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β-Rhenanite (β-$NaCaPO_4$) as Weak Interphase for Hydroxyapatite Ceramics

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Abstract

Hydroxyapatite/bioactive glass laminate has been fabricated by hot pressing of stacked hydroxyapatite and bioactive glass powders at 1000°C (30 min, 30 MPa). This processing resulted in the formation of β-$NaCaPO_4$ *(*β*-rhenanite) interphase layers between each hydroxyapatite and bioactive glass layer. The* β-$NaCaPO_4$ *interphase provided an easy path for debonding and crack deflection in the laminate demonstrating that this material can work as weak interphase in hydroxyapatite ceramics. The* β-$NaCaPO_4$ *exhibits also high biocompatibility and bioactivity. Moreover, it significantly enhances sinterability of hydroxyapatite at 1000°C without formation of any undesired phases, such as tricalcium phosphate or CaO. Our results show that various microstructurally controlled hydroxyapatite-based composites with potentially improved reliability and high biocompatibility can be prepared in the hydroxyapatite/*β-$NaCaPO_4$ *or hydroxyapatite/bioactive glass systems. © 1998 Elsevier Science Limited. All rights reserved*

Keywords: hydroxyapatite, β-rhenanite, bioactive glass, weak interphase, laminates

1 Introduction

Hydroxyapatite [HAp, chemical formula $Ca_{10}(PO_4)_6(OH)_2$] is one of the most biocompatible materials due to similarities with mineral constituents of teeth and bones.[1–3] Mechanical reliability of pure HAp ceramics is not sufficient, especially in wet environments,[1–5] therefore the HAp ceramics can not be used as heavy–loaded implants, such as artificial teeth or bones. Its medical applications are presently limited to small unloaded implants, powders, coatings and low-loaded porous implants.[1–3]

Basic approaches to achieve materials with high mechanical reliability include improved processing and/or improved toughening.[6] The improved processing strategy does not seem to work for the HAp-based ceramics, because it is difficult to control the flaw size for a long time in the material exhibiting high susceptibility to subcritical crack growth.[4,5] The improved toughening strategy seems to be much more promising for the HAp-based biomaterials. This is in fact a classical approach, but not fully exploited yet for the HAp-based materials. The requirements for appropriate bone-replacement implants necessitate fabrication of highly reliable HAp ceramics with high strength while having pores with diameters of minimum 100 μm, to enable bone ingrowth and lower the Young's modulus.[2] It has been known that materials exhibiting the R-curve behavior become less flaw susceptible due to increase of fracture toughness with increasing crack (flaw) size caused by shielding mechanisms acting in the crack wake.[7,8] Therefore such reinforcements as metals,[9] PSZ,[10] fibers/whiskers,[11,12] etc., have been applied in the HAp ceramics to improve its reliability, as reviewed in Refs 3 and 13. However, there are several limitations of possible used reinforcements, because they must not decrease bioactivity and biocompatibility of HAp. Metals and PSZ are not appropriate materials due to bioinertness, corrosion, degradation in wet environments, difficulties with processing etc.[3,14] Finally, only fibers/whiskers remain as possible reinforcements. Among them, long fibers such as Al_2O_3, ZrO_2 or carbon cannot be used mostly due to processing problems (undesired thermal expansion mismatch,[9] decomposition of HAp[15]) and bioinertness.[2,14] Available bioinert whiskers (SiC, Si_3N_4 etc.) must not be used in bioceramics because of their carcinogenic nature.[16,17] Therefore the most promising reinforcements seem to be calcium phosphate fibers, especially the HAp whiskers or HAp long fibers.

HAp reinforced with HAp whiskers has been already prepared.[13,18] Unfortunately, significantly

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*To whom correspondence should be addressed. Fax + 81-45-924-5358; e-mail sucha1@rlem.titech.ac.jp improved flaw tolerance is not expected in this case, because of absence of a bridging zone and pull-out in the crack wake, due to lack of a weak whiskers/matrix interphase. Fabrication of highly reliable HAp reinforced with HAp whiskers and also other microstructurally controlled[19] HAp–based materials (for example fibrous, porous HAp[20]) could be possible if an appropriate weak interphase for HAp is found. The weak interphase must provide an easy path for debonding with subsequent bridging and pull-out phenomena. Moreover, application of such an interphase should not result in introduction of not biocompatible and not bioactive phases into HAp.

In this article we introduce β-$NaCaPO_4$ (β-rhenanite) as 'weak interphase' for the HAp ceramics. The β-$NaCaPO_4$ is a biocompatible and bioactive material. When applied with HAp it provides an easy path for debonding, does not cause decomposition of HAp, moreover it is an effective sintering agent.

