Microstructure and Microcrack Formation at Phase Boundaries in Na₃PO₄-Doped Hydroxyapatite

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Na₃PO₄添加ハイドロキシアパタイトの微細組織とマイクロクラックの生成

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Hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂, doped with 0.3 to 5.0 mass% Na₃PO₄ as external sintering aid was studied by transmission electron microscopy. Densification of the powder blend was performed by hot-pressing at 1200°C for 30 min. The overall microstructure of the material was composed of homogeneous, equiaxed hydroxyapatite grains with an average size of about 1.5 μm. Apart from the matrix grains, a sodium-plus calcium-containing secondary phase, β-NaCa₃(PO₄)₂, precipitated at triple pockets of few hundred nanometer scale. The occurrence of this precipitated phase was typically accompanied by microcrack formation. Microcrack opening typically occurred at one edge of the three or four visible phase boundaries. It should be emphasized that nearly all of the secondary phase pockets revealed such a microcrack. The microcrack formation process is likely to be governed by two interacting material characteristics the thermal expansion mismatch of the adjacent phases and the interface bonding strength.

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1. Introduction

Hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂ (HAp), has gained rather wide interest in the field of biomaterials, owing to its excellent biocompatibility which, in principle, opens the potential for its use as a dense monolithic implant in the human body. One major obstacle of HAp, however, strongly limits its wide spread use, apart from surface coating applications in hip prosthesis, is its relative poor mechanical properties, i.e., the low fracture toughness, toughness. Therefore, intensive work has been performed in order to optimize the densification process of calcium phosphate ceramics and to improve the mechanical response of these materials, however, with limited success. Moreover, there is a serious concern related to observed cracking and spalling of surface coatings, thus putting constraint on the use of HAp as a mere coating material. The inherent brittleness and low strength level combined with spalling of coatings does not only limit the use of HAp, but more importantly narrows this material as a viable candidate serving within mechanically stressed regions in the human body or as a bone replacement.

To overcome the aforementioned limitations, a considered approach is the fabrication of HAp composites with particle, platelet, or fiber reinforcements. This in turn requires a favorable densification behavior of the monolithic material, which is known to be kinetically limited. Simply increasing the sintering temperature, for example above 1300°C, will cause fatal decomposition of HAp and, hence, cannot be employed as an alternative processing route. Therefore, different sintering aids such as the addition of glass or Li₃PO₄ as well as Na₃PO₄ have been investigated. The addition of Na₃PO₄ is anticipated to reduce the sintering temperature and to avoid a decomposition of HAp. Furthermore, the decrease of sintering temperature would lead to a reduction of grain growth. The use of hot-pressing or pressureless sintering, combined with the formation of a liquid phase at elevated temperatures, enhances the densification kinetics and improves the material density, which provides the prerequisite for effective composite processing. In this context, it is also important to understand the behavior of the monolithic matrix material, densified under respective processing conditions and with the appropriate sintering aids, prior to the elaboration of rather sophisticated composites, which in fact is considered as the driving force of the present work.

In this paper, we report on the observation of microcracks formed at phase boundaries in highly Na₃PO₄-doped monolithic HAp. The basic understanding of the underlying mechanism related to crack formation at interfaces in this particular material is may allow to address the general problem of cracking and spalling of similar doped surface coatings.

2. Experimental procedures

A commercially available hydroxyapatite powder (Bioland) was employed for specimen preparation. The starting powder was initially calcined at 750°C for 1 h followed by brief milling to desintegrate possible particle agglomerates. The Ca/P-ratio of the starting powder was measured to equal 1.67, which corresponds to the stoichiometric Ca/P-ratio of pure HAp. The powder was blended with 0.3 to 5 mass% Na₃PO₄·12H₂O as Na₃PO₄ source, acting as sintering aid during further heat treatment. Green bodies were prepared by cold-isostatic pressing (CIP) and subsequently densified by hot-pressing at 1200°C for 30 min under a constant compressive stress of 20 MPa in Ar atmosphere. Heating and cooling rate during hot-pressing was 15°C/min and 10°C/min, respectively. A final relative density of 99.5% was measured for this material employing...
The overall microstructural characterization of the HAp materials investigated was performed by means of transmission electron microscopy (TEM) utilizing a Philips CM20FEG microscope fitted with an ultra-thin window Ge energy dispersed X-ray (EDX) detector. Operating at 200 kV, the instrument revealed a point-to-point resolution of 0.24 nm. TEM-foil preparation followed standard techniques, which involve diamond cutting, ultra-sound drilling, mechanical grinding, dimpling, Ar-ion thinning to perforation, and light carbon coating to minimize electrostatic charging under the incident electron beam. Secondary phase identification was performed by EDX and electron energy-loss spectroscopy (EELS) analysis in conjunction with selected area electron diffraction (SAED) studies.

