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Alpha-tricalcium phosphate (α-TCP): solid state synthesis from different calcium precursors and the hydraulic reactivity

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Abstract The effects of solid state synthesis process parameters and primary calcium precursor on the cement-type hydration efficiency (at 37°C) of α-tricalcium phosphate ($Ca_3(PO_4)_2$ or α-TCP) into hydroxyapatite ($Ca_{10-x}HPO_4(PO_4)_{6-x}(OH)_{2-x}$ $x = 0–1$, or HAp) have been investigated. α-TCP was synthesized by firing of stoichiometric amount of calcium carbonate ($CaCO_3$) and monetite ($CaHPO_4$) at 1150–1350°C for 2 h. Three commercial grade $CaCO_3$ powders of different purity were used as the starting material and the resultant α-TCP products for all synthesis routes were compared in terms of the material properties and the reactivity. The reactant $CaHPO_4$ was also custom synthesized from the respective $CaCO_3$ source. A low firing temperature in the range of 1150–1350°C promoted formation of β-polymorph as a second phase in the resultant TCP. Meanwhile, higher firing temperatures resulted in phase pure α-TCP with poor hydraulic reactivity. The extension of firing operation also led to a decrease in the reactivity. It was found that identical synthesis history, morphology, particle size and crystallinity match between the α-TCPs produced from different $CaCO_3$ sources do not essentially culminate in products exhibiting similar hydraulic reactivity. The changes in reactivity are arising from differences in the trace amount of impurities found in the $CaCO_3$ precursors. In this regard, a correlation between the observed hydraulic reactivities and the impurity content of the $CaCO_3$ powders—as determined by inductively coupled plasma mass spectrometry—has been established. A high level of magnesium impurity in the $CaCO_3$ almost completely hampers the hydration of α-TCP. This impurity also favors formation of β- instead of α-polymorph in the product of TCP upon firing.

1 Introduction

Bone cements are substances used to repair the damaged or diseased parts of bones or to fix prosthesis in the hard tissues. These self hardening materials are mainly composed of various calcium phosphates (CaP) or their composite forms with various polymers [1–5]. The addition of CaPs into polymeric bone cement systems (like acrylic based cements) enhances the mechanical properties and biocompatibility of these hybrid systems [6, 7]. Calcium phosphate cements comprised of different combinations of calcium phosphate salts can form hydroxyapatite (HAp, $Ca_{10}(PO_4)(OH)_2$) and/or brushite ($CaHPO_4{\cdot}2H_2O$) as the reaction products upon mixing with aqueous media.

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Among these, systems resulting in a hardened form of HAp are advantageous in bone defect filling applications due to their chemical resemblance with the mineral component of natural bone tissue. HAp is known as bioactive material since it supports bone ingrowth and osseointegration in orthopaedic and dental applications. Therefore, CaP bone cements are commonly used for the repair and augmentation of osseous tissues and are successfully used in several clinical applications such as dentistry, maxillofacial, orthopedic and spinal surgeries [8–10].

There are a variety of CaP cement systems and α-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_2$) is especially interesting and offers some advantages over other inorganic cement systems. The main advantage of α-TCP is its ability to hydrate and set into monolithic calcium deficient hydroxyapatite (CDHAp, $Ca_{10-x}(HPO)_x(PO_4)_{6-x}(OH)_{2-x}$, $x = 0–1$) at near physiological pH and temperature from a single solid reactant. Majority of the other CaP systems require mixing of various calcium phosphate salts, such as tetracalcium phosphate (TetCP, $Ca_4(PO_4)_2O$) and dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$) [11] or TetCP and anhydrous dicalcium phosphate (DCPA or monetite, $CaHPO_4$) [12] at fixed molar proportions to achieve stoichiometry for the HAp products. Bioactivity of α-TCP, as well as the microstructural and chemical resemblance of its hydration product to the mineral component of natural bone, makes it a good candidate for hard tissue applications [2, 13, 14]. Moreover, the setting reaction is potentially not destructive for the surrounding tissue due to minimal heat release and pH change, which stays almost constant at neutral values during the hydration [15]. However, there are still some limitations for the use of cement-type HAp products obtained from α-TCP due to their poor strength and lack of interconnected macroporosity.

