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Compositional distribution of hydroxyapatite surface and interface observed by electron spectroscopy

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The surfaces of single crystals and polycrystalline specimens of hydroxyapatite were measured by auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Compared to P content, Ca content was found to be enriched near the surface of the hydroxyapatite single crystal. A Ca-deficient and carbonate-containing phase was observed at the grain boundaries of the polycrystalline specimen. Ca content at fracture surface increased as a function of time. It is suggested that Ca ions in the hydroxyapatite crystals migrated from inside the crystal to the surface, and that carbonate ions were incorporated from the gas phase into the crystal interior.

1. Introduction

Hydroxyapatite is similar to the inorganic part of biological bone in composition and structure; therefore it is regarded as a model material for understanding bone minerals [1]. Since biochemical interaction takes place at a surface, and a grain boundary plays an important role in mechanical degradation in aqueous solution, it is necessary to elucidate the chemical composition of the hydroxyapatite surface and grain boundaries.

Biocompatibility of hydroxyapatite is due to biochemical and electrochemical characteristics of the surface. For example, electrochemical surface effects probably contribute to bone formation *in vivo* [2]. In this paper, the compositional distribution of the surface and grain boundaries of hydroxyapatite was measured by auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Ca-deficiency of the surface and CO_3 contamination of the grain boundary were observed.

2. Experimental procedure

2.1. Specimen preparation

Stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ powder was prepared by reaction in aqueous solution of reagent grade $CaCO_3$ and H_3PO_4. Single crystals of hydroxyapatite were grown from the powder at 1000 °C using $Ca(OH)_2$ flux; the crystals obtained were washed using NH_4Cl aqueous solution.

Polycrystalline specimens were prepared by sintering the same powder at 700 °C under Ar gas at a pressure of 600 MPa. The sintered polycrystalline specimen was cut into cylindrical shape, 4 mm^2 × 30 mm in size, and used as the specimen for AES and XPS measurements.

2.2. Measurements

The single crystals were observed by a scanning electron microscope (SEM) and their surfaces were measured by the AES technique. In order to eliminate carbon compounds adsorbed on the surfaces, the specimens were etched by Ar ions accelerated through 3 kV.

AES and XPS measurements were performed with a Microlab-320D. The electron beam accelerating voltage for the AES measurements was 5 kV and its current was 30 μA. The excitation X-ray energy for the XPS measurements was 1253.6 eV (MgK_α). Accelerating voltage and emission current were 15 kV and 20 mA, respectively. The diameter of the X-ray beam was about 2 mm. The polycrystalline specimens were fractured in a high vacuum chamber at 10^{-8} Pa. The fracture surface was measured by AES and XPS techniques just after fracturing. The specimen was kept in the high vacuum chamber at room temperature for 24 days, and XPS measurement was performed 7 and 24 days after.

3. Results

3.1. Auger spectra of single crystals

Fig. 1 shows the SEM image of the synthetic hydroxyapatite single crystals. The crystals had hexagonal pyramid shape of about 200 μm in length and about 100 μm in diameter.

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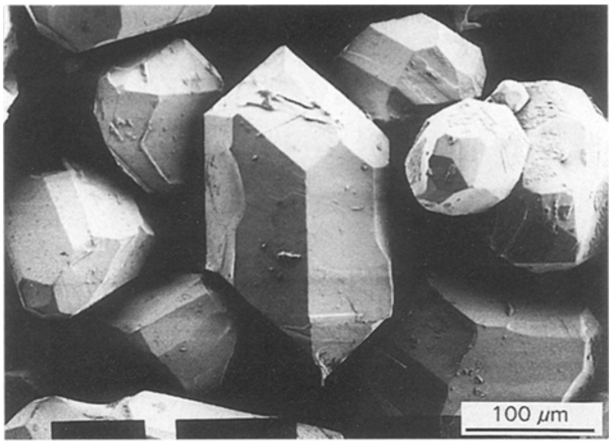

Figure 1 Scanning electron microscope image of single crystals of stoichiometric hydroxyapatite synthesized in $Ca(OH)_2$ flux.

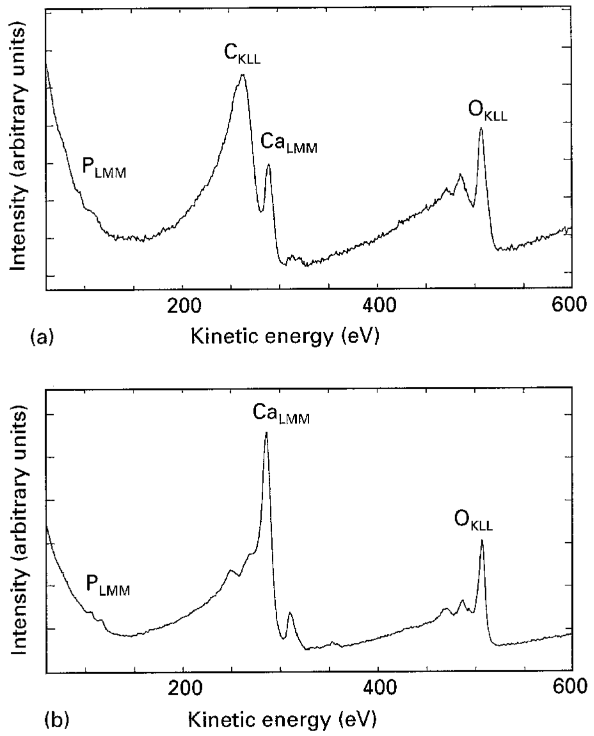

Figure 2 AES spectra hydroxyapatite single crystal surface: (a) before Ar ion etching and (b) after etching.