2 Experimental procedure

HAp powder used in this study has been prepared hydrothermally in our laboratory.[21] It consisted of nonaggregated HAp crystals with a length in the range of 100–200 nm, a diameter of about 30 nm and a Ca/P molar ratio of 1·66. Small quantities of carbonate ions were incorporated in the lattice of HAp. Bioactive glass (Nikon Co. Ltd, Sagamihara, Japan) used in this study had following chemical composition (in mol%): 46·1% SiO_2, 24·4% Na_2O, 26·9% CaO, and 2·6% P_2O_5. β-$NaCaPO_4$ powder was prepared by heating a mixture of Na_2CO_3 and $Ca_2P_2O_7$ powders at 1000°C for 10 h.

The HAp powder and the bioactive glass powder were alternately stacked and pressed under 30 MPa in a graphite die. The laminated powder mixture was hot pressed (HP-ed) at 1000°C for 30 min under a pressure of 30 MPa in flowing argon (Hot Press, Shimadzu Co., Kyoto, Japan). Heating rate was $20° \min^{-1}$. The sample was cooled together with the hot press.

The HP-ed laminate was then cut into bars, notched perpendicularly to the plane of interphases (notch depth to bar thickness was $\approx 0{\cdot}5$) and tested in 3-point bending (loading rate $0{\cdot}01 \text{mm} \min^{-1}$). Subsequently, fracture surface was observed by a scanning electron microscope (SEM: JSM-T200, JEOL Ltd, Tokyo, Japan). Indentation technique using Vickers pyramid has been used to study crack propagation profiles and interactions with the laminate microstructure. A load of 10 N has been applied for 10 s to produce median cracks. Crack propagation was observed using an optical microscope. Phase composition of the composite was characterized by X-ray diffraction (XRD, 40 kV–40 mA, Cu Kα, MAC Science Co. Ltd, Tokyo, Japan). X-ray intensities for silicon, calcium, phosphorus and sodium were analyzed across the HAp/bioactive glass interphase using an energy dispersive X-ray microanalyser (EDX: SIGMA, Kevex Int., USA) connected with a field emission scanning electron microscope (model S-4500, Hitachi, Japan). Raman spectra were obtained across the HAp/bioactive glass interphase using a laser Raman spectrometer (T64000 Atago-Jobin Yvon, France-Japan) working in a micro mode. An Ar laser with a wavelength of 514·5 nm was used for excitation. The laser beam was focused to produce 1–2μm diameter spot.

To investigate influence of β-$NaCaPO_4$ on sinterability of HAp, HAp + 5wt% β-$NaCaPO_4$ powder mixtures were sintered at 1000–1100°C for 2 h in air. Shrinkage, microstructure, and phase composition of the sintered HAp + 5 wt% β-$NaCaPO_4$ materials were investigated.

For comparison, the HAp powder and the bioactive glass powder were separately sintered in air at 1000°C for 30 min. Subsequently, phase compositions of these materials were determined by XRD.

3 Results

The HP-ed laminate consisted of alternated layers (about 100 μm thick) of HAp and bioactive glass (Fig. 1). SEM allowed to distinguish a reaction layer (about 20 μm thick) between each HAp and bioactive glass layer (Fig. 1). Only hydroxyapatite (from the HAp layers), Na, Ca-silicates (from the bioactive glass layers) and β-$NaCaPO_4$ (β-rhenanite) were detected by XRD in the laminate (Fig. 2). β-$NaCaPO_4$ which formed the interface layer, was a product of the chemical reaction between HAp

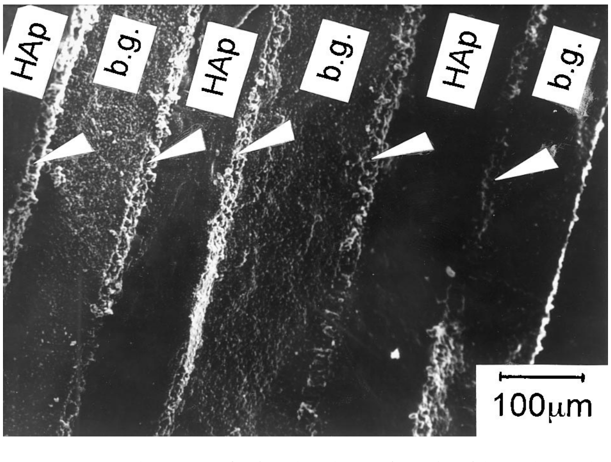

Fig. 1. SEM image of the laminated HAp/bioactive glass composite. Arrows indicate β-$NaCaPO_4$ interphase layers between each HAp and bioactive glass ('b.g.') layer.