The cement-type setting reaction of α-TCP upon reaction with aqueous solutions initially proceeds by surface area controlled dissolution which generates supersaturation of Ca^{+2} and PO_4^{-3} ions in the reactant solution. Then, the nucleation of HAp occurs followed by growth of entangled plate-like crystal precipitates of fully CDHAp [16, 17]. The kinetics and the control of the setting reaction of α-TCP are critical for the efficiency of the cement in clinical applications. There are many researches reporting the effect of different factors on the setting reaction of α-TCP. The effects of morphology [18], crystallinity [19, 20] and particle size of α-TCP [17, 20–22] on the kinetics of setting reaction have been reported. A number of researchers investigated the optimization of the injectability and setting time of α-TCP cements by forming hybrids with the addition of organic components such as gelatin [23], chitosan [24, 25], polylactic acid and glycerol [24]. Among all of these factors, it is well known that chemical composition α-TCP dominantly affects its cement-type setting as well as its final physical properties. Since the natural bone mineral contains trace amount of cation/anion substitutions, synthetic analogs such as bone cements should be also chemically adaptable for substitution of ions of elements such as Mg, Na, Sr, Ba, Al, Cd, Pb, Cr, and Si for bone regeneration. In this respect, many researchers have investigated the effect ionic doping on the structural, physical, and chemical properties of HAp products of cement-type reactions. In recent years Sr-substituted [26–28], Ba-doped [29], Fe-modified α-TCPs [30] as well as Mg- [31–34] and Na-doped CaPs [35, 36] have been reported.

The synthesis of α-TCP is generally realized by solid state reactions. This is achieved by open air firing of homogenously mixed stoichiometric amount of calcium and phosphorus precursors at temperatures higher than 1125°C. This is followed by quenching to avoid formation of equilibrium polymorph of TCP, i.e. beta-TCP (or β-TCP). By this way, phase pure α-TCP can be obtained as shown by many studies [15, 19, 37]. However, direct assessment on the hydraulic reactivity of the α-TCP products of these studies is not possible, as the precursors and firing temperatures usually differ. In addition, despite the large body of previous work, due to inadequate information on chemical composition and physical properties of the starting materials, synthesis of reactive α-TCP becomes a problematic task for those trying to reproduce an available synthesis protocol. Similar to intentional ionic substitutions, a variety of intrinsic impurities present in the starting materials can affect the cement-type hydraulic reactivity, i.e. conversion of α-TCP to HAp accompanied by hardening.

The main objective of this study is to provide a reproducible and well-detailed α-TCP powder synthesis protocol. The synthesis was achieved by solid state reaction using calcium carbonate ($CaCO_3$) and monetite ($CaHPO_4$), which was also obtained from the same $CaCO_3$ source. α-TCP production was attempted using three commercially available $CaCO_3$ sources with different chemical grades, i.e. different amounts of impurities. The chemical phases and hydraulic properties of the resultant products are reported. Another critical synthesis parameter related with the reactivity and setting behavior of α-TCP is the firing temperature, which was also optimized systematically by employing different firing temperature of 1150, 1200 and 1350°C. The findings of the present work are a useful guideline for synthesis of highly reactive α-TCP.

2 Materials and methods

2.1 Materials

Three different $CaCO_3$ precursors were used to prepare α-TCP. They were the commercial grade products of Merck

(Germany, Catalog no. 102066), Sigma-Aldrich (Germany, Catalog no. C4830) and Carlo Erba (Italy, Catalog no. 327059), which will be referred as *CC-M, CC-S* and *CC-C*, hereafter. H_3PO_4 (85 wt%) was received from Merck (Germany, Catalog no. 100573). The hydration solution was obtained from $Na_2HPO_4{\cdot}2H_2O$ (Riedel-de Haen, Germany, Catalog no. 04272) and used as setting medium in cement-type reactions, i.e. in hydraulic property assessments.

2.2 α-TCP synthesis

α-TCP was synthesized by solid state reaction between $CaCO_3$ and pre-synthesized $CaHPO_4$ according to the following reaction.

$$CaCO_3(s) + 2CaHPO_4(s) \rightarrow Ca_3(PO_4)_2(s) + CO_2(g) + H_2O(g).$$

In the preparation of $CaHPO_4$, first $Ca(OH)_2$ was produced by a two-step process; calcination (1015°C for 3 h) of $CaCO_3$ to obtain CaO, followed by hydrolysis of CaO with deionized (DI) water. In these steps the same $CaCO_3$, employed in the above given reaction, was used. Then, the resultant $Ca(OH)_2$ slurry was used in the production of $CaHPO_4$. For this purpose, $Ca(OH)_2$ was mixed with H_3PO_4 solution at 1:1 molar ratio in presence of excess DI-water at 60–65°C for 30 min. The final slurry was vacuum filtered and dried at 80°C for overnight to obtain $CaHPO_4$ powder. For the preparation of α-TCP, this pre-synthesized $CaHPO_4$ was mixed with $CaCO_3$ in 2:1 molar ratio using Turbula T2F mixer (WAB, Switzerland). After 1 h mixing, the solid powder blend was fired in an alumina crucible in an open atmosphere furnace at 1200°C for 2 h (or 24 h). At the end of the soaking period, the chunky product was discharged on a borosilicate glass plate and air quenched to room temperature. After hand grinding with an agate mortar and pestle and sieving through −200 mesh, the obtained powder products were stored in a vacuum desiccator until further use. This synthesis protocol was repeated for all $CaCO_3$ sources of *CC-M, CC-S* and *CC-C*. In addition, for the experiments with *CC-M*, 2 h firing operations of $CaHPO_4$:*CC-M* blends were also performed at 1150 and 1350°C, followed by the same quenching treatment.

