Sintering of HAp precipitated from solutions containing ammonium nitrate and PVA

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ABSTRACT

Bioceramics based on hydroxyapatite (HAp) is known to be a prospective material for biomedical applications. However, sintering of HAp is still understudied in sense of reasonable selection of controlling parameters. In particular, the role of impurities and co-products of powder fabrication is still questionable. The data concerning the role of ammonium nitrate coming to precipitated HAp from the mother liquor, its effect on powder compaction and subsequent sintering, are not available.

Nanosized powders of HAp were fabricated via conventional wet-precipitation technique by dropwise adding of $Ca(NO_3)_2$ solution (0.25 -1.67 M) to the stock solution of $(NH_4)_2HPO_4$ (0.15-1.00 M) with pre-adjusted pH at 60 C in presence of polyvinyl alcohol (PVA). PVA was added to the stock solution in order (i) to block crystal growth during synthesis , (ii) to improve stability of Hap suspension to sedimentation, (iii) to regulate an aggregation of HA nanoparticles during synthesis and in the stage of drying.

NH_4NO_3 – a by-product of the precipitation reaction, presented in as-precipitated powder in amount of 30%, was evaluated as an additive affecting a compaction of the powder and the initial stage of a sintering. The powder samples were tested by XRD, FTIR, light-scattering , TEM and SEM/EDX to get particle sizes, morphology and chemical composition, dilatometry. Ceramics were sintered at 700-1250 C and evaluated with SEM/EDX and density measurements.

Addition of PVA to the stock solution in the course of HAp precipitation is a promising technique to control an aggregation of HAp nanoparticles in the stages of drying and sintering. PVA acting as a surfactant in the solution and as a binder in dry powder can keep highly reactive small HAp particles within large agglomerates providing better molding of the powder and controllable densification of ceramics. The effect of PVA on microstructure of the HAp powder and their sintering behaviour is discussed in terms of self-organisation concept and synergetics.

INTRODUCTION

Ceramics based on calcium phosphates is known to be a prospective material for biomedical applications [1]. Much attention is paid to hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HAp) due to its affinity to a bone mineral. Different precursors have been used to synthesize HAp powders. The most popular reaction consists in precipitation from $(NH_4)_2HPO_4$ and $Ca(NO_3)_2$ solutions. Effect of the principal parameters of the powder fabrication on sintering was extensively discussed (see, e.g., [2]). However, the role of impurities and co-products of powder fabrication is still questionable. Thus, there is no data concerning the role of ammonium nitrate coming to precipitated HAp from the mother liquor, its effect on powder compaction and subsequent sintering, though NH_4NO_3-monitoring of wet precipitates and bulk samples prior to

sintering is considered as a routine [3]. Meanwhile, NH_4NO_3, a low-melting impurity, could cause a beneficial effect on a compaction of the powder and on the initial stage of sintering. Another key is a role of organic (mostly, polymeric) substances acting in the course of HAp preparation. This subject was addressed significant amount of works pointing out a positive influence of these additives, especially surfactants [4-6] which can decrease surface energy due to adsorbtion or decrease aggregation due to decreasing of drying temperature [7]. Besides, they can inhibit [8] a growth of HAp crystals leading to a more active powder in subsequent sintering. Practically important task is to get through the above logic some widely accepted technological additives such as, for instance, polyvinyl alcohol (PVA). PVA is expected (i) to block crystal growth during synthesis, (ii) to improve a resistance of HAp suspension against sedimentation, (iii) to control an aggregation of HAp nanoparticles in the stage of drying. Therefore, the aim of this work is focused on the role of NH_4NO_3 (a by-product of the HAp precipitation) and the effect of PVA (added to the stock solution) on sintering of bioceramics.

