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Slip casting of mechanochemically synthesized hydroxyapatite

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The dispersion behaviour of mechanochemically synthesized hydroxyapatite was investigated. Electrophoretic mobility measurements evidence that $pH_{i.e.p.} = 10.7$ and that pH modification has a poor effect on the mobility. Surface charge reverses as anionic polyelectrolytes are added in considerably high amounts (3 wt %). Polyacrylates are effective in stabilizing 10 vol % suspensions while pourable casting slips are obtained at the maximum solid concentration of 21.4 vol %. The mechanical properties of the sintered bodies were tested and resulted significantly improved in the slip cast samples if compared with the cold pressed samples, thus proving the importance of the application of the colloidal approach to the optimization of cold consolidation of fine powders.

1. Introduction

The use of hydroxyapatite as a ceramic material for osteo-implants is restricted because of its low mechanical strength and low toughness [1–5]. The enhancement of mechanical properties would extend the range of applications in place of the bioinert materials used at the present time.

Recently it was demonstrated that manufacts based on hydroxyapatite containing tricalcium phosphate show rather improved mechanical properties [6, 7]. An optimization of the performance of hydroxyapatite materials, following the mechanochemical synthesis route, can be expected. If it is verified, the new synthesis route can be considered as inductive of the improvement of performance of the powders synthesized chemically. In a recent work Toriyama *et al.* developed a new processing method, based on the mechanochemical reaction [8] that is simply milling a mixed slurry of calcium hydrogen phosphate and calcium carbonate for producing hydroxyapatite containing β-tricalcium phosphate; they obtained hydroxyapatite ceramics having improved mechanical properties on uniaxially pressed mechanochemically synthesized (MCS) powder.

On the other hand, Galassi *et al.* [9] studied slip casting of the hydroxyapatite and reported that the method is suitable to obtain a high density forming body. This work was carried out to clarify the dispersibility of MCS powder into water and the final properties of the MCS powder shaped by slip casting in plaster moulds are studied. The MCS powder was characterized in order to investigate its dispersing behaviour and develop casting slips suitable to produce samples for mechanical characterization and of complex shapes.

2. Materials and methods

Hydroxyapatite powder was synthesized following the mechanochemical synthesis procedure summarized in Fig. 1. The mechanochemical method consists of arousing a chemical reaction within a rotating jar among suitable reagents in powder through the pressure on them of (generally ZrO_2) highly dense spheres ingraining towards the walls of the jar through impact force. In this case, the reaction was obtained among the mixed slurry of $CaCO_3$(5.587 g) and $CaHPO_4 \cdot 2H_2O$(14.413 g) within jars of Teflon with an internal diameter of 70 mm and using as grinding media, balls of 800 g of ZrO_2 with a diameter of 15 mm. The batch was made by weighing the reagents so as obtain a Ca/P ratio of 1.67, to synthesize pure hydroxyapatite. The milling conditions tested as well as the crystalline phase content at the end of the milling step are reported in Table I. The purer powder was obtained in a Teflon jar with ZrO_2 milling media. The powder was then calcined at 700 °C for 1 h (MCS-700) and 720 °C for 10 h (MCS-720). The powder characteristics were investigated with scanning electron microscopy (SEM) analysis, particle size distribution, specific surface area and X-ray diffraction (Table II). The electrophoretic mobility of hydroxyapatite powder

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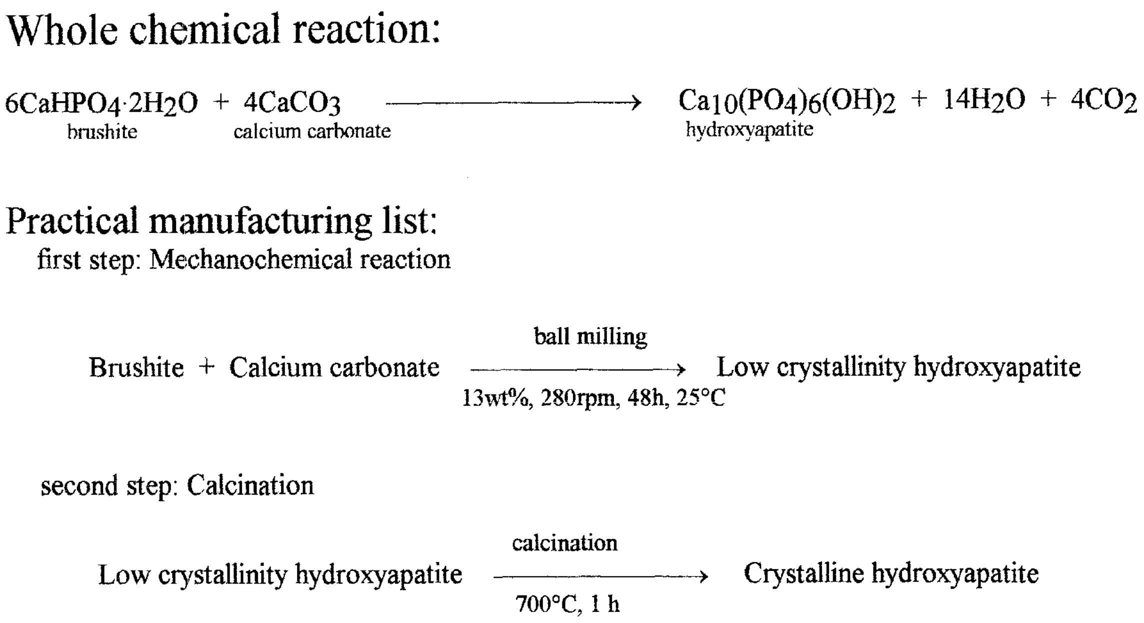

