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Preparation of sintered filter for ion exchange by a doctor blade method with aqueous slurries of needlelike hydroxyapatite

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Abstract

Sintered, needlelike hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$) filters for an ion exchange were prepared by a doctor blade method to use in strongly acidic regions. The best slurry for tape casting was a mixture of 20 mass% HAp, 15 mass% binder, 15 mass% plasticizer, 1 mass% dispersant, and solvent (water). Tapes without cracks, obtained after freeze drying, were sintered at 1200°C for 1 h. Cation exchange between Ca^{2+} and Pb^{2+} was attempted by passing a $Pb(NO_3)_2$ solution at pH2 through a filter cut from the sintered, needlelike HAp tapes. Approximately 59% of the Pb^{2+} ions were removed with the first run, and that figure reached ~100% after five more runs with the same filtering procedure. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

Hydroxyapatite (HAp;$Ca_{10}(PO_4)_6(OH)_2$) has been studied in various ways for use as artificial bone and tooth substitutes, since HAp is the main inorganic component of the bones of human beings and animals [1–5]. HAp, however, also exhibits other important properties of cation exchange between Ca^{2+} ions and heavy metal or harmful ions [6,7], such as Pb^{2+}, Cd^{2+}, Mn^{2+} and $C0^{2+}$, as well as adsorption of proteins [8–10]. The ion exchange properties of HAp become important for removing the heavy metal ions contained in factory waste water, as environmental concerns have increased on a worldwide scale. Sintered filters of needlelike HAp therefore are necessary to facilitate handling in strongly acidic regions [11]. No previously published works, however, have reported needlelike particles of HAp sintered above 800°C. In the present work, filters without cracks after sintering were prepared by a doctor-blade method from aqueous slurries composed of needlelike HAp particles and forming aids, and the cation exchange between Ca^{2+} of HAp and Pb^{2+}, a heavy metal ion, was investigated using the sintered filters.

2. Experimental procedure

Needlelike HAps were synthesized by a wet method for the present study [12]. Aqueous solutions Of $CaCI_2$ (A) and Na_2HPO_4 (B) with a molar ratio of A/B = 1 were slowly and simultaneously dropped, with stirring, into water (C) heated at ~100°C. Needlelike $CaHPO_4$ precipitates first were synthesized, followed by needlelike HAp particles after the addition of KOH solution. The precipitated powders were filtered with suction and washed until they contained no residual ions, then (1) dried at room temperature or (2) freeze-dried. The obtained precipitates were confirmed with all needlelike HAp by X-ray diffraction (XRD) and scanning electron microscopy (SEM) (Fig. 1). Fig. 2 shows an experimental flow chart for preparation of the sintered filters. The aqueous slurries of HAp used for the doctor-blade method were prepared with forming aids such as binder (poly acrylic acid, PAA, average molecular weight (av.) = 2.5×10^5), plasticizer (polyetylene glycol, PEG, (av.):1000), and dispersant (polyacrylic ammonium salt, (av.):1.5×10^4). Mixing was accomplished carefully and without breaking the needlelike shapes of the HAp particles by using the balls coated with resin (17 mm in diameter) and the polypropylene jar. The fluidity of the slurries was checked with viscosity, measured by a rotating cylinder viscometer (MR-500, Rheology Co. Ltd., Japan). Tapes were cast using a doctorblade