EXPERIMENT

2.1. Powder synthesis

Powders of HAp were fabricated via conventional wet-precipitation technique by dropwise adding of $(NH_4)_2HPO_4$ solution (0.15-1.00 M) to the stock solution of $Ca(NO_3)_2$ (0.25 -1.67 M) with pre-adjusted pH at 60 C in presence of polyvinyl alcohol (PVA). The amount of PVA (added to $Ca(NO_3)_2$ solution) was set to 0.25 and 0.5 % with respect to the mass of HAp in two parallel runs. The pH of the mixture was maintained at a constant value (about 9) by addition of NH_4OH. The solution was vigorously stirred. After total addition of the $(NH_4)_2HPO_4$ solution, the suspension was matured during 30 min and then filtered without washing. The resulting precipitates were dried at room temperature during 48 hours. Dry powders were disaggregated by means of ball milling (3 min, acetone media, the proportion liquid:powder: balls was set to 2:1:3). Thus processed powders were passed through the sieve (Saatilene HiTech[TM] polyester fabrics, cells of 200 μm).

2.2 Sintering

The samples (charge of about 1.5 g, without plasticiser) were pressed uniaxially under 25-50 MPa in a stainless steel die into 6x40 mm rectangular bars. Green density and density of sintered samples was determined by geometrical measurements assuming a theoretical density of 3.156 g/cm^3 for the HAp. Thermal treatment of the powder and compacted samples was done with isothermal hold during 4 hours at the temperatures 300-1200˚C. The linear shrinkage was determined with dilatometer LIR-1400 (Russia) on the HAp samples pressed in the form of bars 6x4x10 mm in size. The samples were heated in air up to 1000˚C at a ramp rate of 5˚C/min.

2.3. Samples characterization

XRD patterns were obtained with CuKα radiation using DRON-3M (Russia). FTIR spectra of the powders were recorded on PE-1600 FTIR (Perkin Elmer, USA) in the range of 400-4000 см$^{-1}$ with scanning step 4 см$^{-1}$. TGA of the specimens was conducted with Diamond Pyris (Perkin Elmer, USA) in air up to 1000 °C at a ramp rate 5°C/min. Microstructure of the powders

and dense specimens was observed by FESEM at 5-10 kV (LEO Supra 50 VP, Carl Zeiss, Germany) and TEM at 200 kV (JEM-2000 FXII, JEOL, Japan). Composition of the samples (Ca/P ratio) was determined by SEM/EDX (INCA Energy +, Oxford Instruments, UK).

RESULTS AND DISCUSSION

According to XRD all as-synthesised powders consisted of nanocrystalline HAp (size of crystals accessed from peak broadening was in the range of 15-40 nm) with Ca/P close to 1.67. Besides the apatite phase, a significant amount of NH_4NO_3 in dry powders was revealed by FTIR (pronounced band at $1380\,cm^{-1}$). This amount, rulled out of TG-curves (weight change in the region 20-400°C since NH_4NO_3 decomposes at 210°C) and weight gain of as-precipitated powders against theoretical yield of the reaction, was varied from 5.87 to 27.40 % (Table 1). TEM gave a strong evidence of needle-like morphology of HAp particles, the samples with PVA demonstrating higher aspect ratio compared to the case of powder without PVA ((150…200)x(20…25) and (150…200)x(10…15) nm, respectively). The particles were seemed to be composed of primary crystals with sizes close to that determined by XRD. Another indicative feature deducing the origination of the particles from gel-like amorphous precursor was their microporosity with pore sizes less than 5 nm. The effect of PVA on microstructure of the powders consisted in formation of large aggregates detected by TEM and SEM (Fig. 1 a,b)

As one can see in Fig.1 c,d, demonstrating cleaved surfaces of compacts after thermal treatment (300°C, 4 hs), primary aggregates form bulk sintered agglomerates (in some cases more than 10 μm in size). Formation of such agglomerates was accompanied by shrinkage of the compacts in the range of 200-300°C (Fig.2), increasing with PVA content and starting concentration of salts in the stock solution (i.e., with the amount of NH4NO3 captured by the precipitate) increase. Thus, we believe that observed agglomeration of the HAp powders is a concerted action of NH4NO3 and PVA. According to FTIR and SEM (see distinct pocks in Fig.1 c,d) the former was released from the compacts at 300°C. As it followed from TG and annealing experiments PVA was burnt out at 600-700°C. Its role consisted mainly in formation of the agglomerates, i.e., gentle coarsening of the powders, which provided a close packing of the particles at rather low temperature. Hence we infer that PVA can keep high reactivity of wet-chemistry HAp powders. However, the effect of PVA on the main stage of sintering is non-monotonous one (Fig.2), revealing better sintering for the sample with intermediate content of PVA (0.25 %).

