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Production of macroporous ceramics from fibres dispersed mortars (FDM)

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Abstract

We examined the production of macroporous monolithic ceramic from mortars prepared using aluminate cements, one or two different types of alumina powders, superfluidificant, water and polyurethane fibres. Some relevant parameters for the preparation process of the mortar are: (i) the weight ratio between cement powder and water, (ii) the weight ratio between superfluidificant and cement powder and (iii) that between superfluidificant and water. Thirty-six percent is the upper limit for the volumetric content of the fibres that can be introduced into the mortar without leading to a material that breaks up by handling after the successive thermal cycle. We also optimized the thermal cycle that may be used in order to avoid the spontaneous break-up of the material during the sintering treatment. Materials containing fine and coarse particles of alumina powders exhibit extended ruptures probably dependent on the thermal stresses that grow on cooling after the sintering process, whereas in materials containing only fine alumina powders the presence of ruptures is more limited so that the fired materials have a sufficient strength and can be handled without a particular care. The ageing time at the maximum temperature plays an important role on the microstructure of the sintered material since it has been seen that after 2 h at 1250 °C the residual porosity seems to be completely closed and the large grain size shows the presence of structures which can be due to the presence of aluminates.

Keywords: A. Sintering; B. Microstructure-final; B. Porosity; Mortar

1. Introduction

Porous ceramic materials are actually matter of diffuse attention due to their wide use in industrial and surgical fields. In fact, due to the good mechanical properties at high temperatures and to their chemical inertness, they can be used as filters for hot exhaust gases, catalytic supports and separation membranes [1–3]. More recently, they have been matter of research aimed to reproduce the ceramic structure of human body bones where the inorganic part is mainly constituted of porous hydroxyapatite [4–8].

The general interest devoted to porous ceramic materials has recently increased and many researchers, on the grounds of studies regarding some natural biomaterials and novel production strategies for new materials having a biomimetic approach, have prepared porous ceramics by adapting biological principles, which in nature govern the production of biocomposites, to laboratory production, in order to prepare new materials and/or find new preparation techniques [9–13].

Porosity is actually a fundamental requirement for the good performance of ceramic substrates for solid–gas reactions operating at high temperatures; it should be as stable as possible on use so that, even after several

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treatments at high temperature, densification is minimized [14–16].

Presently monolithic ceramic substrates, prepared for application as catalytic supports, have porosity of two different sizes: macroporosity and microporosity. The former has dimensions of some tens of microns ($10 \div 100$ μm), the latter is roughly ten times smaller, being directly determined by grain size which, in turn, is function of thermal treatments adopted during the production of materials.

Microporosity mainly depends on powder characteristics such as composition and particle size distribution. It follows that powders' thermal history plays an important role on the resulting porosity of sintered material. Macroporosity, on the other hand, depends on the preparation procedure of the ceramic substrates and may be obtained by introducing, in the starting green compacts, some substances that, upon thermal sinterization, can evaporate or burn, leaving place to the equivalent porosity.

Although the production costs of fibres reinforced mortars (FRM) are higher than those of traditional mortars, FRM are actually widely used in the construction industry due to their high mechanical performances. During homogenisation of FRM pastes, it is suggested, in order reach good dispersions of the different components, to add small amounts of advanced fluidificants, normally on sale in the market, which permit to reduce the water quantity close to the stoichiometric amount. It is known, in fact, that the major consequence of a low water content is to determine a high density of the hydrated solid material and, therefore, a high strength.

Market offers a practically unlimited number of fibres for toughening advanced mortars: metallic, ceramic or polymeric short or continuous fibres.

Metallic and polymeric fibres can increase both toughness and/or strength with respect to traditional mortars [17–22]. Ceramic fibres are in general not used for the production of FRM, but sometimes added as external supports coupled with some epoxy resins.

In any case it is clear that, if the production of FRM is only a first step for the preparation of porous ceramic, polymeric materials can be thermally evaporated or burnt, whereas other materials do not.

On the grounds of FRM production procedure, which starts with mixing cement powders, silica sands, superfluidificant, fibres and water, in the present work we have used aluminate cement powders, fine and/or coarse particles of α-alumina, superfluidificant, short fibres of polyurethane and water. The use of aluminate cement powders and highly pure alumina should give products suitable for high temperature applications and could lead to sintered materials displaying a high softening temperature. At the same time, highly pure alumina permits to minimize the number of variables that intervene during the preparation procedure. In particular, we have prepared two different types of mortar: one containing only fine alumina powders, the other containing both fine and coarse particles. Increasing amounts of fibres were added to the mortars in order to determine the upper limit of their content before a catastrophic degradation of the materials might take place during the sintering process. We have accorded the preference to polyurethane with respect to other polymeric materials substantially because, as we have observed in our experiments, they are not wetted by the cementitious solutions [23], it is not required an additional amount of water and fibres can be burnt, on sintering, at moderate temperatures.