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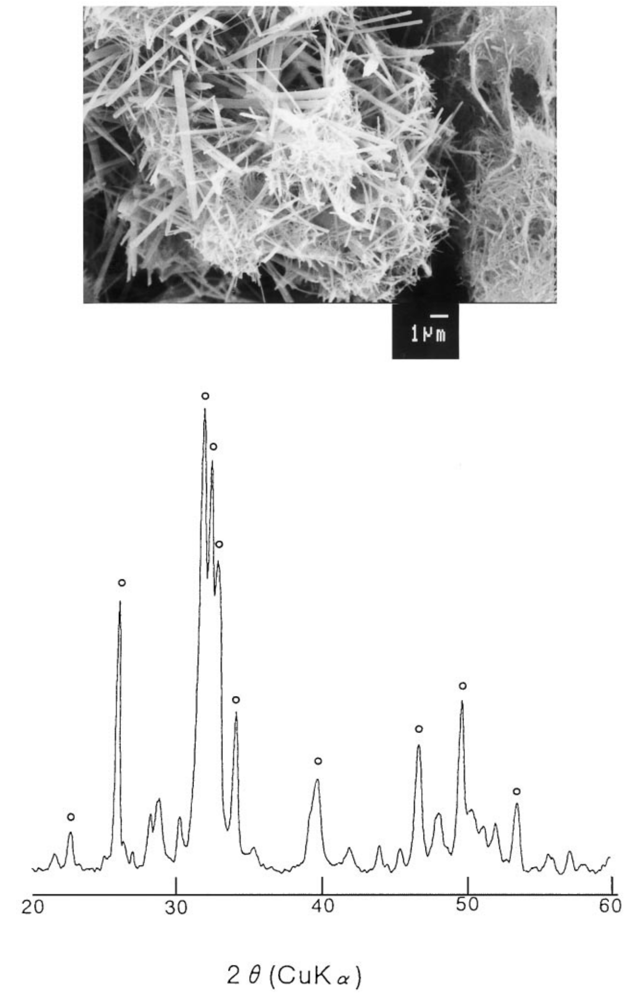


Fig. 1. SEM photo and X-ray diffraction pattern of precipitates. (○): HAp.

apparatus (DP-150, Tsugawa Seiki Co.Ldt., Japan) at a blade gap of 1 to 2 mm. After doctor-blading, half of the tapes were dried at room temperature and the remaining half freeze-dried. The obtained green tapes were burned out at 650°C, then sintered at 1200°C for 1 h. Cation exchange between Ca^{2+} and Pb^{2+} was investigated at pH2 using the sintered HAp filters cut from the doctor-bladed tapes.

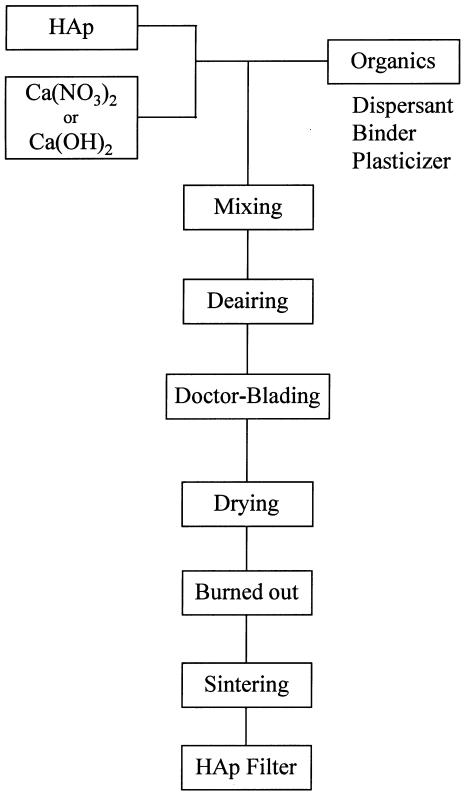


Fig. 2. Experimental flow chart for a preparation of sintered HAp filters.

