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Processing of hydroxyapatite ceramic foams

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A novel method of producing highly porous hydroxyapatite ceramics vía the foaming of ceramic slips is discussed. Foams with densities $\geq 15\%$ and an open cell structure have been produced.

1. Introduction

Hydroxyapatite (HA) is currently receiving considerable attention owing to its potential for use as a bioactive bone substitute [1]. Recently it has also begun to receive attention as a potential water filter due to its capacity for removing heavy metal ions [2]. For both applications there is a need for high-porosity HA ceramics. A number of routes for producing such ceramics have been investigated in the past (see [3] for a review); however, all of these techniques are felt to be too complicated or too expensive for commercial production.

It is well established that without the presence of a surfactant, surface charges on ceramic particles cause the latter to agglomerate in ceramic slips [4]. Hence it is generally acknowledged that such slips will have a high viscosity and poor packing behaviour during consolidation [5]. It is thus favourable for the production of dense ceramics to use powder of colloidal dimensions in deagglomerated dispersions.

However, if the mechanical strength of the component is not of prime importance it is less important to work with fully dispersed colloidal suspensions. Kingery *et al.* [5] have shown that a non-dispersed slip produces clusters during sintering which lead to an increased surface area due to pore formation. This effect would be quite beneficial for the production of filters for example, because a high surface area increases the effectiveness of the filter, as long as the strength of the filter is sufficient.

This paper thus describes a novel method of producing hydroxyapatite-based ceramic foams via the foaming of ceramic slips which are not fully dispersed.

2. Experimental procedure

Hydroxyapatite (HA) ceramic foam bodies were produced using the following four basic steps: (i) production of ceramic slips; (ii) foaming of the slips; (iii) drying of the foamed slips; (iv) sintering of the green body.

Three different grades of HA-based powder (Jesse Shirley and Son, Stoke-on-Trent, UK) of different purity were used to produce ceramic foam bodies. The purest grade was a white powder coded H. The other two grades were grey–brown powders and designated M and L, the latter representing the lowest purity. This powder had a residual water content of approximately 12%. Upon drying, this caused the powder to cake and form pellets which had to be broken up either mechanically or by using ultrasonic dispersion before the powder could be used. The Ca/P ratio was 1.67 for the H and M powders and 1.66 for the L grade. Further information on the powders may be found in Tables I and II.

Four methods for producing foamed slips were investigated. These are summarized in Fig. 1 and are described in the following sections.

2.1. Simultaneous production of slip and foam

The required amount of HA powder was added to a specific volume of deionized water and subsequently a known amount of Decon 75 (a general purpose surfactant added to deagglomerate the powder and encourage the foaming of the slip; Decon Laboratories Ltd, Sussex, UK) was added under constant stirring at 1200 r.p.m. for 1 min. The slip was then transferred to an ultrasonic unit where the powder was dispersed for 2 min (this procedure was only used to deagglomerate powder particles if the purity of the final product was not crucial. The tip of the ultrasonic probe was subject to wear during use and this introduced metal impurities into the slip). The optimum settings were found to be an amplitude of 24 μm at a frequency of 20 kHz. The slip was then stirred with a high-speed stirrer at 1200 r.p.m. By this means, remaining agglomerates were broken down, the slip was further homogenized, and air bubbles were simultaneously introduced. After 2 min stirring the maximum foam volume was reached and the bubble size was homogeneous. The foamed slip was then transferred into boxes made of filter paper for drying.

2.2. Separate slip and foam production

Water and Decon 75 were mixed in a predetermined ratio and whisked at 1200 r.p.m. for 1 min. Previously prepared slip, consisting of powder, water and Decon

TABLE I Physical properties of the three grades of HA-based powders

	Grade H	Grade M	Grade L
Particle size (μm)	42% < 1	40% < 1	36% < 1
Crystal size (μm)		1	1
Moisture content	Dry	Dry	12.5% ± 1%
Density ($g\,cm^{-3}$)	3.11	3.11	3.11

TABLE II Chemical analysis of the three grades of HA-based powders

Chemical analysis (wt%)	Grade H	Grade M	Grade L
SiO_2	0.05	< 0.2	1.81 ± 0.23
TiO_2		< 0.01	< 0.01 ± 0.002
Al_2O_3	< 0.01	< 0.2	0.10 ± 0.03
Fe_2O_3	< 0.01	0.03	0.04 ± 0.016
CaO	54.4	54.8	53.18 ± 0.24
MgO	0.95	1.12	1.17 ± 0.03
Na_2O	0.75	0.95	0.60 ± 0.04
K_2O	0.02	0.01	0.02 ± 0.008
P_2O_5	40.9	41.0	39.91 ± 0.19
BaO		0.03	0.02 ± 0.005
SrO		0.09	0.10 ± 0.015

75, was added to the foam under constant stirring at 1200 r.p.m. The foamed slip was then poured into filter-paper boxes for drying.