2. Experimentals

2.1. Starting materials and procedures

As starting materials, we have used the following products: calcium aluminate cement, Electroland (San Vicenc Dels-Horts, Barcelona-Espana); α-alumina 99.6%, Cristalba HP (P.E.M.-Pechiney) with average particle size of 500 μm; α-alumina 99.6%, Cristalba HP (P.E.M.-Pechiney) with average particle size of 3 μm; superfluidificant Mapefluid X504 (Mapei) in solution with 34 vol.% of water, containing mainly acrylic polymers and free from formaldehyde; polyurethane short fibres having 0.5 mm diameter and 20 mm length, self extinguishing temperature <300 °C, tensile rupture strength of 70 MPa and elastic moduli of 0.5 GPa.

For the preparation of mixtures we used a 5 l Hobart planetary mixer normally used for the laboratory production of mortar samples (conform to the EN 106/1 and ASTM C305 standards).

The preparation protocol, reported below, was defined after several attempts of optimising mixing speeds and procedure parameters, i.e. water/cement ratio (α), superfluidificant/water ratio (β) and superfluidificant/cement ratio (γ) and alumina/cement ratio (δ). In the present work δ was kept fixed at 0.25 in order to minimize the number of variables, which must be examined during the preparation procedure. This value corresponds to the amount of silica sand added to some high performance cements [17,18]. In some samples the total amount of alumina was shared into equal quantities of fine and coarse powders whereas in others the total amount of alumina consisted of only fine powders.

We have introduced into the container, keeping the mixer still, cement and fine alumina powders ($\delta = 0.25$), superfluidificant ($\beta = 0.02$, $\gamma = 0.0042$) and free water ($\alpha = 0.21$), afterwards we started to mix at slow speed for 5 min. This procedure is necessary to allow for a good homogenisation of cement and alumina powders. At the end of this initial mixing different quantities (7, 12, 18, 25 and 36 vol.% of the total amount of mixture) of polyurethane fibres were added to the paste and the mixing was further protracted for 5 min. The eventual addition of coarse alumina powders was carried out at the end of this second mixing and this was

followed by further mixing for 2 min. The mixer was then stopped and the mortar paste kindly detached from the container walls and from the blades. The mixing was subsequently restarted at high speed for further 6 min.

In the present work we adopted a modified version of the slump test, according to the following procedure: a metallic die shaped as a truncated cone (inner diameter of the major base 70 mm, inner diameter of the minor base 50 mm, height 85 mm) is filled with the mortar paste; the major base of the die is leant on a Vebe vibrating plate, lifted and the mortar is left to expand for 20 s, afterwards the plate starts vibrating for 5 s. At this point the width of the cake over the plate is measured with a rule. The paste is said to have the correct viscosity, and may be poured into the mould, if the cake width is 150 (±10) mm. Pastes were poured under vibration into a mould having dimensions of 40 mm × 40 mm × 160 mm and aged 24 h for the first hydration.

Afterwards samples were demoulded and aged 28 days in common water at 40 °C and then dried in atmospheric environment for 24 h. Dried materials were washed with acetone and dried again in an oven at 80 °C for 24 h. They were finally cut into small specimens (10 mm × 10 mm × 30 mm).

The sintering process took place in a Netzsch muffle furnace heated by $MoSi_2$ elements at different temperatures for 1 or 2 h following the thermal cycle reported in Fig. 1. The thermal cycle is discussed in the next point.

X-ray diffractions were done on an XRG 300 INEL powder diffractometer equipped with CPS 120 detector. Monochromatic Co $K\alpha_1$ was obtained by setting 35 kV and 20 mA as operating conditions. Fired samples were analysed by a Cambridge Stereoscan scanning electron microscope (SEM).

