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Molten Salt Synthesis of Calcium Hydroxyapatite Whiskers

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Calcium hydroxyapatite (HA) whiskers and crystals were produced by the route of molten salt synthesis. The effects on whisker morphology of chosen flux, flux-to-HA ratio, synthesis temperature, and reaction time were investigated. The thermal stabilities of the produced whiskers were tested at 1300°C in an air atmosphere. A tentative X-ray diffraction pattern was proposed for the HA whiskers. Molten salt synthesis with a K_2SO_4 flux was found to be a simple and sturdy technique for manufacturing short ($\leq$60 μm) HA whiskers in the temperature range from 1080° to ~1200°C. The alternative use of fluxes such as KCl, KBr, $CaCl_2$, or Na_2SO_4, rather than K_2SO_4, over the temperature range 850°–1000°C resulted in the formation of large (~25 μm) single crystals of HA.

I. Introduction

CALCIUM HYDROXYAPATITE ($Ca_{10}(PO_4)_6(OH)_2$) is one of the most biocompatible ceramics, because of 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 ~1 MPa·m$^{1/2}$, in contrast to the values observed for human bones, in the range 2–12 MPa·m$^{1/2}$.[1]

Reinforcement by whiskers has been considered as a way of improving the fracture toughness of pure HA bioceramics; thus, whiskerlike or needlelike crystals of HA have been synthesized in recent years, mainly by the hydrothermal method or precipitation routes.[2–9] However, the whiskers synthesized by these methods[4–6] suffer from nonstoichiometry (i.e., calcium deficiency) and have low thermal stability, i.e., they partially decompose into a β-TCP phase (5–35 vol% TCP), even after 1 h of heating at 1100°C. Moreover, Suchanek *et al.*[5] have reported that, for HA composite ceramics reinforced with hydrothermally synthesized HA whiskers (~30 vol% whiskers), the whiskers disappear within the HA matrixes at sintering temperatures ≥1000°C and turn themselves into large, equiaxed grains.[6] The fracture toughness values of these samples have been reported[5] to remain only in the modest range of 1.4–2.0 MPa·m$^{1/2}$.

Molten salt synthesis (MSS) is reported to be one of the simplest techniques for preparing ceramic powder bodies with whiskerlike, needlelike, or platelike morphology and, as well, complex stoichiometry.[10] The MSS technique is based on the use of low-melting solvents, such as alkali chlorides, sulfates, carbonates, or hydroxides, as the medium of reaction for the ceramics. The literature on molten salt synthesis is quite extensive and, to name just a few cases, this technique has been used (with different alkali salts) to prepare ferrites,[10] titanates,[11–13] niobates,[14–17] mullite,[18] aluminum borate,[19,20] wollastonite,[21] and carbonated apatite ($Ca_{9.8}((PO_4)_{5.6}(CO_3)_{0.4})(CO_3)$, by using a high-melting flux of $CaCO_3$).[22] The selection of the salt in MSS is critical for obtaining desirable powder morphology and characteristics. There are two major requirements for the selection of a salt:[16] First, the melting point of the salt should be low and appropriate for the synthesis of the required phase; second, the salt should have sufficient aqueous solubility that it will be eliminated easily by simple washing, after synthesis.

In the present study, we used submicrometer-sized HA powders synthesized by a previous method[23–25] as the starting material for the MSS method. The effects on whisker morphology of the alkali salt chosen, the temperatures/times of synthesis, and the salt-to-HA powder ratio used were studied. To our knowledge, this report is the first describing the successful preparation of monodisperse HA whiskers, using K_2SO_4 salt, by the simple technique of MSS.

II. Experimental Procedure

(1) *Preparation of HA Powders*

The single-phase calcium hydroxyapatite powders used as the starting material for the MSS of the HA whiskers were synthesized as follows.[23–25] (The following procedure is the derivative of a route described earlier by Hayek and Newesely,[26] Moreno *et al.*,[27] and Jarcho *et al.*[28]) A 3 mL aliquot of 0.1 g/L methyl cellulose solution (99% purity, Sigma–Aldrich Corp., St. Louis, MO) was mixed (to act as a dispersant) with 1440 mL of deionized water. Next, 0.152 mol of $Ca(NO_3)_2·0.4H_2O$ (99.8% purity, Merck, Darmstadt, Germany) was dissolved in the above-described solution. Then, 0.090 mol of $(NH_4)_2HPO_4$ (99.8% purity, Merck) was dissolved in that solution. Following that step, 115 mL of 24 vol% NH_4OH was added, in its entirety, to the above-described opaque solution. The solution was heated and vigorously stirred at 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 deionized water. The filtrates were dried at 100°C overnight. Finally, the HA precursors were calcined in an air atmosphere at 1000°C for 6 h and then lightly ground by hand, with an agate mortar and pestle.