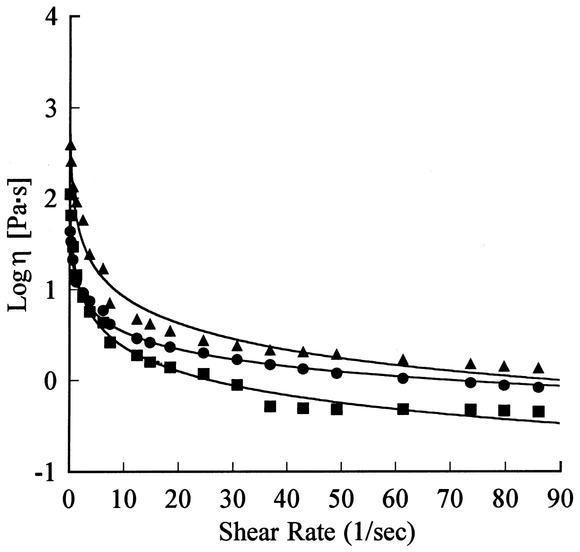
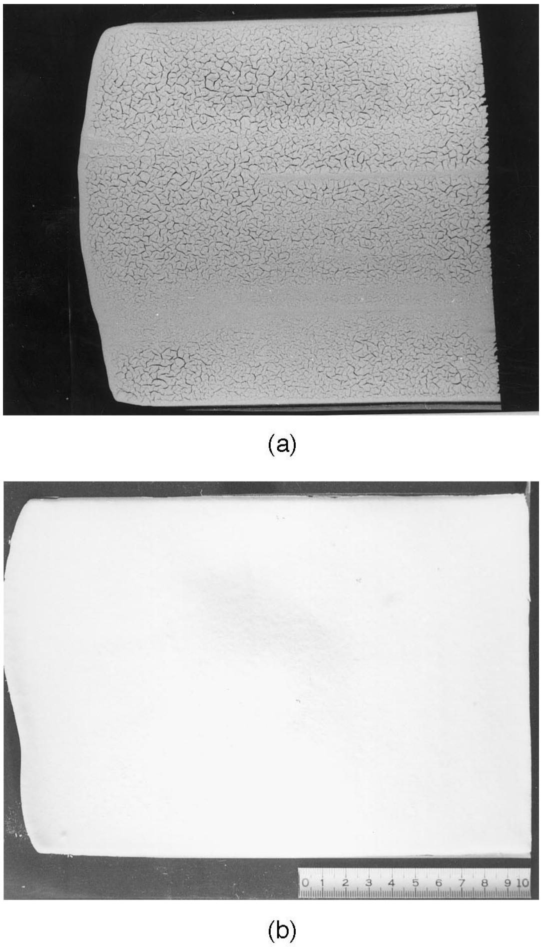


Fig. 3. Viscosities of aqueous slurries as a function of shear rate, for slurries added with $Ca(NO_3)_2$, (■): 0 mol, (●) : 1 mol and (▲): 2 mol.

3. Results and discussion

Shear thinning behaviour occurred in all of the present slurries containing forming aids (Fig. 3). The aqueous slurries could be cast with the present doctor-blade apparatus when the viscosity was less than ~10 Pa s or the HAp concentration below ~28 mass%. Tape casting therefore was conducted at a shear rate of 20–80 s^{-1}. The state of the obtained green tapes indicated that the best aqueous slurry for the present tape casting was a combination of 20 mass% HAp, 15 mass% binder, 15 mass% plasticizer, 1 mass% dispersant, and water. Many of the tapes cracked after drying at room temperature [Fig. 4(a)], but the freeze drying produced excellent tapes without cracks, as shown in Fig. 4(b). Cracks in the tapes prepared with needlelike particles



(a)

(b)

Fig. 4. Green tapes prepared by a doctor-blade method. (a): dried at room temperature; (b): freeze-dried.

may have been caused by heterogeneous shrinkage during drying at room temperature, since the freeze-dried tapes, which exhibited no shrinkage, had no cracks. The freeze-dried-tapes without the cracks were sintered at 1200°C for 1 h. The needlelike particles obtained by the present wet synthesis were only nonstoichiometric or Ca-deficient HAps, with a Ca/P ratio of ~1.54, as determined by inductively coupled plasma emission spectrometry (ICP). Nonstoichometric HAp converts to β and/or α tricalclum phosphate (TCP: $Ca_3(PO_4)_2$) above 700°C [11,13], and ion exchange and adsorption functions generally worsen after conversion to TCP. $Ca(OH)_2$ or $Ca(NO_3)_2$ thus was added in aqueous slurries to supply specified amounts of Ca-deficient HAps. Practically, the tapes added with 1 or 2 mol of $Ca(OH)_2$ or $Ca(NO_3)_2$ to 1 mol of HAp remained as HAp after sintering at 1200°C, but the untreated tapes converted into β and/or α TCP (Fig. 5). Detailed observation by SEM of the texture of the sintered tapes added with $Ca(OH)_2$ or $Ca(NO_3)_2$ showed porous structures composed of needlelike HAps, but the untreated tapes lost their needlelike shapes and exhibited grain growth

