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Development of multiphase bioceramics from a filler-containing preceramic polymer

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Abstract

Multiphase bioceramics based on wollastonite and wollastonite/hydroxylapatite (W/HAp) have been successfully prepared by the heat treatment of a filler-containing preceramic polymer. CaO-bearing precursors (Ca-carbonate, Ca-acetate, and CaO nano-particles) were dispersed in a solution of silicone resin, subsequently dried and pyrolysed in nitrogen. The reaction between silica, deriving from the oxycarbide (SiOC) residue of the silicone resin, and CaO ‘‘active filler’’ led to the formation of several calcium silicates, mainly consisting of wollastonite ($CaSiO_3$), in both low and high temperature forms. The phase assemblage of the final ceramic varied with the pyrolysis temperature (varying from 1000 to 1200 °C). HAp was additionally inserted, as ‘‘passive filler’’ (i.e. not reacting with SiOC), for the preparation of bioceramics based on W/HAp mixtures.

The use of a filler-containing preceramic polymer to obtain bioceramics is favourable, besides for the simplicity of the procedure, for the possibility of achieving complex shapes. In fact, we demonstrated the possibility of fabricating an open-celled microcellular foam, prepared by mixing the filler-containing preceramic polymer with sacrificial PMMA microbeads. The proposed approach, due to the well-known bioactivity of wollastonite, W/HAp composites, and secondary calcium silicates, could be profitable for manufacturing various ceramic components for medical use.

Keywords: A. Shaping; B. Nano-composites; B. X-ray methods; E. Biomedical applications

1. Introduction

Preceramic polymers are well known for their use in the production of advanced ceramic components (fibers, coatings, micro-components, foams, membranes), especially based on the Si–O–C, Si–C and Si–(B)–N–C systems [1,2]. These ceramics, also known as polymer-derived-ceramics (PDCs), rely on a particular microstructure, generally consisting of nano-crystalline domains (based on SiC or C) embedded within an amorphous matrix, which yields unusual properties (such as very low creep, high chemical resistance etc.) [3,4]. A key advantage of PDCs is the possibility of shaping ceramic components by using conventional plastic-forming techniques (spinning, blowing, injection-molding, warm pressing, resin transfer-molding), applied to the precursor polymers. The main drawbacks, however, are the poor control of the shrinkage and the formation of cracks deriving from the gas release occurring during the polymer-to-ceramic conversion upon pyrolysis. The pioneering research carried by Greil [5] showed the possibility of both controlling the shrinkage and obtaining relatively dense and crack-free components by simply adding to preceramic polymers so-called ‘‘active fillers’’. Metal (or intermetallic) particles, upon pyrolysis in inert atmosphere, may react with the gaseous decomposition products coming off the preceramic polymer or with the pyrolysis gas, to yield mainly carbide or nitride ceramics. The volume expansion occurring upon conversion of metal particles into ceramics (e.g. Ti to TiC) limits both the formation of defects and the large shrinkage otherwise occurring upon pyrolysis. As an alternative, inert filler powders (in particular SiC or Si_3N_4), which do not react with the preceramic polymer decomposition products, can be added. In this case, the fillers simply partially reduce the total shrinkage in the component, by diluting the transforming mass [6]. Oxide powders have rarely been added as fillers to produce all-oxide ceramics [7–9], probably due to the fact that typically preceramic polymers are processed in inert atmosphere in order to retain the C atoms which play a key role in the development of the unique microstructure and properties of PDCs [10]. However, some

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papers have very recently highlighted the potentialities of using such oxide fillers in combination with polymethylsiloxanes. In particular, the use of highly reactive nano-sized fillers, such as γ-Al_2O_3 nano-particles, allowed to produce a large amount of mullite at low temperature (by reaction in oxidative atmosphere) [11,12] and SiAlON ceramics (in nitrogen atmosphere) [13]. These papers are based on a new concept of ''active filling'', consisting in the reaction of the whole ceramic residue deriving from the pyrolysis (in air or in nitrogen) of the polysiloxanes with the fillers. In particular, the synthesis of mullite from a preceramic polymer containing nano-sized fillers appears promising as it shows a simple and fast route to obtain components from ceramics which possess a poor solid state sinterability (due to the slow interdiffusion of the components). In particular, an homogeneneous dispersion of the fillers allows a rapid conversion of the composite system into the desired ceramic, even at relatively low temperatures [12].