Table I Synthesis conditions and properties of powders.

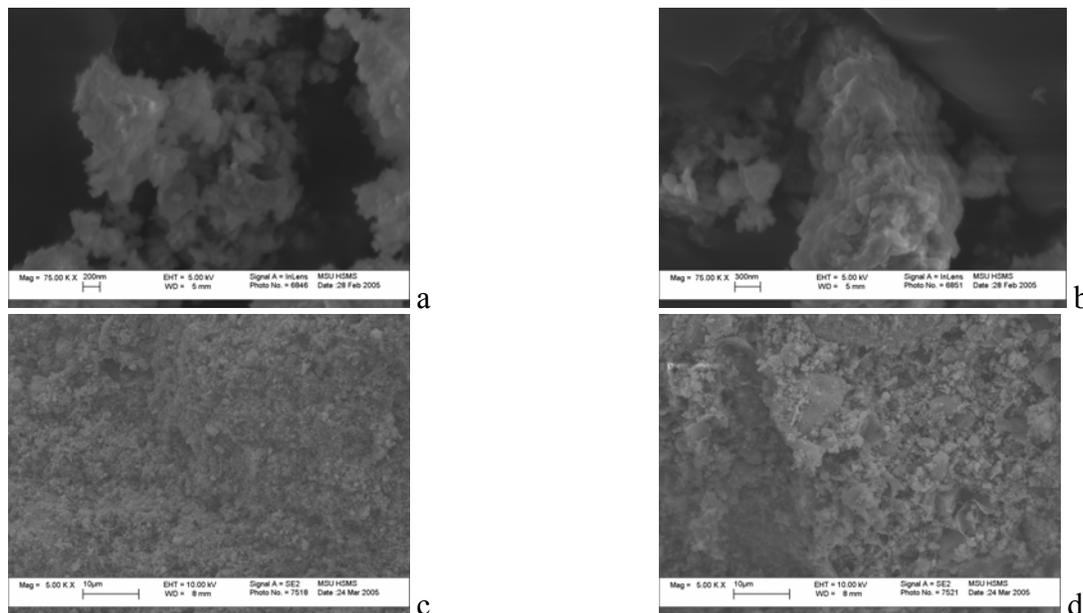| Starting concentrations			Weight loss of the samples at 400˙C, %	Apparent density of powders, g/cm3	Green density of compacts, % (P=50 MPa)
$c(Ca^{2+})$, M	$c(PO_4^{3-})$, M	c(PVA), %			
0.25M	0.15M	0	5.87	0.28	39
0.5M	0.3M	0	13.55	0.36	40
1.0M	0.6M	0	23.99	0.42	42
1.0M	0.6M	0.25	25.39	0.56	47
1.0M	0.6M	0.5	27.40	0.67	48
1.6M	1.0M	0	27.40	0.40	46

Figure1. SEM micrographs of as-synthesised powders (a) without PVA, (b) with 0.25% PVA; and treated at 300°C powders (c) without PVA, (d) with 0.25% PVA

Viable explanation of this phenomenon could be done in terms of self-organization approach. Highly dispersed powders agglomerate during molding giving rise to local densification regions due to self-organisation processes [9-12]. This implies that preliminary stages of ceramics technology can be regarded as mass-transfer process, which determine further structural evolution of the system via plastic deformation or brittle disintegration. If the amplitude of external and internal factors influencing the system in an unstable state exceeds that of noises (i.e., weak uncontrollable external perturbations and internal fluctuations), they can turn into control signals.