Homogenisation of the components during mortars preparation is the first important step for the production of fired bodies with good properties. It is known that, if the mortars pastes are fluid, the components are better dispersed. From this point of view the amount of free water plays a very important role. It seems reasonable that a high water content should benefit the dispersion, but conversely it causes a high porosity of the hydrated samples. We found that α ratio of 0.21 represents the better amount of water for our components. In fact, if α exceeds 0.21 the mortar pastes display high fluidity and fibres can be well dispersed, but mixed pastes are very fluid, the slump test cannot be performed, and the hydrated materials contain high porosity. If the α ratio is below 0.20, pastes are not sufficiently fluid and it is difficult to obtain a rapid homogenisation of fibres and alumina powders. It follows that using long mixing times a partial hydration of the cement cannot be avoided thus making it impossible to pour the paste and fill the mould. Moreover the mortar, placed into water for ripening, tends to break up.

The second parameter, which had to be investigated during the preparation of specimens, is the amount of superfluidificant expressed as β (superfluidificant/water ratio) or as γ (superfluidificant/cement ratio). We observed that if β is greater than 0.02 and, in turn, γ greater than 0.0042, fibres tend to emerge from the fluid mixture and to float on top of the mortar paste during hydration in the mould; in this case part of the added superfluidificant diffuses to the samples surface giving rise to a plastic film when the partially hydrated samples are exposed to the air. After ripening in water, mortar samples break up when they are extracted from the mould. Moreover, when the paste is still fluid, the slump test cannot be carried out since the fluidity of the mixture is too high.

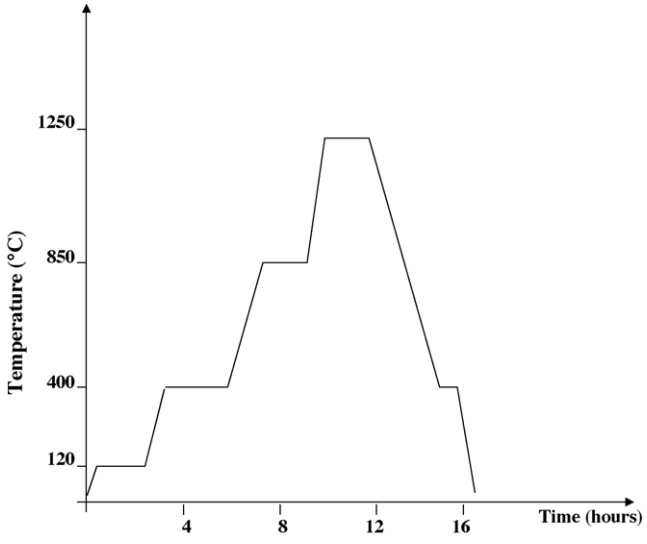

Fig. 1. Qualitative representation of the thermal cycle followed for the sintering process. *X*-axis reports time in hours, while *Y*-axis reports the most significant temperatures.

2.2. The thermal cycle

The definition of a sintering procedure for a ceramic material is a very delicate task since no general rule exists that may help to find the best conditions in terms of maximum temperature, time and steps on heating. DTA, TGA and dilatometry measurements often represent a valid experimental approach to acquire data about the heating cycle, but results are hardly transferable to the experiment in a muffle furnace since, in this case, the temperature is not uniformly distributed. Moreover, the thermal analysis, which is normally carried out under dynamic conditions, often reveals only a temperature range where a particular phenomenon occurs, and in this case the precise temperature of the phenomenon can be hardly deduced. It is known that several phenomena often occur in the same range of temperatures and we have observed that from 80 to 500 °C materials studied by us undergo a continuous weight loss. We concluded that the best way to find a good thermal cycle is the direct experiment in the muffle furnace itself. The more so if we consider that our green materials contain several components, a large amount of water that must evaporate on heating and some polymeric fibres which

should burn at temperatures higher than that of water evaporation and that their complete burning cannot be investigated by dilatometry. We must also consider that, during hydration of the mortar paste, some product can react with the CO_2 present in air giving rise to an undefined amount of carbonates that must decompose on heating, before the beginning of the final shrinkage in the sintering process.

In Fig. 1, we display the thermal cycle used for the sintering process. It is the result of several attempts that were carried out by varying heating rates, final temperatures, ageing time at the final temperatures and three intermediate steps at 120, 400 and 850 °C with their relative ageing times, which were necessary in order to preserve the integrity of the monolith during the several reactions that intervene on heating.

First of all we made some experiments to determine the best final temperature of sintering. It is the maximum temperature that the hydrated mortar can withstand without losing its shape when fired into a ceramic body. In our experiments we have observed that if the green materials are fired at the temperature of 1300 °C, for any ageing time, the result of the sintering process is a vitreous solid; the shape of the starting sample is lost. Sintering temperatures between 1260 and 1290 °C show a fired body that is extremely deformed relative to the starting green sample, thus denoting the presence of a liquid phase at high temperature. Therefore, we assumed that at 1260 °C the material starts softening, and is completely liquid at 1300 °C.

