwave susceptor. For lower temperatures, the material is heated indirectly, due to the heat released from the susceptor. After reaching its critical temperature, the stoneware absorbs the microwave radiation efficiently and is directly heated by the absorption of the microwave radiation [9]. The interior of the microwave furnace has a sandwich insulating wall, with 75 mm thickness. The layout displaying the distribution of the mugs over the SiC plate, inside the microwave furnace, is shown in Fig. 1.

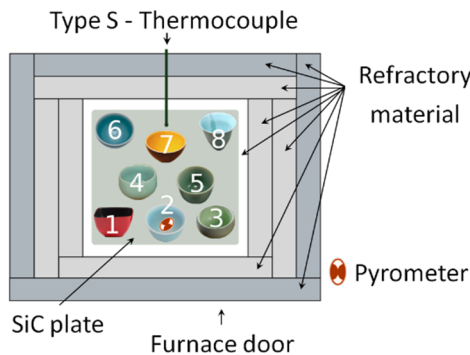


Fig. 1. Mugs distribution inside the microwave furnace.

Electric furnace: The electric furnace is a standard furnace with a nominal power of 4.5 kW. Due to the reduced availability of the samples' material and the reduced size of the electric furnace, only an aliquot taken from stoneware mugs was electrically fired. The temperature during the firing process was measured by the electric furnace thermocouple.

Employed techniques and analysed features

Rupture energy analysis: Stoneware mugs were tested by impact at the rim, according to ASTM 368/ISO 12980. Samples were repeatedly impacted increasing hammer's energy until fracture occurrence [10]. Results are presented in Fig. 2.

Water absorption analysis: Water absorption was determined based on the mass of aliquots samples impregnated with boiling water, following the porcelain tableware standard (BS5416) [11]. Aliquots were drawn from two different parts (the base and the rim) of the mugs. Results are presented in Fig. 2.

Simultaneous Thermo Analysis (STA): Differential Scanning Calorimetry (DSC) and ThermoGravimetry Analyses (TGA) were performed on stoneware powder from room temperature up to 1250 °C. Some of the transformations occurring in the stoneware during firing were studied and results compared with those found in the literature. Results are presented in Fig. 3.

Optical microscopy analysis: Olympus BH2 optical microscope was used to perform microstructure (closed porosity) analysis. Prior to optical analysis, stoneware aliquots were grinded with sandpaper and water, and subjected to a final polishing with a 1 µm ultra pure alumina suspension. Results are presented in Fig. 4.

Scanning Electron Microscopy (SEM - EDS) analysis: After optical analysis the aliquots were etched with a 10% HF solution during 60 s, then carbon coated and analyzed using the TESCAN-Vega 3 SBM SEM instrument. Results are presented in Fig. 5.

X-Ray diffraction (XRD) analysis: For detection of the phases present during firing, the powder aliquots of the samples fired at different temperatures, including green and gas fired references, were analyzed by powder X-Ray Diffraction (XRD). Data were collected using Empyrean Panalytical Diffractometer (CuK α radiation) with a Ni filter. Intensity data of diffraction peaks were provided by the continuous counting method in the range of 5° to 80° of 2 θ angles. Results are presented in Fig. 6.

Results

The rupture energy and the water absorption determined on aliquots drawn from mugs rim and from mugs base are presented in Fig. 1. The rupture energy of the reference is over the curve of the microwave fired samples. Aliquots taken from the base of microwave fired mugs show lower water absorption than the reference. Aliquots taken from the rim of microwave fired mugs provided results contradicting the results corresponding to the basal ones. Comparing results with those of the electrically fired samples, it is clear that microwave fast fired samples present characteristics closer to that of the reference than the

electrically fired ones, Table 1. At 1180 °C the electrically fired samples provide water absorptions values of 7.5 %, much higher than the water absorption obtained for microwave fired and reference samples. The firing test with a 115 minutes cycle (marked in Fig. 1 in green) did not present significant differences when compared to the samples fired in 70 minutes cycles, the rupture energy being lower for this case.

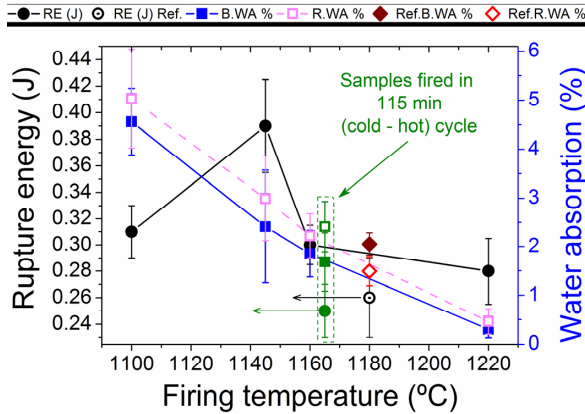


Fig. 2. Rupture energy (RE (J)) and water absorption (WA %) as a function of the firing temperature (measured by the pyrometer). Ref. refers to the reference samples. B.WA% refers to the water absorption of aliquots from the mugs base. R.WA% refers to the water absorption of aliquots from the mugs rim.