(2) *Synthesis of HA Whiskers*

HA powders calcined at 1000°C were dry-mixed in an agate mortar with potassium sulfate (K_2SO_4, 99.9% purity, Merck) at K_2SO_4-to-HA weight ratios in the range 1.2–3.0, for a total sample weight of 2 g. In several experiments, the K_2SO_4 (melting point (MP) = 1069°C) flux was replaced by sodium sulfate (Na_2SO_4, MP = 884°C), calcium chloride ($CaCl_2$, MP = 782°C), potassium chloride (KCl, MP = 771°C), or potassium bromide (KBr, MP = 734°C). The mixtures, as loose powder compacts, were then placed into clean alumina boats with a volume of 7.5 cm^3 and set inside a box furnace. The samples were heated from the ambient to the peak temperature of whisker synthesis at a rate of 5°C/min. Following soaking times ranging from 0.5 to 3.5 h at the peak temperatures (850°–1190°C), the samples were cooled naturally to room temperature within the shut-off furnace. The single-crystal whiskers or particles were separated from the solidified mass by washing the mass several times with hot (~90°C) deionized water.

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Washing was repeated until the specific conductance of the decanted liquid fell to <2.4 μS, measured[11] using a conductance meter (Model No. Digi610, WTW, Weilheim, Germany), knowing that the conductance of deionized water was 1.4 μS. Finally, the washed whiskers were dried in an oven, at 100°C, overnight.

(3) Investigation of Thermal Stability of Whiskers

The morphology and phase stability of the HA whiskers after heating (with heating/cooling rates of 5°C/min) at 1300°C for 9 h, as a loose powder compact, in an air atmosphere, were evaluated by scanning electron microscopy (SEM), X-ray diffractometry (XRD), and Fourier transform infrared spectrometry (FT-IR).

(4) Sample Characterization

The phase constitution of the whiskers was analyzed by XRD (Model No. D-5000, Siemens Aktiengesellschaft, Karlsruhe, Germany) and CuK_α radiation (40 kV, 30 mA). For lattice-parameter determinations, a scan rate of 0.2° 2θ/min (over the range 10°–70° 2θ), using a silicon external standard to correct for systematic errors, was used, along with the Appleman Least-Squares Refinement Program.[29] The morphologic and semiquantitative elemental distribution information on the samples were obtained by SEM (Model No. DSM 982-Gemini, Karl Zeiss, Inc., Oberkochen, Germany), and by energy dispersive X-ray spectroscopy (EDS), respectively. Quantitative chemical analyses were performed by inductively coupled plasma atomic-emission spectroscopy (ICP-AES; Model No. JY-70Plus, Jobin Yvon S.A., Longjuveau, France). An FT-IR spectrophotometer (Model No. IFS66, Bruker, Karlsruhe, Germany) was used to measure the infrared transmission spectra of the whiskers, after the whiskers had been mixed with dry KBr (1 wt%), to form pellets.

III. Results and Discussion

The SEM micrographs given in Fig. 1 show the morphology of the starting HA powders used in this study in molten salt whisker synthesis. The chemically precipitated HA precursors, following filtration from the mother liquor and 100°C drying, consisted of nanosized, but aggregated, particles, as depicted in Fig. 1(a). These precursors were poorly crystalline, but not completely amorphous. Their crystallization behavior, as a function of calcination temperature, has been published elsewhere.[25] Figure 1(b) shows the microstructure of the same powders after calcination (as a loose powder compact) in air at 1000°C for 6 h. The average particle size was ~100 nm. Calcined HA powders were determined, by XRD, to be "single-phase" HA (with only a small amount of CaO, not readily detectable by rapid XRD scans) with a Ca/P atomic ratio (measured by ICP-AES) of 1.68 ± 0.01.[24,25] This Ca/P ratio in the calcined powders was intentionally adjusted to that value by the specific Ca/P ratio used in the chemical precipitation of precursors. The XRD pattern of the calcined (1000°C, 6 h) HA powders is shown as the bottom trace of Fig. 2.