2.3. Slip production with a Buchner funnel

A different approach to those described above involved the use of a Buchner funnel. This device is normally employed to filter water through a ceramic disc with very fine pores (10–16 μm) when a partial vacuum is applied. Here the concept was reversed. The slip was prepared by mixing the powder, water and Decon 75 and using ultrasonics to disperse the powder if required. The slip was then poured into the mouth of the funnel which was connected to a compressed air line so that gas bubbled up through the fine pores of the filter disc and into the slurry. Special care had to be taken to keep the air pressure as low as possible to prevent damage to the funnel. After approximately 20 s the slip was foamed completely and was poured into filter-paper boxes. Extremely large bubbles were destroyed manually to obtain a more even pore-size distribution.

2.4. Separate slip and foam production with stabilizing agent

Settling and drainage were common problems encountered during the first part of the drying stage for all the above routes. This caused the foam lamellae to thin and ultimately to collapse. Agar powder was found to be a suitable stabilizing agent to prevent this and three levels of addition, 0.03, 0.067 and 0.1 g/g ceramic powder, were investigated. Agar is a linear polymer which is extracted from seaweed and is thus a heterogenous material. It does not dissolve in water at room temperature, but gelling can be initiated at temperatures above about 70 °C. A stable, heat-resistant gel is then formed on subsequent cooling to below 20 °C [6, 7]. Although gel strength is primarily determined by the agar concentration and its molecular weight, different batches can contain impurities such as polysaccharides, salts and proteins and a range of additives. The latter are generally used to produce special grades of low gelling-temperature agar and hence the temperatures quoted above can vary slightly.

The use of the stabilizing agent required a slight modification to the processing route. Hence after preparing slips with the required amounts of HA powder, water, Decon 75 and agar powder, the mixture was homogenized and then slowly heated up to 80 °C on a hotplate under constant stirring with a laboratory mixer. Meanwhile a separate water/Decon 75 foam was prepared as described above. The hot slip

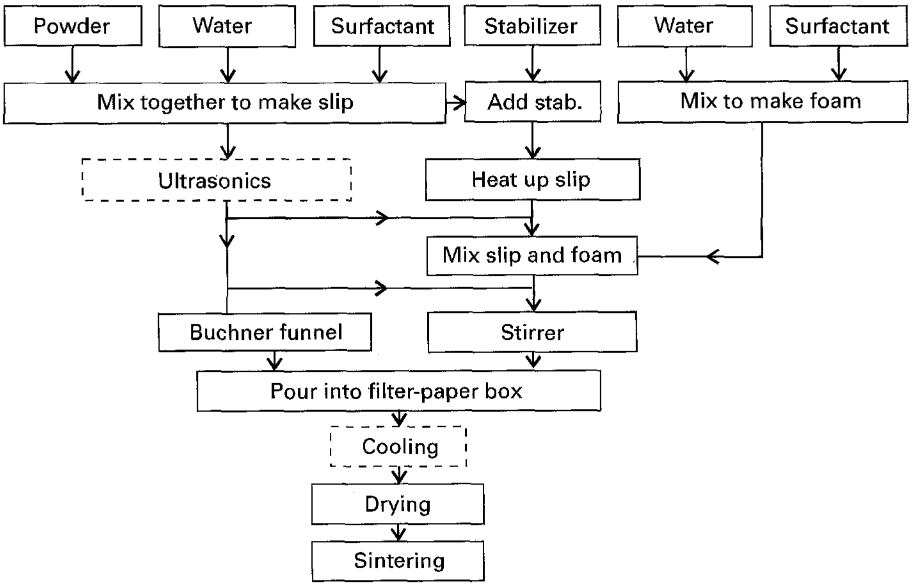

Figure 1 Flow chart of production routes.

was then added to the foam under constant stirring at 1200 r.p.m. This homogenized and foamed the mixture further. After approximately 2 min the foam structure became uniform and the foamed slip was then poured into filter-paper moulds. These containers were transferred to a refrigerator to cool the green body down to 6 °C and set the gel before drying.