Table 1. Water absorption of aliquots fired in the electric furnace.

Temperature (°C)	Water Absorption (%)
1100	18.6
1140	10.3
1180	7.5
1225	2.9
1300	0.2

Differential Scanning Calorimetry (DSC) and ThermoGravimetry (TG) analyses presented in Fig. 3, show that the loss of free and bound water represent about 1.8% of the total weight loss. Below 450 °C and under oxidizing conditions [12], burning of organic matter may occur, mainly in less pure clays. This could explain the continuous TG decrease, associated also to the continuous release of water from the stoneware raw materials. It is followed by the release of structural water from kaolinite leading to the formation of metakaolinite, endothermic reaction expressed by a peak at 510 °C. The onset of the kaolinite structure collapse is observable from ~450 °C upwards, which according to [13] might extend up to temperatures close to 1000 °C. This transformation comprises a weight loss of 5.6%. The $\alpha \rightarrow \beta$ transformation of quartz occurs at 573 °C [4]. The pre-mullite and liquid phase formations occur at approximately 990 °C and 1100 °C, respectively [2,4]. Formation of the liquid phase lowers to the eutectic temperature of 985 °C [14], or of 990 ± 20 °C according to [15], for the $K_2O-Al_2O_3-SiO_2$ system.

The residual quartz, which is part of the initial composition, only reacts with the liquid phase at higher temperatures, beginning to be dissolved for temperatures above 1200 °C [4,14].

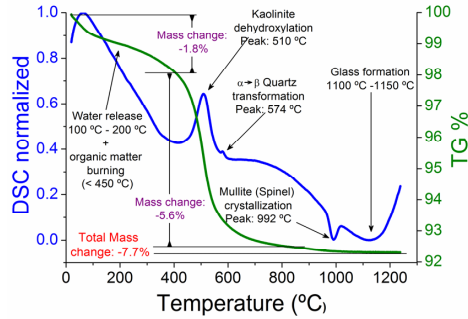


Fig. 3. Differential Scanning Calorimetry (DSC) and ThermoGravimetry (TG) curves of dry stoneware raw materials composition.

At temperatures close to 990 °C mullite is formed due to a solid state reaction consisting of a rearrangement of the constituents, silica and alumina, released from metakaolinite. Above 1200 °C recrystallization occurs, with the consequent development of mullite crystals exhibiting needles' shape. With the dissolution of quartz the liquid phase content increases and its viscosity decreases, having an enhanced effect on the growth of mullite crystals [4,16]. In Fig. 4 the set of images show the microstructures of aliquots of several samples fired between 1000 °C and 1300 °C in both the microwave (MW) and electric (E) furnaces. The gas fired reference is also shown for comparison.

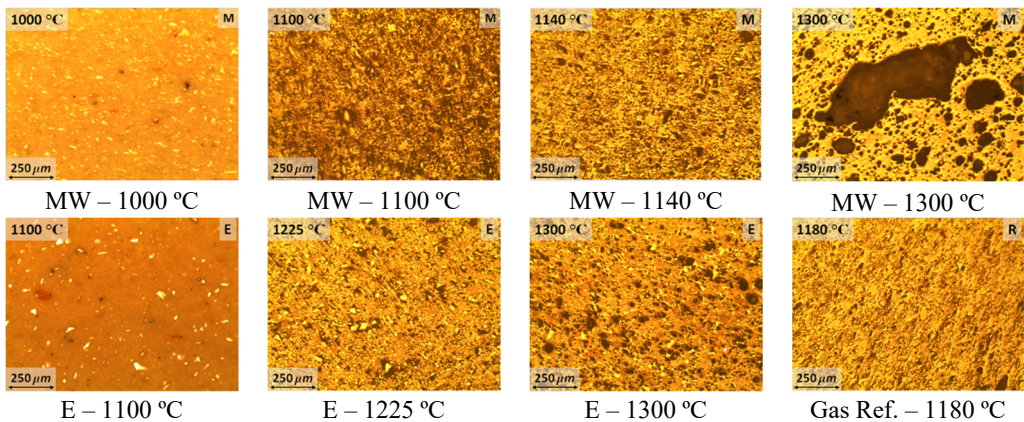


Fig. 4. Optical microscope images of samples microwave fired (M), electrically fired (E) and gas fired (Gas Ref.) at several temperatures.