HA powders precalcined at 1000°C (to ensure that the starting materials consisted of single-phase hydroxyapatite) were then mixed with the alkali salts listed in Table I for MSS. K_2SO_4 was first[20] tested as the fluxing agent in MSS runs at four different salt-to-HA weight ratios and four different temperatures. The samples, labeled W1–W12 (see Table I), all produced single-phase HA whiskers. The XRD pattern of the W4 sample is shown by the middle trace of Fig. 2. The same XRD trace was observed for all of the samples, labeled as W*xx* in Table I. That trace represents the characteristic XRD pattern for calcium hydroxyapatite, although the intensities of the 211 and 300 planes are changed, because of whisker orientation. This result was also the case for previously reported[3–6] hydrothermally synthesized HA whiskers, and the whiskers were apparently elongated along the *c* axis. Moreover, all of the HA whiskers of samples W1–W12 were totally transparent, according to examination by optical microscopy.

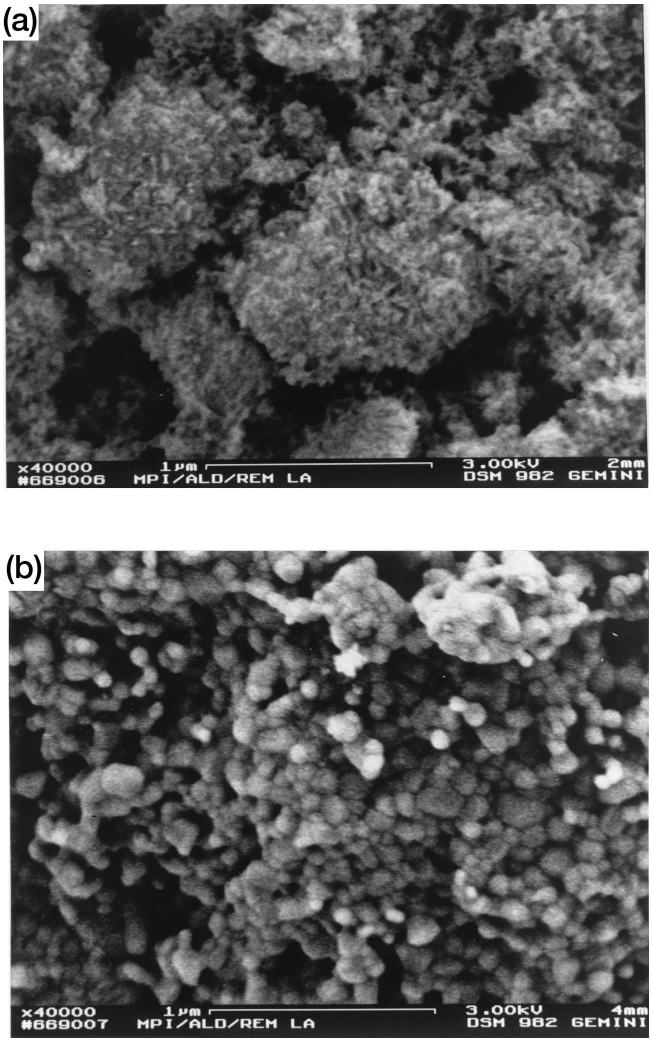

Fig. 1. SEM micrographs of HA powders at (a) 100° and (b) 1000°C.

ICP-AES analyses performed on the W*xx* samples showed the presence of 0.55–0.60 wt% potassium in the whiskers, regardless of the salt-to-HA ratios and synthesis temperatures/times used in this study. Potassium was expected to substitute the calcium sites of the HA lattice. No sulfur was detected in the whiskers by the ICP-AES analyses. Thus, the crystals produced in the present study could not be regarded as "pure" calcium hydroxyapatite whiskers, and they had the typical formula of $Ca_{1-x}K_x(PO_4)_6(OH)_{2-x}$, where *x* varied between 0.140 (i.e., 0.55 wt%) and 0.155 (i.e., 0.60 wt%).

