X-ray diffraction data for flux-grown calcium hydroxyapatite whiskers

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Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) whiskers were prepared by using the technique of molten salt synthesis with the fluxing agent of potassium sulphate (K_2SO_4). A tentative x-ray diffraction (XRD) pattern was suggested for the produced whiskers. Phase purity, composition, and morphology of the whiskers were investigated by powder XRD, inductively coupled plasma-atomic emission spectroscopy, Fourier transform infrared spectroscopy, and scanning electron microscopy, respectively. © *2001 International Centre for Diffraction Data.* [DOI: 10.1154/1.1330273]

I. INTRODUCTION

Calcium hydroxyapatite (HA:$Ca_{10}(PO_4)_6(OH)_2$) is a biocompatible ceramic, owing to its significant chemical and physical resemblance to the mineral constituents of human bones and teeth. For load-bearing orthopedic and dental applications, densified HA ceramics are needed. However, dense HA ceramics manufactured by using synthetic HA powders have always exhibited a low fracture toughness of about 1 MPa $m^{1/2}$, in contrast to values observed for human bones in the range of 2–12 MPa $m^{1/2}$ (Hench, 1991).

Reinforcement by whiskers has been considered as a way of improving the fracture toughness of pure HA bioceramics, and whisker- or needle-like crystals of HA have thus been synthesized in recent years mainly by using the hydrothermal method/precipitation routes (Yubao *et al.*, 1994; Yoshimura *et al.*, 1994; Suchanek and co-workers, 1995, 1997, 1998; Iizuka and Nozuma 1998, 1999; Nakahira *et al.*, 1999; Aizawa *et al.*, 2000). However, some of the whiskers synthesized by these methods were reported (Suchanek and co-workers, 1995, 1997, 1998) to suffer from being nonstoichiometric (i.e., Ca-deficient) and to have low thermal stability, i.e., they partially decomposed into β-TCP ($Ca_3(PO_4)_2$, tricalcium phosphate) phase (5–35 vol % TCP) even after 1 h of heating at 1100 °C.

Molten salt synthesis (MSS) technique is known to be one of the simplest routes to prepare ceramic powder bodies with whisker-, needle-, or plate-like morphology and as well with complex stoichiometry (Arendt, 1973). The MSS technique is based on the use of low-melting solvents, such as alkali sulphates, chlorides, carbonates or hydroxides, acting as the medium of reaction for ceramics. The literature on molten salt synthesis is quite extensive and this technique has frequently been utilized (by using different alkali salts) to prepare ferrites (Arendt, 1973), titanates (Fuierer and Newnham, 1991; Aboujalil *et al.*, 1998; Katayama *et al.*, 1999), niobates (Li *et al.*, 1991; Wan *et al.*, 1998; Yoon *et al.*, 1998; Brahmaroutu *et al.*, 1999), mullite (Hashimoto and Yamaguchi, 2000) and aluminum borate (Wada *et al.*, 1996; Gonenli and Tas, 2000).

In the present study, submicron HA powders synthesized by us (Tas, 1995; Tas *et al.*, 1997; Mavis and Tas, 2000) were used as the starting material in the MSS method. To our knowledge, this report is the first one describing the preparation of monodisperse HA whiskers by using K_2SO_4 salt via the technique of molten salt synthesis.

II. EXPERIMENTAL

A. Preparation of HA powders

Single-phase calcium hydroxyapatite powders used as the starting material in the molten salt synthesis of the HA whiskers were synthesized as described in the following (Tas, 1995; Tas *et al.*, 1997; Mavis and Tas, 2000). It should hereby be mentioned that the following procedure is basically the modification of a route described earlier by Hayek and Newesely (1963), Moreno *et al.* (1968), and Jarcho *et al.* 1976). A 3 mL aliquot of 0.1 g/L methyl cellulose solution (99% pure, Sigma, St. Louis, MO) was mixed (to act as a dispersant) with 1440 mL of de-ionized water. 0.152 mol of $Ca(NO_3)_2 \cdot 4H_2O$ (99.9% pure, Merck, Darmstadt, Germany) and 0.090 mol of $(NH_4)_2HPO_4$ (99.9%, Merck, Germany) was then dissolved in the above-given solution. Following that step, 115 mL of 24 vol % NH_4OH was added, in its

TABLE I. Powder diffraction data for phase characterization.