The pH of the slips was monitored with a pH meter with an automatically compensating temperature probe prior to agar addition and the foaming stage. In addition, the viscosity and zeta potential of various slip compositions was measured to determine their rheological properties.

The drying time varied from 1–2 days depending on room temperature and humidity. The use of filter-paper boxes as moulds promoted even drying from all sides because water from the slip could penetrate the filter paper and evaporate. Some specimens were dried in an environmental cabinet in order to work under more controlled conditions. Various temperatures and humidities were used within the ranges 45–70 °C and 50%–95% relative humidity.

Once dry, the green bodies were carefully removed from the filter-paper boxes and placed on to alumina plates in a furnace for sintering at temperatures ranging from 1000–1350 °C. Unless otherwise stated, a heating rate of 1 °C min^{-1} and a hold time of 90 min were used. The cooling rate averaged 4–5 °C min^{-1}.

The sintered samples were examined with an optical microscope and an image analysing system. A video camera transferred optical information from the microscope into a computer where the analysis was performed by PC Image (Foster Findlay, Newcastle-upon-Tyne, UK). This technique allowed the percentage of porosity of the specimens to be determined. Pore-size distributions were calculated using a purpose-written computer program which allowed for the fact that when a porous body is cut in any particular plane, the statistical probability that the pores are cut at the maximum diameter is very low.

A scanning electron microscope operating in secondary electron imaging mode was used to obtain micrographs of the powders and the sintered porous ceramics. All samples were sputter coated with either gold or aluminium and an accelerating voltage of 10 kV was used.

3. Results and discussion

3.1. Viscosity

The viscosity of all the slips was found to be influenced by two principal parameters: (i) the pH of the powder, which itself depends on the Decon 75 concentration in the slip and the grade of powder, and (ii) the solid content of the slips. Although the pH of the slips was slightly affected by the various water-soluble salts present as impurities in the powders, slip pH was mainly influenced by the addition of Decon 75. It is a strongly alkaline surfactant with a pH of 13.8 and hence its presence increased the slip pH irrespective of the solids content of the slips. An increased Decon 75 concentration thus resulted in a decrease in slip viscosity due to an increase in particle repulsion and hence a decrease in flocculation.

However, if the level of Decon 75 was increased above approximately 50 mg/g powder no significant further decrease in slip viscosity was observed. When combined with zeta potential measurements, this suggests that complete coverage of the powder particles was achieved preventing particle coagulation. For Decon 75 concentrations above 60 mg/g powder increasing slurry viscosities were noted and dilatant slip behaviour was observed at higher shear rates. This suggests that the excess Decon 75 in solution interacted with the surfactant molecules already coating the powder particles. Hydrogen-bond formations or entanglements between the polymer chains in solution and those adsorbed on the particle surface will have increased the effective diameter of the powder particle and hence disturbed the flow of the particles. Micelles and hemimicelles formation was another unwanted effect at high surfactant concentrations.

An increase in the solid content of the slips increased their viscosity, albeit not linearly. Thus high solid content slips were generally favoured for producing ceramic foams because: (i) the resulting foams exhibited a high green strength due to an increased amount of ceramic between each bubble and a reduction in the tendency of the bubbles to coalesce; and (ii) they displayed pseudoplastic behaviour, i.e. during shearing the viscosity decreased significantly but increased again when stirring stopped.

Unfortunately above a certain limit for each slip, the viscosity became too high to entrap air bubbles preventing foaming. The Buchner funnel method was most susceptible to this effect, hence the impossibility of using this method with the high-viscosity agar-stabilized slips.

3.2. Foam production without stabilizing additions

The simplest method of producing a foamed slip of controlled volume and narrow range of pore-size distribution involved the use of the stirrer. No specialized equipment was needed, it was easy to clean and the blade design could be changed to match various requirements. For example, if propeller-shaped blades were chosen, a fairly dense body was produced, whilst a whisk-type blade produced foams of lower density. A blade speed of 1200 r.p.m. and a stirring time of 2 min was found optimum for the latter blade design. All other factors being equal, the separate slip and foam production route yielded green foams with a higher level of porosity compared with the simultaneous production of slip and foam.

High-viscosity slips could not be foamed using the Buchner funnel because an air pocket formed underneath the slip. Other disadvantages compared with the stirring method were the relatively large (> 2000 μm) pores created by air bubbling through the slip which limited the green strength of the foam. The only benefit of this technique was the simultaneous foaming and drying of the slip by the air bubbling through it.

