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Short communication

Internal friction of hydroxyapatite and fluorapatite

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Abstract

Internal friction was measured by a forced torsional vibration method at 0.1–10 Hz in the temperature range of −100 to 400 °C on both hydroxyapatite (HAp) sintered at 1300 °C for 3 h under fluent H_2O vapor and fluorapatite (FAp) sintered at 1200 °C for 3 h in the F_2 atmosphere. Three peaks of internal friction appeared at approximately −40, 80 and 130 °C for HAp. However, for the FAp, no internal friction peak was obtained in the measured temperature range. It is considered that the difference of F^- and OH^- positions in each FAp and HAp structure greatly influences internal friction.

Keywords: B. X-ray methods; C. Friction; D. Apatite; Fluorapatite

1. Introduction

Hydroxyapatite (HAp:$Ca_{10}(PO_4)_6(OH)_2$) and fluorapatite (FAp:$Ca_{10}(PO_4)_6F_2$) are investigated as multiple function materials such as artificial bones, teeth and ion exchange substrates. HAp is similar to the stiff tissue of bones and teeth of vertebrate animals [1–5]. HAp exhibits also other important properties of cation exchange between Ca^{2+} ions and heavy metal or harmful ions [6–9], such as Pb^{2+}, Cd^{2+}, Mn^{2+} and CO^{2+}, as well as adsorption of proteins [10–13]. FAp is chemically more stable than HAp, and is investigated in order to clarify its fundamental properties like absorbing phosphorus and fluorine ions selectively in waste water [14,15]. In the present work, internal friction was measured on polycrystalline HAps and FAps.

2. Experimental procedure

The particles synthesized to stoichiometric HAp [16] were mixed with wax (LUVAX-1266, Nippon Seiro Co. Ltd., Japan) in toluene by a ball mill. After drying at 70–80 °C, 50 mm × 5 mm × 0.5 mm test pieces were formed to at 100 MPa, and then sintered at 1300 °C for 3 h under fluent H_2O vapor. FAp particles were synthesized by reaction sintering with CaF_2 and $Ca_3(PO_4)_2$ (β-TCP) [17,18] under fluent N_2 gas at 1100 °C for 2 h. FAp test pieces were also pressed as HAp pieces, and then sintered at 1200 °C for 3 h in the F_2 atmosphere. The composition ratios of FAp test pieces were adjusted as $Ca/P = 1.68$ and $P/F = 2.99$ and confirmed by ion chromatography. The internal friction ($\tan\delta$) was measured by a forced torsional vibration method (MR-500, Rheology Co. Ltd., Japan) at −100 to 400 °C at 0.1–10 Hz.

3. Results and discussion

The internal friction ($\tan\delta$) is shown in Fig. 1 for HAp and Fig. 2 for FAp. For the HAp, three peaks of internal friction appeared at approximately −40, 80 and 130 °C (Fig. 1). On the other hand, no peak appeared at the investigated temperature range for FAp (Fig. 2). In the case of HAp, both peaks, at approximately −40 and 130 °C, agree well to the results obtained at −40 °C for Ca-deficient ($Ca/P = 1.5$) HAp and at 110 °C for stoichiometric ($Ca/P = 1.7$) HAp [16]. It was assumed that the peak at −40 °C occurred from a phase transition [19] of β-TCP since the Ca-deficient HAp converted to β-TCP after sintering, and the peak at 110 °C was explained by the behavior of structural OH^-ions in the stoichiometric HAp ($Ca/P = 1.7$) sintered at 1200 °C [16]. The peaks obtained at ∼130 °C in the present work depend on the frequency although the peaks at around −40 °C are not related to the frequency. So, the present

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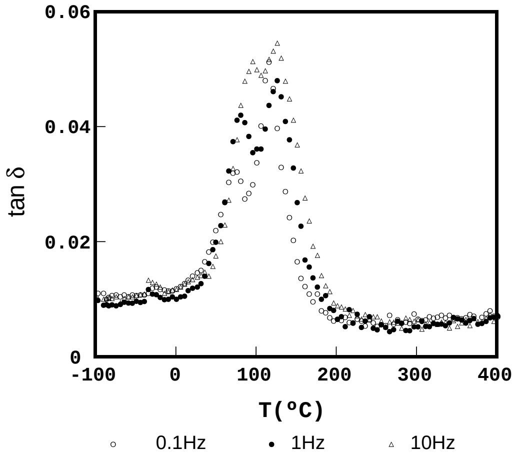

Fig. 1. Internal friction measured as a function of temperature and frequency by the forced torsional vibration method on the HAp sintered at 1300 °C for 3 h under fluent H_2O vapor.

