INTRODUCTION

Hydroxyapatite (Ca_{10}(PO_4)_{6}(OH)_2; HAp) is well-known as inorganic components of biological hard tissue, and it has directly-bonding ability with hard tissue of host. Therefore, the HAp ceramics are clinically applied as materials of artificial bone and tooth root. In addition, because of the stability of the crystal structure, the HAp can include various kinds of ions in the Ca^{2+}, PO_4^{3-} and OH^{-} sites. In fact, biological apatite presented in bone and teeth of mammals contains various minerals, for instance: Na^{+}, K^{+}, Mg^{2+}, F^{-} and CO_3^{2-} ions. Thus, it has lots of strains and defects with nano-scale sizes in the crystal structure. It is known that the HAp lattice can easily accommodate a variety of substituents both cationic and anionic, inducing modifications of the crystallinity, morphology, lattice parameters and stability of the apatite structure.

Many studies of substituted apatite have been conducted so far, and numerous reports on Mg^{2+}, F^{-} and CO_3^{2-}-substituted apatite have been reported. However, there are few studies on potassium-substituted apatite. The importance of potassium (K) in bone composition is its major influence on biomineralization process. Several studies have demonstrated the versatile nature of potassium in the control of biochemical processes and the important role in the apatite mineral nucleation process.

In this study, an ultrasonic spray-pyrolysis (USSP) technique was used for the synthesis of HAp powders. The USSP technique is one of the powder preparation methods via the liquid phases. The advantage of this method is that one can prepare stoichiometric and homogeneous compounds instantaneously by spraying the solutions with the desired amounts of cations into the hot zone of an electric furnace. Especially, this method is effective for the preparation of HAp-like materials containing the hydroxyl group in the crystalline structure, and the powders can be prepared directly in a steam atmosphere during spray-pyrolysis.

We prepared potassium-substituted HAp (KAp) powders using the USSP technique in the present study. Furthermore, in order to examine the effects of substitutions of potassium on material properties of the HAp ceramics, the KAp ceramics with desired potassium content were fabricated and characterized using various analysis techniques.

MATERIALS AND METHODS

1) Preparation of KAp powders
Three kinds of KAp powders were synthesized by the USSP technique, together with pure HAp one. The starting solutions were prepared by mixing the following chemicals: Ca(NO\(_3\))\(_2\)·4H\(_2\)O, (NH\(_4\))\(_2\)HPO\(_4\), KNO\(_3\), and HNO\(_3\), as given in Table 1. The sample powders were prepared by spray-pyrolyzing the starting solution using the ultrasonic vibrator with frequency of 2.4 MHz in the hot zone. The hot zone in the present USSP apparatus was composed of two electric furnaces; the lower furnace was used for the pyrolysis (850 °C) and the upper furnace was used for the pyrolysis (850 °C)\(^{14}\).

2) Characterizations of resulting powders

Crystalline phases of the powders were identified by X-ray diffractometry (XRD; Miniflex, Rigaku, Japan) using Cu-K\(_\alpha\) radiation at 30 kV and 15 mA. The XRD data were collected under the following conditions: 2\(\theta\) range of 10–50°, scan rate of 2° per minute and sampling width of 0.02°. The infrared spectrum of the specimens was obtained using a Fourier transform infrared (FT-IR; IR Prestige-21, Shimadzu Co., Japan) spectrophotometer, in the region of 400–4000 cm\(^{-1}\) using potassium bromide pellets with a spectral resolution of 4 cm\(^{-1}\). The Ca, P and K contents of the powders were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS7800, SII Nano Technology, Japan). The morphology of the KAp powder particles was observed by scanning electron microscopy (SEM; JSM6390LA, JEOL, Japan) at 10 kV. The SEM samples were prepared by fixing the powders on pieces of double-sided carbon tape, which were then deposited with platinum particles in a vacuum.

3) Fabrication of KAp ceramics and their properties

The resulting KAp powders were uniaxially compressed at 100 MPa in disks (diameter: ~12 mm, thickness: ~2 mm). The resulting compacts were fired with an electric furnace at 1250 °C for 5 h at the heating rate of 5 °C/min in steam atmosphere.