2.3 Cement-type setting of α-TCP

The cement-type setting of α-TCP products was performed by exposing the α-TCP powders to 2 wt% aqueous solution of $Na_2HPO_4{\cdot}2H_2O$. The hydration was achieved at 37°C for 24 h, at a solid to liquid weight ratio of 1:2. At the end of 24 h, the solid reaction products were washed with acetone and dried by air blowing to finalize hydration.

2.4 Material characterization

The chemical composition of $CaCO_3$ sources were investigated by inductively coupled plasma-mass spectrometer (ICP-MS, Perkin Elmer DRC II model). X-Ray diffraction (XRD) analyses were performed for phase analysis of the α-TCP products and their hydration products. XRD analyses were carried out using Rigaku X-ray diffractometer (Ultima D/MAX 2200/PC). CuKα radiation was used at 40 kV voltage and 40 mA current. The scanning range of the samples was 20–40° and the scanning speed was 2°/min. The morphologies of all $CaCO_3$ precursors, α-TCP products and resultant HAp were examined with a FEI Quanta 400F scanning electron microscope (SEM). The samples were coated by Au–Pd thin film by a Hummle VII sputter prior to SEM investigations. The surface area of selected α-TCP powders were determined by nitrogen gas adsorption using Autosorb-1-C/Ms analyzer. The powders used in the analyses were approximately 0.40 g and were degassed using high purity N_2 at 80°C for 6 h prior to measurements.

3 Results and discussion

XRD diffractograms of the α-TCP powders synthesized from *CC-M* by firing at 1150, 1200 and 1350°C, and the hydration products of these α-TCP powders are given in Fig. 1a and b, respectively. The XRD patterns of the samples fired at 1200 and 1350°C exhibited the characteristic peaks of α-TCP (JCPDS card no. 9-348). These products contained very small amount of HAp as evidenced by very low intensity set of peaks at around $2\theta \approx 31$–$33°$ matching with the characteristic peak positions of HAp (JCPDS card no. 9-432). These α-TCP products seem to have negligible amount of HAp, and for practical purpose they were considered as phase pure α-TCP. No other crystalline phase was observed. So, after firing at these relatively high temperatures, α-TCP was obtained by the solid state reaction between $CaCO_3$ and $CaHPO_4$. The XRD pattern of the sample fired at 1150°C, on the other hand, reveals formation of some *β*-TCP (JCPDS card no. 9-169) as a second phase besides the main α-TCP product. The *β*-polymorph, the room temperature equilibrium phase of TCP, does not illustrate any cement-type setting as observed for α-polymorph. For TCP *β*-polymorph is the stable phase up to 1125°C and at this critical temperature transformation of *β* to α-phase occurs [38, 39]. However, regardless of firing temperature, conservation of the metastable α-TCP phase at room temperature requires effective quenching. So, for the sample fired at 1150°C the presence of *β*-polymorph is a combined result of various factors. A firing temperature around