However, human bones and tooth enamel are also known[30] 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 ~1.3 wt%, whereas, in enamels, the same figure has been reported[30] to be ~1 wt%. On the other hand, the Ca/P molar ratio of the present MSS whiskers was found, by ICP-AES analyses, to be 1.64 ± 0.01. These whiskers may also be regarded as calcium-deficient, in comparison with stoichiometric HA, which has a Ca/P molar ratio of 1.667. However, the Ca/P ratios of dental enamel and human bones are known[30] to be 1.62 and 1.65, respectively.

The lattice parameters of the W4 whiskers (middle XRD trace in Fig. 2) were determined, by least-squares analysis,[29] to be $a = 9.4189$ and $c = 6.8827$ Å. The hexagonal unit cell (of the space group of $P6_3/m$) had a cell volume of 528.79 Å^3. The lattice parameters of these whiskers resembled those reported previously[30] for the apatite of human bones, although these whiskers and human bones do not have the same chemical constitution. The

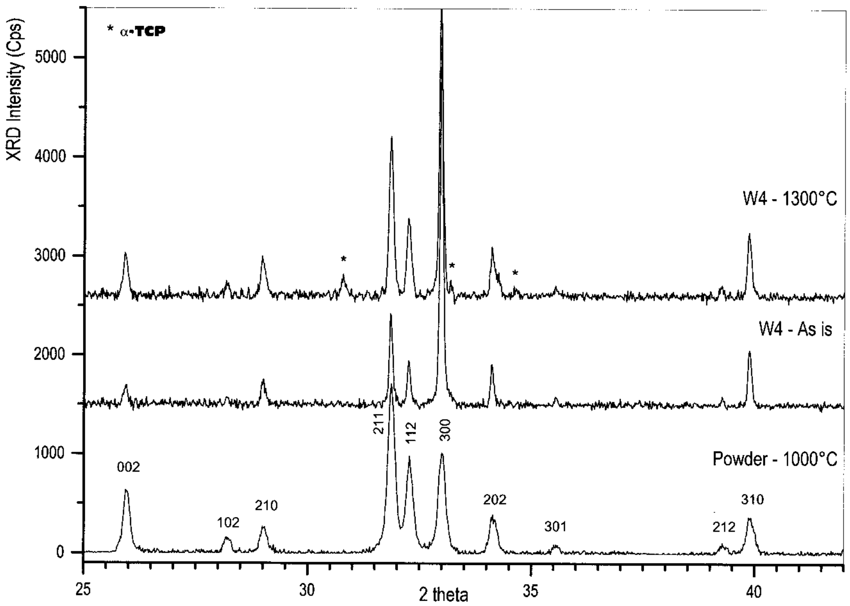

Fig. 2. XRD patterns of HA powders and whiskers.

Table I. Molten-Salt-Synthesized Samples

Sample	Salt	Salt/HA (by weight)	Reaction temperature (°C)	Reaction time (h)
W1	K_2SO_4	1.2	1190	3.5
W2	K_2SO_4	1.2	1150	2.0
W3	K_2SO_4	1.2	1100	1.0
W4	K_2SO_4	1.6	1190	3.5
W5	K_2SO_4	1.6	1150	2.0
W6	K_2SO_4	1.6	1100	1.0
W7	K_2SO_4	2.4	1190	3.5
W8	K_2SO_4	3.0	1190	3.5
W9	K_2SO_4	3.0	1150	2.0
W10	K_2SO_4	3.0	1100	2.0
W11	K_2SO_4	3.0	1100	1.0
W12	K_2SO_4	3.0	1080	0.5
P1	KCl	1.6	880	3.0
P2	KCl	1.6	1000	3.0
P3	KBr	1.6	850	3.0
P4	KBr	1.6	1000	3.0
P5	Na_2SO_4	3.0	1000	3.0
P6	$CaCl_2$	3.0	850	3.0
P7	$CaCl_2$	3.0	1000	3.0

presence of K^+ in the lattice also has been reported previously[30] to have no influence on the lattice parameters of hydroxyapatite. Therefore, a tentative XRD pattern for the HA whiskers (with the strongest XRD peak assigned to the 300, rather than the 211, plane) was created and is given in Table II.