Figure 1 Preparation procedure of hydroxyapatite by mechanochemical method.

TABLE I Preparation conditions of hydroxyapatite powders

Apparatus	Milling media	Milling time (h)	Powder content of slurry (wt %)	Crystalline phase
Ball mill (Teflon made)	ZrO_2	24	20	1-HA, $CaHPO_4 \cdot 2H_2O$, $CaCO_3$
Ball mill (Teflon made)	ZrO_2	48	13	1-HA
Ball mill (Porcelain made)	Al_2O_3	24	20	$CaHPO_4 \cdot 2H_2O$, $CaCO_3$

1-HA: low crystallinity hydroxyapatite.

TABLE II Calcined low crystallinity hydroxyapatite powder properties

Sample	Calcination condition	Specific surface area ($m^2 g^{-1}$)	Calculated particle diameter (nm)	Average diameter (μm)	Crystalline phase
MCS-700	700 °C, 1 h	43.9	43.3	1.0	HA, β-TCP
MCS-720	720 °C, 10 h	22.0	86.3	–	HA, β-TCP

HA; hydroxyapatite; β-TCP, β-tricalcium phosphate.

calcined at 700 °C was measured in dilute dispersion as a function of pH in the range of pH 7–12. In order to maintain the ionic strength constant the suspension was prepared in 1.0×10^{-3} mol dm^{-3} KNO_3 solution. The pH for dilute dispersions was adjusted by adding either 1 mol dm^{-3} HNO_3–NH_4OH to the KNO_3 solution. The preparation of suspensions of microelectrophoresis involved two steps. First, about 0.5 g powder was put into 100 ml of electrolyte solution and ultrasonically dispersed for 1 h in order to reduce the presence of the agglomerate. Dispersions suitable for microelectrophoresis experiments were then obtained by mixing 1 ml of the starting powder dispersion with 49 ml of pH-adjusted KNO_3 solution followed by thorough mixing using an ultrasonic bath. Prepared dilute dispersions were introduced into a microelectrophoretic cell which was maintained at 25 °C. The velocity of the particles was measured at the upper stationary level in a capillary cell. Each mobility value was calculated from the average of 30 velocity measurements. Moreover, electrophoretic mobility measurements were carried out after addition of two polyelectrolytes with and without KNO_3.

In the supernatant liquid of the MCS-700 suspension adjusted at pH 10 with NH_4OH, the content of ions Ca^{2+}, PO_4^{3-}, was determined with the inductively coupled plasma atomic emission (ICP) analysis on the solution of 1 g of powder in 100 ml of water, and CO_3^{2-} through a thermogravimetric analysis.

Sedimentation tests were carried out in 10 vol % suspensions of the hydroxyapatite powder calcined at 700 °C for 1 h added to different deflocculants as reported in Table III. The suspension was ultrasonically

TABLE III Tested deflocculants

Sample ID	Composition	Molecular weight	pH of deflocculant	Concentration (wt %)	pH of suspension
A-1	Ammonium ligninsulphonate		8.0	0.5	–[b]
A-2				3.0	–[b]
B-1	Ammonium Polymethacrylate	14000	7.5–9.0	0.5	–[b]
B-2				3.0	8.7
C-1	Sodium polycarboxylate		9.5–10.5	2.0	9.5
C-2				3.0	9.7
C-3				4.0	9.9
D-1	Ammonium polymethacrylate	15000	8.0–9.0	2.0	9.0
D-2				3.0	9.0
D-3				4.0	8.9
E-1[a]	Sodium polyacrylate	2100		3.0	9.5
E-2[a]		5000		3.0	9.3
E-3[a]		15000		3.0	9.5
E-4		2100		3.0	9.4
F-1	Graft copolymer of methoxy methacrylate	2000		3.0	–[b]
G-1	2-Amino-2-methyl-l-propanol	89.1	11.3	0.5	–[b]
G-2				3.0	11.0

Weight ratio of hydroxyapatite/water = 5/15.