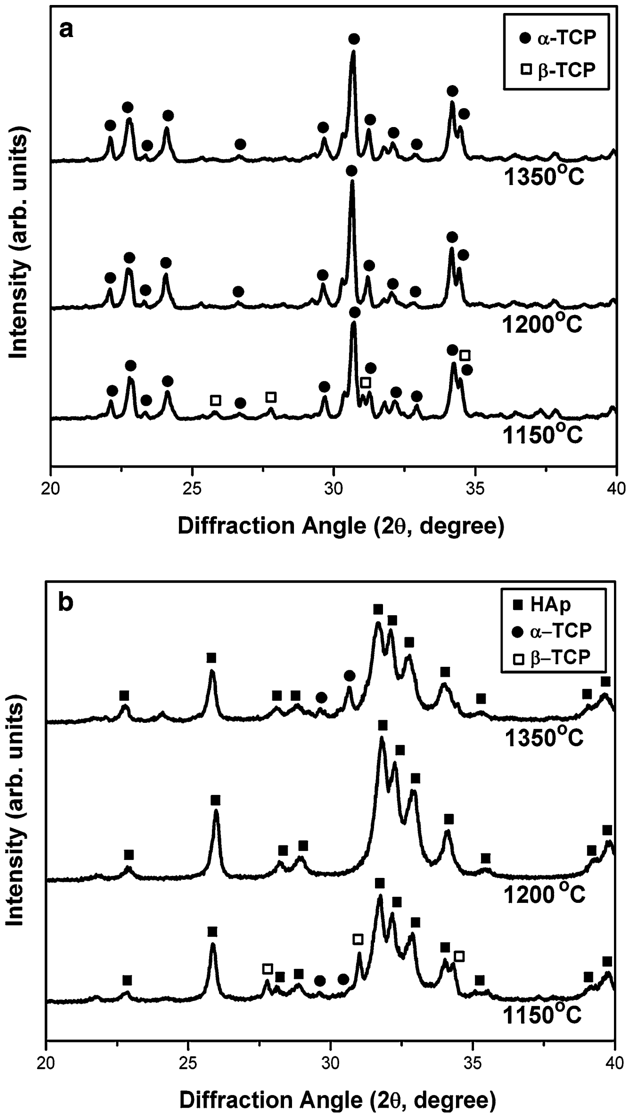

Fig. 1 The XRD diffractograms of **a** α-TCP powders synthesized from *CC-M* by firing at 1150, 1200 and 1350°C for 2 h, and **b** their hydration products

1150°C is at close proximity of the equilibrium phase transformation temperature for β-to-α transition (1125°C), and this is thermodynamically more tolerant condition for the presence of β-TCP compared to its existence during firing at relatively higher temperatures. In addition, this situation also requires much more aggressive supercooling to avoid formation of the equilibrium phase (β-polymorph) upon cooling down to room temperature, which was most likely not accomplished by moderately effective air quenching for the samples fired at 1150°C. Therefore, some β-TCP together with α-TCP was formed in the end product.

The XRD pattern of the hydration products of the α-TCP powders synthesized from *CC-M* and fired at 1150°C suggests a complete transformation of α-TCP to HAp and small amount of β-TCP remained in the end product (Fig. 1b). Similarly, for the sample fired at 1350°C, again formation of HAp was observed, but some α-TCP remained unreacted. The α-TCP synthesized at 1200°C showed the best hydraulic property and was almost completely transformed to HAp. Firing at higher temperatures leads to dead-burning associated with microstructural coarsening, which is known to occur in high temperature solid state reactions [15, 40]. It is worth to emphasize that the surface area of α-TCP powders synthesized from *CC-M* fired at 1150, 1200 and 1350°C was determined as 1.47, 0.99 and 0.69 m^2/g, respectively. A decrease in the surface area for the powders fired at 1350°C due to coarsening hampers the initial dissolution of α-TCP, therefore limiting the overall hydraulic reactivity and transformation to HAp. Thus, the XRD analyses and preliminary hydraulic reactivity evaluations illustrated that the firing temperature of 1200°C to be high enough to avoid the formation of β-TCP, while producing highly reactive α-TCP powder. Therefore, this temperature was chosen as the optimum firing condition and all other firing operations for the remainder of the experimental work were carried out at 1200°C.

XRD diffractograms for the α-TCP powders synthesized from three different $CaCO_3$ sources—*CC-M, CC-S, CC-C*—all fired at 1200°C for 2 h, and for the hydration products obtained from these α-TCP powders are given in Fig. 2a and b, respectively. All the α-TCP products were almost identical in terms of the phase identity and crystallinity. They were all phase pure α-TCP (Fig. 2a), except the one obtained from *CC-C* which had negligible amount of β-TCP. The possible reason for the formation of this additional phase will be discussed later. Despite the similar chemical and phase characteristic of the three α-TCP products, their hydraulic reactivities were distinctly different as revealed by the XRD data shown in Fig. 2b. Upon 24 h hydration with sodium phosphate solution, they all converted to HAp to some extent, but at different completion efficiencies. The α-TCP synthesized from *CC-M* source exhibited the highest reactivity among three products and was completely set to HAp after hydration. The α-TCP of *CC-S* again hydrated to HAp, however, the hydraulic reactivity was relatively poor compared to the α-TCP obtained from *CC-M* and some remained as it is. On the other hand, α-TCP obtained from *CC-C* source showed almost no hydraulic reactivity and the majority of α-TCP stayed unreacted after hydration. The observations in regard to hydraulic reactivity are promising for the α-TCP of *CC-M* source, compared with α-TCPs of other $CaCO_3$ sources. It is considered that the observed differences in hydraulic reactivities are arising from the different quantities of impurities in $CaCO_3$ sources, therefore this point was searched in detail and will be also clarified.