In this paper we discuss the application of this ''novel filler'' approach to another system which is well known for its poor solid state sinterability, that of wollastonite [14]. Wollastonite (W), i.e. calcium (mono-)silicate ($CaSiO_3$, i.e. $CaO \cdot SiO_2$ or C.S.), in its different polymorphic forms (α or β), possesses excellent bioactivity [14–19], and thus it constitutes the basis for several ceramic biomaterials. Due to the difficulties in sintering, wollastonite is generally obtained by complex techniques (such as devitrification of glass [20,21], sol–gel processing [22], spark plasma-sintering [14–17], solution combustion processes [23] etc.). The formation of calcium silicates, not intended for biological applications, from silicones filled with CaO precursors was pioneered by Russian researchers in 1980s [24]; a more recent work, specifically dedicated to medical applications, was carried by Paluszkievicz et al. [25], who investigated a polymethylphenylsiloxane, filled with $Ca(OH)_2$, $CaCO_3$, Na_2HPO_4 micro-powders and silica nano-powders (of about 100 nm). The present approach is based on the reaction of the silica deriving from the pyrolysis of a polymethylsiloxane with several precursors of calcium oxide (calcium carbonate micro-powders, calcium acetate in aqueous solution, calcium oxide nano-powders) and expands what reported in [26].

Together with the ''active filler'' approach, in these experiments hydroxylapatite (HAp) powder was also introduced as a secondary phase, thus obtaining wollastonite–hydroxylapatite (W–HAp) composites. These are one of the most attractive types of biomaterials [27–29], featuring a bioactive phase, wollastonite, coupled to a bioresorbable phase, HAp, which constitutes the mineral component of natural bones. Finally, the precursor mixtures were used to fabricate microcellular foams, which could be useful for bone replacement applications.

2. Experimental procedure

The polymethylsiloxane was a commercial resin (MK, Wacker-Chemie GmbH, Munchen, Germany), available in powder form. When pyrolysed in inert atmosphere MK yields a SiOC ceramic residue, whose composition was estimated to correspond to the atomic proportions 31.6% Si–48.1% O–20.2% C, from data reported in the literature [30]. More precisely, the SiOC is reported to consist of amorphous silica in which some bridging oxygens, linking two silicon atoms, are substituted by carbon atoms connecting four silicon atoms (forming a silicon-oxy-carbide phase); some SiC as well as some carbon nano-sized clusters are also present in the material, and their amount is related to the pyrolysis temperature [31]. On the basis of the reported atomic balance, the yield of SiO_2 of MK is about 64% (while the total ceramic yield is about 84%).

For the preparation of wollastonite-based ceramics, CaO-bearing compounds (Ca-carbonate, Ca-acetate, and CaO nano-particles) were added in different forms, but always keeping the molar ratio CaO/SiO_2 equal to 1 (i.e. identical to that in wollastonite, $CaSiO_3$ or $CaO \cdot SiO_2$). Ca-carbonate ($CaCO_3$) was used in the form of micro-powders (Sigma–Aldrich Co. Ltd., Gillingham, UK, reagent grade, 10 μm), directly mixed in the MK silicone solution. Ca-acetate ($Ca(CH_3COO)_2 \cdot H_2O$, Sigma–Aldrich, Ltd., Gillingham, UK) was used after dissolution in distilled water (10% solid content). The acetate solution was added drop-wise to the silicone solution, under magnetic stirring; in some cases a non-ionic surfactant (Pluronic P 123, BASF Corporation, Florham Park, NJ) was added to the silicone solution (1 g for 80 ml solution), under magnetic stirring, before adding the acetate solution. CaO nano-powders (DGTech, Grenoble, France, 170 nm mean particle size) were directly added in the form of suspension in ethanol (20% solid content). For the preparation of ceramics based on both wollastonite (W) and hydroxylapatite (HAp), hydroxylapatite was added to the silicone/CaO-bearing compound mixture in the form of micro-powders (Sigma–Aldrich, reagent grade, 10 μm). The content of HAp was designed to yield a molar ratio W/HAp equal to 1. All the mixtures were ultrasonicated for 10 min, then dried.