[a] Weight ratio of hydroxyapatite/water = 0.5/15.

[b] Cream-like suspension.

TABLE IV Characteristics of mechanochemically synthesized hydroxyapatite ceramics

Sample	Calcined condition	Optimum sintering temperature (°C)	Flexural strength (MPa)	Fracture roughness[a] (MPa m$^{1/2}$)	Bulk density (g cm^{-3})	Shrinkage (%)
MCS-700	700 °C, 1 h	1250	152.7	0.93 ± 0.07	3.03	31.8
MCS-720	720 °C, 10 h	1250	96.4	–	3.11	31.2

[a] Chevron-notched beam method.

dispersed and poured in a cylinder and sediment height and transparency of the supernatant were recorded as a function of time.

Casting tests were performed with the slurry produced dispersing 46.2 wt % (21.2 vol %) of powders calcined at 700 °C for 1 h and at 720 °C for 10 h with 3.0 wt % deflocculant D. The slurry was poured into plaster moulds and cylindrical samples (ϕ 6 × 60 mm) were produced. The samples were fired at different temperatures for 1 h and flexural strength of as-fired samples and fracture toughness were measured by a 4-point bending method and by a chevron-notched beam method. The final properties are reported in Table IV.

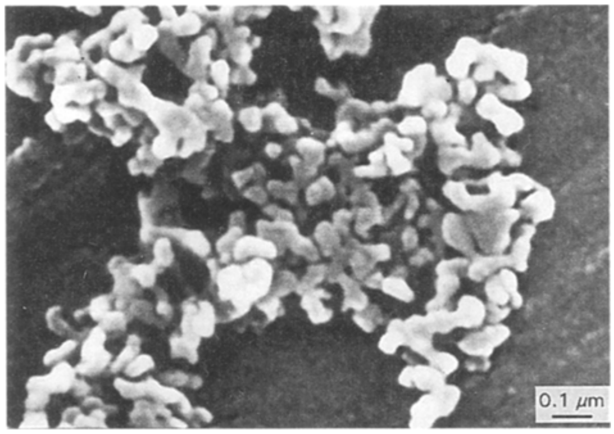

Figure 2 SEM morphology of the mechanochemically synthesized hydroxyapatite powder calcined at 700 °C for 1 h.

3. Results and discussion

The characteristics of the MCS powder calcined at 700 °C and 720 °C are reported in Table II; the SEM morphology is shown in Fig. 2. It is a very fine powder with primary particles rounded and interconnected in agglomerates in which the mean size is 1 μm. Eventually Teflon debris can be easily removed by sieving off before any thermal treatment and burning out in calcination procedure, because Teflon decomposes completely at 600 °C. The electrophoretic mobility

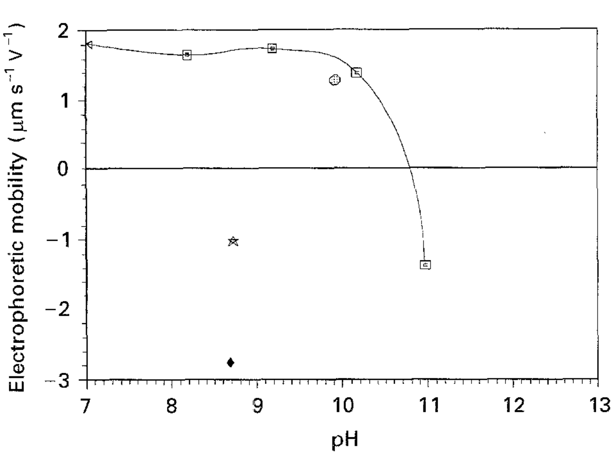

Figure 3 Electrophoretic mobility of mechanochemically synthesized hydroxyapatite powder calcined at 700 °C for 1 h against pH: ☐ HA; * HA + D 0.5 wt %; ◆ HA + D 3 wt %; △ HA + D 3 wt %; ○ HA + G3 wt %.

measurements in dilute suspensions with KNO_3 is poor electrolytic evidence that the powder is positively charged for pH values lower than 10.7 (Fig. 3) and becomes negatively charged for higher values of pH. In any case the mobility is quite low evidencing a poor effect of the modification of pH on the dispersion of the powder. The different behaviour from that previously reported [9, 10] could be probably correlated with the surface species present at different calcination temperatures. The addition of the cationic polyelectrolyte (amino alcohol, Table III (G)) does not produce any relevant modification of the mobility while after addition of the anionic polyelectrolyte (polymethacrylate deflocculant, Table III (D)) the surface charge reverses and the mobility doubles when the relative deflocculant concentration increases from 0.5 to 3.0 wt % (Fig. 3).