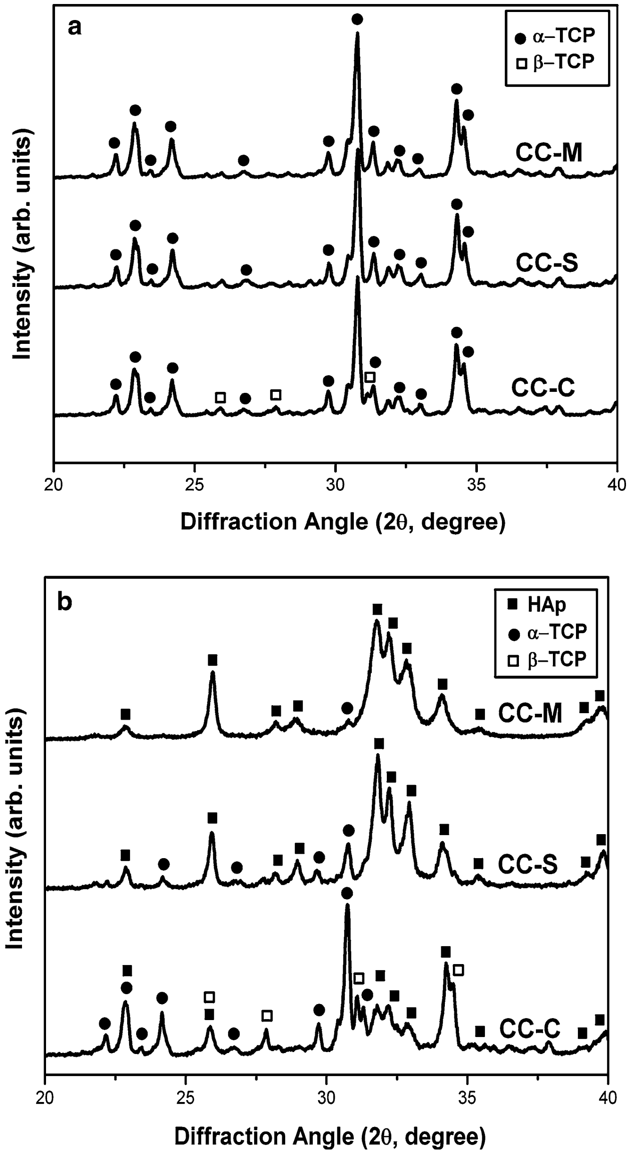

Fig. 2 The XRD diffractograms of **a** α-TCP powders synthesized from different $CaCO_3$ sources—*CC-M, CC-S, CC-C*—by firing at 1200°C for 2 h, and **b** their hydration products

In order to have more definite conclusion about the effect of firing operation on reactivity of α-TCP powders, longer firing treatments extending to 24 h were performed and the hydraulic reactivities of the products were evaluated. The results are summarized by the XRD data shown in Fig. 3. This figure illustrates the XRD diffractograms of the α-TCP powders (obtained from different $CaCO_3$ sources) as synthesized (Fig. 3a) and after hydration (Fig. 3b). Extending the firing operation does not lead to any apparent change in the chemical nature and phase identity of α-TCP in as synthesized condition. The 24 h-fired and 2 h-fired α-TCPs were identical, as revealed by the similarity of the XRD data presented in Figs. 3a and 2a. Meanwhile, similar trends in hydraulic reactivity were observed for the α-TCPs obtained after prolonged firing operations. Again, α-TCP of *CC-M* exhibited the highest reactivity while α-TCP of *CC-C* had the least. Besides these general observations one important finding associated with the prolonged firing is the recognition of a marginal decrease in the overall hydraulic reactivities of all α-TCP products. In all cases relatively more α-TCP remained in the hydrated product as shown by the XRD data in Fig. 3b. This change is valid both for α-TCP of *CC-M* and of *CC-S,* however more obvious for the latter. This observation is related with the microstructural coarsening simply due to excessively long firing operation, as also discussed earlier in firing temperature studies. In this case, time factor becomes dominant instead of temperature leading to coarsening. This microstructural