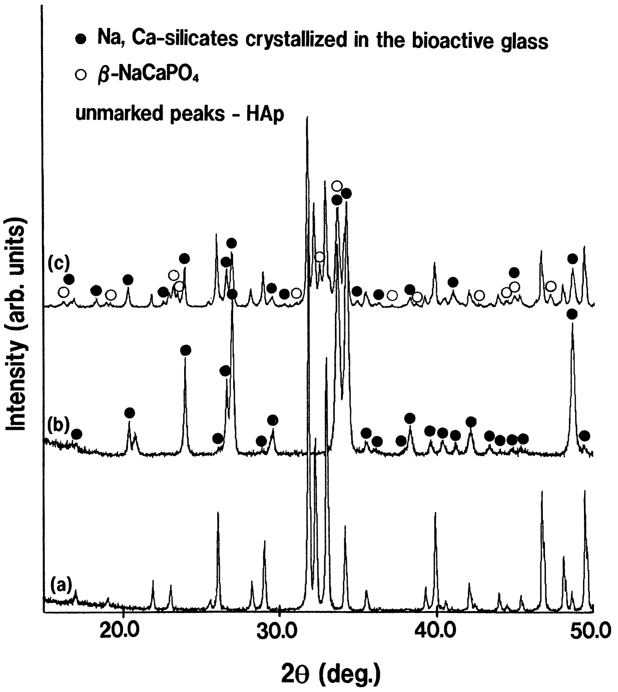

Fig. 2. XRD patterns of (a) HAp powder used in this study, after sintering at 1000°C (30 min) in air; (b) bioactive glass used in this study, after sintering at 1000°C (30 min) in air; (c) the HAp/bioactive glass laminate, after HP-ing at 1000°C (30 min, 30 MPa) in flowing argon.

and bioactive glass, as already reported in the literature.[22] Peaks derived either from β-$Ca_3(PO_4)_2$ (β-TCP) or $CaSiO_3$ (wollastonite) were not observed (wollastonite may be present, but its detection by XRD is difficult due to peak overlapping).

The interphase layer was characterized in detail using Raman spectroscopy (Fig. 3) and EDX (Fig. 4). Raman measurements gave us direct evidence that the interphase layer consists of β-$NaCaPO_4$ (β-rhenanite). Spectra acquired in the central part of the interphase layer [Fig. 3(c)] were almost identical to those obtained from the β-$NaCaPO_4$ standard [Fig. 3(d)]. However, some HAp-derived bands (PO_4-bands at 600–620 cm^{-1}; OH-band around 3570 cm^{-1})[23] have still been detected in the interphase layer near the HAp layer, suggesting presence of HAp/β-$NaCaPO_4$ mixture in this region.

Load–deflection curve of the laminated HAp/bioactive glass composite indicates not fully brittle fracture due to delamination and crack deflection (Fig. 5). Delamination and crack deflection occurred exactly on the β-$NaCaPO_4$ interphase layer (Fig. 6). Cracks propagating from both the HAp and bioactive glass sides were arrested at the β-$NaCaPO_4$ layer (Fig. 7). They were spread along the β-$NaCaPO_4$ layer forming arrays of cracks in both sides of the main crack in a similar way to that reported by Morgan and Marshall for the $Al_2O_3/LaPO_4$ laminate.[24]

