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Densification additives for hydroxyapatite ceramics

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Abstract

The present work is aimed at the elucidation of the role played by $CaCl_2$ and NH_4NO_3 (the latter is a by-product of the solution synthesis of hydroxyapatite, hereinafter referred to as HAp) in the densification of nano-sized HAp powder in the course of the pressureless sintering. Nanocrystalline HAp powder was fabricated via the wet-precipitation technique by the dropwise addition of an $(NH_4)_2HPO_4$ solution to a $Ca(NO_3)_2$ mother solution at a pre-adjusted pH at 60 °C. The pH of the aqueous mixture was maintained at a constant value (either 7 or 9) by the addition of an appropriate amount of NH_4OH. The Ca/P ratio was set to 1.67, 1.61, and 1.48; 10 wt% of $CaCl_2$ was added to dry HAp powder. NH_4NO_3 remaining in unwashed HAp powder can act as a fluxing agent that promotes partial melting at a relatively low temperature (150–250 °C) thus allowing the particles to rearrange into a denser packing. Several mechanisms of the $CaCl_2$ action as a densification additive might be envisaged: (i) a decrease in the melting temperature; (ii) the surface wetting of grains; (iii) a change in the growth morphology owing to the high-temperature surfactant properties; (iv) a possible reaction with HAp on the surface of grains giving rise to the decomposition of HAp and yielding chlorapatite (ClAp), which can convert back to HAp over a wide temperature range and at any level of H_2O.

Keywords: Sintering; Powders-solid state reaction; Grain size; Apatite; Biomedical applications; Peritectic melting

1. Introduction

Ceramics based on calcium phosphates is widely recognized as a highly promising material for the human tissue restoration due to its excellent biocompatibility. Numerous works have been devoted to the conventional pressureless sintering of HAp ceramics in the solid-state regime under surface or volume diffusion control.[1–7] Another direction in the fabrication of HAp ceramics is based on the utilization of the liquid-phase sintering. There are two ways to improve on the densification of powder compacts in the course of the liquid-phase sintering. One of them consists in the addition of a fine glass powder, which is inert with respect to the main component(s). Another way consists in the addition of a powder, which can interact with the main crystalline phase of the compact after melting yielding a multi-component melt, presumably, an eutectic liquid. Typically, the liquid-phase sintering proceeds faster than the solid-state one.[8–12]

Various types of additives specific to HAp sintering have been considered by Suchanek et al.[13] They included different salts, *e.g.*, $CaCl_2$, KCl, KH_2PO_4, $(KPO_3)_n$, $Na_2Si_2O_5$, K_2CO_3, Na_2CO_3, KF, sodium phosphates; compounds within bi- and three-component oxide systems, including P_2O_5 and CaO. These additives were added to HAp powders in an amount of 5%. Takami and Kondo[14] described sintering and reinforcing additives (in the form of a frit) in the system P_2O_5–CaO near the eutectic composition (Ca/P = 0.2–0.7) in an amount of 5%. The phase formation in ceramics based on HAp and frit in the system P_2O_5–CaO in amount of 10–40% was also described.[15] Georgiou and Knowless[16] used additives from the ternary Na_2O–P_2O_5–CaO system. Tancred et al.[17] used glasses from the CaO–P_2O_5 system (with a CaO to P_2O_5 molar ratio of 1) in quantities of 2.5, 5, 10, 25, and 50 wt.%. A borosilicate

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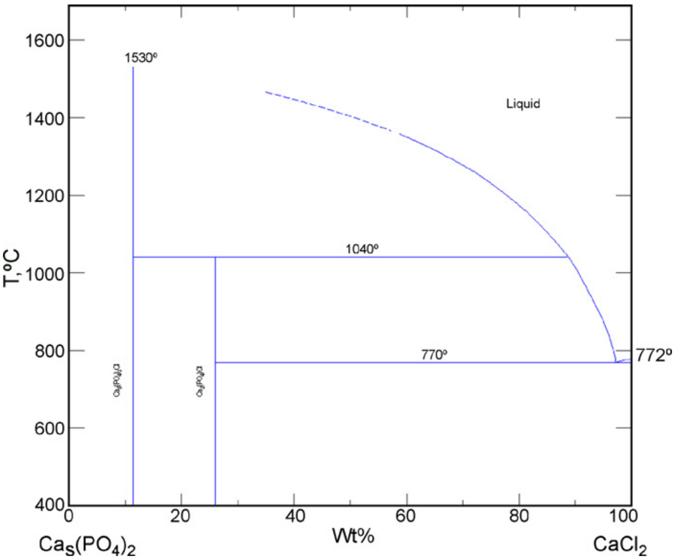

Fig. 1. Phase diagram $CaCl_2$–$Ca_5(PO_4)_3Cl$ for the $CaCl_2$–$Ca_3(PO_4)_2$ system.[20]

glass in an amount of 50% was also tested as a sintering additive.[18] In the case of biocompatible HAp-based ceramics, components constituting the additive should either be present in natural bones or belong to the group of bioinert materials. Note, however, that in most cases of the liquid-phase sintering, the concomitant formation of tricalcium phosphate (TCP) or CaO occurs. The presence of TCP is not crucial for biomedical purposes. Meanwhile, if CaO is present in ceramics, it readily reacts with water to yield $Ca(OH)_2$, which can give rise to undesirable changes in pH *in vivo*. Furthermore, this reaction induces volume changes and the resultant mechanical stresses can give rise to microcracking thus decreasing the strength of the target material.