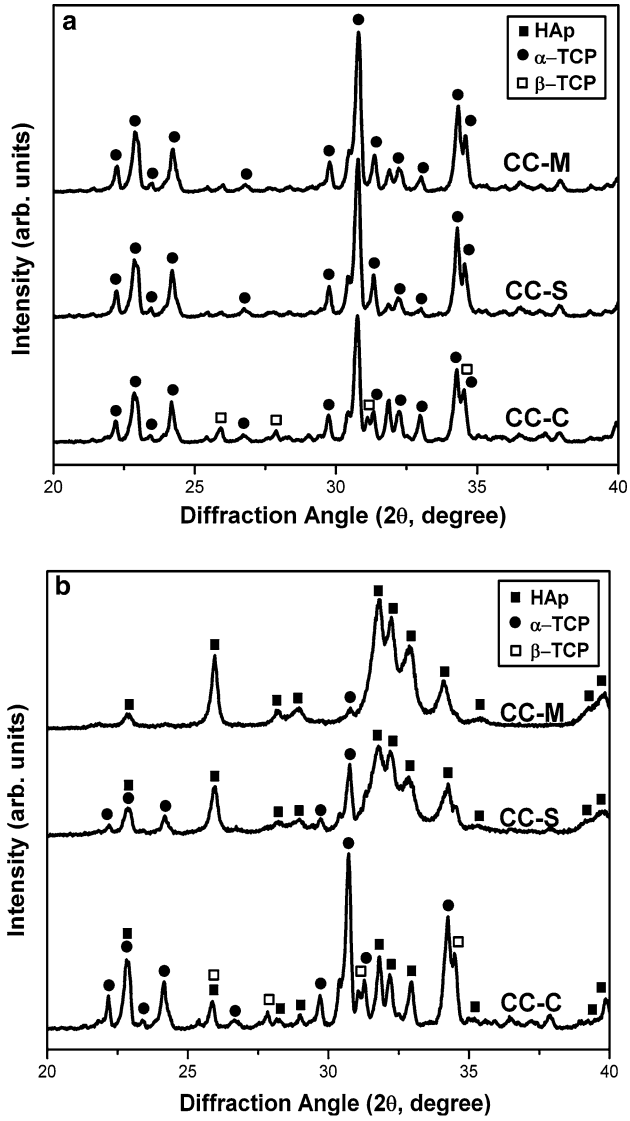

Fig. 3 The XRD diffractograms of **a** α-TCP powders synthesized from different $CaCO_3$ sources—*CC-M, CC-S, CC-C*—by firing at 1200°C for 24 h, and **b** their hydration products

change impedes dissolution of α-TCP, which is essential for the cement-type hydraulic reactivity.

The SEM micrographs of the $CaCO_3$ sources**,** α-TCP powders synthesized from these sources (fired at 1200°C for 2 h) and the cement-type products obtained by hydration of respective α-TCPs are given in Fig. 4. The $CaCO_3$ sources of *CC-M* and *CC-S* exhibit prismatic/cubic crystal morphology typical to highly crystalline $CaCO_3$ mineral, as shown by the micrographs in Fig. 4a–c. The average particle sizes were determined as approximately 5 and 8 μm, for *CC-M* and *CC-S*, respectively. The morphological appearance of *CC-C* is distinctly different, exhibiting irregularly shaped submicron crystals. The morphologies of the α-TCP powders, as shown in Fig. 4d–f, are identical with slightly distorted and equiaxed-like shape without any sharp discontinuities or features. This morphology is common for the ceramic powders obtained by high temperature solid state reactions at conditions approaching to sintering temperatures. The average particle size of the α-TCP powders produced from *CC-M* was around 2 μm, meanwhile α-TCP of *CC-S* and *CC-C* sources had comparable particle sizes at around 3 μm. The relatively small particle size is certainly a favorable factor for the high hydraulic activity observed for α-TCP obtained from *CC-M*. However, the particle size does not directly correlate with the observed overall hydraulic activity, as α-TCPs of *CC-C* and *CC-S* with almost identical particle size exhibiting an obvious difference in hydraulic reactivities.

SEM micrographs showing the morphologies of the cement-type products, i.e. the HAp crystals, obtained by hydration of respective α-TCP samples are given in Fig. 4g–i. For the hydration products of α-TCP obtained from *CC-M* and *CC-S* (which were shown to be completely converted to HAp by the XRD analyses) the morphologies resemble the typical equiaxed-like shape of α-TCP powders. However, the surfaces of the α-TCP particles are completely covered with newly formed small sub-micron size reticulated need-like HAp crystals. On the other hand, the morphology of the α-TCP of *CC-C* seems to be relatively unchanged upon hydration. There are some very small need-like HAp crystals partially covering the α-TCP particle surfaces, but distinctly at a much smaller extent compared to those of α-TCP of *CC-M* and of *CC-S*. The SEM findings in general correlate with the XRD analyses, suggesting relatively poor hydraulic reactivity for α-TCP of *CC-C*. It is worth to emphasize that, no significant