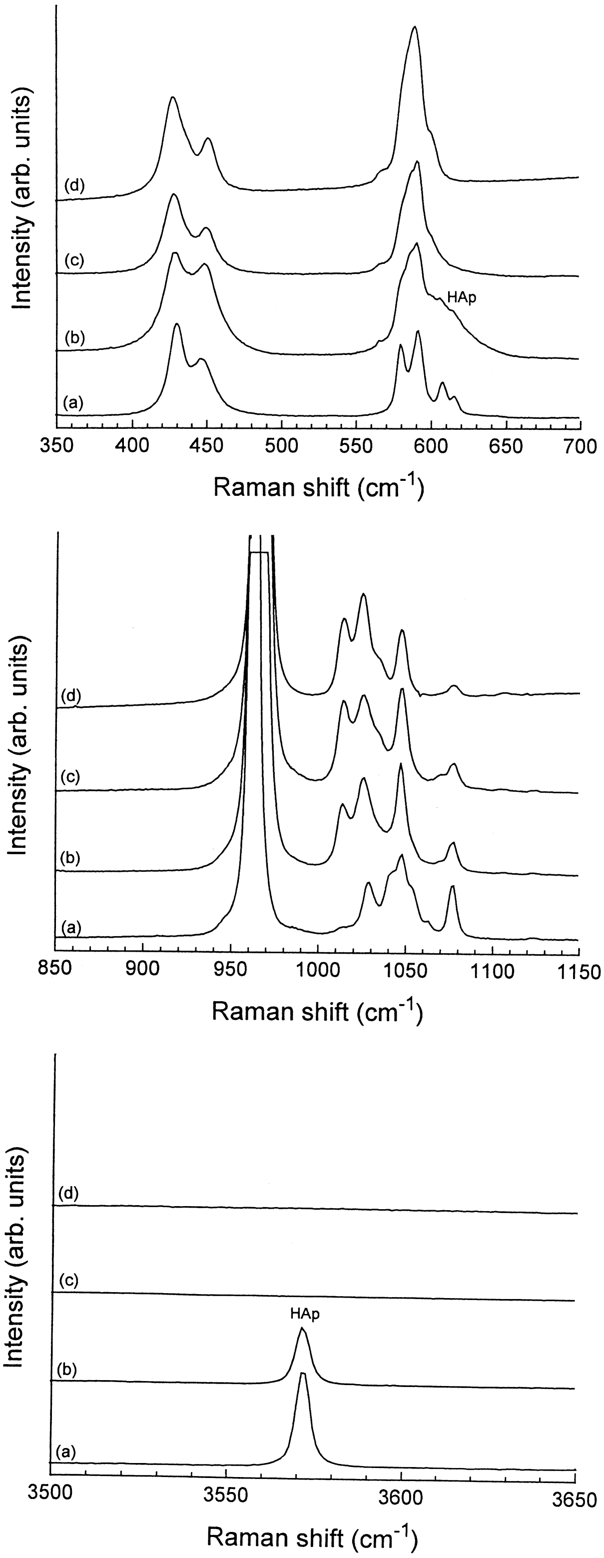

Fig. 3. Raman spectra of (a) HAp layer; (b) interphase layer close to the HAp layer; (c) center of the interphase layer; (d) β-$NaCaPO_4$ standard powder.

Five wt% of β-$NaCaPO_4$ (β-rhenanite) significantly enhanced sintering of the HAp powder at 1000°C (Fig. 8). This effect was less distinct when sintering was carried out at 1100°C. Only HAp- and β-$NaCaPO_4$-derived peaks were detected by XRD in the HAp + 5 wt% β-$NaCaPO_4$ materials sintered at 1000°C [Fig. 9(a)]. When sintering was

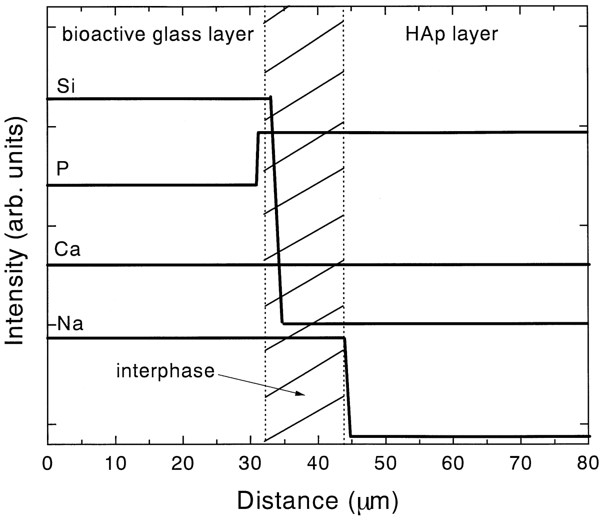

Fig. 4. Concentration profiles of selected elements measured by EDX across the interphase layer between HAp and bioactive glass layers.

carried out at 1100°C, also small quantities of CaO were formed [Fig. 9(b)]. The present sintering study of the HAp/β-$NaCaPO_4$ mixtures is in a good agreement with previous reports.[25]

4 Discussion

β-$NaCaPO_4$ (β-rhenanite) has been found in this study to act as weak interphase for HAp ceramics. Debonding abilities of the β-rhenanite have been demonstrated using the HAp/bioactive glass laminate. Generally speaking, the weak interphase determines mechanical properties of any microstructurally-controlled ceramic materials. Laminates, fiber (whiskers)-reinforced composites, fibrous monoliths with weak interphases belong to high-toughness and high-strength ceramic composites.[19] Good examples are SiC/SiC materials with a graphite interphase[26] or Si_3N_4 ceramics having rod-like grains, with a glassy interphase derived from sintering additives.[27] In such composites, the weak interphase is essential for debonding and subsequent bridging and pull-out effects thus improving considerably toughness of the material. On the other hand, in the whiskers–reinforced composites without a weak interphase (for example Si_3N_4 (whiskers)/Si_3N_4,[28] HAp(whiskers)/HAp[13,18]), crack propagates through the whiskers without debonding and related effects, thus significant improvement of mechanical reliability does not occur.