3. Results
TEM observation of both low and highly sodium phosphate doped hydroxyapatite material revealed a homogeneous and fine grain microstructure after densification. HAp matrix grains of about 1 to 2 μm in size with an equiaxed morphology were observed as the major crystalline phase in all the materials, as depicted in Fig. 1. The results of an analysis of lattice parameter and crystal structure from selected area electron diffraction patterns agreed with those of β-NaCaPO₄. Therefore, SAED evaluation identified the phase precipitation at the triple-grain junctions as β-NaCaPO₄ (the arrow in Fig. 1). The matrix grains were typically well faceted, however, on a less macroscopic scale, a slight curvature of the grain boundaries was commonly observed. Therefore, HREM imaging of interfaces at two-grain junctions was limited owing to the slight overlap of adjacent grains. Using the diffuse dark field (DDF) imaging technique, the Fresnel fringe technique as well as HREM imaging revealed no amorphous interlayer at the interfaces. Moreover, no amorphous phase was observed at any of the multi-grain pockets studied in this material. Indirect chemical analysis of the HAp matrix grains was performed by convergent beam electron diffraction (CBED), which allows to determine the space group of the crystal. This, in turn, is indicative of the Ca/P-ratio of the crystal investigated. No difference in the Ca/P-ratio was determined among the highly doped, the low doped and an undoped HAp material. The formation of a solid solution between Na₃PO₄ and HAp was outruled based on EDX analysis, although the detection of traces sodium by EDX is complicated, owing to possible electron-beam-induced cation migration.

The lack of any residual glass phase in this material implies that the liquid phase, formed at elevated temperatures during heat treatment and promoting densification, must have been transient. This assumption is in accordance with the observation of a crystalline secondary phosphate present only at triple pockets in the highly doped material, which contained sodium plus calcium as cations. EDX analysis in addition to SAED evaluation identified the phase as β-NaCaPO₄. Figure 2 shows the EELS spectrum of the precipitated phase in the HAp material (doped with 5 mass % Na₃PO₄). In this figure, the carbon ionization edge was a result of light carbon coating on the TEM foil. This EELS spectrum confirms that the secondary phase in the HAp material was β-NaCaPO₄. All of the multi-grain pockets analyzed in the highly doped material gave the same result, so that the highly doped HAp material was composed of a fine grained HAp matrix with β-NaCaPO₄ precipitations at grain pockets. Typically, the triple pockets were filled with one single crystal of the secondary phase only, which indicates a low probability of nuclei formation. The average size of the

Fig. 1. Low magnification TEM bright field image of a HAp material doped with Na₃PO₄ (employing 5 mass% Na₃PO₄·12H₂O as sintering aid) hot-pressed at 1200°C for 30 min. The material reveals a homogeneous microstructure with equiaxed and faceted apatite grains with a grain diameter of about 1-2 μm.

Fig. 2. (A) EDX spectrum of the NaCaPO₄ secondary phase which clearly locates the presence of Na. (B) EELS spectrum of the NaCaPO₄ secondary phase. Note the carbon ionization edge is a result of light carbon coating of the TEM foil.

triple pockets, determined over about 15 measurements, was \( d = 300 \) nm. The most surprising and therefore unexpected experimental observation was the formation of microcracks along phase boundaries. Nearly all of the triple pockets observed revealed one single microcrack at either side of the pocket, as depicted in Fig. 3. The average microcrack opening at triple pockets was averaged on about 15 different sites observation and estimated to be about \( l = 5 \) nm. Hence, a simplified model was constructed showing one crystal of \( \beta \)-NaCaPO₄ at a multi-grain pocket with the surrounding HAp crystals being fixed in position. Local stress relaxation is achieved by the formation of an isolated microcrack (probably during cooling from processing temperature), as shown in the schematic of Fig. 4. There is no data available in literature about the thermal expansion coefficient of \( \beta \)-NaCaPO₄ phase. However, based on the present microscopic observation, the microcracking phenomenon can be unequivocally rationalized according to the mismatch between the thermal expansion coefficients of the HAp matrix and the precipitated sodium calcium phosphate phase.

4. Discussion

The result of SAED evaluation identified the phase as \( \beta \)-NaCaPO₄ at the triple grain junctions, as confirmed by both EDX and EELS on the crystalline secondary phase. The results of both EDX and EELS revealed the corresponding chemical composition, which matches the electron diffraction patterns, actually being that of \( \beta \)-NaCaPO₄.