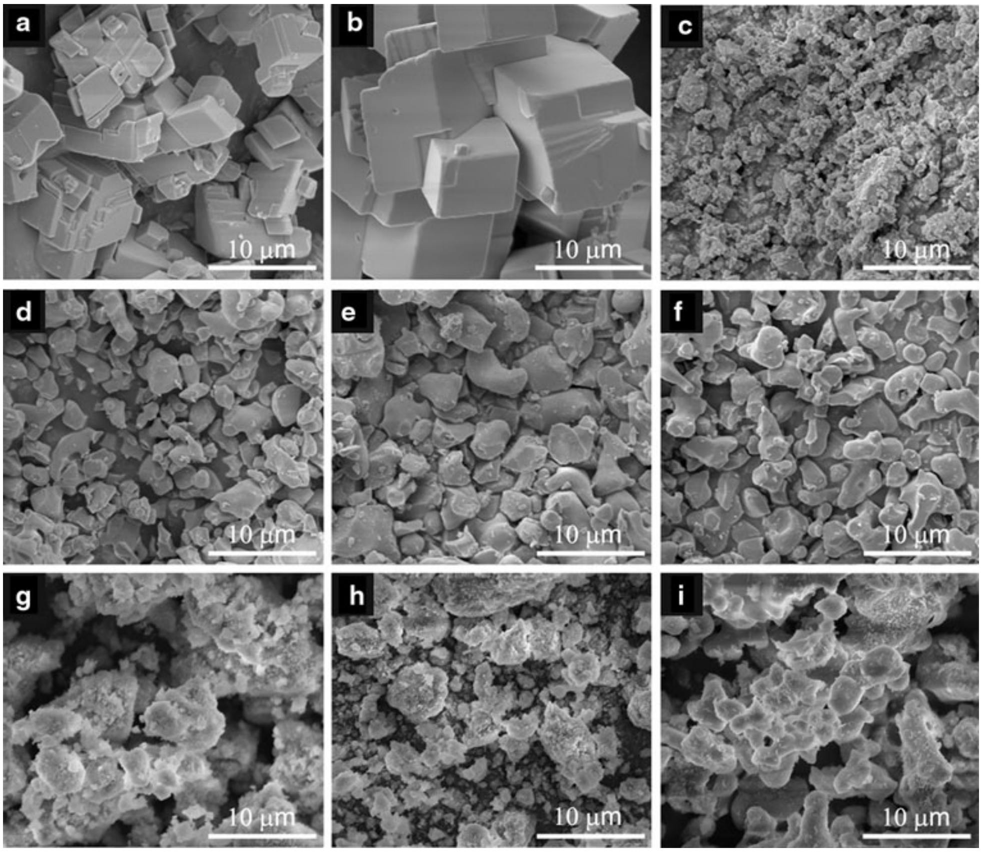

Fig. 4 The SEM micrographs of $CaCO_3$ precursors **a** *CC-M*, **b** *CC-S*, **c** *CC-C*, α-TCP powders synthesized at 1200°C for 2 h from **d** *CC-M*, **e** *CC-S*, **f** *CC-C*, and HAp products obtained by hydration of these α-TCP powders (**g–i**)

morphology and particle size differences were observed for the α-TCPs synthesized from different $CaCO_3$ sources (*CC-M, CC-S* and *CC-C*). Therefore, it is reasonable to suggest that the differences in the hydraulic reactivities of α-TCPs are not directly related with physical factors, but most likely with chemical characteristics, initiating from the differences in impurity content of starting mineral precursor of $CaCO_3$.

The amounts of some impurities for the $CaCO_3$ precursors obtained by ICP-MS analyses are given in Table 1. The total amounts of the impurities are different for each $CaCO_3$ source. The highest amount of impurity was detected for *CC-C*, which turned out to α-TCP product with the poorest hydraulic reactivity. In fact, the morphological investigations of the $CaCO_3$ precursors with SEM provided some foresee for such chemical differences. The crystals of *CC-C* were submicron in size, much smaller compared to crystals of the other $CaCO_3$. On the other hand, *CC-M* and *CC-S* crystals were in the form of large planar facets with cubical resemblance as shown in Fig. 4a and b. This difference is most likely due to the ionic impurities, which can effectively change the crystal growth mechanism during mineral formation, leading to differences in the shape and size of the $CaCO_3$ crystal deposits.

As shown in Table 1, the contents of sodium (Na), potassium (K), strontium (Sr), lead (Pb) and cadmium (Cd) impurity are slight different, however are at comparable level for all three $CaCO_3$ sources. Meanwhile, magnesium (Mg) content is significantly different in all $CaCO_3$ sources. For *CC-C,* Mg content was detected as 1054.8 $\mu g\ g^{-1}$, order of magnitude higher than Mg content of *CC-M* (30.4 $\mu g\ g^{-1}$) and *CC-S* (93.5 $\mu g\ g^{-1}$). This is the main possible reason for the poor reactivity of *CC-C*. It is known that Mg doping changes the crystal structure of TCP. The substitution of Ca^{2+} by smaller sized Mg^{2+} ions in the TCP crystal, leads to a more relaxed geometry for the crystal lattice. Due to the higher electronegativity of Mg^{2+} compared to Ca^{2+} a stronger interaction forms between Mg and O weakening the Ca–O bonding [31]. Therefore, presence of Mg^{2+} results in an enhancement in the chemical stability and consequently decreases the solubility of TCP [32, 34, 41] limiting its cement-type conversion by hydration. This was the case for the α-TCP synthesized from *CC-C* source containing high level Mg which exhibited no hydraulic reactivity and poor setting characteristic. In addition, high Mg content of *CC-C* also becomes a determining factor for the crystal nature of fired α-TCP product thereof synthesized by high temperature solid state reaction. It has been showed that the Mg ion doping stabilizes the low temperature β-polymorph of TCP and increases the β to α-TCP phase transformation temperature (1125°C) to higher values [32, 33, 42, 43]. In this respect, the formation of β-TCP phase from *CC-C* reactant after firing at 1200°C is quite reasonable, again attributed to its considerable high Mg impurity content.