Figures 3(a) and (b) show the SEM micrographs of molten-salt-synthesized HA whiskers of samples W1 and W4, respectively. The aspect ratios (i.e., length/diameter) varied in the range 2–18, with the median whisker diameter and length 9 μm and 55 μm, respectively. Whiskers were monodisperse and were not fused to one another. Interestingly, samples W2, W3, and W5–W11 produced almost the same microstructures and whisker morphologies. Thus, the K_2SO_4-to-HA weight ratio (in the range 1.2–3.0), the reaction temperature (in the range 1100°–1190°C), and the reaction time (in the range 1–3.5 h) were almost unable to influence the resultant HA whisker morphology. On the other hand, Fig. 3(c) shows that sample W12 (i.e., 1080°C, 0.5 h, K_2SO_4-to-HA weight ratio = 3.0) exhibited the formation of monodisperse, but much thinner, HA whiskers, with an aspect ratio >30 and a typical diameter and length of 2 μm and 65 μm, respectively. The XRD

Table II. Experimental XRD Pattern of HA Whiskers[†]

2θ	*d* (Å)	*hkl*	I/I_0
10.8335	8.1600	100	8
16.8416	5.2601	101	4
18.8287	4.7092	110	3
21.7654	4.0800	200	9
22.8615	3.8868	111	8
25.8647	3.4419	002	7
28.1278	3.1699	102	2
28.9355	3.0832	210	8
31.7870	2.8128	211	26
32.1873	2.7788	112	13
32.9093	2.7194	300	100
34.0553	2.6305	202	12
35.4751	2.5284	301	3
39.1983	2.2964	212	3
39.8151	2.2622	310	18
42.0046	2.1492	311	2
42.3272	2.1336	302	3
43.8628	2.0624	113	6
44.3859	2.0393	400	3
45.3132	1.9997	203	2
46.7025	1.9434	222	9
48.0899	1.8905	312	4
48.6156	1.8713	320	3
49.4793	1.8406	213	9
50.5031	1.8057	321	6
51.2834	1.7800	410	9
52.0951	1.7542	402	4
53.1910	1.7206	004	3
54.4593	1.6835	104	2
55.8807	1.6440	322	7
57.1331	1.6109	313	5
58.0628	1.5873	501	2
59.9570	1.5416	420	3
60.4326	1.5306	331	3
61.6848	1.5025	214	7
63.0029	1.4742	502	8
63.4444	1.4650	510	2
64.1687	1.4502	323	9
65.0382	1.4329	511	6
66.3987	1.4068	422	2
69.7071	1.3479	512	1

[†] For W4 at 1190°C.