The β-$NaCaPO_4$ provides an easy path for debonding, additionally is biocompatible and bioactive.[22,29] It is worth to note that biodegradation rate of sintered bars of β-$NaCaPO_4$ *in vivo* is higher than biodegradation rate of HAp ceramics but lower than that of β-TCP ceramics.[30] However, particulate β-$NaCaPO_4$ does not exhibit resorption 6 months after implantation into teeth sockets but transforms fully into HAp.[31] Presently, it is difficult to say, whether the β-$NaCaPO_4$ would be an

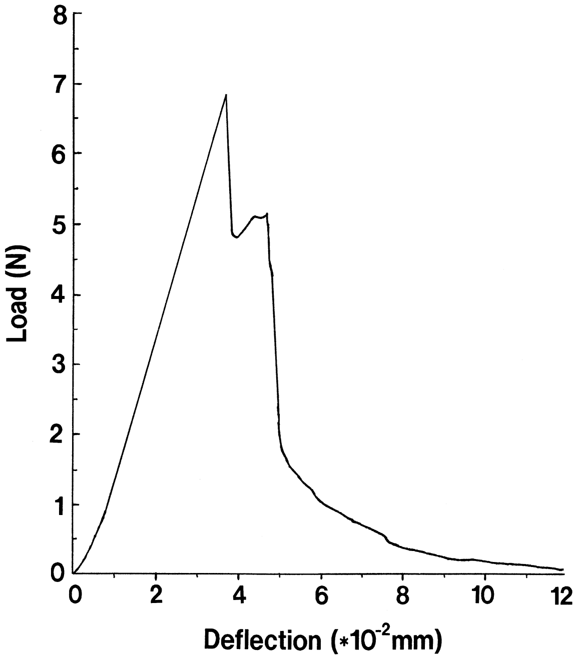

Fig. 5. Load–deflection curve of the notched HAp/bioactive glass composite.

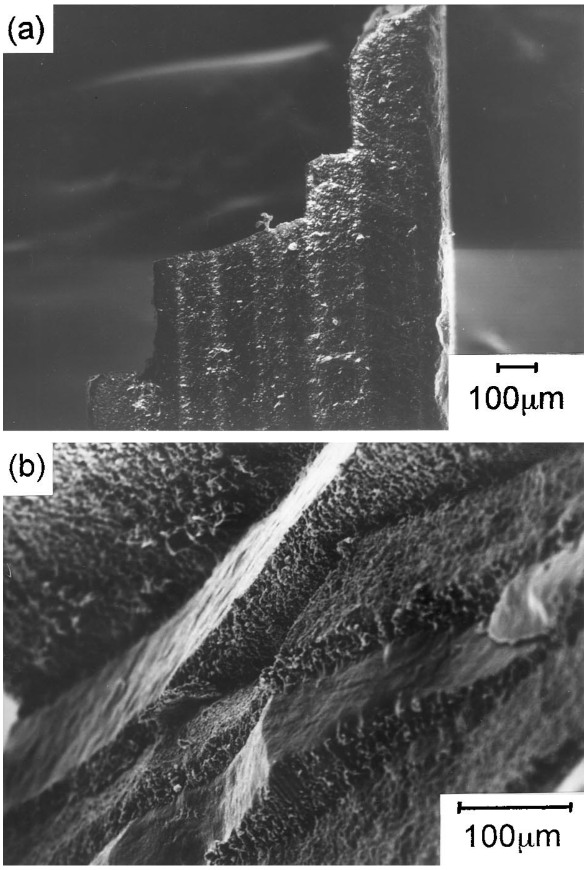

Fig. 6. SEM images of the fracture surface of the HAp/bioactive glass composite. Notice crack deflection on the β-$NaCaPO_4$ interphase layers.