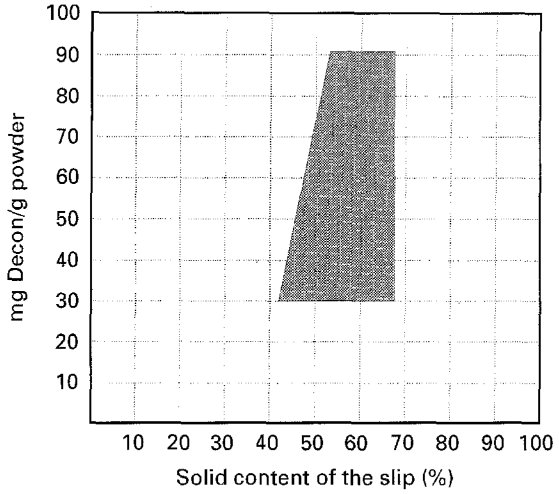

Figure 2 Production range of foamed H grade slips without stabilizing additions.

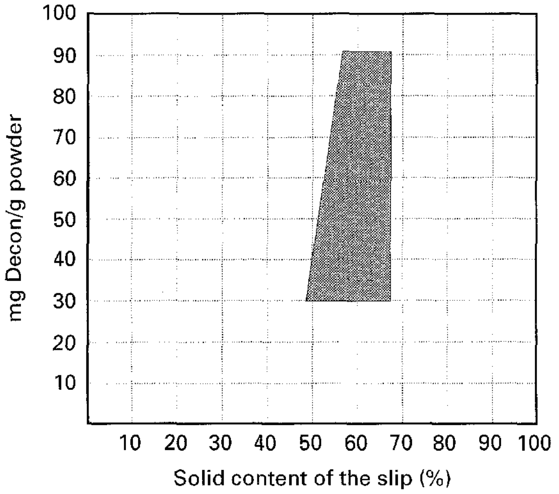

Figure 3 Production range of foamed M grade slips without stabilizing additions.

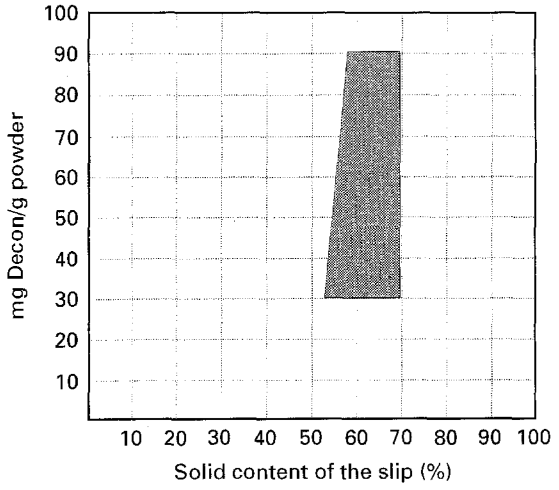

Figure 4 Production range of foamed L grade slips without stabilizing additions.

Figs 2–4 show the range of processing conditions which yielded successful production of foamed green bodies by the separate slip and foam production route. Although it was easier to foam slips with lower solid contents due to a lower viscosity, these foams were not stable below the limits shown in the figures and collapsed while drying. This was due to high drainage rates and very high porosity which decreased stability. In other words the solid content was so low in these cases that the foam was not able to support its own weight during drying.

Within the permitted range the slips with the lower solid content displayed a gradient in the size of the bubbles from the bottom to the top of the foamed slurry. The bottom region of the foam was under higher pressure due to the weight of the foam on top, so that the bubbles became smaller. Larger bubbles also rose in the slip due to their larger buoyancy forces.

The upper limit of the solid loading was determined by the ability of the water to coat the particle surfaces of the ceramic. Thus the upper loading limit was not only influenced by the solid content but also by the particle size of the ceramic powder. Because the H grade powder had the smallest particle size it showed the smallest maximum production range.

3.3. Foam production with stabilizing agent

Although highly porous foams were produced without the addition of stabilizing agents, the green strength of these specimens was not always sufficient for handling. The use of stabilizing agents increased the slip viscosity and so yielded higher green strengths and reduced drainage of water during the drying stage. Unfortunately, the higher viscosity also made it more difficult to foam the slips, necessitating a compromise between the conflicting requirements.