Mixtures containing $CaCO_3$ or CaO nano-powders were dried overnight at 60 °C, while the dispersion based on Ca-acetate was dried by means of a rotary vacuum evaporator, at 40 °C for 1.5 h. After drying, the mixtures were finely ground (into particles $<$10 μm) and cold pressed at 40 MPa in a cylindrical steel die. The pressed samples (diameter ∼31 mm, height ∼1.5 mm) were fired under flowing nitrogen (2 l/min), at a temperature in the range of 1000–1200 °C, with a heating rate of 10 °C/min and a holding time of 1 h.

It has to be mentioned that in this paper we carried out the pyrolysis of the samples in nitrogen, rather than in air, as experiments carried out by firing in air did not allow for the development of such a favourable crystalline phase assemblage in the ceramic components, and led in some cases to the presence of a network of cracks in the samples.

Disc-shaped samples were investigated by X-ray diffraction (XRD; Philips PW 3710), using Cu Kα radiation ($\lambda = 0.15418$ nm). Data were collected between 15° and 75° 2θ in step scan mode with step of 0.05° and a counting time of 2 s/step. The XRD patterns were first analysed by means of the Match! software package, which allows for phase identification and quantification [32], supported by the JCPDS-ICDD (International Centre for Diffraction Data, Powder Diffraction File PDF2) database, then refined by applying the Rietveld method using the MAUD (Material Analysis Using Diffraction) program package [33], supported by the ICSD (Inorganic Crystal Structure Database, v. 2005-1, Fachinformationszentrum Karlsruhe, Germany) structural database.

Microcellular foams were obtained by mixing the silicone resin, filled with CaO nano-powders and HAp micro-powders, with PMMA sacrificial microbeads (Cray Valley Waterborne Polymers Department, Atofina Italia, Milan, Italy), having a dimension of 100 μm, in a concentration of 40% by wt., following a procedure similar to that employed for SiOC microcellular foams [34,35]. After dry ball-mixing, the powders were warm-pressed at 170 °C, under a pressure of 20 MPa. After a pre-treatment in oxidative atmosphere at 300 °C (with a heating rate of about 0.5 °C/min), for burning out the PMMA microbeads, the foams were produced by a thermal treatment at 1200 °C (with a heating rate of 2 °C/min), in nitrogen atmosphere.

The density of discs and foams was determined geometrically. The true density of the various samples was measured by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA), operating with He gas on samples in powdered form.

3. Results and discussion

3.1. Wollastonite-based ceramics

All the CaO-bearing compounds were effective in reacting with silica deriving from the preceramic polymer, thus yielding wollastonite. However, many differences among them were found, in terms of the phase assemblage. In particular the overall content of wollastonite, the balance between wollastonite polymorphs (α- and β-phases), and the balance between wollastonite, i.e. calcium monosilicate ($CaO\cdot SiO_2 = C.S.$) and other secondary calcium silicates ($C_x\cdot S_y$, with $x \neq y$) varied depending on the type of CaO precursor employed.

The use of calcium carbonate as CaO precursor yielded dense samples (with a porosity of about 10%) having a limited amount of wollastonite at temperature below 1200 °C, as shown in Fig. 1a; at 1000 °C and 1100 °C most of crystal phases correspond to β-C_2S and C_3S. This fact is attributable to the distribution of CaO within the preceramic polymer: starting from macro-sized CaO precursors, i.e. $CaCO_3$ micro-powders, the calcium oxide was not mixed in a quasi-molecular way with the silica deriving from the ceramization of the preceramic