Crystalline phases of the crushed ceramics were identified by XRD using Cu-K\(_\alpha\) radiation at 30 kV and 15 mA. The XRD data were collected under the same conditions as for the KAp powders. The FT-IR spectra of the KAp ceramics were recorded in a range of 400–4000 cm\(^{-1}\) by potassium bromide pellets method. The lattice constants of the crushed ceramics were determined by refinement of XRD data collected under the following conditions: 2\(\theta\) range of 10–50°, scan rate of 0.1° per minute and sampling width of 0.02° (40 kV, 40 mA; Ultima IV, Rigaku, Japan). The refinement software PDXL2 was used according to the manufacturer’s instructions (Rigaku). The Ca, P and K contents of the KAp ceramics were determined by ICP-AES. The microstructure of the KAp ceramics was observed by SEM at 10 kV. The SEM samples were prepared by fixing the thermally-etched ceramics on pieces of double-sided carbon tape. The grain sizes were measured by an intercept method using the SEM images, and calculated as follows:

\[
G_{\text{true}} = d_a \times F
\]

where \(d_a\) is the apparent grain size, and \(F\) is Fullman constant.

RESULTS AND DISCUSSION

1) Characterizations of KAp powders

Figure 1 shows the XRD patterns of KAp powders obtained by spray-pyrolyzing the solutions with various concentrations of potassium. The XRD patterns of KAp powders indicated that the crystalline phase was of HAp single phase with low crystallinity. The addition of potassium had almost no effect on the powder synthesized by spray pyrolysis.

FT-IR spectra of KAp powders with various potassium contents are shown in Figure 2. These spectra indicated typical HAp absorptions. The absorption bands were observed at 960, 1030 and 1100 cm\(^{-1}\) assigned to P-O stretching vibration, and at 570 and 600 cm\(^{-1}\) assignable to O-P-O bending. The absorption bands at 630, 1650 and 3570 cm\(^{-1}\) showed the existence of OH\(^-\) groups was detected in all samples. Furthermore, the peak of NO\(_3\)\(^-\) at 1400 cm\(^{-1}\) derived from the starting solutions was detected.
Table 2 gives quantitative results of Ca, P and K elements of KAp powders. The actual amounts of K in the KAp powders increased depending on the K contents of starting solutions.

The morphology of the KAp powder particles was observed by SEM (Fig. 3). The SEM micrographs showed that all of the samples consisted of spherical-shaped particles with a diameter smaller than 2 µm. There were no significant differences among KAp powders regardless of potassium concentration in the starting solution.

| Samples     | Ca (mass%) | P (mass%) | K (mass%) | K/(Ca+K) mol% | (Ca+K)/P |
|-------------|------------|-----------|-----------|----------------|-----------|
| Pure HAp    | 36.99      | 17.62     | 0.00      | 0              | 1.62      |
| KAp(2.5)    | 37.75      | 17.71     | 0.79      | 2.10           | 1.68      |
| KAp(3.75)   | 36.28      | 16.96     | 1.06      | 2.92           | 1.70      |
| KAp(5.0)    | 36.53      | 17.58     | 1.54      | 4.14           | 1.68      |

FIGURE 1 XRD patterns of KAp powders: (a) pure HAp powder, (b) KAp(2.5) powder, (c) KAp(3.75) powder, (d) KAp(5.0) powder.

FIGURE 2 FT-IR spectra of KAp powders: (a) pure HAp powder, (b) KAp(2.5) powder, (c) KAp(3.75) powder, (d) KAp(5.0) powder.

FIGURE 3 SEM micrographs of KAp powders: (a) pure HAp powder, (b) KAp(2.5) powder, (c) KAp(3.75) powder, (d) KAp(5.0) powder.
2) Material properties of KAp ceramics

Figure 4 shows the XRD patterns of KAp ceramics sintered at 1250 °C for 5 h. All of the KAp ceramics were of single phases of hydroxyapatite still after firing. The KAp ceramics prepared in this study was prepared so that the charged amount of (Ca+K)/P ratio was 1.72. On the other hand, the crystalline phase consisted of biphase of HAp and β-TCP when (Ca+K)/P ratio was 1.67. Excess of Ca + K conditions suppressed the formation of Ca-deficient apatite, and it seems that HAp single phase could be achieved.