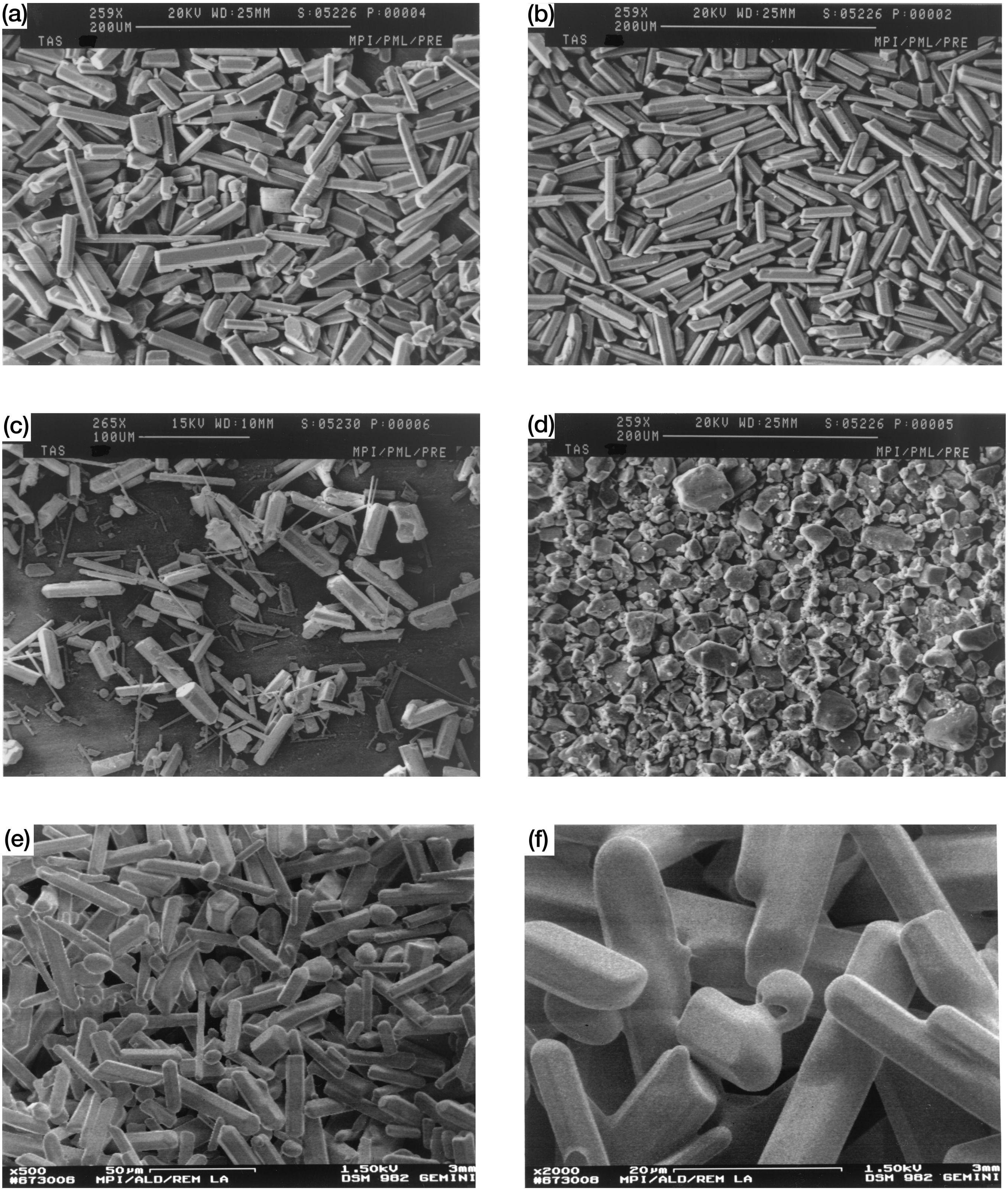

Fig. 3. SEM micrographs of HA whiskers and crystals: (a) W1, (b) W4, (c) W12, (d) P1, (e) and (f) W4 at 1300°C (see Table I for sample designations).

pattern of this sample again showed the presence of calcium hydroxyapatite only.

The above set of experimental data, obtained using K_2SO_4 as the fluxing agent, implies the following process:

(1) The liquid phase formed during the MSS process by the molten K_2SO_4 (i.e., the flux) first dissolves all of the initial ceramic raw material.

(2) With further heating, particles of the apatite phase are formed through the nucleation and growth processes.[16]

(3) As the molten ionic bath cools, while passing through its melting point down to room temperature, rapid crystallization occurs along the preferred growth axes of the ceramic phase.

(4) HA whisker growth occurs during MSS, by a sequential "dissolution–crystallization–whisker-growth" process.

(5) Solubility of the ceramic raw material in the molten flux (which is a function of temperature) must have a significant role in the crystallization process to follow.

Fig. 4. FT-IR spectra (transmittance) of HA whiskers.

(6) The extent of superheating of the molten flux must also have a rather strong effect on the resultant aspect ratio of the formed whiskers (as evidenced by the case of sample W12).

(7) The morphology of the whiskers growing out of the cooling molten salt bath must be strongly dependent on soaking time at the peak temperature.

Whiskers with the highest aspect ratio were obtained at the lowest temperature and time combination, i.e., sample W12 of Table I, a result suggesting that time and temperature are the most significant variables in altering the whisker morphology, along with the use of an appropriate fluxing agent, in which the ceramic raw material has sufficient solubility.

To test the feasibility of decreasing the MSS temperature, we also tried using KCl, KBr, Na_2SO_4, and $CaCl_2$, rather than K_2SO_4, with the MSS parameters given in Table I. These samples were labeled P1–P7. Interestingly, none of the samples were able to produce HA whiskers, and the reason(s) for this failure may also be found in the above paragraph. Figure 3(d) shows the SEM micrograph of the P1 powders, and this morphology was also encountered with the other samples, P2–P7. The product phase in all of these P*x* samples was, again, calcium hydroxyapatite, with an average particle size of 25 μm. The finer portion of the powder body (of Fig. 3(d)) is believed to have been the undissolved, initial HA powder, and the larger portion consisted of single crystals of HA. Such hydroxyapatite powders, with a large average particle size, may be useful for applications such as plasma-spraying. However, ICP-AES analyses performed on the P1 and P2 samples indicated the presence of chlorine (in the range 1.5%–1.7%) in the final powders. It can be inferred that using KCl as the molten salt facilitates at least the partial transformation of hydroxyapatite into chloroapatite.