If the samples are sintered at 1250 °C or at a lower temperature, the sintering process leads to porous ceramics, more or less consistent as function of the followed thermal cycle and of the maximum temperature set.

Heating from room temperature to 120 °C can be fast since, after drying in the oven at 80 °C, green samples contain only a small amount of free water, whereas crystallization water evaporates at higher temperatures (around 120 °C or more), therefore the step at this temperature is sufficiently long in order to enable the evaporation of a significant amount of crystallization water. The heating rate between 120 and 400 °C is lower, because in this temperature range the residual crystallization water evaporates and most of the organic compounds decompose. The next stop at 400 °C must be quite long, because fibres burn and the material tends to loose coherence and breaks up. The best heating rate between 400 and 850 °C is 5 °C/min since in this temperature range no critical event takes place. Only some carbonates, grown during hydration, some organic compounds not yet decomposed, and further oxydrilic groups still entrapped in the sample must evaporate without damaging the materials.

The heating rate between 850 and 1250 °C (10 °C/min) can be quite fast since it represents only a heating step for the material, which at this point of the thermal treatment contains high melting oxides, which are driven to shrink. Sulphates group, if present, evaporates at temperatures above 1000 °C when the materials are already partially sintered and, consequently, they are strong enough to support the evaporation without catastrophic ruptures.

On cooling we maintained a moderate cooling rate down to the temperature of 400 °C in order to preserve the integrity of the sintered materials under the action of some possible thermal stresses, which develop in the presence of several phases in the fired ceramic. The stop of 40 min at 400 °C is due to the $MoSi_2$ elements that heat the muffle furnace and have a phase transition in that temperature range. From 400 °C to room temperature the cooling rate was 10 °C/min since it was considered not particularly critical for the integrity of the porous fired materials.

We have observed that materials containing more than 36 vol.% of fibres break up during the thermal cycle and the fired materials, if handled after firing, break up for any thermal treatment and for any composition of the starting mortars. We can therefore assume 36% to be the maximum content of fibres that can be introduced in the starting mortars.

3. Results and discussion

Fig. 2, a and b report the SEM microstructures of a materials containing both fine and coarse alumina powders and containing 12 vol.% of fibres before the thermal treatment and maintained at the final sintering temperature for 1 h. The presence of diffuse fractures in the material can be observed (Fig. 2a), whereas Fig. 2b shows, at higher magnification, why coarse alumina particles (dark zones) can be considered responsible for the fractures. All visible fractures, in fact, start from the dark zones and, consequently, coarse particles tend to detach from the surrounding matrix. It is possible to explain this fact by taking into account two synergic effects that occur during the thermal cycle. The first is that coarse alumina particles lay, almost unreacted, embedded into the surrounding matrix during the thermal cycle. Of course a partial reaction cannot be excluded for very long ageing times at the maximum sintering temperature. However the sintering process, in our case, must be considered a shrinkage in presence of rigid inclusions just like in the sintering of most of ceramic matrix composites (CMC) [24]. The second effect is due to the presence of thermal stresses, grown on cooling, and caused by the different thermal expansion coefficients of alumina and of the matrix. Such stresses probably exceed the strength of the matrix and cause extended ruptures [25–28]. In order to extend the present research to evaluate also the effects in the bulk of the fired samples, some specimens were broken and the fracture surfaces examined by the SEM. Fig. 3 shows the fracture surface of a sample obtained by sintering for 1 h at 1250 °C a material containing 36 vol.% of fibres and no coarse alumina particles. Macroporosity appears to be randomly distributed and the mean diameter of pores is about 0.5 mm. Remembering that the diameter of the starting polyurethane fibres, burnt during the thermal cycle,