Radiation type, source	X-rays, Cu, 40 kV, 30 mA
Wavelength used	1.540 598 Å $K_{\alpha 1}$, monochromatic
λ Discrim.	Diffracted beam, graphite-mono
λ Detector	Scintillation
Instrument description	Div.: 1° Rec.: 0.2°
Instrumental profile breadth	0.10° 2θ
Temperature (°C)	21 ± 1
Range of 2θ from	10°–70°
Specimen form	Side-loaded powder, packed for 2θ's
Specimen motion	None
Step size	0.02° 2θ
Count time	10 s
External 2θ standard	Si (Starck Co., Germany)
Lattice parameter of 2θ standard	5.4310 Å
2θ error correction procedure	Linear interpolation from nearest 2θ's of std.
Intensity meas. technique	Peak heights, automated computer software (Siemens) and "PEAKFIT 3.0" (Jandel Scientific, USA)
Peak heights error	~3%
Cell refinement method	Least-squares, Appleman and Evans (1973).

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entirety, into the above-described opaque solution. The solution was heated and vigorously stirred at a temperature of 60–70 °C for 3 h on a hot plate. The precipitates that formed were recovered from the supernatant by filtering and washed five times with de-ionized water. The filtrates were dried at 100 °C overnight. HA precursors were finally calcined in an air atmosphere at 1000 °C for 6 h, followed by light grinding by hand with an agate mortar and pestle.

B. Synthesis of HA whiskers

HA powders calcined at 1000 °C were dry mixed in an agate mortar with potassium sulphate (99.9% pure, Merck) at the K_2SO_4/HA weight ratio of 3.0, for a total sample weight of 2 g. The mixtures were then placed, as loose powder compacts, into clean alumina boats having a volume of 7.5 cm^3 prior to setting in a box furnace. The samples were heated from the ambient to the peak temperature of whisker synthesis at the rate of 5 °C/min. Following soaking for 3 h at the peak temperature of 1150 °C, the samples were cooled naturally to room temperature within the shut-off furnace. The whiskers were separated from the solidified mass by washing several times with hot (~90 °C) de-ionized water. Washing was repeated until the specific conductance of the decanted liquid fell below 2.0 μS, measured (Fuierer and Newnham, 1991) using a conductance meter (Model Digi610, WTW, Weilheim, Germany), knowing that the conductance of de-ionized water was 1.4 μS. Washed whiskers were finally dried in an oven at 100 °C, overnight.

C. Sample characterization

The phase constitution of the whiskers was analyzed by using an (model D-5000, Siemens, Karlsruhe, Germany) X-ray diffractometer (XRD). Further details of the XRD work are given in Table I. The morphological and semiquantitative elemental distribution information on the samples were obtained by scanning electron microscopy, SEM (model DSM 982-Gemini, Zeiss, Oberkochen, Germany), and by energy dispersive X-ray spectroscopy (EDS), respectively. The samples for SEM and EDS investigations were, first, sputter coated with an approximately 20-nm-thick layer of gold. EDS runs were believed to be accurate to about ±2 wt %. Quantitative chemical analyses were performed by inductively coupled plasma atomic emission spectroscopy, ICP-AES, (model JY-70Plus, Instruments SA, France). A Fourier transform infrared spectrophotometer (model IFS66, Bruker, Karlsruhe, Germany) was used to measure the infrared transmission spectra of the whiskers, following their mixing (1 wt %) with dry KBr to form pellets.