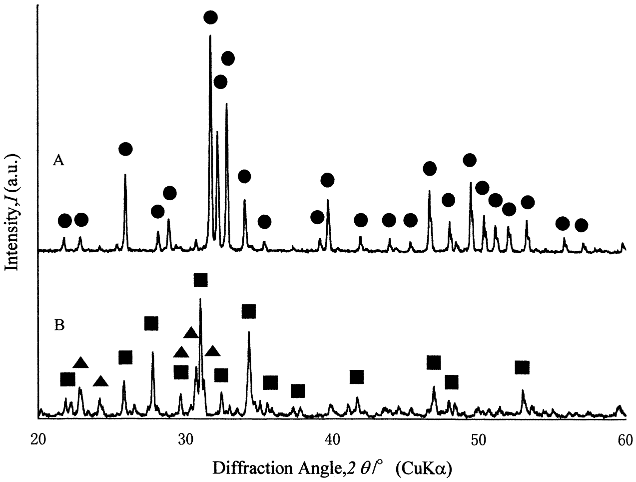
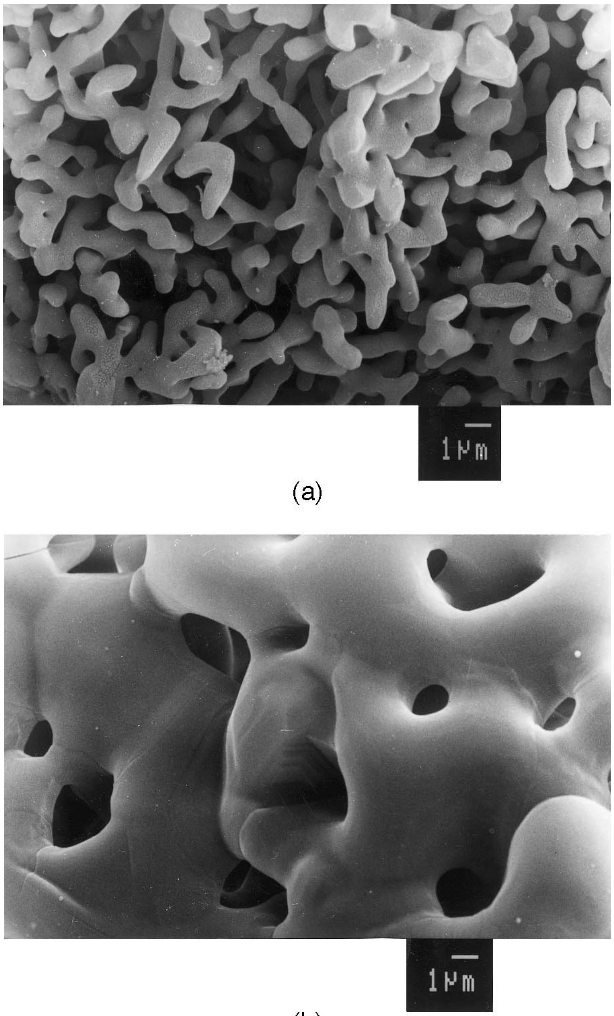


Fig. 5. X-ray diffraction patterns of HAp particles after sintering at 1200°C. A: added with 2 mol Ca $(NO_3)_2$; B: untreated (●) : HAp (■): β -TCP (▲): α -TCP.



(a)

(b)

Fig. 6. Tapes after sintering at 1200°C for 1 h. (a) : added with 2 mol Ca $(NO_3)_2$; (b): untreated.

