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PRESSURE SINTERING OF APATITE-COLLAGEN COMPOSITE*

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Abstract—Preparation of a composite consisting of apatite and collagen was attempted. Starting from an aqueous solution of collagen, phosphoric acid, and calcium hydroxide suspension, an apatite (90wt%)-collagen (10wt%) composite of 1.75 g/ml in apparent density, with 2 GPa in Young's modulus, and 6.5 MPa in compression strength was synthesized at 40°C, 200 MPa, successfully. It was found that the presence of liquid water in the system was essential for the sintering of the composite under high pressures. Without liquid water, the specimen that was pressure treated and brought in atmospheric pressure, broke into small pieces due to residual strain. The prepared composite could be cut by a razor blade, and was stable against immersion in water. The mean size of the apatite crystals in the composite was 10 nm in width and 40 nm in length.

Key Words—collagen, hydroxyapatite, composite, pressure, sintering

INTRODUCTION

IT IS well-known that the apatite phase found in living bodies exists as very small crystals that are bonded with organic high polymers such as collagen. Trials to examine the possibilities of apatite-collagen composite as an implant material have been reported by many authors (1–13). Advancement of mechanical properties of a collagen-apatite mixture have also been investigated by means of various technologies, such as γ-rays irradiation (3), UV irradiation (5,6,8,9,11,12), mineralization of collagen sheets (10), or adoption of sintered porous hydroxyapatite (4,13).

For the advancement of mechanical properties of the collagen-apatite mixture, application of pressure was attempted as described below.

MATERIALS AND METHODS

Five hundred grams of commercially available collagen solution (concentration 2 wt%, isoelectric point 9, pH 3) was diluted up to 8 liters and mixed with 0.6 mole of phosphoric acid.

The $CaCO_3$, 1 mole was kept at 900°C in air for 10 h. The CaO thus formed was crushed in a mortar into fine powder and mixed with 3 liters of water. The $Ca(OH)_2$ aqueous suspension thus formed was mixed vigorously and collagen-phosphoric acid mixed solution was slowly added at room temperature to the aqueous suspension. In this case, the mixing ratio of collagen to hydroxyapatite thus formed was 1 to 10.

The precipitate thus formed was filtered and partly freeze-dried until the water content of the precipitate became suitable for sintering. Then, the precipitate was mounted in a metal capsule. The capsule was evacuated and sealed by welding, after which it was kept for 8 h at 200 MPa, 40°C.

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The specimen thus formed was examined by 5 MHz sound velocity measurement and compression strength measurement using INSTRON model 1123. The cross head speed was 0.5 mm/min. during the measurement.

RESULTS

After the pressure treatment, the metal capsule made from lead was removed. In every run, the specimen was slightly yellow and solid. When the water content of a specimen during the pressure treatment was about 10 wt%, for example, the resultant solid specimen was stable in air, but unstable in water. When the specimen was immersed in liquid water, it broke vigorously into small pieces.

When the water content was near 50 vol%, the pressure-treated specimen was stable in liquid water. The solid feature of the specimen was unchanged during a period of one month of immersion in water at room temperature. The results of the compression test are shown in Fig. 1. The results were compared with apatite powder compact treated under the same conditions as those of the apatite-collagen composite, i.e., 200 MPa, 40°C, and 8 h of run duration, and the presence of liquid water.

The apparent density of the apatite powder compact thus obtained was 2.1 g/ml, and was hard and brittle. In this case, without collagen, the load-displacement curve in Fig. 1 is almost a straight line until it breaks, while in the case of collagen-apatite composite, the load-displacement line in Fig. 1 shows small and varying gradients, indicating large deformation of the specimen.

These results coincide with the sound velocity measurement, from which 2 GPa of Young's modulus was calculated.