In our case, the powder after synthesis was agglomerated in the presence of a surfactant (PVA), which simultaneously acted as a binder. An increase in the PVA content from 0.25 to 0.5% makes the aggregates larger, stronger, and denser. Aggregates with high densities can be regarded as control signals. They provide a higher apparent density of the powder. Consequently, density of the green compact after molding also appears higher (Table I). The aggregates preserved after molding start to sinter at a lower temperature and thus densification occurs dominantly in already densified regions, which gives rise to a strong inhomogeneous framework composed of local densification regions. Shrinkage proceeds slowly, the crystals forming the framework undergo densification and rapidly loose activity towards further sintering. As a result, low-density ceramics is produced.

In contrast, in the case of a low PVA content (0.25%), the aggregates are smaller, less strong and dense; apparent density of the powder is lower; and density of the green compact after molding is respectively lower (Table 1). These aggregates do not play a role of the control signal. Although particles constituting the aggregates can loose activity during sintering, the aggregates are small and start to move upon shrinkage-induced deformations. Substantial deformations disintegrate the aggregates that are characterised by a low strength. This results in large shrinkages (Fig.2) and, consequently, high-density ceramics.
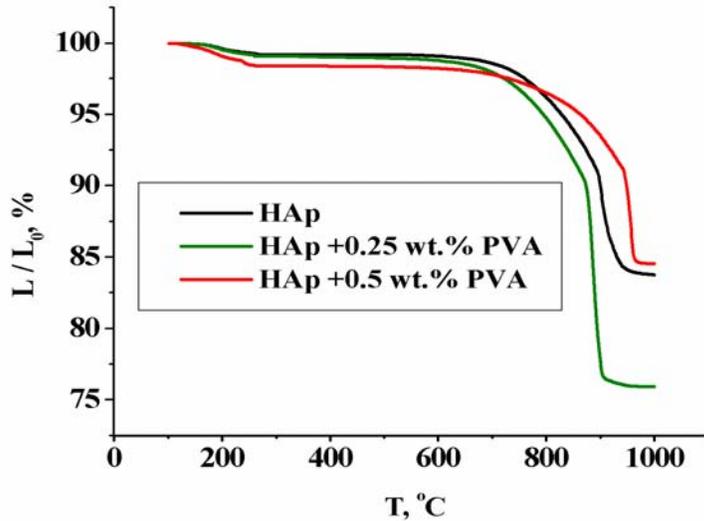
Figure 2. Linear shrinkage of the compacts (P=25 MPa) with different amount of PVA

Finally, in the absence of PVA, strong interparticle friction favours formation of local densification regions during molding. Then, the local densification regions are sintered giving rise to a strong framework, like in the case of the high PVA content (0.5%), the total shrinkage is reduced and ceramics produced appears porous. This occurs due to self-organisation, in contrast to the case of the high PVA content, where the granules were pre-prepared in the molding stage.

Reduction of sintering temperature from 1150°C according to the data [13] down to 900-950°C in our work (which is of special interest) can originate from higher sintering activity of the powder under study. Sintering activity of a powder is a qualitative characteristic depending mostly on the fabrication route.The increasing of crystal lattice imperfection and increasing of specific surface area of powder, reduction of the aggregation extent make the sintering activity of the powder higher. In our case sintering activity was enhanced due to shortening of duration of precipitation and subsequent aging of the precipitate, lowering of drying temperature and using special program of desaggregation of the powder.

CONCLUSIONS

Addition of PVA to the stock solution in the course of HAp precipitation is a promising technique to control an aggregation of HAp nanoparticles in the stages of drying and sintering. PVA acting as a surfactant in the solution and as a binder in dry powder can keep highly reactive small HAp particles within large agglomerates providing better molding of the powder and controllable densification of ceramics. Ammonium nitrate coming from the mother liquor facilitates the agglomeration of the powders due to melting at 180°C and subsequent evaporation at 210°C. However, in order to obtain high green density of the compacts the amount of NH_4NO_3 has to be diminished in comparison to that found in unwashed precipitates.

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