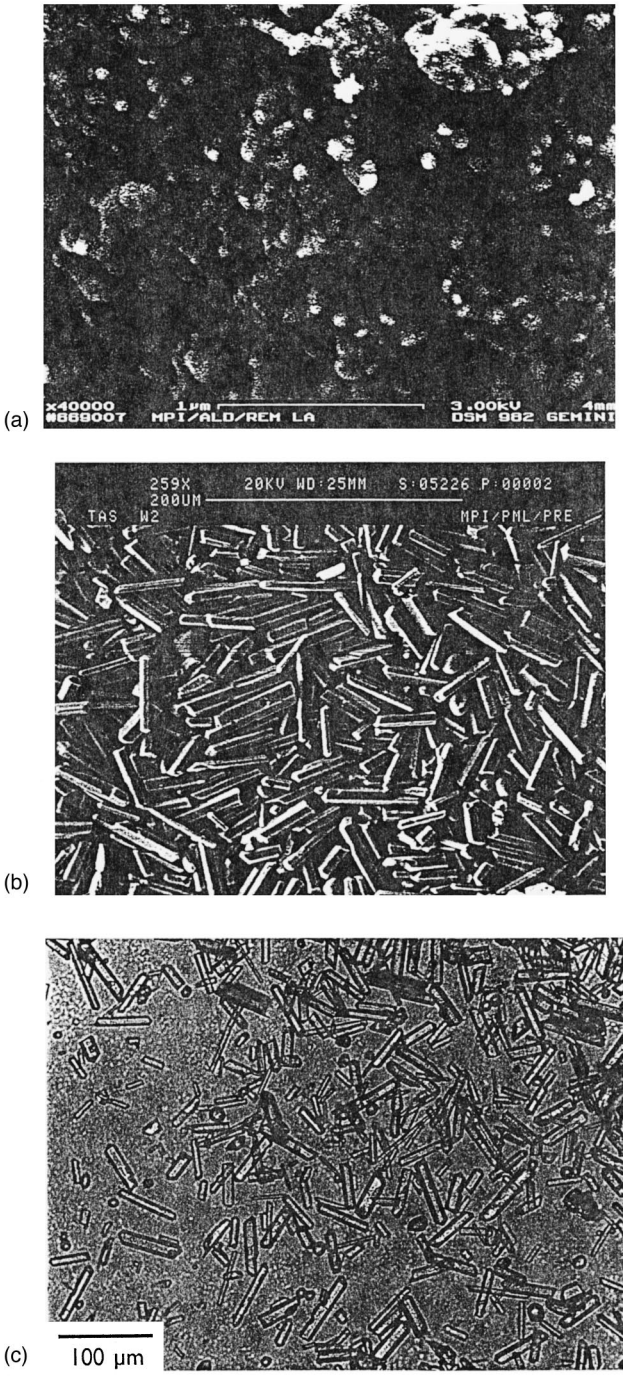

Figure 1. (a) SEM micrograph of starting HA powders after calcination at 1000 °C for 6 h, (b) SEM micrograph of flux-grown HA whiskers, (c) polarized light optical microscope photograph of the HA whiskers shown in (b).

III. RESULTS AND DISCUSSION

The SEM micrograph given in Figure 1(a) shows the morphology of starting HA powders (after calcination in air at 1000 °C for 6 h as a loose powder compact) used in the molten salt whisker synthesis. The as-is precursors (following their separation from the mother liquors and drying at 100 °C) were poorly crystalline, but not completely amorphous, and their crystallization behavior as a function of calcination temperature was published elsewhere (Mavis and Tas, 2000). Average particle size was found to be around 100 nm for the calcined, single-phase HA powders. Ca/P ratio of the same powders was determined by ICP-AES as 1.682.

Produced whiskers had the typical SEM morphology as depicted in Figure 1(b). The aspect ratio (i.e., length/diameter) of the transparent [see Figure 1(c)] whiskers was found to vary in the range of 2–18, with median whisker diameter and length being 9 and 55 μm, respectively. Whiskers were monodisperse and were not fused to one another. The XRD pattern of flux-grown whiskers is given in Figure

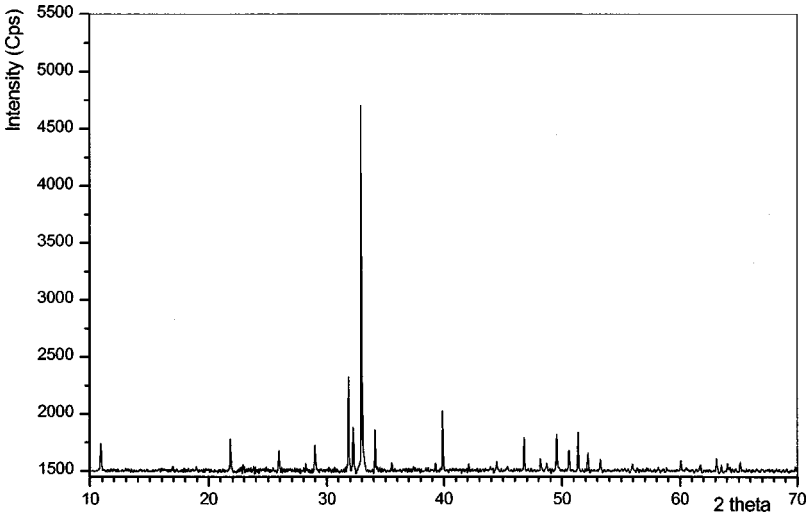

Figure 2. XRD pattern of flux-grown HA whiskers.