The collagen-apatite composite could be cut with a razor blade (Fig. 2). The blade-cut

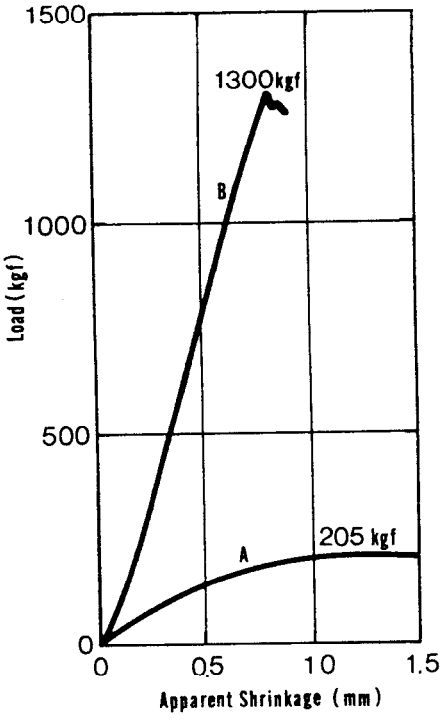

FIG. 1. Load-displacement relation in compression strength test. A: collagen-apatite composite, 22 mm in diameter and 50 mm length. B: apatite powder compact, 23 mm in diameter and 50 mm length. Both are sintered at 40°C, 200 MPa, under the presence of liquid phase water.

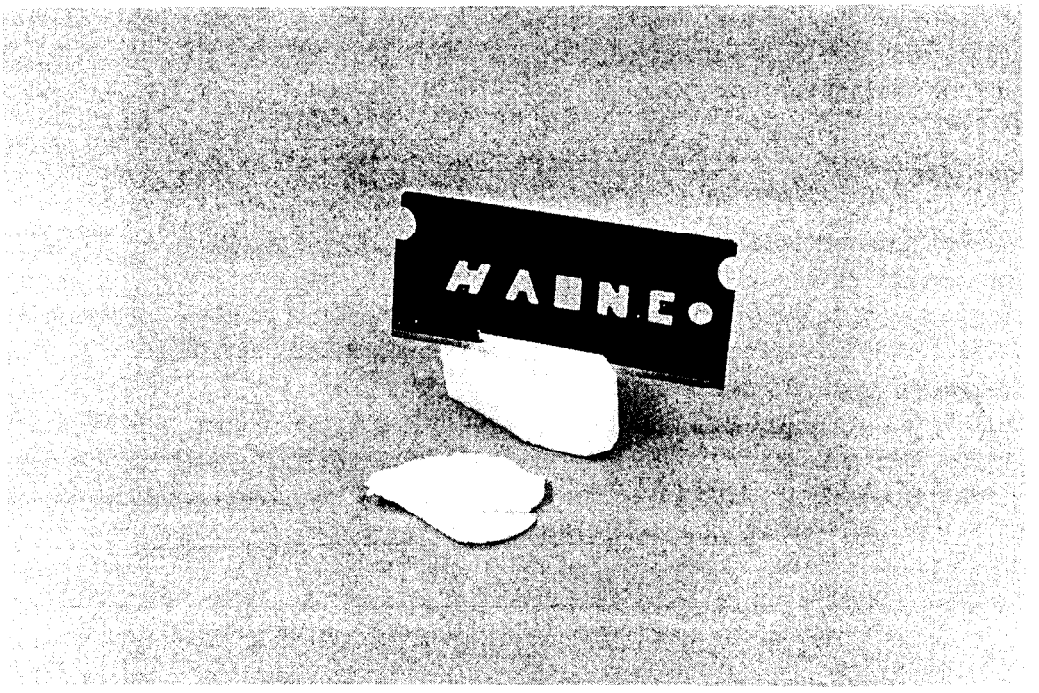

FIG. 2. Collagen-apatite composite can be cut by razor blade.

surface is shown in Fig. 3. The average size of the apatite crystal was 10 nm in diameter and 40 nm in length.

DISCUSSION

Sintering temperature suitable for hydroxyapatite is known to be 1200 ± 100°C. Under a pressure of 200 MPa, a fully dense sintered specimen can be obtained at 800°C.

Presence of water in the system lowers the sintering temperature of hydroxyapatite. In a stream of steam at 300°C and atmospheric pressure, grain growth of hydroxyapatite can be found, and also a powder compact of hydroxyapatite shows small shrinkage in volume due to its sintering.

Previously, we reported that calcium deficient hydroxyapatite, which has bonded water at the calcium-deficient site, sinters up to full density at 300°C under a pressure of 600 MPa (14,15). At that time, 300°C was the lowest limit to obtain a stable sintered specimen. At 200°C or lower, full density could not be obtained and strain remained in the pressed powder by treating it at 600 MPa. It was found that such an obtained specimen, placed in air, gradually broke into small pieces.