From Fig. 4 the microwave fired samples, in fast cycles of 70 min or less, have a more developed microstructure that those electrically fired, microwave fired samples at 1140 °C already presenting features very similar to those of the reference. The electrically fired samples at this same temperature have an underdeveloped microstructure, the sample fired at 1225 °C being closer to the reference. For a better and deeper understanding of the main

reasons for the observations made so far, SEM observations were carried out (Fig. 5). At 1050°C an advanced state of melting and dissolution could be observed in feldspar grains from samples fired in the microwave furnace. This melting and dissolution is just incipient in the electrically fired samples, which still present structures/agglomerates of platy particle relics derived from kaolinite structural collapse, and that are just starting transformation to mullite. At 1140 °C the mullite is more developed in the microwave fired samples than in the electrically fired ones, already presenting mullite type-II, yet not so developed as in the reference sample.

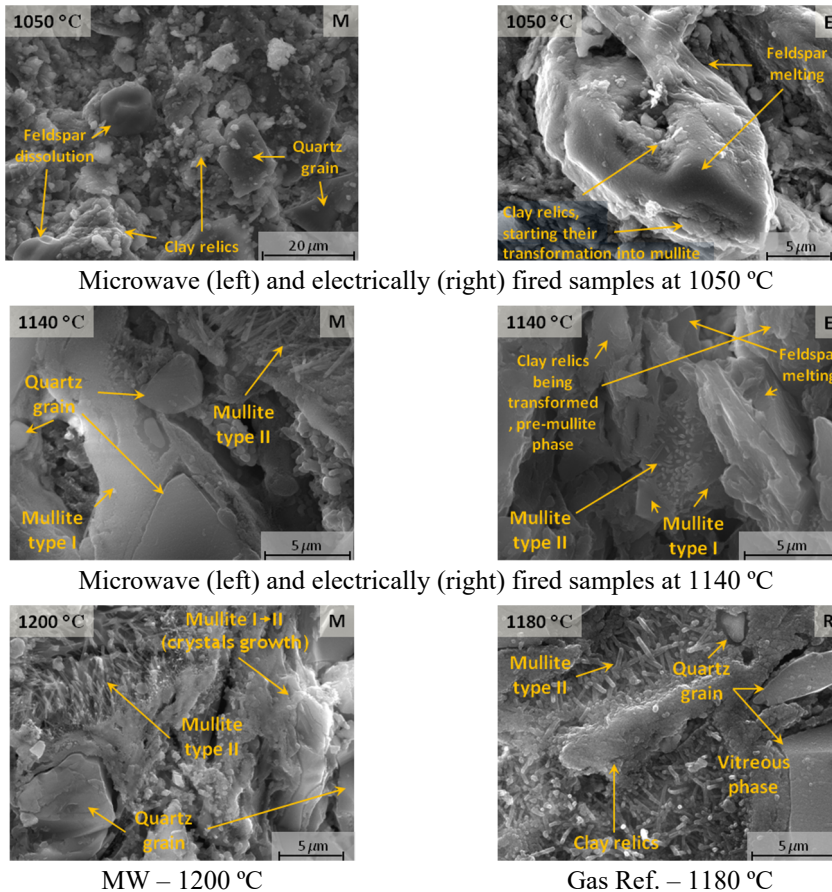


Fig. 5. SEM images of microwave fired, electrically fired and gas fired reference samples, fired at 1050 °C, 1140 °C, 1180 °C and 1200 °C. (M)=Microwave; (E)=Electrically; (R)=Gas reference.

The results of the XRD analysis presented in Fig. 6 show that the electrically fired samples exhibit less intense mullite peaks than those microwave fired at the same temperature, the diffractograms of microwave fired samples at 1140 °C being very similar to the one of the reference sample. XRD results also show that some transformations occur earlier, i.e., for lower temperatures, in the case of microwave fired samples. Kaolinite dehydroxylation is a

paradigm, the collapse of kaolinite structure being completely accomplished at 500 °C. Electrically fired samples still show residual kaolinite at 800 °C, although not visible in Fig. 6. The same is observed for talc and muscovite, which structural changes comparatively occur at lower temperatures for microwave firing.