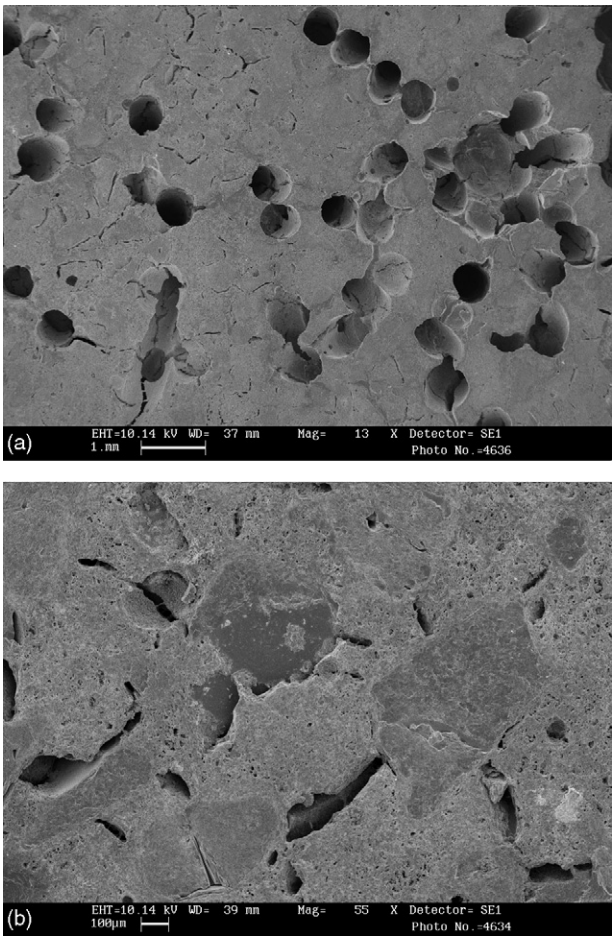

Fig. 2. SEM images of a sample obtained by sintering for 1 h at 1250 °C a hydrated mortar prepared using a cement powder, fine alumina powders, coarse alumina powders, superfluidificant, water and 12 vol.% polyurethane fibres. Fig. 2a shows the free surface of the as fired sample, while Fig. 2bshows a detail of Fig. 2a at higher magnification. In Fig. 2b dark zones are coarse alumina particles.

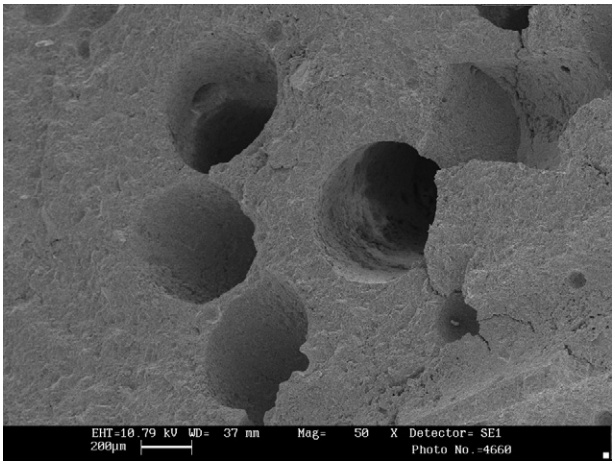

Fig. 3. SEM images of the fracture surface of a sample obtained sintering for 1 h at 1250 °C a hydrated mortar prepared using cement powder, fine alumina powders, superfluidificant, water and 36 vol.% polyurethane fibres.

is very close to this value, we can state that, during the shrinkage of the material, the dimensions of the macroporosity changed very little. This is an unexpected and interesting result that leads us to assume that it is possible to prepare materials having a desired macroporosity just by adding fibres of proper diameter. It can be also observed that few fractures are still present, but their quantity is sensibly lower than that present in samples reported in Fig. 2b. Moreover they probably depend on the fracture process and are not a consequence of the difference between the thermal expansion coefficients of the phases present after the sintering. The presence of free, unreacted alumina was excluded by the X-ray diffraction data of the fired samples. In fact, Fig. 4a and b show the microstructures of two samples prepared using mortars containing fine alumina and 36 vol.% of fibres after sintering for 1 h (4a) and 2 h (4b) at 1250 °C. These figures show the free surface inside one of the several tubular macropores produced by the evaporation of the fibres. As expected, it can be observed that the grain size of the material shown in Fig. 4a is smaller than that shown in Fig. 4b, and is accompanied by a residual micrometric porosity not visible in Fig. 4b. The presence of