2. It is the characteristic XRD pattern for calcium hydroxyapatite (see ICDD PDF 24-33 and 34-10), although the intensities of 211 and 300 planes are changed due to whisker orientation. This has also been the case for previously reported (Yoshimura *et al.*, 1994; Suchanek and co-workers, 1995; 1997; 1998) hydrothermally synthesized HA whiskers, and the whiskers were apparently elongated along the *c* axis.

ICP-AES analyses performed on the flux-grown HA whiskers showed the presence of potassium in the samples in the range of 0.55–0.60 wt %. Potassium is expected to substitute the Ca sites of the HA lattice. No sulphur has been detected in the whiskers by the ICP-AES analyses. It has thus been confirmed that the hereby produced crystals cannot be regarded as ''pure'' calcium hydroxyapatite whiskers, and their chemical formula may also be regarded as $(Ca_{1-x}K_x)_{10}(PO_4)_6(OH)_{2-x}$. However, human bones and tooth enamel are also known (LeGeros and Legeros, 1993) to contain significant quantities of alkali and alkali earth cations, such as Na^+, K^+, and Mg^{2+}. The sum of these three ions in human bones reaches to about 1.3 wt %, while in enamels the same figure has been reported (LeGeros and LeGeros, 1993) to be around 1 wt %. On the other hand, Ca/P ratio of the MSS whiskers of this study were experimentally found to be 1.645 by ICP-AES analyses. These whiskers can be regarded as Ca deficient, when compared with the same ratio of 1.667 in stoichiometric HA. However, the Ca/P ratios of dental enamel and human bones are known (LeGeros and LeGeros, 1993) to be 1.62 and 1.65, respectively.

The lattice parameters of the HA whiskers (from the XRD data given in Figure 2) were determined, by a least-squares analysis (Appleman and Evans, 1973), to be $a = 9.4189(1)$ and $c = 6.8827(2)$ Å. The hexagonal unit cell (of the space group of $P6_3/m$) had a cell volume of 528.79 Å^3. The figure of merits (deWolf, 1968; Smith and Snyder 1979) for this tentative pattern were found to be $M_{20} = 205$, $F_{20} = 254$, $M_{30} = 203$, and $F_{30} = 284$. The lattice parameters of these whiskers were in perfect agreement with the parameters reported (LeGeros and LeGeros, 1993) for human bones. The presence of K^+ in the lattice has also been previously reported (LeGeros and LeGeros, 1993) not to influence the lattice parameters of hydroxyapatite. Therefore, a tentative XRD pattern for flux-grown HA whiskers (with the

TABLE II. Powder diffraction data for flux-grown HA whiskers.

$2\theta_{exp}$ (°)	I/I_0	d_{exp} (Å)	hkl	$\Delta 2\theta^a$ (°)
10.8335	8	8.16	100	0.002
16.8416	4	5.2601	101	−0.001
18.8287	3	4.7092	110	0.001
21.7654	9	4.0800	200	0.004
22.8615	8	3.8868	111	0.004
25.8647	7	3.4419	002	0.002
28.1278	2	3.1699	102	−0.004
28.9355	8	3.0832	210	0.001
31.7870	26	2.8128	211	−0.005
32.1873	13	2.7788	112	0.001
32.9093	100	2.7194	300	0.002
34.0553	12	2.6305	202	0.002
35.4751	3	2.5284	301	−0.003
39.1983	3	2.2964	212	0.001
39.8151	18	2.2622	310	−0.001
42.0046	2	2.1492	311	−0.001
42.3272	3	2.1336	302	0.001
43.8628	6	2.0624	113	−0.001
44.3859	3	2.0393	400	0.001
45.3132	2	1.9997	203	0.002
46.7025	9	1.9434	222	0.001
48.0899	4	1.8905	312	0.001
48.6156	3	1.8713	320	−0.001
49.4793	9	1.8406	213	0.001
50.5031	6	1.8057	321	−0.001
51.2834	9	1.7800	410	−0.001
52.0951	4	1.7542	402	−0.002
53.1910	3	1.7206	004	−0.001
54.4593	2	1.6835	104	−0.002
55.8807	7	1.6440	322	0.001
57.1331	5	1.6109	313	0.001
58.0628	2	1.5873	501	−0.002
59.9570	3	1.5416	420	0.002
60.4326	3	1.5306	331	0.002
61.6848	7	1.5025	214	−0.001
63.0029	8	1.4742	502	0.001
63.4444	2	1.4650	510	−0.001
64.1687	9	1.4502	323	0.002
65.0382	6	1.4329	511	−0.001
66.3987	2	1.4068	422	−0.001
69.7071	1	1.3479	512	−0.002