Fig. 2 shows the Auger electron spectra of the crystal surface of hydroxyapatite. Fig. 2(a) and (b) were measured before and after Ar ion etching (about 30 nm), respectively. The peak located at 250 ~ 320 eV is the Ca_{LMM} auger transition, and the peak at 460 ~ 510 eV is the O_{KLL} transition. The peaks observed at 90 ~ 120 eV and near 260 eV correspond to the P_{LMM} and C_{KLL} transitions, respectively. After the Ar ion etching, the content of P increases while the content of C decreases.

3.2. Auger spectra of fracture surfaces

Fig. 3 shows the AES spectra for the fracture surface of a polycrystalline specimen measured just after fracturing. According to SEM observations, fracturing occurred both intra-grain and along grain boundaries.

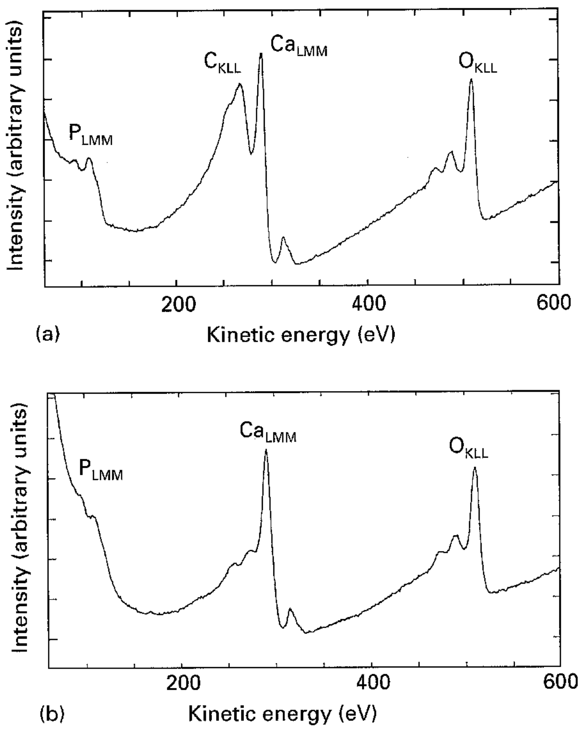

Figure 3 AES spectra of fracture surface of hydroxyapatite polycrystalline specimen: (a) inter-grain and (b) intra-grain fracture surface.

The proportion of intra-grain fracturing was comparatively dominant. Fig. 3(a) and (b) were obtained from the grain boundary and intra-grain, respectively. Three peaks, P_{LMM}, O_{KLL} and Ca_{LMM} are observed in both figures, while an intense C_{KLL} peak is especially noticeable at the grain boundary as shown in Fig. 3(a).

3.3. X-ray photoelectron spectra of fracture surfaces

XPS spectra for the polycrystalline specimen just after the fracture and after 24 days are indicated in Fig. 4(a) and (b), respectively. P_{2p}, Ca_{2p} and O_{1s} peaks are observed at 130, 350 and 530 eV, respectively. A peak at 290 eV corresponds to C_{1s} photoelectron transition. It is found from Fig. 4 that the peak intensity ratio of Ca_{2p}/P_{2p} increases with time after fracturing.

4. Discussion

4.1. Composition of crystal surface

As seen in Fig. 2, the compositional ratio Ca/P of the surface of the as-grown crystal is about twice as large as that of the crystal surface etched by Ar gas. It is therefore concluded that a Ca-enriched layer is formed at the surface of hydroxyapatite single crystal. As the excess amount of Ca is assumed to result from Ca migrated from the inside of the crystal, it is plausible to suppose that a Ca-deficient layer is formed inside the Ca-enriched layer.