Agar was found to stabilize the foamed green bodies in two ways. Firstly, the slip viscosity was increased in the initial gelling process because water was entrapped in the gel structure and consequently could not drain as quickly from the foamed body. Secondly, the agar gel gave the foam structure sufficient mechanical strength to support its own weight. Agar also increased the drying times of the green bodies from approximately 24 h to approximately 48 h. Hence there was a reduced risk of cracking due to high moisture gradients.

It was found that the 0.067 g agar/g ceramic powder addition level was generally the most successful compromise concentration. Even slips with low solid contents, for example 35 wt %, were stabilized. Slips with a solid content as high as 60 wt % were generally more stable anyway, and in fact the addition of agar in these cases could be detrimental as the slip viscosity was increased too much, leading to poor foaming characteristics. Production ranges of the three different slip compositions are shown in Figs 5–7 for two stabilizing additive levels. If these are compared with Figs 2–4 it can be seen that, in general, use of agar powder increased the production range towards slips with lower solid contents.

3.4. Drying

For slips with a lower solid content, a higher drying temperature (60 °C) was favourable, because this

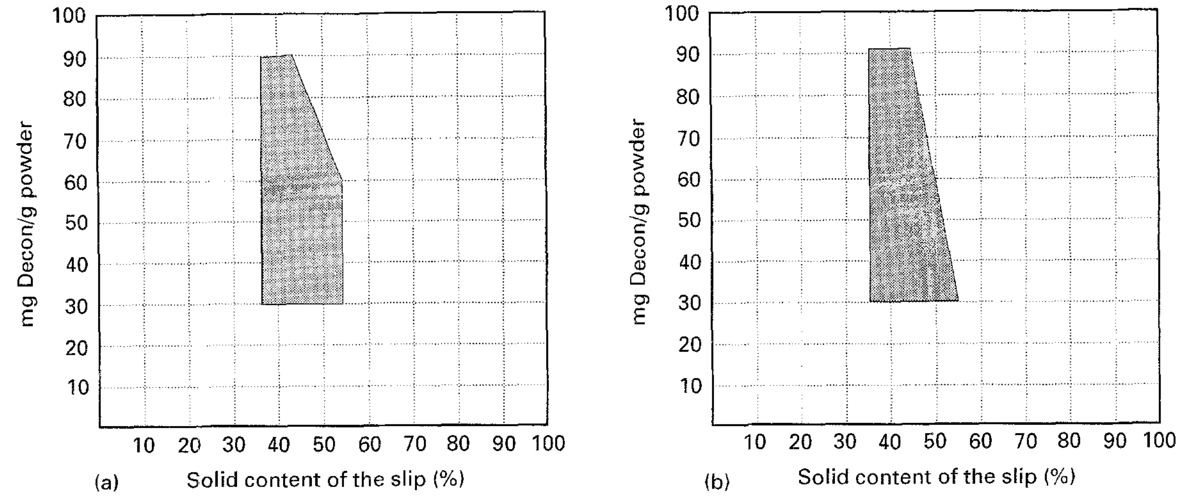

Figure 5 Production range of foamed H grade slips with agar: (a) 0.067 g agar/g powder, (b) 0.1 g agar/g powder.