In order to understand the dispersing behaviour of the powder, the effect of all the ionic species in solution must be considered; in fact the presence of the ions Ca^{2+} (2.5×10^{-5} mol dm^{-3}), PO_4^{3-} (2.1×10^{-4} mol dm^{-3}) and CO_3^{2-} (4.4×10^{-3} mol dm^{-3}) was detected in the supernatant of the powder itself at pH 10. Considering the formula of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] (in which an appreciable content of CO_3^{2-} was detected with i.r. spectroscopy measurements, substituting at the phosphate site) and β-tricalcium phosphate [$Ca_3(PO_4)_2$], it is evident that there is a poor dissolution of calcium compared with phosphate and that the carbonate dissolves preferentially its existence in the solution being more than an order of magnitude higher than that of phosphate.

The powder being positively charged until high values of pH are reached, the sequence of deflocculants reported in Table III was chosen for settling tests. At first anionic polyelectrolytes with different functional groups (acrylate, carboxylate, lignosulphonate) and with different molecular weight (2100, 5000, 15 000) were tested.

All the acrylic or carboxylic dispersants (B, C, D, E) deflocculated the suspension so that it was still cloudy after 100 h. The sediment height slightly increased with the trend reported in Fig. 4. For all of them it was found that they were not effective at the low concentration typically used (< 1%) but only if used in the concentration of 2–4 wt %. They all produced suspensions with high pH values, quite near to the $pH_{i.e.p.}$ of the powder itself.

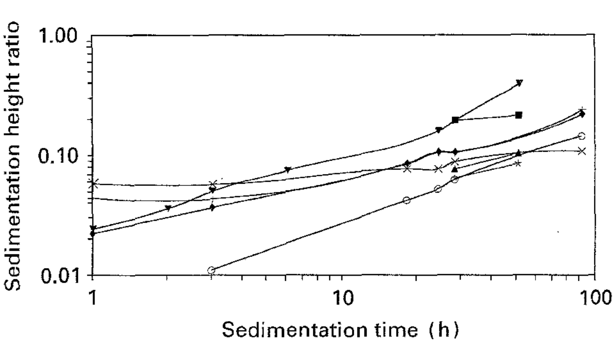

Figure 4 Sedimentation height ratio versus sedimentation time for MCS 700 powder with several deflocculants: + C1; * C2; × C3; ◆ D1; ▲ D2; O D3; ▼ E4; ■ G2.

In the case of the polycrylic acid three different molecular weights (Table III (E)) resulted in a slightly smaller sediment height of the suspension deflocculated with the lower molecular weight deflocculant. In any case deflocculant E shows the poorer effect within that group (Fig. 4 (E4)).

The lignosulphonate (Table III (A)) resulted in a cream-like dispersion either at 0.5 or 3.0 wt % concentration. An amino alcohol (Table III (G)) as a cationic polyelectrolyte was then tested and it deflocculates the suspension and the sediment height increases with a trend similar to that found for anionic dispersions. The pH value is higher (11) and it implies a negatively charged surface of the powder. Finally, a graft copolymer (F) was tested and it produced immediate flocculation of the suspension. When tested at volume fraction of solids suitable for slip casting, the maximum volume fraction that still produces castable suspensions is 21.4 vol % with 3.0 wt % (Table III (D-2)) a too small concentration to provide high density of the green bodies.

Casting tests were performed on the powder calcined at 700 °C with the deflocculant D which produces the best dispersion at the concentration of 3.0 wt %; the maximum volume fraction was about 21 vol %. For comparison, slips with the powder calcined at 720 °C were prepared with the same volume fraction and deflocculant. Samples were produced changing the deflocculant concentration. The firing tests were carried out so as to optimize the sintering temperature and to provide evidence of the effect of the dispersion state (i.e. varying the concentration of deflocculant) on the final properties of the ceramics. In Fig. 5 the flexural strength reported as a function of sintering temperature provides evidence that the best results are obtained for powder MCS-700 fired at 1250 °C and this temperature gives results also optimal for sample MCS-720, although it shows lower values of flexural strength.

