DEVELOPMENT OF STABLE DICALCIUM PHOSPHATE AGAINST NaF BY USE OF A SURFACE MODIFICATION TECHNOLOGY (I)

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Abstract Stable dicalcium phosphate (DCP) against NaF was prepared by heat treatment at 200°C with adding Mg compound and condensed phosphate to DCP anhydrous. The stability of the improved DCP against NaF was higher than that of hydroxyapatite and fluorapatite. It was approximately equal to the SiO<sub>2</sub> anhydrous.

INTRODUCTION

Dicalcium phosphate (DCP) is manufactured for toothpaste. Much toothpaste contains NaF for the prevention of dental caries but can not use DCP, because DCP reacts with NaF easily to form CaF<sub>2</sub>. There have been many efforts to resolve the problem but they have not obtained a sufficient stability against NaF.<sup>1), 2), 3)</sup>

We looked at the particular DCP anhydrous which showed the improvement of the stability against NaF after heat treatment at 200°C for 2hr. The improvement depends on the Mg content in DCP.

We analyzed the particular DCP anhydrous and developed a surface modification technology to get the improved DCP which showed the higher stability against NaF than that of hydroxyapatite and fluorapatite by the storage test for 90days at 40°C. It was approximately equal to the SiO<sub>2</sub> anhydrous.

EXPERIMENTAL

Preparation of Sample

Typical DCP anhydrous was our manufactured product. We added Mg compound to the DCP anhydrous. Mg/DCP (wt ppm) = 971, 985, 1040, 1109, 1660, 2343. Heat treatment was at 200°C for 2hr in an oven.

The improved DCP anhydrous was prepared by adding Mg compound and condensed phosphate. Mg/DCP (wt ppm) = 3500, P<sub>2</sub>O<sub>7</sub>/DCP (wt ppm) = 12500. Heat treatment was at 200°C for 2hr in an oven. Mg content was analyzed by an
atomic absorption spectrometer (AAS), Shimazu AA-6800.

Reference sample was standard DCP anhydrous, hydroxyapatite, fluorapatite and SiO2.

Thermal analysis

We analyzed several DCP anhydrous with some Mg content by thermogravimetry (TG) and differential scanning calorimetry (DTA) (SEIKO INSTRUMENTS INC., EXSTAR 60200). Reference material was α-Al2O3 and temperature was increased from room temperature to 350°C at a heating rate of 20°C /min. Carrier gas was nitrogen and flow rate was 250ml/min.

Volatile material was identified by pyrolysis Gas Chromatography/Mass Spectrometry (Py-GC/MS). Pyrolysis was carried out using a Frontier Lab PY-2010D and temperature was increased from 50°C to 300°C at a heating rate of 5°C/min. GC/MS system was Hewlett Packard HP-G1800A with 1.5mmi.d. x 5m capillary column and temperature was 280°C. Carrier gas was helium, flow rate was 1ml/min and split ratio was 1/50.

X-ray diffraction

Crystalline phase was evaluated by an X-ray diffractometer (XRD; RIGAKU, GEIGERFLEX RAD-C SYSTEM, CuKα radiation and 40kV and 30 mA power condition)

Storage test

The stability of a compound against NaF was evaluated by the analysis of the concentration of residual F⁻ in the mixture of a compound, NaF and glycerin. A compound for evaluation (19.59g), NaF (0.11g) and glycerin (30.3g) were mixed in polyethylene container (100ml). The initial concentration of F⁻ was prepared at 1,000ppm in the mixture.

Keep the sample at 40°C in a thermostatic chamber. Storage period was 7, 30, 60 and 90 days. The stored sample was mixed again and centrifuged to get supernatant liquid. The supernatant liquid (2ml) was taken to a flask and mixed with the pH5.3 buffer solution (38ml), TISAB solution (1) from Kanto Kagaku (2ml), perchloric acid (3ml) and ion-exchange water (5ml).