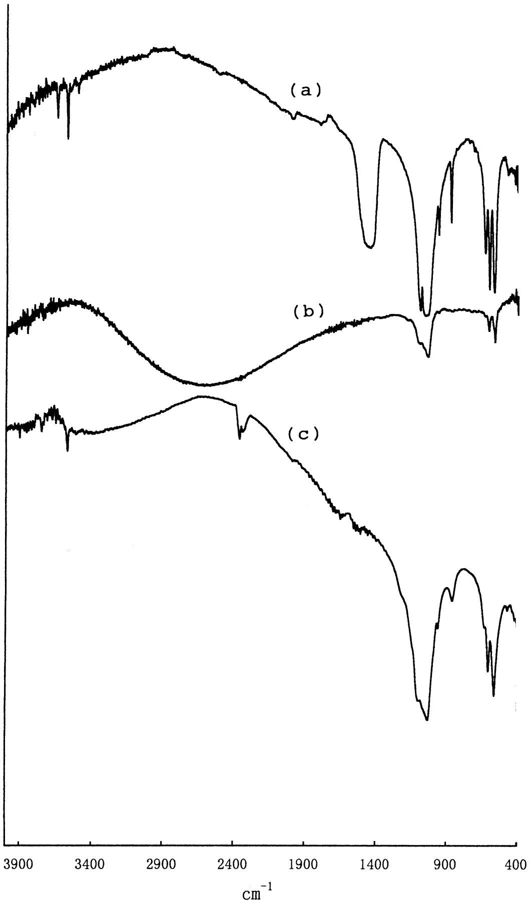


Fig. 7. Infrared spectroscopy of HAps before and after sintering at 1200°C. (a): before sintering (b): after sintering, untreated (c): after sintering, added with 2 mol $Ca(NO_3)_2$.

(Fig. 6). Moreover, after sintering at 1200°C, even the HAp with 2 mol of added $Ca(OH)_2$ or $Ca(NO_3)_2$ may have converted into an oxyapatite. Since such a conversion could not be distinguished clearly from the XRD patterns, the sintered tapes also were investigated by infrared spectroscopy (IR) (Fig. 7). A peak of structural OH groups of HAp unmistakably existed in the 3550 cm^{-1} region [13–15] in the HAp with 2 mol of added $Ca(NO_3)_2$ [Fig. 7(c)], but that peak disappeared in untreated HAp, as shown in Fig. 7(b).

Cation exchange between the Ca^{2+} and Pb^{2+}, a heavy metal ion, was attempted at $pH=2$ in the strongly acidic region, using filters cut from the sintered HAp tapes. Pb^{2+} solutions (0.025M) prepared with $Pb(NO_3)_2$ and using HCl to maintain the acidity at $pH=2$ were passed slowly through the filters at a rate of 0.12 dm^3/h. The same permeation procedure was repeated several times with the filtrates. Each filtrate was analyzed for Pb^{2+} ions using EDTA (ethylenediaminetetraacetic acid) titration. The results are shown in Fig. 8 as a function of the repeated runs. The removal of Pb^{2+} ions was ~59% with the first run and reached ~100% after repeated five repeated runs in the dilute $Pb(NO_3)_2$ solution, with far fewer Pb^{2+} ions than Ca^{2+} ions composing the HAp filter. After the removal measurement of Pb^{2+} ions, the structure of the HAp filters was investigated by XRD. Cation exchange between Ca^{2+} and Pb^{2+} ions had occurred without the adsorption of Pb^{2+} ions on to the HAp particles, since Pb-Cl-apatite was identified, as shown in Fig. 9. Sintered filter of HAp for ion exchange in strongly acidic regions therefore could be prepared using a doctor-blade method.

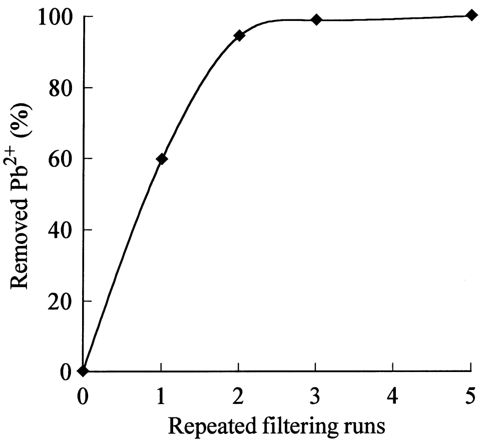


Fig. 8. Removal of Pb^{2+} ions as a function of repeated filtering runs.