The tests on powder MCS-720 at various deflocculant concentrations provide evidence that 3.0 wt %

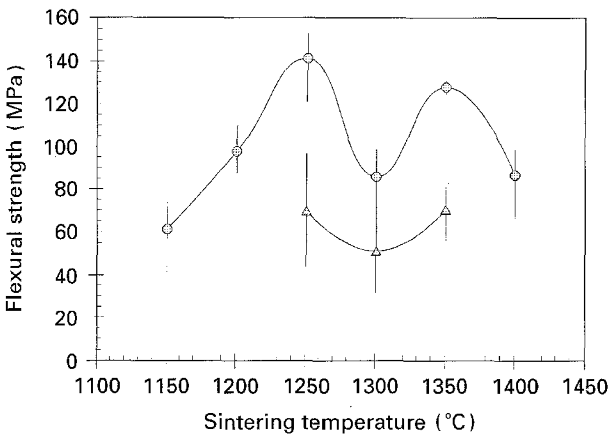

Figure 5 Flexural strength of MCS ceramics as a function of the firing temperature. △ MCS-720; ⬡ MCS-700.

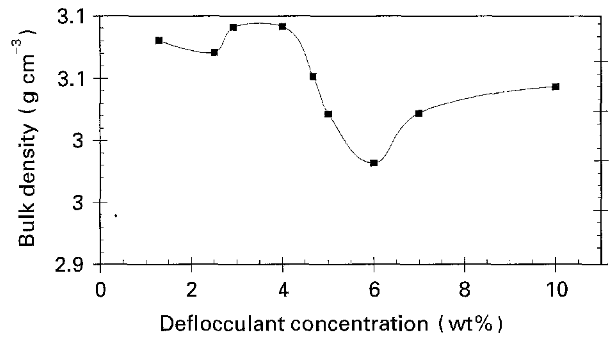

Figure 6 Effect of deflocculant concentration on bulk density of MCS-720 ceramics.

still produces the higher final density (Fig. 6) corresponding to the higher flexural strength with a strong dependence on the deflocculant concentration (i.e. on the dispersing state of the suspensions); in fact, flexural strength increases with concentration of the deflocculant up to 3.0 wt %. However, in excess of 3.0 wt % the values suddenly decreased. The phenomenon could be explained by the existence of the excess deflocculant bringing about a formation of agglomerates of hydroxyapatite particles which compromise the packing properties of the cast body. The maximum flexural strength was 152.7 MPa for the calcined hydroxyapatite at 700 °C for 1 h; above 700 °C initial sintering phenomena take place with formation of "necks" among grains, while below 700 °C the grain growth appears too low thus leaving amorphous phase. Therefore the best condition to obtain fine and totally crystalline grains was found to be a temperature of 700 °C for 1 h.

The optimum sintering temperature was the same (1250 °C) as that for the die-pressed one. But the flexural strength of the sintered body formed by the slip casting method was about 50% higher than that of the die-pressed sample. That is, it showed that mechanical properties of hydroxyapatite ceramics were improved by the introduction of a slip casting method as a forming technique because it allows the control of the green body texture and also of the defects governing the mechanical properties.

4. Conclusions

The observed dispersing behaviour of mechanochemically synthesized hydroxyapatite allows us to draw the following conclusions.

1. The surface area of the powder calcined at 700 °C is very high so it is in any case difficult to produce very high solids volume suspension. An increase of temperature involves a strong surface area reduction but the maximum solid content of the slip casting suspension does not improve and the properties of the sintered body are compromised.
2. The powder can easily be dispersed for a long time at low concentration of solids through adsorption of polyelectrolytes on the surface that means that an electrosteric mechanism takes place.
3. Ions are present in solution due to a partial dissolution of the powder leaching in the particular anions CO_3^{2-}, PO_4^{3-}. They compete in the adsorption on the particle surface with the added polyelectrolytes. The weak charge of the surface and this competition implies a need to use high concentration of deflocculant to allow a higher probability of its adsorption. The electrostatic repulsion prevails on the steric effect as confirmed by the mobility measurement on the powder deflocculated with polymethacrylate. Consequently a low volume of powder can be dispersed by still maintaining flowability of the suspension.

The use of powders prepared by the mechanochemical synthesis method resulted in better mechanical properties, for both samples formed by the slip casting or by the die-pressing methods, than other ones obtained in the same manner but now using commercial or conventional precipitation method powders. As a result, the mechanochemically synthesized hydroxyapatite calcined at 700 °C for 1 h has, when formed by the slip casting method using 3 wt% ammonium polymethacrylate as a deflocculant and sintered at 1250 °C for 1 h, a flexural strength of 152.7 MPa, which is about 50% higher than that of the same uncalcined powder formed by the die-pressing method.

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