Table 1 ICP-MS analyses results for the $CaCO_3$ sources; *CC-M, CC-S and CC-C*. The values are in $\mu g\ g^{-1}$

Element	*CC-M*	*CC-S*	*CC-C*
Na	33.0 ± 2.8	20.3 ± 3.7	38.7 ± 2.3
K	≪9.3	51.7 ± 3.4	25.0 ± 3.8
Mg	30.4 ± 0.5	93.5 ± 1.4	1054.8 ± 12.0
Sr	92.1 ± 1.1	87.4 ± 1.9	73.6 ± 0.6
Ba	0.8 ± 0.03	1.61 ± 0.12	1.51 ± 0.1
Fe	≪5.5	≪5.5	75.1 ± 1.2
Al	≪3.0	≪3.0	73.3 ± 4.9
Pb	≪0.1	≪0.1	0.5 ± 0.1
Cd	≪0.075	≪0.075	1 ± 0.1

Another compositional difference between $CaCO_3$ sources (*CC-M* and *CC-S)* leading to highly reactive α-TCP, and *CC-C* source that yields to poorly reactive α-TCP, is in the amount of Fe impurity. The amount of Fe was found less than 5 $\mu g\ g^{-1}$ both for *CC-M* and *CC-S,* and at around 75 $\mu g\ g^{-1}$ for *CC-C*. Fernandez et al. investigated the effect of iron citrate modification on setting characteristics of α-TCP and they reported shorter initial and final setting times with Fe modification [30]. In this regard, the poorest reactivity of α-TCP of *CC-C* suggests that the inhibitory effect of Mg seems to be more dominant than synergetic effect of Fe.

The amount of Al was also much higher for *CC-C* (73.3 $\mu g\ g^{-1}$) compared to that for *CC-M* and *CC-S* which was less than 3.0 $\mu g\ g^{-1}$. It is not possible to propose an educated guess about the direct effect of Al on hydraulic reactivity from the data of the present study. However, if Al had an effect on reactivity this should be inhibitory, as it is the highest in *CC-C*. However, this conclusion is just vague, as there is no data for the effect of Al on reactivity of α-TCP in the literature for the best of our knowledge.

The effect of Sr, which is a common impurity for the all calcium precursors employed in this study, on hydraulic reactivity of α-TCP has been also investigated by others. A decrease in hydraulic reactivity was reported for α-TCP containing more than 1 mol% Sr substitution [28]. Similarly, decrease in α-TCP reactivity was observed when Sr ion was present in the hydration media [27]. The Sr impurity content of the $CaCO_3$ precursors used in present study was found to be almost identical; in the order of 70–90 $\mu g\ g^{-1}$. This Sr amount is much lower than the amount of Sr substitution (1–10 mol%) achieved in the previous reports [28]. The sufficiently high reactivity of α-TCPs, obtained from *CC-M* and *CC-S* containing trace amounts of Sr impurity suggest that there at least a critical content of Sr is required to cause an obvious decrease in the reactivity of α-TCP.

4 Conclusions

The overall hydraulic reactivity of α-TCP is controlled by combination of several interrelated synthesis parameters, but predominantly by the chemical composition of the primary calcium precursor. The experimental approach in making reactive α-TCP by solid state reaction relies on a simple systematic optimization in regard to choosing proper firing temperature and time. The present study highlights some general findings in regard to determination of these parameters for the $CaCO_3$–$CaHPO_4$ solid reactant system. It has been found that the firing temperature higher than 1200°C and prolonged firing both reduce the hydraulic reactivity. These two factors are most likely valid for any solid reactants co-fired for obtaining α-TCP. However, system specific assessments on hydraulic reactivity of α-TCP require precise information about the chemical identity of the precursors. Some impurities conveyed from the calcium precursor completely annihilate the setting of α-TCP. The results obtained in this study indicated that magnesium impurity content, leading to a significant and adverse effect on the hydration of α-TCP, is one of the primary concerns for the selection of proper calcium precursor.

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