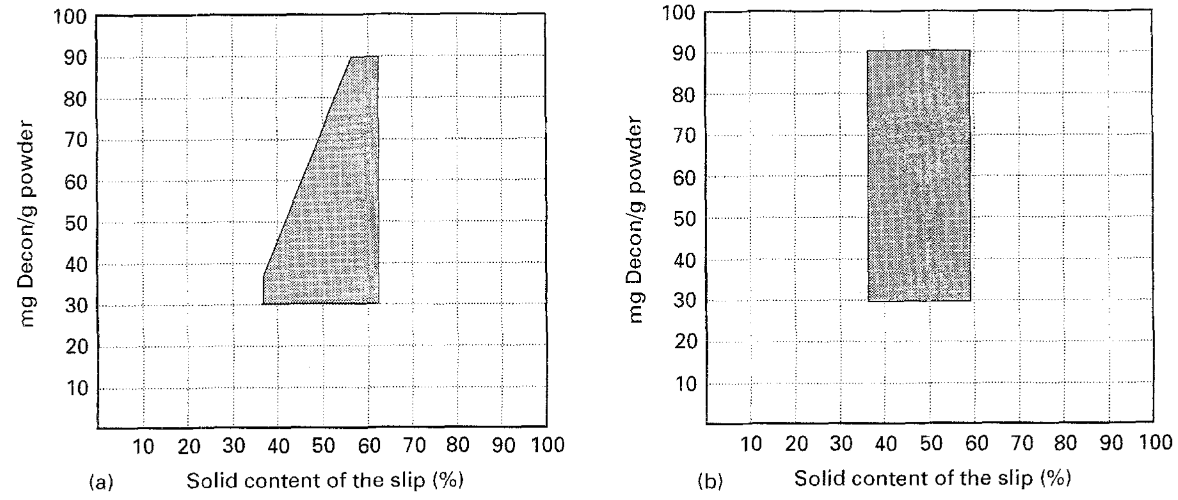

Figure 6 Production range of foamed M grade slips with agar: (a) 0.067 g agar/g powder, (b) 0.1 g agar/g powder.

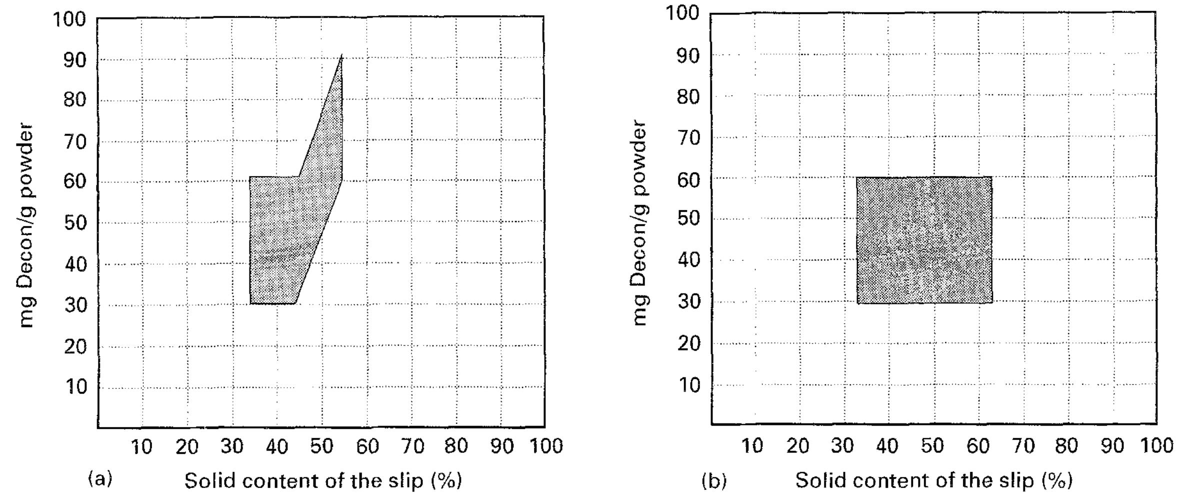

Figure 7 Production range of foamed L grade slips with agar: (a) 0.067 g agar/g powder, (b) 0.1 g agar/g powder.

meant that the time to immobilize the particles was shorter and less drainage would occur. For higher solid content slips, a lower temperature (40 °C) was chosen, because a low moisture gradient was desired to prevent cracking. Drainage was not the main problem in these cases.

Specimens containing no stabilizing agent had to be dried very slowly in a humidity chamber at > 45 % relative humidity to prevent uneven drying which caused surface cracks. If agar was used to stabilize the slips it was found unnecessary to dry specimens in the humidity chamber because the gel gave the specimens sufficient stability. In all cases, the shrinkage of the foam volume during drying was typically approximately 30%.

3.5. Sintering

The optimum sintering temperature was found to be 1350 °C with a heating rate of 4–5 °C min^{-1}. Specimens sintered at lower temperatures were not sufficiently strong. In these experiments, it was found necessary to maintain the sintering temperature for 90 min and then allow the furnace to cool at an average rate of approximately 1 °C min^{-1}. In this way thermal stresses in the sintered foams were reduced. The average shrinkage in volume of the porous specimens during sintering was approximately 60%.

3.6. Microstructures

The H grade ceramics did not show well-defined pores (see Fig. 8a) due to the thin walls between the pores rupturing during processing as a result of drainage. During sintering, the edges of these ruptured walls were rounded off, producing a network of open channels which made it impossible to determine pore-size distributions. The bridges showed "microporosity" in the range of < 1–2 µm at high magnifications (see Fig. 8b). These micropores arose from the non-fully dispersed nature of the ceramic slip and resulted in a higher surface area. The grain size was fairly uniform at about 3 µm.