When specimens with remaining strain were dipped into water at room temperature, they broke vigorously into small pieces within several seconds. The water content in these apatite specimens were determined. It was found that these specimens were intensely dried. The bonded water molecules in the calcium deficient site had been partly lost.

In the present experiment, therefore, wet apatite powder was used for the pressure treatment. The pressure treated apatite specimen thus obtained did not break at the immersion in water. The stable solid specimens were obtained by the pressure treatment at room temperature.

It seemed obvious that in the liquid water, the strain in the apatite phase due to the pressure treatment could be released at room temperature. This phenomenon led us to the further

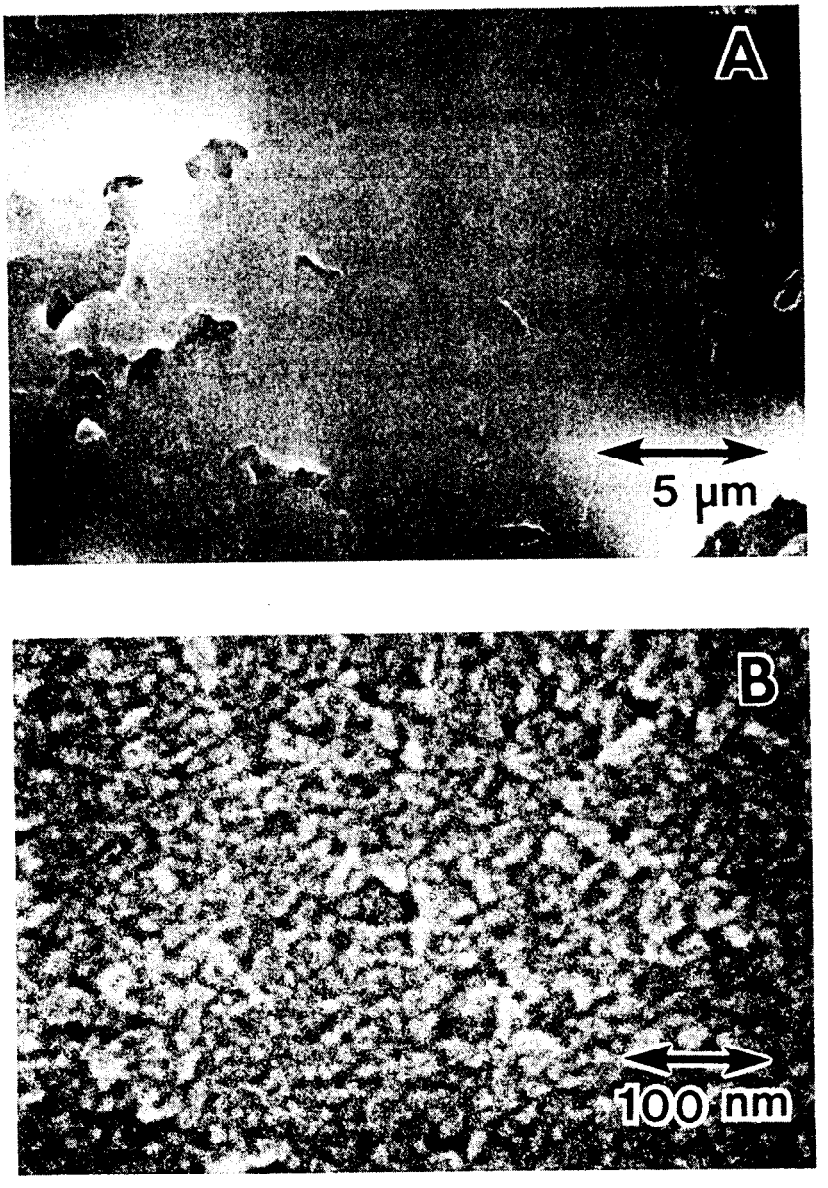

FIG. 3. Blade cut surface of collagen-apatite composite. A: SEM image, ×5,030, B: SEM image, ×203,000.

possibility of pressure-sintering of hydroxyapatite mixed with organic compounds at room temperature.

These results also suggest that the higher pressures make it possible to obtain collagen-apatite composite of higher density, and of higher strength at room temperature.

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