Compared to an undoped HAp reference material, sintering with Na₃PO₄ as densification aid enhances both densification rate and grain growth. It is thought that the increase in sinterability as well as in grain size is a result of enhanced diffusion, in particular, at elevated hot-pressing temperature. Ababou and Bernache-Assolant⁴⁰ reported that the addition of Na₃PO₄ appears to be a promising sintering aid because the HAp with 5 to 10 mass% Na₃PO₄ showed an increase in grain growth associated with NaPO₄ addition. Also, they showed that HAp with 5 to 10 mass% Na₃PO₄ has the straight phase boundaries and no liquid phase at grain boundary.

TEM/HREM observations gave no clear indication of a residual glass phase within the material in the present study, indicating that a transient liquid was formed at high sintering temperatures promoting densification. During high-resolution imaging, however, small regions of 0.3 to 0.5 nm in width were typically imaged which appeared to be non-crystalline. Under the given electron optical conditions, it is impossible to unequivocally exclude the presence of an amorphous, Na-containing segregation at the interface (one monolayer), because the phase contrast of an amorphous material seen at high resolution cannot be distinguished from the phase contrast given by a crystalline phase, oriented out of diffraction conditions. Therefore, based on the HREM imaging technique in addition to the difficulty of Na detection by TEM techniques, it cannot conclusively be stated that no amorphous residue is present upon sintering. However, taking into account that diffuse dark field (DDF) imaging as well as out-of-focus Fresnel fringe imaging did also indicate no amorphous phase, it is concluded that the proposed liquid, present at high sintering temperatures and promoting both grain growth and densification, is a transient liquid phase, which undergoes complete crystallization upon cooling to room temperature, leading to the pocket filling precipitation of \( \beta \)-NaCaPO₄. It is thought that the formation of \( \beta \)-NaCaPO₄ is supported by the presence of partly amorphous HAp crystallites in the starting powder with Ca deficiency, which would lead to a chemical reaction between Na₃PO₄ and Ca₃(PO₄)₂(OH)₂.

In this experiment, there was no difference in the Ca/P ratio was determined among the highly doped, the low doped and an undoped HAp material by EDX and EELS analyses. Riboud reported the result of solid solution of Na into HAp, in which Ca was substitute by Na in HAp. Ababou and Bernache-Assolant⁴⁰ indicated that the addition of Na₃PO₄ decreased \( a \), lattice parameter, of HAp, which value was constant in the region of 5 to 10 mass% Na₃PO₄, whereas \( c \) remained constant, compared to monolithic HAp. According to the present result that the glassy phase must be transient and \( \beta \)-NaCaPO₄ phase segregate at triple point only, there may be a limit for solid solution of Na into HAp in this HAp-Na₃PO₄ system. Therefore, most of Na content was thought to be precipitated as \( \beta \)-NaCaPO₄ phase though in part Ca was replaced with Na.

TEM observation showed the occurrence of a phase-boundary microcrack at each triple pocket filled with \( \beta \)-NaCaPO₄ in the highly doped system, while no microcracking was observed in undoped HAp. However, Halouani et al. reported about the occurrence of spontaneous microcracking caused by thermal expansion anisotropy of hexagonal lattice of HAp, \( \alpha_h = 13 \times 10^{-6}/K \), \( \alpha_c = 22 \times 10^{-6}/K \). Hence they speculated that the addition of Na₃PO₄ as a sintering aid would facilitate the accommodation of thermal mismatch and reduce the microcracking by formation of glassy intergranular films. However TEM observation in this study indicated the presence of spontaneous microcracking in the HAp with Na₃PO₄, not in pure HAp, and furthermore no
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glassy interlayer phase at the interfaces. Though there was no precise data of thermal expansion coefficient on β-
NaCaP₄, it was reported that NaCaP₄ showed approximately 3% of rapid volume expansion around at 700°C.²² Therefore the occurrence of a phase-boundary microcrack at each triple pocket filled with β-NaCaP₄ in the highly doped system can be attributed to the thermal mismatch between HAp and β-NaCaP₄ as the precipitated phase and also the weak interface bonding of HAp and β-NaCaP₄, which might result in the microcracking.

5. Conclusions

Compared to an undoped HAp reference material, sintering with Na₃PO₄ as densification aid enhances both densification rate and grain growth. The densification of HAp through the liquid phase as well as grain growth is strongly promoted by the addition of Na₃PO₄ as a densification aid. However, from the given results it can be concluded that Na₃PO₄ derived HAp materials do not overcome the general concern regarding the intrinsic mechanical behavior of undoped HAp samples mainly for one reason: the addition of 5 mass% of Na₃PO₄ as sintering aid leads to an enhanced intergranular embrittlement of the material, i.e., the formation of microcracks at phase boundaries which in turn also limits the potential application of such a biocompatible material.

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