The M grade bone ash exhibited more structured pores (see Fig. 9a) compared to the pure H grade filters but a less uniform microstructure. Again the interpore walls ruptured at their thinnest parts during production; however, the sharp edges remained during subsequent processing. Higher magnifications (see Fig. 9b) revealed that the average grain size was larger than in the H grade filters, individual grains varying between 2 and 12 µm in size, and the majority of the grains were not spherical. The bridges showed microporosity, but were denser than the H grade filters.

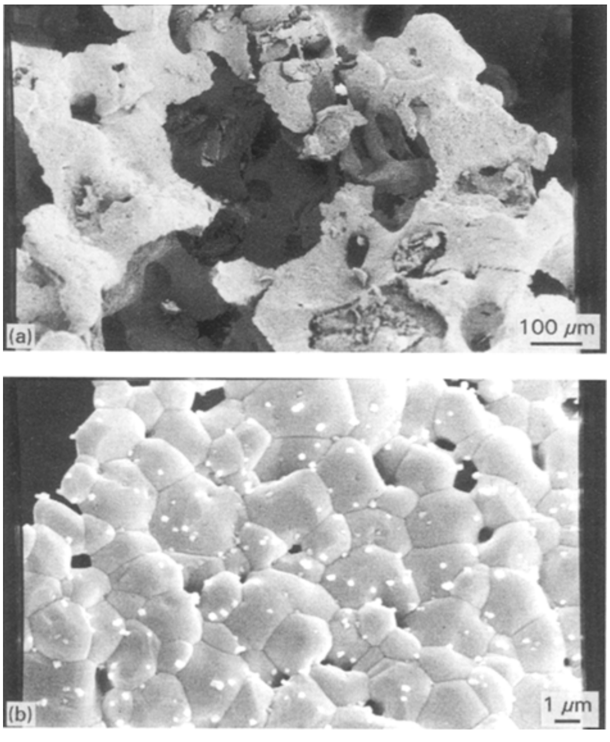

Figure 8 (a) Micrograph of an H grade filter. (b) Higher magnification of (a).

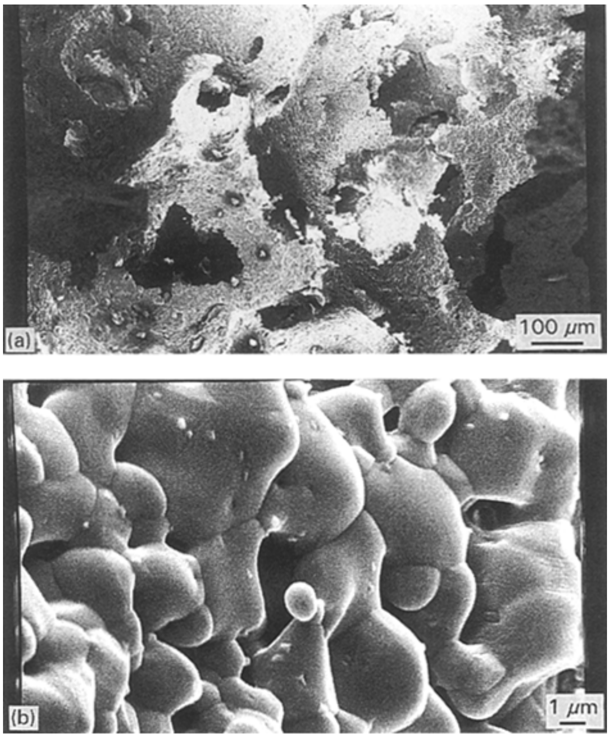

Figure 9 (a) Micrograph of an M grade filter. (b) Higher magnification of (a).