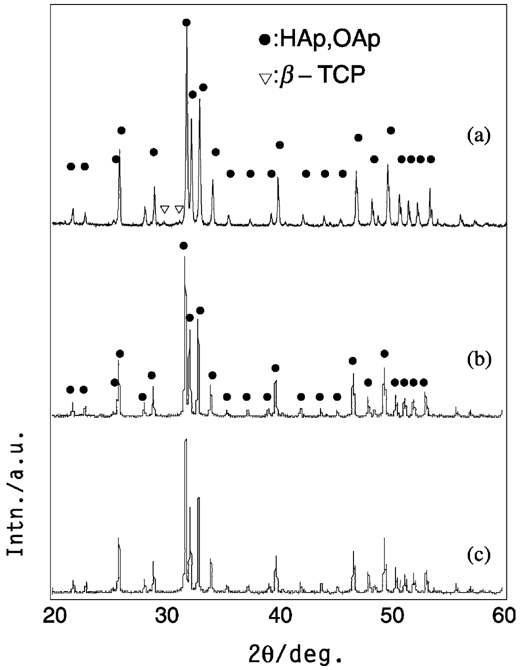

Fig. 3. XRD patterns on the Hap: (a) HAp sintered at 1200 °C for 3 h [16], (b) HAp (OAp) sintered at 1200 °C for 3 h in N_2 gas and (c) HAp sintered at 1300 °C for 3 h under a current of H_2O vapor.

HAp were also identified by X-ray diffraction (XRD). The XRD pattern was shown in Fig. 3c, and the existence of β-TCP phase was confirmed although most of peaks fitted well to the HAp phase. Furthermore, the existence of the structural OH^- ions was investigated by infrared spectroscopy (IR). An absorption peak of structural OH^- groups of HAp existed in the 3570 cm^{-1} region [20–22] as shown in Fig. 4b. As investigated above, it can be assumed similarly as in the conclusion of the previous paper [16], that the two kinds of peaks at approximately −40 and 130 °C in the present HAp were due to the phase transition of β-TCP and the behavior of structural OH groups, respectively. Next, it was investigated, on what the peak appearing at ∼80 °C is based, since there was no such peak in previous experiments [16]. The peaks showed frequency dependence (Fig. 1). We questioned whether the internal friction peak was influenced by oxyapatite containing vacancies on the hydroxy sites since the present HAps sintered at 1300 °C would convert partially to oxyhydroxyapatite (OAp), $Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_y$ ($\square$: vacancy, $x < 1$), with vacancies located on hydroxy sites [1,23–25]. So, the HAp test pieces were sintered in N_2 gas at 1200 °C for 3 h to confirm the appearance of OAp containing vacancies [23], and were investigated by XRD and IR. The XRD pattern (Fig. 3b) fitted excellent to the HAp phase without any β-TCP phase [17,26]. But it was found, that the absorption

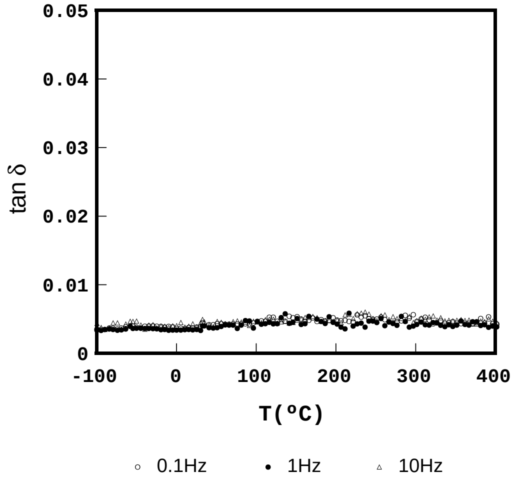

Fig. 2. Internal friction measured as a function of temperature and frequency by the forced torsional vibration method on the FAp sintered at 1200 °C for 3 h in the F_2 atmosphere.