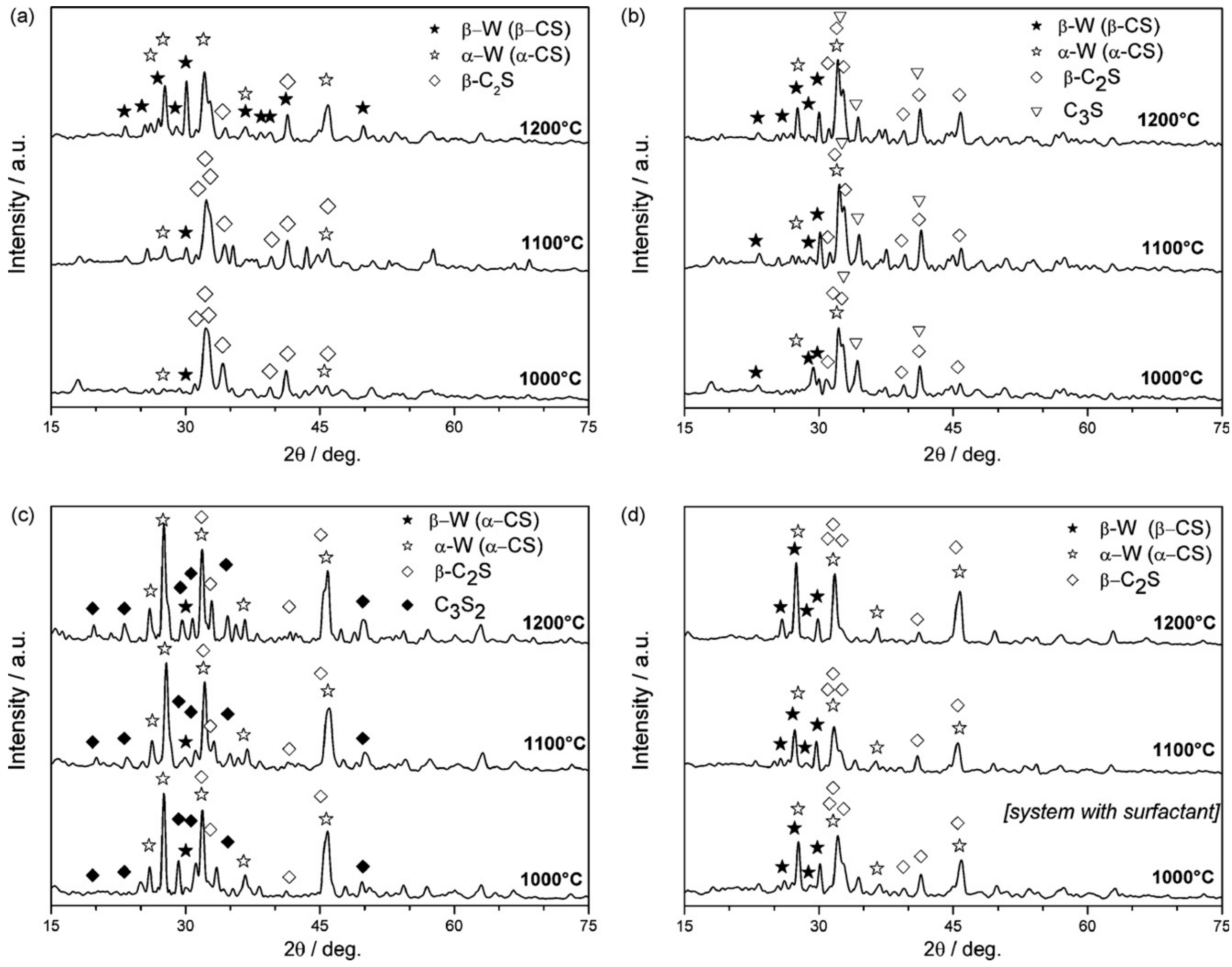

Fig. 1. X-ray diffraction patterns of wollastonite ceramics, obtained from different CaO precursors: (a) $CaCO_3$, (b) Ca-acetate aqueous solution without surfactant (upper graph) and with surfactant (lower graph) and (c) CaO nano-powders.