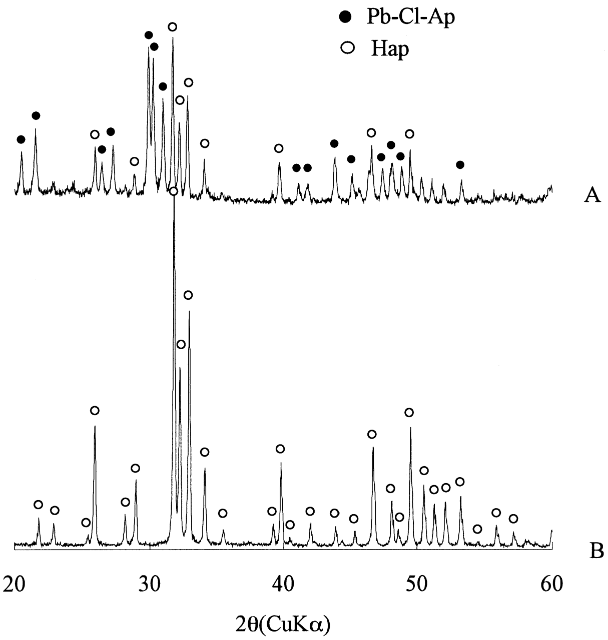


Fig. 9. X-ray diffraction patterns of HAp filters after and before removal measurements of Pb^{2+} ions. A: after; B: before.

4. Summary

Sintered, needlelike HAp filters for an ion exchange were prepared by a doctor-blade method to employ in strongly acidic regions. The results of the present study were as follows.

1. The best aqueous slurry for tape casting was a combination of 20 mass% HAp, 15mass% binder, 15 mass% plasticizer, 1 mass% dispersant, and-water containing specific amounts of $Ca(OH)_2$ or $Ca(NO_3)_2$.
2. Shear-thinning behaviour appeared in all of the aqueous slurries.
3. Tapes without cracks were obtained by sintering at 1200°C for 1 h after freeze drying.
4. The removal of Pb^{2+} ions was investigated by passing Pb^{2+} solutions through sintered, needlelike HAp filters at $pH = 2$. In the first run, ~59% of the Pb^{2+} ions were removed, and that amount reached ~100% after five runs under the same procedure.

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References

[1] T. Yamamuro, L.L. Hench, J. Wilson (Eds.), Handbook of Bioactive Ceramics, vol. II: Calcium Phosphate and Hydroxyapatite Ceramics. CRC Press, Boca Raton, FL, 1990 p. 39.
[2] M. Jacho, C.H. Bolen, M.B. Thomas, J.F. Kay, R. Doremus, J. Mater. Sci. 11 (1976) 2027.
[3] M. Akao, H. Aoki, K. Kato, J. Mater. Sci. 16 (1981) 809.
[4] M. Toriyama, S. Kawamura, S., Shiba, Yogyo-Kyokaishl 95 (4) (1987) 456.
[5] P.W. Brown, M., Fulmer, J. Am. Ceram. Soc. 74 (5) (1991) 934.
[6] T. Suzuki, K. Ishigaki, M., Miyake, J. Chem. Soc., Faraday Trans. 1 (80) (1984) 3157.
[7] J. Reicher, J.P. Binner, J. Mater. Sci. 31 (1996) 1231.
[8] A. Tiselius, S. Hjerten, O. Levin, Arch. Blochem. Biophys. 65 (1956) 132.
[9] T. Kawasaki, M. Nikura, Y. Kobayashi, J. Chromatography 515 (1990) 91.
[10] T. Kawasaki, M. Nikura, Y. Koibayashi, J. Chromatography 515 (1990) 125.
[11] S. Suzuki, T. Fujita, T. Maruyama, M. Takahashi, Y. Hikichi, J. Am. Ceram. Soc. 76 (1993) 1638.
[12] H. Hirano, T. Nishijima, T. Iwamura, Anal. Biochem. 150 (1985) 228.
[13] J.A.S. Bett, L.G. Christer, W. Keith Hall, J. Am. Chem. Soc. 89 (1967) 5535.
[14] D. Walsh, J.L. Kingston, B.R. Heywood, S. Mann, J. Cryst. Growth, 133 (1993) 1.
[15] L. Yubao, C.P.A.T. Klein, J. Dewijin, S. Van De Meer, K. De Groot, J. Mater. Sci.: Materials in Medicine, 5 (1994) 263, 326.