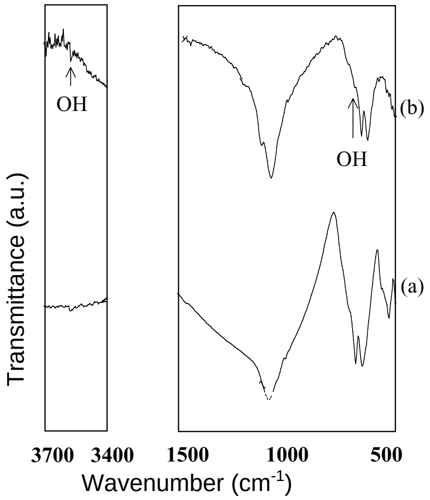

Fig. 4. Infrared spectrum: (a) HAp (OAp) sintered at 1200 °C for 3 h in N_2 gas and (b) HAp sintered at 1300 °C for 3 h under fluent H_2O vapor.

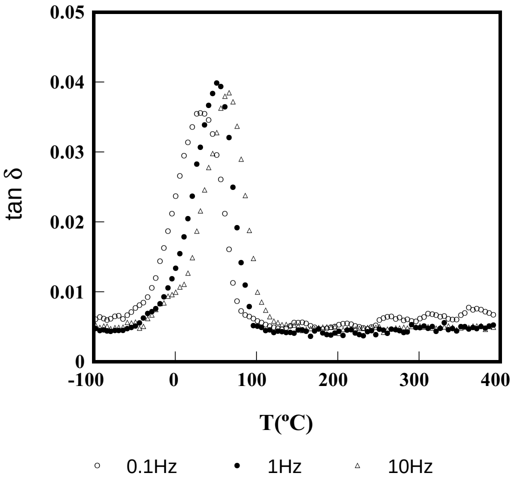

Fig. 5. Internal friction measured as a function of temperature and frequency by the forced torsional vibration method on the HAp sintered at 1200 °C for 3 h in N_2 gas.

(3570 cm^{-1}) of structural OH groups was neglectable according to the result of IR (Fig. 4a). Therefore we assumed that the oxyapatite with vacancies located on hydroxy sites to be dehydroxylated at 1200 °C was produced after sintering in N_2 gas. For the treated test specimens, internal friction was measured, and the results are shown in Fig. 5. Only one internal friction peak appeared only at about 60 °C, but showed also the frequency dependence. From the results of internal friction and IR, it was guessed that the internal friction peaks shown at ∼80 °C in Fig. 1 were influenced by vacancies located on OH sites in the oxyhydroxyapatite [23,26]. As the peak temperatures at ∼130 °C (high temperature peak) and at ∼80 °C (intermediate temperature) shifted as a function of frequency, the activation energies (ΔH) of the relaxation behavior were obtained from the peak temperature (T) and frequency (ω). The results were ∼150 kJ mol^{-1} at ∼130 °C (high temperature peaks) and ∼120 kJ mol^{-1} at ∼80 °C (intermediate temperature peaks).

For the internal friction of FAp, no peak appeared as shown in Fig. 2, and rather low values of about 0.005 were obtained in the present temperature range. A real difference in the tendency of the internal frictions obtained with FAp and HAp may result in a different behavior of the F^- ion compared to the OH^- ion, since arrangement of the F^- ion and the OH^- ion around the vertical axis (c-axis) at the corners of the apatite unit cell differ in each structure of FAp and HAp although the difference of structure could not be confirmed by XRD [26]. The F^- ion is at the center of the triangle of Ca(2) ions, but the OH^- ion is above this position [26–28]. Therefore, it was considered that the difference in the positions of F^- and OH^- ions in each structure, FAp and HAp, had an great influence on the internal friction.

4. Conclusion

Internal friction was measured by a forced torsional vibration method at 0.1–10 Hz in the range of −100 to 400 °C on both, HAp sintered at 1300 °C for 3 h under a flow of H_2O vapor and FAp sintered at 1200 °C for 3 h in the F_2 atmosphere. The results are summarized as follows: (1) Three peaks of internal friction appeared at approximately −40, 80 and 130 °C on the HAp. (2) No internal friction peak appeared at the measured temperature range on the FAp.

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