The FT-IR spectra of KAp ceramics showed absorption attributable to PO$_4^{3-}$ as well the case of KAp powders (Figure 5). The peak of NO$_3^-$ at 1400 cm$^{-1}$ detected with KAp powders was disappeared by firing. Although there was almost no difference depending on the potassium contents in the case of powders, the peak intensity of OH$^-$ groups at 630 and 3570 cm$^{-1}$ of KAp(3.75) and (KAp5.0) was lower than that of pure HAp and KAp(2.5). Substitution of monovalent cations like Na$^+$ and K$^+$ ions cause a charge imbalance that can be neutralized by creating supplementary vacancies, or by the occurrence of simultaneous substitutions of cations and anions without the formation of any vacancy or loss of the charge balance.$^{15}$ Since carbonate ions were not detected in KAp ceramics, the decrease in the OH$^-$ band observed at KAp(3.75) and KAp(5.0) may have resulted in the formation of OH vacancies.

Table 3 gives the contents of Ca, P and K determined by ICP-AES. Compared to the value of KAp powders, the K contents of each ceramics further decreased. The K/(Ca+K) molar ratios in three types of KAp powders are given in Table 2. These values were at 2.10 in KAp(2.5), 2.92 in KAp(3.75), and 4.14 on KAp(5.0). After sintering at 1200 °C for 5 h, the K/(Ca+K) molar ratios in the KAp ceramics decreased down to 0.38 in KAp(2.5), 1.40 in KAp(3.75), and 2.42 on KAp(5.0). The differences in the K/(Ca+K) molar ratios before and after sintering are in the ranges of 1.5 to 1.7, and these values are nearly close. Since ionic radius of potassium (0.133 nm) is larger than that of calcium (0.099 nm), potassium ions are hard to be substituted into HAp structure compared to calcium ions. Thus, during sintering, parts of potassium in the starting KAp powder may be vaporized before the potassium is substituted with calcium in the HAp structure. Furthermore, the potassium content of KAp(2.5), which did not shown a reduction in OH$^-$ band in the FTIR spectrum, was as small as 0.38 mol%, suggesting that substitution of a certain amount of potassium is necessary for the formation of OH vacancy.

Figure 6 shows constants of HAp obtained by refining the XRD pattern of KAp ceramics. As the K content increased, the lattice constants of a-axis slightly increased, and that of c-axis expanded. Contrary to this result, Kannan et al.$^9$ showed contraction in the a-axis of potassium-substituted apatite synthesized by wet
precipitation method. This may be due to the formation of vacancies in the channel through the substitution of a bivalent cation by a monovalent cation. Decrease in the diameter of the channel lead to decrease the $a$-axis parameter. Furthermore, the location of substituting cations in the apatitic structure is generally correlated to their ionic radius. Site Ca(I) (Columnnar Ca) is smaller in volume than site Ca(II) (Screw axis Ca), potassium with a large ionic radius is assumed to preferentially occupy site(II). However, Feki et al. reported that 83% of the potassium atoms were located in site (I), which is causes expansion of the $c$-axis when large ions are replaced in. Thus, the variation of the lattice constants of the KAp ceramics fabricated in this study is thought to be due to the result of the substitution of the Ca(I) site for most of the potassium although the reduction of the OH$^-$ channel due to vacancy formation also occurs.

Figure 7 shows SEM images of the surfaces of KAp ceramics. The grain sizes of pure HAp, KAp(2.5), KAp(3.75) and KAp(5.0) ceramics measured by the intercept method were at 1.38, 1.64, 3.58 and 4.14 $\mu$m. Compared with pure HAp and KAp(2.5) ceramics, the grain size of KAp(3.75) and KAp(5.0) ones was bigger. This could be caused by liquid phase sintering and/or an increase of diffusion coefficients of HA due to incorporation of monovalent ions into calcium sites of the HA structure, with formation of OH vacancies. This result also proved that OH vacancies were formed by incorporation of potassium.

CONCLUSION

Effect of incorporation of potassium into the HAp structure was examined. The addition of potassium had little effect on the properties of the powder synthesized by ultra sonic spray-pyrolysis technique. By setting the (Ca+K)/P ratio of the starting solution to 1.72, KAp ceramics remained as HAp single phase regardless of the added concentration of K even after firing. The FTIR results showed that substitution of K cause OH vacancies to be formed by charge compensation. The lattice constants of KAp ceramics via spray-pyrolysis increased in both $a$- and $c$-axes,
suggesting that K+ ions occupied site Ca(1). However, it is necessary to pay attention to the substitution form of ions to HAp because it varies depending on the synthesis method or the presence of simultaneously substituted ions. The findings of this study are expected to lead to the development of research on substituted apatite for high-performance artificial bone.

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