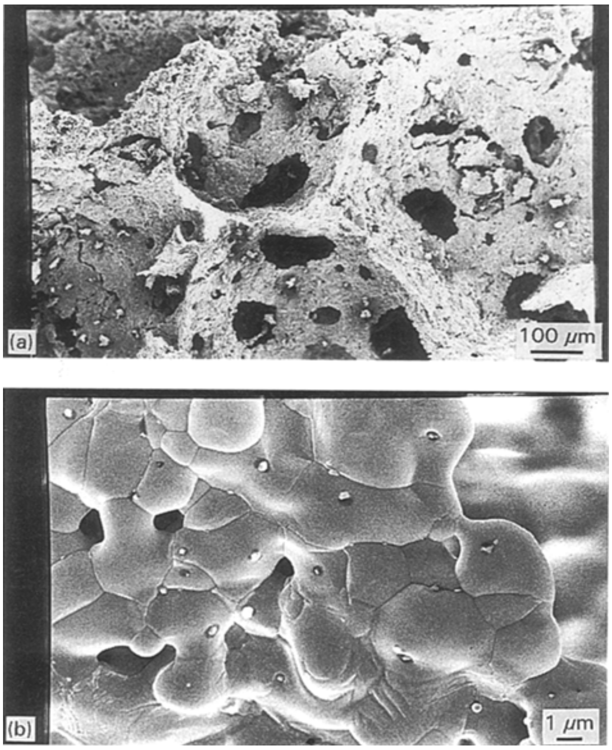

Figure 10 (a) Micrograph of an L grade filter. (b) Higher magnification of (a).

For the L grade ceramics, well separated pores were clearly detected at low magnifications (see Fig. 10).

Again the pore walls ruptured during production at the thinnest part. The entire network appeared less structured than the M grade ceramics but more structured than for the H grade material. The pore bridges exhibited a very small amount of microporosity and showed a grain size of 2–5 μm. The grains seemed well bonded and the struts denser than those of the other filters.

Nodules of approximately 0.3 μm diameter were visible at very high magnifications (see, for example, Fig. 8b) with their highest concentration being on the H grade filters. It was impossible to detect any difference in the chemical composition of these nodules compared to the matrix by either back-scattered electron imaging or energy dispersive X-ray analysis (EDX). Hence it is suspected that they were HA crystals growing on the surface by dissolution and reprecipitation of the bulk material. It is believed unlikely that they were water-soluble salts which precipitated out on the surface because it was impossible to remove them by washing the ceramics.

All three grades of hydroxyapatite-based foam produced showed substantial evidence of the pore walls rupturing during production at the thinnest part. This is believed to have been caused by one or both of two well-known mechanisms [4] : (i) gravity, which causes the liquid to drain to the bottom of the foam (this results in thinning of the upper lamellae first until they eventually collapse); (ii) liquid also drains from the lamellae into the region where more than two bubbles touch. This is due to a pressure gradient within the film towards the Gibbs triangle due to the different radii of curvature of the cell walls and the Gibbs triangle. This thinning of the lamella can eventually cause it to collapse.

4. Conclusion

Hydroxyapatite-based ceramic foams with densities $> 15\%$ and an open cell structure have been produced by the foaming of unstabilized and stabilized hydroxyapatite-based ceramic slips.

The unstabilized slips exhibited a low viscosity and were easily foamed but resulted in bodies with a low green strength due to (i) the thin struts containing the slip not being strong enough to support the weight of the foam, (ii) thinning of the foam lamellae by drainage of water and powder particles. This, in turn, was caused by gravitational forces and/or a difference in pressure between the cell wall and the Gibbs triangle, resulting in high moisture gradients. A network of interconnecting struts was left behind which had almost completely collapsed; (iii) the coalescence of bubbles in the wet state of the slip. Gas passed through the cells walls and thus larger bubbles expanded at the expense of the smaller ones. This increase in pore size decreased the foam stability.

The agar-stabilized slips exhibited a higher viscosity. They showed a correspondingly higher green strength (they were quite handleable) and a lower drainage rate, but entrapment of air was difficult.

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References

1. J. C. HEUGHEBAERT and G. BONEL, in “Biological and Biomechanical Performance of Biomaterials”, edited by P, Christel, A. Meunier and A. J. C. Lee (Elsevier Science, Amsterdam, 1986) pp. 9–14.
2. J. REICHERT and J. G. P. BINNER, *J. Mater. Sci.* **31** (1996) 1231.
3. A. SLÓSARCZYK and J. PARZUCH, *Sprechsaal* **122** (1989) 745.
4. M. J. ROSEN, “Surfactants and Interfacial Phenomena”, 2nd Edn (Wiley, New York, 1989) Ch. 9 and pp. 276–303.
5. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, “Introduction to ceramics” 2nd Edn (Wiley, New York, 1976) pp. 484–85.
6. H. D. BELITZ and W. GROSCH, “Lehrbuch der Lebensmittelchemie” (Springer, Heidelberg, 1982) pp. 48–52.
7. HILKEN DE GROOT-BÖHLHOFF, *Europa Lehrmittel* (1990) 238.

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