polymer (as it would happen with other precursors—see later). The formation of di- and tri-calcium silicates is thus the result of local over-concentration of calcium oxide (di- and tri-calcium silicates in fact correspond to a CaO/SiO_2 molar ratio far exceeding 1). The formation of secondary silicates is confirmed by the findings of Paluszkievicz et al. [25] even if the quantitative details of the phase assemblage of their samples were not reported. A further corroboration of our hypothesis concerning the behaviour of the system with $CaCO_3$ is given by the results obtained with Ca-acetate aqueous solution, when used without any surfactant added to the silicone solution. The immiscibility of the aqueous solution with the silicone solution in acetone resulted again in the formation of CaO-rich domains embedded in the preceramic polymer. As illustrated by Fig. 1b (upper part), the phase evolution for the system with Ca-acetate is similar to that with $CaCO_3$. In particular, as shown in Table 1, the best condition for the formation of wollastonite is a treatment at 1200 °C, for which the amount of crystalline phases is about 73 wt.%, and the overall content of wollastonite is about 70 wt.% of the total crystalline phases. At 1200 °C, the most important crystal phase is α-$CaSiO_3$, the high temperature polymorph of wollastonite (pseudo-wollastonite).

The addition of a surfactant determined a dramatic change in the reactions occurring between the preceramic polymer and calcium oxide, deriving from the calcium acetate aqueous solution. The surfactant allowed a homogeneous dispersion of calcium acetate, leading to a transparent solution after mixing the two components (the surfactant likely acted as a coupling agent between the silicone solution in acetone and the acetate solution in water, by placing its hydrophobic end towards acetone and its hydrophilic end towards water). This allowed the silica from the preceramic polymer to react with CaO in the expected molar ratio ($CaO/SiO_2 = 1$), yielding wollastonite in relevant quantities even at 1000 °C and 1100 °C, and greatly limiting the formation of di- and tri-calcium silicates ($C_x{\cdot}S_y$, with $x > y$). Table 1 reports that the estimated crystallinity reached the maximum value (80 vol.%), with a dominant content of α-$CaSiO_3$ (67% of the crystalline phase). Compared with the system containing $CaCO_3$, the system using Ca-acetate as a precursor led to more porous samples (porosity of about 20 vol.%), consistently with the fact that the decomposition of Ca-acetate into CaO yields a larger amount of gas than Ca-carbonate.

The system with CaO nano-powders combined the features of the systems with $CaCO_3$ and Ca-acetate (with surfactant). As in the case of calcium carbonate, the CaO nano-powders allowed a very easy processing and the fabrication of rather dense samples (porosity of about 10 vol.%); as in the case of Ca-acetate (with surfactant), the CaO nano-powders led to a high yield of wollastonite, even at low temperature. The limited dimensions of the filler were again suitable for achieving a homogeneous distribution of CaO within the preceramic polymer, favouring an equimolar reaction with silica. A specific feature of this last filler was the formation of rankinite, as the main secondary phase. Rankinite, as di- and tri-calcium silicates, is a silicate with a higher content of CaO than expected ($C_x{\cdot}S_y$, with $x > y$); however, the degree of over-concentration of calcium oxide is clearly lower (rankinite corresponds to the formula $C_3{\cdot}S_2$). As previously reported for silicone resins containing γ-Al_2O_3 nano-powders [11,12], the use of nano-sized fillers in preceramic polymers is effective in providing a quasi-molecular mixing. An example of the XRD refinements applied to the analysis of the diffraction data for the sample from the system with Ca-acetate and surfactant (pyrolized at 1200 °C), useful for phase quantification, is given in Fig. 2.

3.2. W/HAp ceramics

The best conditions for the development of wollastonite (Ca-acetate with surfactant and CaO nano-powders) were also the most suitable for the preparation of composites based on both wollastonite and hydroxylapatite. HAp micro-powders were intended to act as ‘‘passive fillers’’, and they were inserted in all the silicone–CaO precursor mixtures in a weight percentage theoretically leading to a W/HAp weight balance equal to 1. This was done in order to approach the conditions of bioactive W/HAp glass–ceramics, where the W content is almost equal to