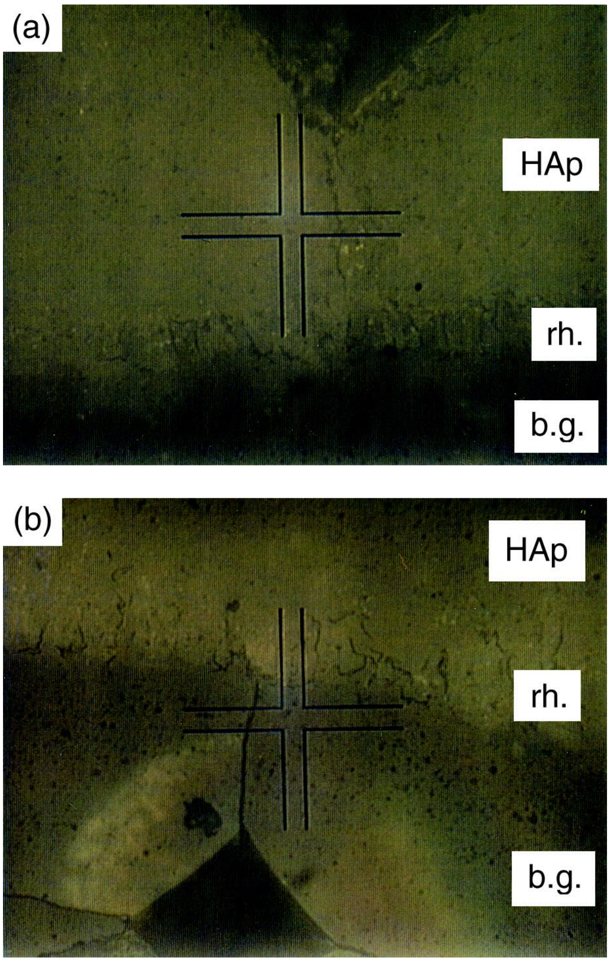

Fig. 7. Optical micrographs showing crack arrest at the β-NaCaPO$_4$ interphase layer and arrays of cracks spread along the interphase layer [b.g. denotes bioactive glass; rh. denotes β-rhenanite (β-NaCaPO$_4$)].

easy path for slow crack growth in the future HAp-based composites or not.

Especially important for further processing of HAp-based composites is that application of the β-NaCaPO$_4$ directly with HAp (without using the bioactive glass) at 1000°C does not cause formation of β-TCP, CaO, or other undesired phases. Moreover, the β-NaCaPO$_4$ is an effective sintering agent for HAp thus it could be also used to enhance densification of the HAp-based composites.[32]

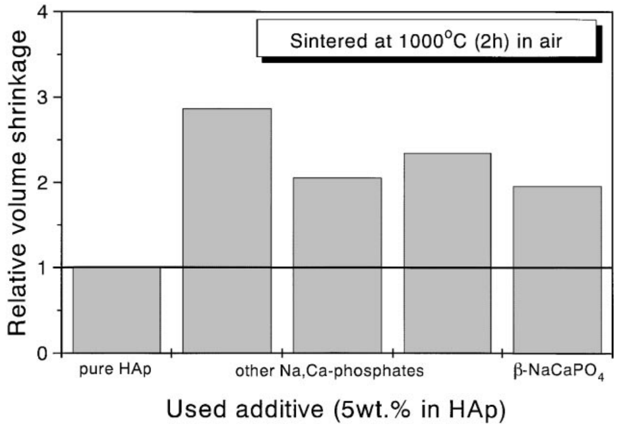

Fig. 8. Volume shrinkage of the HAp + 5 wt%Na,Ca-phosphates materials relative to shrinkage of pure HAp sintered under the same conditions (1000°C, 2 h, air). Data for other Na,Ca-phosphates were taken for comparison from Ref. 32.

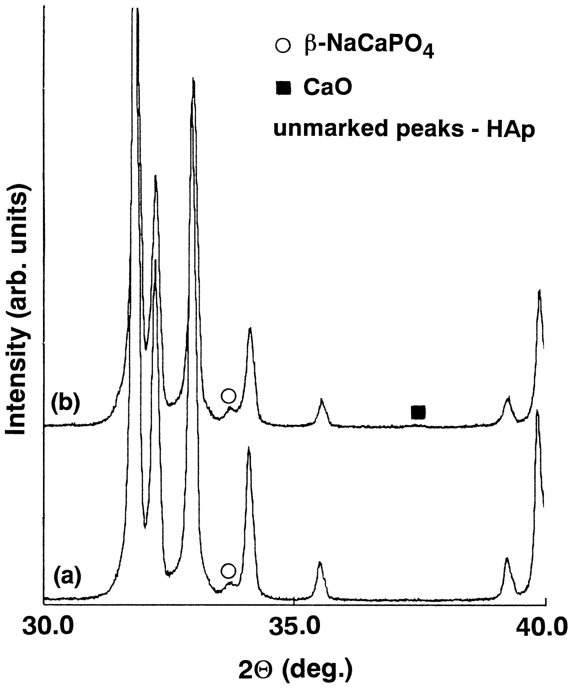

Fig. 9. XRD patterns of the HAp + 5 wt%β-NaCaPO$_4$ mixtures sintered in air at: (a) 1000°C (2 h); (b) 1100°C (2 h).