[a] $2\theta_{exp} - 2\theta_{calc}$.

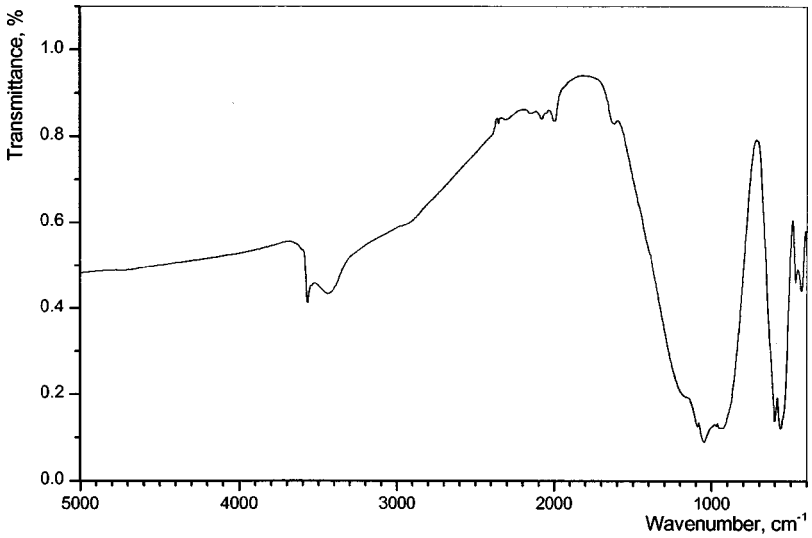

Figure 3. FTIR spectrum (*transmittance*) of flux-grown HA whiskers.

strongest XRD peak being assigned to the 300, instead of 211 plane) has been created and given in Table II.

The FTIR spectrum of the as-synthesized whiskers, shown in Figure 3, is characteristic for calcium hydroxyapatite. All bands originated from PO_4 and OH groups are clearly visible. The absence of any distinct bands in the range of 1500–1400 cm^{-1} means that the HA whiskers do not contain significant quantities of carbonate ions (Tas, 2000). Bands in the region of 1190 to 975 cm^{-1} are due to v_3 vibrational mode of phosphate group. Phosphate v_1 band is present near 962 cm^{-1}. The phosphate v_4 band is present in the region of 605–560 cm^{-1}, and two sites are observed for these whiskers at 602 and 569 cm^{-1}. Phosphate vibration v_2 is observed in the form of two discrete peaks at 471 and 433 cm^{-1}. The OH vibrations at 3571 (stretching) and 634 (bending) cm^{-1} are well defined, and the band in the region of 1638–1600 cm^{-1} is due to H–O–H deformation. Atmospheric CO_2 is detected by the band at 2349 cm^{-1}.

Biocompatible HA whiskers prepared by the MSS technique could be useful for numerous applications involving the reinforcement of hydroxyapatite-based bioceramics. The MSS process for calcium hydroxyapatite whisker manufacture is quite a robust one, since it does not require the achievement of a precise, up-to-the-last-digit control over many of the processing parameters [to produce the typical morphology given in Figures 1(b) and 1(c)], such as flux-to-HA ratio (over the range of 1.2–3.5), reaction temperature (1100–1200 °C) and soaking time (0.5–4 h).

IV. SUMMARY

Monodisperse whiskers of calcium hydroxyapatite have been synthesized by the molten salt technique. The use of K_2SO_4 as the fluxing agent was found to be suitable for this process. A tentative XRD pattern has been suggested for these whiskers, which had an aspect ratio of 2 to 18. Ca/P ratio in the whiskers were found to be 1.645, and the whiskers also contained 0.55–0.60 wt % K.

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