A prominent trend in the development of structural ceramics (*e.g.*, Al_2O_3-based) consists of the search for the preparation conditions, which would enable a decrease in the sintering temperature (down to 1450 °C in the case of alumina) not compromising the strength of the target material, in particular, using appropriate advanced sintering additives.[19] For the densification driven by the formation of an eutectic melt, it is possible to use either an additive of the eutectic composition or a compound, which is capable of reacting with powder grains of the main phase to afford an eutectic melt. To adapt the strategy mentioned above to the sintering of HAp, it seems promising to explore the $Ca_{10}(PO_4)_6Cl_2$ (chlorapatite, hereinafter referred to as ClAp)–$CaCl_2$ system, which is characterized by an eutectic point of about 750 °C (Fig. 1).[20] This means that the reaction of calcium chloride (acting as an additive to HAp powder) with HAp shifts the overall composition of the sample, located inside the triangle HAp–ClAp–$CaCl_2$ in the vicinity of HAp corner, toward the ClAp–$CaCl_2$ side. In order to overcome the problem of a possible collapse of the apatite structure due to the reaction with $CaCl_2$ excess leading to a formation of chlorspodiosite, $Ca_2(PO_4)Cl$,[21] at $T \leq 1040\,°C$, Ca-deficient HAp (CDHAp) should be used as a starting material. It is believed that Ca vacancies are filled with extra Ca atoms coming from the sintering additive according to the summary process (not reflecting details of the transformation):

$$\begin{aligned}&Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} + xCaCl_2\\&\quad = Ca_{10}(PO_4)_6(OH)_{2-x}Cl_x + xHCl \uparrow .\end{aligned}$$

Calcium chloride was tested as a sintering additive earlier.[13] However, this trial was unsuccessful, likely due to its small amount (*ca.* 5%) and a non-uniform distribution over the sample. Consequently, in order to observe the effect of a liquid-phase formation, we have chosen to increase the quantity of this additive up to 10 wt.% (or 12 vol.%), being the lowest limit for the complementary CDHAp (the reaction above needs then *ca.* 12 vol.% of $CaCl_2$ for the CDHAp with Ca/P = 1.5; note, however, that this amount does not meet the percolation threshold for a liquid phase exceeding 16 vol.%). As has been shown elsewhere,[22] the crystallization of HAp from $CaCl_2$ melts proceeds rather sluggishly and does not yield whiskers (*i.e.*, only crystals with small aspect ratios are formed), which implies that the presence of $CaCl_2$ induces the formation of nearly isotropic particles. From the viewpoint of ceramics microstructure development, the formation of virtually equiaxed particles may be regarded as a positive result. It means that the $CaCl_2$ melt interacts with nanosized HAp particles (100 nm) by the sequential "dissolution-crystallization-growth" mechanism providing the growth of HAp grains up to 200 μm for 3 h at 850–1000 °C and selectively inhibiting the growth along the *c*-axis owing to efficient wetting of the basal faces of HAp grains. The present work is aimed at the elucidation of the role played by NH_4NO_3 (a by-product of the solution synthesis of HAp) and $CaCl_2$ in the densification of nanosized HAp powder in the course of the conventional sintering. It is of note that significant amount of NH_4NO_3 captured by HAp precipitate can be removed (and this is commonly held step in HAp preparation) by washing the precipitate with water. Here, we report on the HAp powder obtained without this washing with water-step.

2. Experimental

2.1. Powder synthesis and samples preparation

HAp powder samples were fabricated via conventional wet-precipitation technique by a dropwise addition of an $(NH_4)_2HPO_4$ solution (0.15–1.00 M) to a starting solution of $Ca(NO_3)_2$ (0.25–1.67 M) with a pre-adjusted pH at 60 °C. The pH of the mixture was maintained at a constant value (about 9 and 7) by addition of appropriate amounts of NH_4OH. The solution was vigorously stirred. After addition of the specified amount of the $(NH_4)_2HPO_4$ solution, the suspension was matured for 30 min and then filtered without washing. The resulting precipitate was dried at room temperature for 48 h. Dry powder was disaggregated in a ball mill for 3 min in acetone or alcohol media with a liquid: powder: balls proportion set to 2:1:3. A surplus of $CaCl_2$, in amount of 10 wt.% to a powder charge, was added at the stage of disaggregating (alcohol media, ratio liquid:powder:balls = 1:1:3, 3 min). The powder processed in this way was sieved (Saatilene HiTechTM polyester fabrics, cells of 200 μm). The samples (charges of about 0.5 or 1.5 g,