Table 1
Estimated phase assemblage for wollastonite ceramics

CaO precursor	Pyrolysis temperature (°C)	Crystallinity (wt.%)	Distribution of crystal phases (wt.%) (±2%)		
			β-W	α-W	Other phases
$CaCO_3$	1000	66	10	21	40 C_2S, 29 C_3S
	1100	71	23	29	28 C_2S, 20 C_3S
	1200	75	27	42	18 C_2S, 13 C_3S
Ca-acetate	1000	67	19	15	38 C_2S, 28 C_3S
	1100	71	20	34	27 C_2S, 19 C_3S
	1200	73	20	43	24 C_2S, 13 C_3S
Ca-acetate (+surfactant)	1000	76	20	52	18 C_2S, 10 C_3S
	1100	77	21	54	19 C_2S, 6 C_3S
	1200	80	16	67	12 C_2S, 5 C_3S
Nano-CaO	1000	79	6	66	10 C_2S, 4 C_3S, 14 C_3S_2
	1100	79	18	54	11 C_2S, 4 C_3S, 13 C_3S_2
	1200	78	17	49	9 C_2S, 6 C_3S, 19 C_3S_2

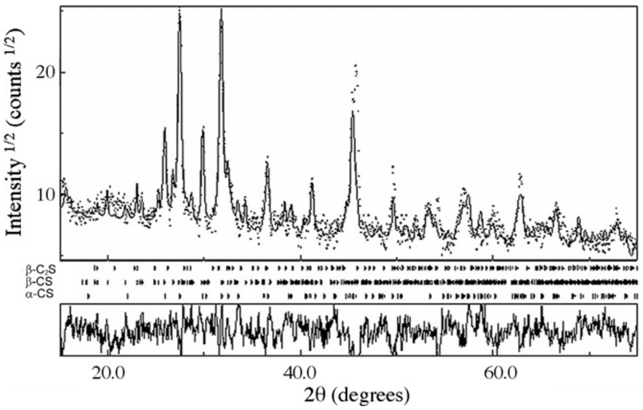

Fig. 2. Typical Rietveld refinement of XRD pattern for a wollastonite-based ceramic from MK resin and Ca-acetate (with surfactant), pyrolized at 1200 °C (dots: experimental data; continuous line: refinement).

that of HAp, being about 35%, while the glass phase is about 30% [29].

As previously observed for the systems based only on wollastonite, secondary silicates, with a CaO/SiO_2 molar ratio higher than 1, formed; this fact was probably important in affecting the stability of HAp. In fact, as shown in Table 2, HAp partially dissolved upon the heat treatments (crystalline HAp is present in relatively low quantities); moreover, some tricalcium phosphate (β-TCP) formed, reasonably due to CaO release from HAp (according to the following reaction: $Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO4)_2 + CaO + H_2O$, i.e. HAp - → TCP + CaO + H_2O). In our opinion, the calcium oxide was extracted from HAp by reaction with the ceramic residue of the silicone resin. In fact, the formation of secondary silicates did not allow for the complete consumption of the reactive silica from the silicone resin, so that the unreacted fraction reacted with HAp, driving its decomposition. The best condition for HAp stability was reached for the system employing Ca-acetate, and this could be attributed to the higher yield of wollastonite ($CaO/SiO_2 = 1$), which in turn depends on the homogeneity of distribution of CaO within the ceramic residue. Thus, the data indicate that the higher is the amount of silica reacting with CaO precursors, the lower is the reaction of residual silica with CaO deriving from HAp decomposition. This point obviously would need further experiments, which could be carried out for example by adding HAp to silicone/CaO precursor mixtures with other CaO concentrations, and this will be the subject of future work. Some promising data have been already reported by the present authors in a previous paper [26], where the concentration of CaO (from Ca-acetate) was slightly lower than that giving a ratio $CaO/SiO_2 = 1$, leading to a more extensive formation of wollastonite instead of other calcium silicates.

Although not composed of pure wollastonite, which is well known for its bioactivity (in both α and β forms), the ceramics from the pyrolysis of silicone + CaO precursor mixtures feature phase assemblages that could still be profitable for medical applications. In fact, both C_2S [36] and C_3S [37] have recently been shown to be bioactive. In addition to that, the amorphous SiOC matrix embedding the crystalline phases has recently been found to exhibit an anti-trombogenic behaviour similar to that of pyrolytic carbon [38]. Thus, the similar materials obtained by Paluszkievicz et al. [25] which featured the additional presence of cristobalite phase and were found to show bioactivity when immersed in simulated body fluid, constitute indeed an important reference.