Apart from the use of β-NaCaPO$_4$ as weak interphase, we introduce in this paper also laminate approach applied to both HAp and bioactive glass. Heat treatment of the HAp/bioactive glass system results in formation of β-NaCaPO$_4$ at the interphase, without decomposition of HAp. Raman and EDX measurements (Figs 3 and 4) strongly suggest following model for the reaction between HAp and bioactive glass: (1) diffusion of Na from the bioactive glass layer into HAp layer; (2) diffusion of Ca from HAp layer into bioactive glass layer; (3) transformation of HAp grains (Ca-deficient, Na-rich) into β-NaCaPO$_4$ and formation of the interphase layer by consumption of the HAp layer; (4) limited diffusion of Si from bioactive glass layer to HAp (β-NaCaPO$_4$) layer. Our observation is consistent with earlier reports of Kangasniemi *et al.*[22] who studied reaction between single HAp crystals embedded in a bioactive glass matrix.

We have not observed any distinct porosity in the β-NaCaPO$_4$ interphase layers. We suppose that the β-NaCaPO$_4$ intephase has sufficiently low fracture resistance to satisfy conditions of debonding in the propagating crack.[6] Nevertheless debonding mechanism in the HAp/β-NaCaPO$_4$ system requires more detailed study in the future.

The β-NaCaPO$_4$ should find application, both as a weak interphase and an efficient sintering aid, in various microstructurally controlled HAp composites with improved mechanical reliability, high biocompatibility and bioactivity. Moreover, results of this study demonstrate that except already existing HAp-containing glass-ceramics,[33] also other microstructures with potentially improved reliability can be prepared in the HAp/bioactive glass system. It is worth mentioning that similar results to these presented in the present paper have been observed in the HAp/bioactive glass systems also in the case of glasses with different chemical compositions (Haberko *et al.*, unpublished data).

5 Summary

β-$NaCaPO_4$ (β-rhenanite) has been found in this study to act as weak interphase for HAp ceramics. The β-$NaCaPO_4$ provides an easy path for debonding as demonstrated using the HAp/bioactive glass laminate. The β-$NaCaPO_4$ exhibits also high biocompatibility and bioactivity. Moreover, it significantly enhances sinterability of HAp at 1000°C without formation of any undesired phases. Results of this study show that various microstructurally controlled HAp-based composites with potentially improved reliability and high biocompatibility can be prepared in the HAp/β-$NaCaPO_4$ or HAp/bioactive glass systems.