The concentration of residual F⁻ in the prepared sample was analyzed by ion meter (TOA-IM40S). Fluoride ion standard solution (1000mg/l) was provided by Kanto Kagaku.
RESULTS AND DISCUSSION

Effect of adding of Mg compound

Figure 1 shows the result of analysis of residual F⁻ in the mixture after storage test at 40°C for 7 days. The sample with Mg content more than 1600 (wt ppm) was improved the stability against NaF.

Effect of the heat treatment time

We studied the effect of the heat treatment time on the stability against NaF. DCP anhydrous with Mg content 1711 (wt ppm) was heated at 200°C for 15 min, 30 min, 1 hr, 2 hr and 3 hr. Figure 2 shows the result of analysis of residual F⁻ in the mixture after storage test at 40°C for 7 days. The concentration of residual F⁻ reached at stable level after more than 1 hr of heat treatment.

![Figure 1](image1.png)

**Figure 1** The effect of Mg content in DCP on the concentration of residual F⁻ after storage test at 40°C for 7 days.

![Figure 2](image2.png)

**Figure 2** The effect of heat treatment time at 200°C on the concentration of residual F⁻ after storage test at 40°C for 7 days.
We analyzed the DCP anhydrous with Mg content 970 (wt ppm) and 1711 (wt ppm) by TG-DTA. Figure 3 shows the result of TG-DTA. The DCP anhydrous with Mg content 970 (wt ppm) showed gradual weight loss 0.173 (wt%) between room temperature and 200°C. There was no change on DTA curve. The DCP anhydrous with Mg content 1711 (wt ppm) showed rapid weight loss around 130°C. There was typical endothermic peak on DTA curve around 130°C.

Figure 3 TG-DTA curves of DCP anhydrous.
(a) Mg content was 970 (wt ppm), (b) Mg content was 1711 (wt ppm)
--- : TG (wt%), - - - - : DTA (µV)

We supposed that the endothermic reaction depended on the Mg content in DCP. We added MgHPO₄ · 3H₂O to the DCP anhydrous with Mg content 970 (wt ppm) to prepare Mg content 2360 (wt ppm). Figure 4 shows the result of TG-DTA. The DCP anhydrous with additional Mg showed rapid weight loss around 130°C. There was typical endothermic peak on DTA curve as same as that of the DCP anhydrous with 1711 (wt ppm).
The volatile material was identified as water by use of Py-GC/MS. Figure 5 shows the result of Py-GC/MS by comparison of the sample pattern with water pattern.

We compared the XRD pattern of DCP anhydrous with 10wt% MgHPO₄·3H₂O to that after heat treatment at 200°C for 2hr. Results are shown in Figure 6. There is no peak of MgHPO₄·3H₂O after heat treatment. We supposed that heat treatment caused dehydration of MgHPO₄·3H₂O to make an amorphous Mg₂P₂O₇.

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\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{Mg}_2\text{P}_2\text{O}_7 + 7/2\text{H}_2\text{O}
\]
Surface modification of DCP

We tried to make Mg$_2$P$_2$O$_7$ on the surface of DCP anhydrous artificially. Mg compound and condensed phosphate were added to DCP anhydrous as dry powder and the mixture was heated at $200^\circ$C for 2hr in an oven. Mg/DCP (wt ppm) = 3500, P$_2$O$_7$/DCP (wt ppm) = 12500. The result of storage test at 40$^\circ$C for 90 days is shown in Figure 7. The improved DCP showed higher stability against NaF by comparison with hydroxyapatite and fluorapatite. It was approximately equal to the SiO$_2$ anhydrous.

Figure 6  XRD patterns of DCP with 10wt% MgHPO$_4$·3H$_2$O
(a) Standard sample, (b) Heat treatment sample at 200$^\circ$C for 2hr
▲ : MgHPO$_4$·3H$_2$O
Figure 7 The comparison of the results of analysis of residual F⁻ in the mixture at 40°C for 90 days.

REFERENCES

1) K. Kuma, JP Patent, Tokukai 2001-278760