The time dependence of the compositional ratio Ca/P at the crystal surface was estimated from the intensity change of Ca_{2p} (350 eV) and P_{2p} (130 eV) shown in Fig. 4. Background was subtracted using

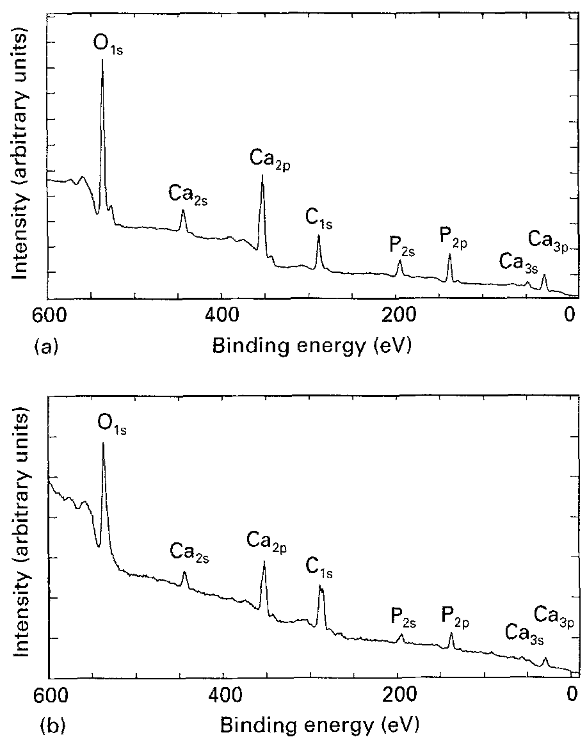

Figure 4 XPS spectra of fracture surface of hydroxyapatite polycrystalline specimen: (a) just after the fracture and (b) 24 days after the fracture.

a linear approximation. The Ca/P ratios were measured 7 days and 24 days after fracturing; the ratios were respectively about 1.14 and 1.18 times larger compared to the ratio measured just after the fracture. This indicates that the Ca content at the surface of hydroxyapatite crystal increases with time even at room temperature: i.e. the Ca ions migrate from inside the crystal to the surface at room temperature. Therefore, the Ca content just inside the surface is considered to decrease inversely, though change in the Ca-content was not obviously observed in the present measurement; probably the content-changed region is broadly distributed.

4.2. Composition of grain boundary

As shown in Fig. 3, the AES measurement shows that carbon is present at the grain boundary of the sintered polycrystalline specimen.

Carbon was also observed by XPS of the fracture surface. As SEM observation of the fracture surface indicated that the fracturing predominantly took place intra-grain, the result of XPS measurement is consistent with the AES result.

The carbon observed is considered to be due to carbonate ions since the polycrystalline specimens were fractured in a high vacuum and therefore hydrocarbon could not be adsorbed onto the fracture surface. In addition, carbon can be contained in the apatite structure, generally as carbonate ions [3].

Comparing Fig. 3(a) and (b), it is suggested that the carbonate ion is segregated along the grain boundary. Since the starting powder for the sintering was synthesized by a wet method, carbonate ions could be incorporated into hydroxyapatite grains from aqueous solution during the preparation. On the other hand, the polycrystalline specimens were sintered in the air: thus, carbon dioxide gas could be incorporated from the air. In any case, the carbonate ions were finally segregated at the grain boundaries where there probably exist structural disorders that stabilize the carbonate ions.

4.3. Effect of Ca-deficiency and carbonate contamination

The XPS and AES measurements indicate that a Ca-deficient and carbonate containing apatite phase is formed at the surface and the grain boundaries. Mineral in biological bone is conjectured to be a Ca-deficient and carbonate-containing phase of hydroxyapatite [4]. The effect of Ca-deficiency and carbonate contamination are considered to be important for surface activity and mechanical strength of the grain boundary. The surface structure of hydroxyapatite could be modified by the Ca-deficiency, which might especially affect chemical adsorption of organic compounds in living bodies. On the other hand, contamination by carbonate ions is considered to increase the solubility product of apatite to water [5, 6]; thus the stability in aqueous solution or velocity of dissolution are varied by the carbonate ion contamination. It is known that intra-granular fracturing predominantly occurs when a sintered apatite is fractured in the air, while grain boundary fracturing takes place when fractured in water [7]. This phenomenon is related to the segregation of carbonate ions at the grain boundaries, which plausibly vary the mechanical properties in aqueous solution via the solubility change.

The formation of the Ca-enriched layer at the surface, derived from Ca migration is related to the electrochemical properties of hydroxyapatite in aqueous solution. When the hydroxyapatite crystal is immersed in water, Ca ions at the surface are dissolved into the water. Then, the carbonate ions in water may also be incorporated into the surface. Consequently, the surface of apatite tends to be negatively charged by the Ca^{2+} dissolution and the incorporation of CO_3^{2-}, especially in acid. Such chemical behaviour of the surface results in the formation of an electrical double layer at the interface of the apatite and solution. It is considered that this double layer influences the formation of a hydration shell around fine apatite powder and possibly causes osteogenesis and osteoclasis via an electrochemical reaction and/or streaming potential [8].

5. Conclusions

Compositional distributions at the surface and the grain boundary of stoichiometric hydroxyapatite were analyzed by electron spectroscopy. A Ca-enriched layer was observed at the surface. This phenomenon was explained in terms of Ca ion migration from the inside of the crystal to the surface and related to electrochemical properties such as the formation of an electric double layer around fine hydroxyapatite.

Carbonate ions were detected at the grain boundary. This compositional distribution was related to mechanical properties in aqueous solution via grain-boundary fracturing of sintered apatite.

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