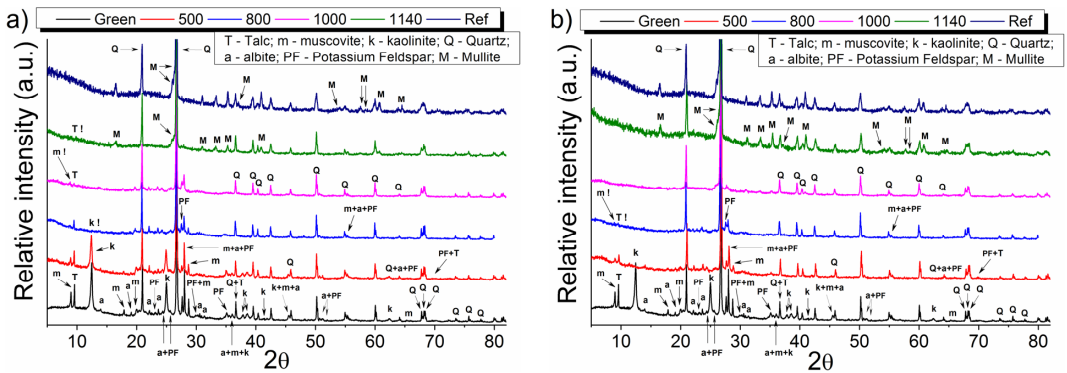


Fig. 6. X-ray diffractograms of aliquots fired at 500 °C, 800 °C, 1000 °C and 1140 °C: a) in electric furnace, and b) in microwave furnace. Dried (“Green”) stoneware reference and the gas fired reference (“Ref”) are also presented.

Discussion

The water absorption analysis shows that aliquots taken from the basal surface of microwave fired mugs provide values below those of the reference; the opposite is observed for the aliquots taken from the mugs rim. This might be related to the temperature differences between the mugs’ base and rim, which depends on the heat technology, allowing the higher temperature in the mug’s base than in the mug’s rim. Since SiC is a very good microwave absorber, the mug’s base contacting the SiC plate can be at a higher temperature than the mug’s rim, and being denser at the base they are less water permeable there.

Microstructural analysis shows that the microstructures of the microwave processed samples are similar to those of the gas reference, for a firing cycle of only 35% of that required by the reference and for a temperature ~50 °C lower (Fig. 4). For the same temperatures, the electrically fired aliquots will require more time to reach the same features or characteristics as the reference. Microwave fired samples at 1300 °C present greater closed porosity, already presenting coalescence and the lost of pores rounded shape. Electrically fired samples at 1300 °C only show the beginning of the closed porosity growth, still very close to the microstructure of the reference sample.

SEM analysis show that at 1050 °C there is some feldspar grains dissolution in microwave fired samples, 60 °C above the formation of the liquid phase at 990 ± 20 °C according to [15]. Although it has not been clearly detected through SEM analysis, from XRD analysis it is shown the existence of mullite type-I in samples fired at 1050 °C, as some peaks characteristic of the presence of mullite in the microwave fired samples are already visible. From XRD analysis, the electrically fired samples at 1140 °C present mullite peaks less intense than those microwave fired, the last ones having very similar diffractogram to the one of the reference sample. From SEM analysis, at 1140 °C, the mullite is more developed in the microwave fired samples than in the electrically fired ones, already presenting mullite type-II, yet not so developed as in the reference sample. XRD analysis shows also that for temperatures lower than the beginning of the vitrification temperature, some transformations

occur considerably earlier in the microwave fired samples. Kaolinite dehydroxylation is a case study, already fully accomplished at 500 °C. Electrically fired samples still show residual kaolinite at 800 °C, not observable from the figures. It could be also observed that talc and muscovite structures full transformation and collapse occur for lower temperatures in microwave fired samples than in electrically fired samples.

Conclusions

Microwave stoneware firing provides similar, or even better, macroscopic features comparatively to those obtained by electrical and gas firing technologies. Microstructure analysis, optical and SEM, provide a better understanding of what was observed on the macroscopic features, microwave fired samples showing more advanced stages of development comparatively to the electrically fired ones, for the same temperatures and/or firing times. DRX analysis shows that some transformations are completed at lower temperatures when microwave firing is used, kaolinite, talc and muscovite transformations being the most notorious cases. The potassium and sodium feldspars seem to completely melt earlier in the microwave fired samples than in the electrically fired ones, presenting less intense peaks. At 1140 °C the mullite crystals become more developed in the microwave fired samples than in the electrically fired ones, already presenting mullite type-II, with a diffractogram similar to that of the reference sample. The full transformations occur at temperatures closer to those referred to in the literature when microwave firing is used when compared with electric firing.

Acknowledgments

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