A specific feature of ceramics based on the usage of CaO nano-powders is the reduced content of C_3S, with the formation of rankinite (C_3S_2). Rankinite is not a bioactive phase, but it has been recently found in bioactive wollastonite-based glass–ceramics [21]. Although the bioactivity of our samples have to be verified through specific biological tests, the formation of C_3S_2 instead of significant amounts of C_3S appears advantageous, since the bioactivity of C_3S could be affected by an excessive heat-release upon hydration, caused by the interaction with body fluids.

The addition of HAp micro-powders, as previously described, resulted in an even more complex phase assemblage. Also in this case, however, the assemblage could be quite

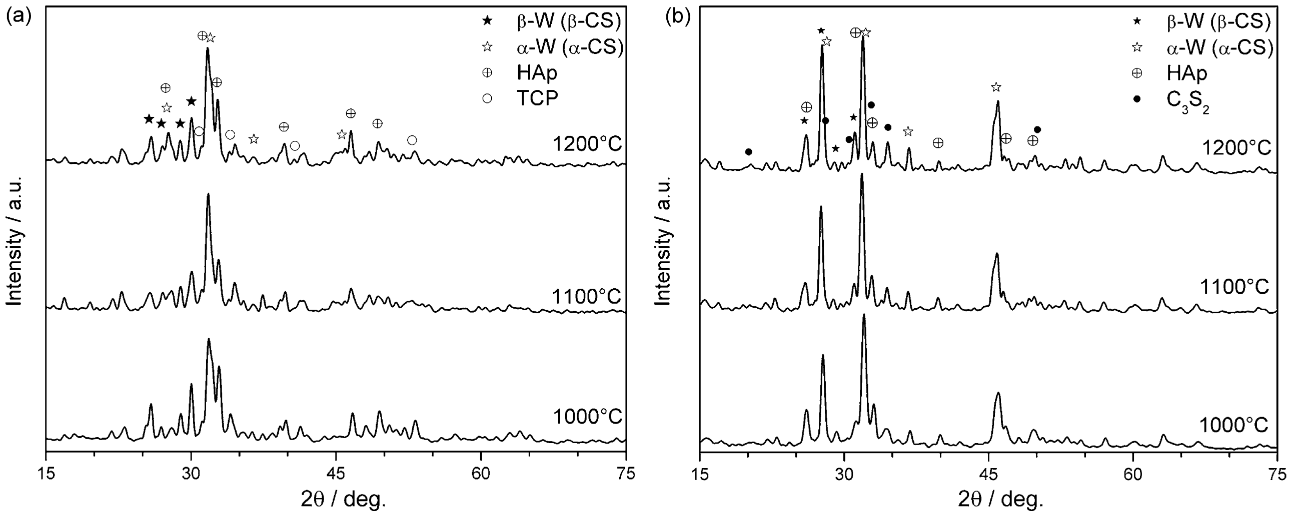

Fig. 3. X-ray diffraction patterns of W-HAp ceramics, obtained from Ca-acetate (a) and CaO nano-sized powders (b).

Table 2
Estimated phase assemblage for W-HAp ceramics

CaO precursor	Pyrolysis temperature (°C)	Crystallinity (wt.%)	Distribution of crystal phase (wt.%) (±2%)				
			β-W	α-W	C_2S	HAp	Other phases
Ca-acetate (+surfactant)	1000	68	21	32	18	17	3 TCP, 9 C_3S
	1100	67	15	39	17	18	2 TCP, 9 C_3S
	1200	67	14	42	15	16	2 TCP, 11 C_3S
Nano-CaO	1000	60	5	53	17	12	2 TCP, 12 C_3S_2
	1100	59	6	56	13	12	2 TCP, 11 C_3S_2
	1200	59	7	57	12	11	3 TCP, 10 C_3S_2