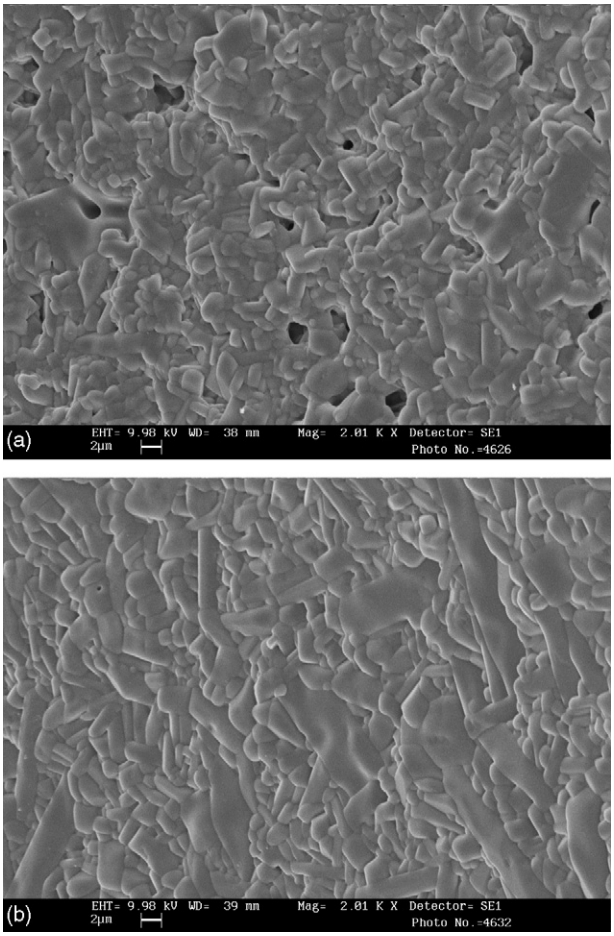

Fig. 4. SEM microstructures of two samples obtained sintering for 1 h (4a) or 2 h (4b) at 1250 °C a hydrated mortar prepared using cement powder, fine alumina powders, superfluidificant, water and 36 vol.% polyurethane fibres.

elongated grains is likely due to the growth of several aluminates structures that are present also in the starting cement powder [29–32]. The presence of free alumina particles is neither documented in Fig. 4a, nor in Fig. 4b. It follows that the effect of free alumina as a rigid inclusion in the matrix, during the shrinkage cannot be excluded, but is certainly limited.

We can therefore conclude that if alumina is present as small particles, the reaction, at high temperature, with the dehydrated mortar particles to form a matrix containing aluminates having a different stoichiometry from that of the starting cement [33] is more probable. For example, it could be reasonable to expect the presence of $CaAl_4O_7$ and $CaAl_{12}O_{19}$ in spite of simple calcium aluminate ($CaAl_2O_4$). The presence of $CaAl_4O_7$ was documented by our X-ray investigations, that of $CaAl_{12}O_{19}$ was not. Nevertheless the presence of this phase cannot be excluded since it is known that if the quantity is small, it is possible that it is not revealed by the diffractometric analysis. This statement is emphasized in our work since we have used commercial cement powders.

On the other hand, if alumina is present as coarse particles the sintering treatment is not sufficient to cause a full reaction between alumina and the other oxides. The major consequence is that the presence of free alumina induces the growth of residual thermal stresses, which exceed the material strength and cause extended fractures, which break up the fired materials. Of course this research is not exhaustive and further experiments are now in progress in order to optimize the thermal cycle for samples of different geometry and dimensions and to clarify if the use of different amounts of starting components (i.e. Al_2O_3 powders, polyester or polyamide fibres) during room temperature preparation can allow for an easier preparation of fired materials having better properties. Moreover the use of pure calcium aluminate instead of commercial aluminate cements could lead to fired samples having a higher softening temperature than those produced in the present work.

4. Concluding remarks

The present work shows that it is possible to prepare monolithic macroporous ceramics by sintering mortars containing dispersed organic fibres, alumina powders, water and superfluidificant. We have observed that the thermal cycle must allow for the evaporation of some components without causing catastrophic ruptures. The final sintering temperature was fixed at 1250 °C. Higher temperature values cause the softening of the materials, whereas lower values lead to materials having a high quantity of microporosity. Also the ageing time at 1250 °C has effects on the microstructure of the materials since after 1 h the materials contain an important amount of micrometric porosity. The ageing time of 2 h revealed the presence of several elongated grains reasonably due to the growth of some aluminates during the sintering. The upper limit for the quantity of fibres is 36 vol.% since higher quantities lead to materials that cannot be handled without catastrophic rupture after sintering.

The main advantage of this technique is that it requires only one high temperature process (1250 °C) and allows for a simple handling of the infiltrated performs (FRM can be easily manipulated since they possess non-negligible mechanical properties).

Another advantage of this preparation is that some of the starting materials used for the production of porous ceramics are relatively cheap and consequently the production of porous ceramic from mortars with dispersed organic fibres is economically valuable.

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