Figures 3(e) and (f) show the microstructures of W4 whiskers at two different magnifications, after heating as loose powder compacts in alumina boats, at 1300°C, for 9 h in a stagnant air atmosphere. For the molten-salt-synthesized HA whiskers of the present study, the previously mentioned problem (for the whiskers synthesized by the hydrothermal method)[3–6] of morphologic degradation apparently was not present. The W4 whiskers retained their shapes perfectly, formed a skeleton of HA, and just fused together at the points of mutual contact. However, the XRD pattern of the whiskers heated at 1300°C (see Fig. 2) showed the presence of a second phase of α-TCP (ICDD No. PDF 9–348[‡]), the high-temperature orthorhombic polymorph of tricalcium phosphate, $Ca_3(PO_4)_2$. The formation of TCP, as a decomposition product of HA, in samples heated at 1300°C in an air atmosphere, is well-known and normal.[1,30] Previous reports[31] have also noted that, for synthetic hydroxyapatites cooled rapidly (as in the present study) from temperatures >1250°C, the crystallographic form of TCP observed will always be the high-temperature polymorph.

The FT-IR spectrum of the as-synthesized W4 whiskers shown in the bottom trace of Fig. 4 is characteristic for calcium hydroxyapatite. All bands originating from PO_4 and OH groups are clearly visible. The absence of any distinct bands in the range 1500–1400 cm^{-1} means that the HA whiskers do not contain significant quantities of carbonate ions.[32] Bands in the region 1190–975 cm^{-1} result from the ν_3 vibrational mode of the phosphate group. A phosphate ν_1 band is present at ~962 cm^{-1}. A phosphate ν_4 band is present in the region 605–560 cm^{-1}, and two sites are observed for these whiskers at 602 and 569 cm^{-1}. A phosphate vibration, ν_2, is observed in the form of two discrete peaks at 471 and 433 cm^{-1}. The OH vibrations at 3571 cm^{-1} (stretching) and 634 cm^{-1} (bending) are well-defined, and the band in the region 1638–1600 cm^{-1} is a result of H–O–H deformation. Atmospheric CO_2 is indicated by the band at 2349 cm^{-1}.

The infrared spectrum of the W4 whiskers calcined in air at 1300°C for 9 h (depicted by the top trace in Fig. 4) shows, as well as all of the above-mentioned bands, a unique band at 743 cm^{-1}, which is characteristic of the P–O–P vibrational mode of pyrophosphates,[32] although their XRD patterns did not indicate the presence of $Ca_2P_2O_7$ as a decomposition product. The band at 1933 cm^{-1} could not be identified.

Biocompatible HA whiskers prepared by the MSS technique could be useful for numerous applications involving the reinforcement of hydroxyapatite-based bioceramics. As shown in this report, the MSS process for calcium hydroxyapatite whisker manufacture is quite robust, because it does not require the achievement of precise, up-to-the-last-digit control over many of the processing parameters, such as the flux-to-HA ratio, reaction temperature, and time.

IV. Summary

Molten salt synthesis (MSS) of monodisperse calcium hydroxyapatite whiskers was accomplished using a K_2SO_4 flux. Single-phase, potassium-doped HA whiskers proved possible to synthesize over the temperature range 1080°–1190°C, and the K_2SO_4-to-HA ratios in the initial mixtures could be varied between 1.2 and 3.0 without significantly affecting the whisker morphology.

[‡] Powder Diffraction File, No. PDF 9–348. International Centre for Diffraction Data, Newtown Square, PA.

HA whiskers produced by the K_2SO_4 flux retained their initial shapes and aspect ratios, even after heating in air at 1300°C for 9 h, although they started to decompose into TCP. Fluxing agents such as KCl, KBr, $CaCl_2$, and Na_2SO_4, when used in place of K_2SO_4, produced large single crystals of HA, with an average particle size of 25 μm, rather than whiskers, over the MSS temperature range 850°–1000°C.

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