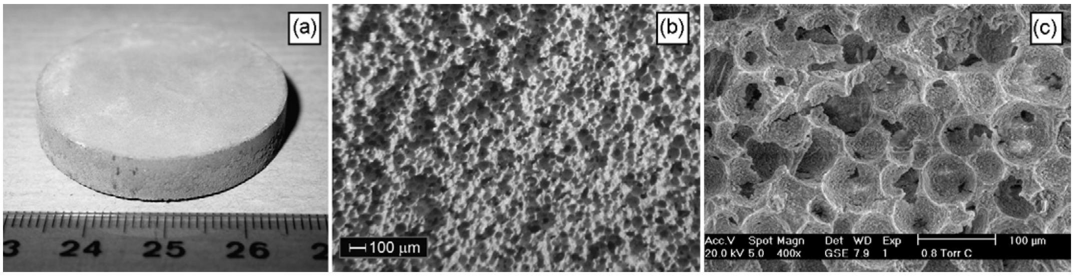

Fig. 4. W-HAp ceramic in the form of microcellular foam: (a) sample after pyrolysis, (b) cross-section (optical stereo-microscope image) and (c) microstructure (SEM micrograph).

profitable for medical use, since both TCP and the amorphous phases would possess favourable biocompatibility characteristics. TCP in fact, as HAp, is a well-known bioresorbable phase [39]. The amorphous phase, which is formed mostly from the decomposition of HAp, should be enriched in both calcium and phosphorous; we can estimate that the CaO/P_2O_5 molar ratio is in the range 0.75–1, so that the Ca/P ratio is in the range 1.5–2, consistent with the optimum ratio (1.67) of ACP (amorphous calcium phosphate) used as Ca and P sources for bone regeneration [40] (Fig. 3).

The possibility of achieving complex shapes from filled silicone resin was verified by the manufacturing of microcellular foams, whose general morphology is shown in Fig. 4. The density of the foams was ~0.4 g/cm^3, corresponding to a porosity content of about 85 vol.%. Fig. 4c shows that a good microstructural homogeneity was obtained, due to the infiltration of the preceramic mixture (i.e. silicone resin and fillers) between the voids created by the packing of the microbeads. The cell walls appeared dense and without cracks, and this is consistent with the measured good compressive strength value of 3.9 ± 0.8 MPa. Similar foams, produced by mixtures in which CaO was given by Ca-acetate, were much weaker (0.7 ± 0.2 MPa), and this could be attributed to the previously mentioned larger release of gas from the CaO precursor upon pyrolysis (with CaO there is no release from the calcium oxide precursor), yielding somewhat porous and cracked walls.

The produced microcellular foams could be an important starting point for the preparation of porous open-celled materials for bone tissue regeneration. However it should be mentioned that our ‘‘filler approach’’ could also be exploited for the coating of several substrates (for example, metal scaffolds, used as mechanically strong bone substitutes [41]) to improve their biocompatibility.

Future investigations will be dedicated for the modification of phase assemblage, by changing the CaO/silicone ratio and the size of the CaO precursors. As an example, CaO nano-sized powders (with an average diameter 100 nm) could be promising, since they could possess an enhanced reactivity towards the silica deriving from the polymer, while at the same time giving a limited gas release upon pyrolysis. As a secondary goal, the morphology of cellular ceramics will be optimised, especially focusing on the specific requirements for bone substitutes, by producing foams using different PMMA microbead contents and sizes.

4. Conclusion

We may conclude that:

- the present approach represents a suitable way for the fabrication of wollastonite-based ceramics and of multiphase biocompatible ceramics, based both on wollastonite and hydroxyalapatite;
- varying the type of precursor for CaO, different crystalline phases formed, depending on the degree of homogeneity of the dispersion of the reacting CaO within the siloxane-derived matrix;
- despite the phase assemblage of ceramics obtained from the pyrolysis of a silicone resin containing CaO precursors and HAp micro-powders being rather complex, the developed crystalline phases are all biocompatible;
- the easy processing of preceramic polymers could be applied to a silicone resin containing a large volume of fillers, as demonstrated by the fabrication of W/HAp microcellular foams.

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