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References

1. Aoki, H., *Science and Medical Applications of Hydroxyapatite*. Takayama Press System Center Co., Inc., Tokyo, 1991.
2. Hench, L. L., Bioceramics: from concept to clinic. *J. Am. Ceram. Soc.*, 1991, **74**, 1487–1510.
3. Suchanek, W. and Yoshimura, M., Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants. *J. Mater. Res.*, 1998, **13**, 94–117.
4. de With, G., Van Dijk, H. J. A., Hattu, N. and Prijs, K., Preparation, microstructure and mechanical properties of dense polycrystalline hydroxy apatite. *J. Mater. Sci.*, 1981, **16**, 1592–1598.
5. Nonami, T. and Wakai, F., Evaluation of crack propagation in hydroxyapatite by double-torsion method in air, water and toluene. *J. Ceram. Soc. Jpn. Int. Ed.*, 1995, **103**, 639–643.
6. Rühle, M. and Evans, A. G., High toughness ceramics and ceramic composites. *Progress in Mater. Sci.*, 1989, **33**, 85–167.
7. Mai, Y.-W., Fracture resistance and fracture mechanisms of engineering materials. *Materials Forum*, 1988, **11**, 232–267.
8. Ziegler, G., Advanced ceramic development trends. *Ber. DKG*, 1991, **68**, 399–404.
9. de With, G. and Corbijn, A. J., Metal fibre reinforced hydroxy-apatite ceramics. *J. Mater. Sci.*, 1989, **24**, 3411–3415.
10. Ioku, K., Somiya, S. and Yoshimura, M., Hydroxyapatite ceramics with tetragonal zirconia particle dispersion prepared by HIP post-sintering. *J. Ceram. Soc. Jpn. Int. Ed.*, 1991, **99**, 191–198.
11. Ioku, K., Noma, T., Ishizawa, N. and Yoshimura, M., Hydrothermal synthesis and sintering of hydroxyapatite powders dispersed with Si_3N_4 whiskers. *J. Ceram. Soc. Jpn. Int. Ed.*, 1990, **98**, 1348–1353.
12. Nonami, T., Study on diopside whiskers precipitation type hydroxyapatite. *Mater. Res. Soc. Symp. Proc.*, 1990, **175**, 71–76.
13. Suchanek, W., Yashima, M., Kakihana, M. and Yoshimura, M., Processing and mechanical properties of hydroxyapatite reinforced with hydroxyapatite whiskers. *Biomaterials*, 1996, **17**, 1715–1723.
14. Hench, L. L. and Ethridge, E. C., *Biomaterials. An Interfacial Approach*. Academic Press, New York, 1982.
15. Ruys, A. J., Milthorpe, B. K. and Sorrell, C. C., Short-fibre-reinforced hydroxyapatite: effects of processing on thermal stability. *J. Aust. Ceram. Soc.*, 1993, **29**, 39–49.
16. Davies, J. M. G., A review of experimental evidence for the carcinogenity of man-made vitreous fibers. *Scand. J. Work. Environ. Health*, 1986, **12**, 12–17.
17. Warheit, D. B., A review of some biophysical factors and their potential roles in the development of fiber toxicity. *Regulatory Toxicology and Pharmacology*, 1994, **20**, S113–S120.
18. Suchanek, W., Yashima, M., Kakihana, M. and Yoshimura, M., Hydroxyapatite/hydroxyapatite-whisker composites without sintering additives: mechanical properties and microstructural evolution. *J. Am. Ceram. Soc.*, 1997, **80**, 2805–2813.
19. Harmer, M. P., Chan, H. M. and Miller, G. A., Unique opportunities for microstructural engineering with duplex and laminar ceramic composites. *J. Am. Ceram. Soc.*, 1992, **75**, 1715–1728.
20. Suchanek, W. and Yoshimura, M., Preparation of fibrous porous hydroxyapatite ceramics from hydroxyapatite whiskers. *J. Am. Ceram. Soc.*, 1998, **81**, 765–767.
21. Ioku, K. and Yoshimura, M., Stoichiometric apatite fine single crystals by hydrothermal synthesis. *Phosphorus Res. Bull.*, 1991, **1**, 15–20.
22. Kangasniemi, I., de Groot, K., Wolke, J., Andersson, O., Luklinska, Z., Becht, J. G. M., Lakkisto, M. and Yli-Urpo, A., The stability of hydroxyapatite in an optimized bioactive glass matrix at sintering temperatures. *J. Mater. Sci. Mater. Med.*, 1991, **2**, 133–137.
23. Elliot, J. C., *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates.*, Studies in Inorganic Chemistry 18, Elsevier, Amsterdam, 1994.
24. Morgan, P. E. D. and Marshall, D. B., Ceramic composites of monazite and alumina. *J. Am. Ceram. Soc.*, 1995, **78**, 1553–1563.
25. Doi, Y., Wakamatsu, N., Shimizu, Y., Adachi, M., Goto, T., Kamemizu, H. and Moriwaki, Y., Effect of rhenanite on sintering of apatite. *The Journal of the Japanese Society for Dental Materials and Devices*, 1996, **15**, 218–225 (in Japanese).

26. Clegg, W. J., Kendall, K., McN. Alford, N., Button, T. W. and Birchall, J. D., A simple way to make tough ceramics. *Nature*, 1990, **347**, 455–457.
27. Pyzik, A. J. and Carroll, D. F., Technology of self-reinforced silicon nitride. *Annu. Rev. Mater. Sci.*, 1994, **24**, 189–214.
28. Tanaka, I., Pezzotti, G., Miyamoto, Y. and Okamoto, T., Fracture toughness of Si_3N_4 and its Si_3N_4 whisker composite without sintering aids. *J. Mater. Sci.*, 1991, **26**, 208–210.
29. Kangasniemi, I. M. O., Vedel, E., de Blick-Hogerworst, J., Yli-Urpo, A. U. and de Groot, K., Dissolution and scanning electron microscopic studies of Ca, P particle-containing bioactive glasses. *J. Biomed. Mater. Res.*, 1993, **27**, 1225–1233.
30. Ramselaar, M. M., Driessens, F. C. M., Kalk, W., de Wijn, J. R. and Van Mullem, P. J., Biodegradation of four calcium phosphate ceramics; *in vivo* rates and tissue interactions. *J. Mater. Sci. Mater. Med.*, 1991, **2**, 63–70.
31. Ramselaar, M. M., Van Mullem, P. J., Kalk, W., Driessens, F. C. M., de Wijn, J. R. and Stols, A. L. H., *In vivo* reactions to particulate rhenanite and particulate hydroxylapatite after implantation in tooth sockets. *J. Mater. Sci. Mater. Med.*, 1993, **4**, 311–317.
32. Suchanek, W., Yashima, M., Kakihana, M. and Yoshimura, M., Hydroxyapatite ceramics with selected sintering additives. *Biomaterials*, 1997, **18**, 923–933.
33. Rawlings, R. D., Bioactive glasses and glass-ceramics. *Clin. Mater.*, 1993, **4**, 155–179 .