JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 2 (1991) 149–152

# Sintering mechanism of hydroxyapatite by addition of lithium phosphate

T. GOTO, N. WAKAMATSU, H. KAMEMIZU, M. IIJIMA, Y. DOI, Y. MORIWAKI
*Department of Dental Materials and Technology, School of Dentistry, Asahi University, 1851 Hozumi-cho Motosu-gun, Gifu 501-02, Japan*

The sintering mechanism of hydroxyapatite (HAp) by addition of lithium phosphate ($Li_3PO_4$) has been investigated. Using the X-ray diffraction method, HAp was confirmed to decompose into β-$Ca_3(PO_4)_2$ (β-TCP) by addition of $Li_3PO_4$. The measurement of shrinkage rate by the isothermal firing made it clear that the densification process at the initial stage of sintering took place in the presence of liquid phase. Furthermore, the examination of the phase diagram on the binary system β-TCP–$Li_3PO_4$ revealed that there was an eutectic point at 1010 °C in the composition of 60 wt% $Li_3PO_4$. From these evidences, we concluded that β-TCP produced by the decomposition of a part of HAp has formed the liquid phase by reacting with $Li_3PO_4$ above 1010 °C, and that this liquid phase has largely promoted the densification by the rearrangement of HAp particles at the initial stage of sintering.

## 1. Introduction

It is well known that the hydroxyapatite, $Ca_5(PO_4)_3OH$, (HAp) is the most attractive materials for hard tissue implant, because of its superior bicompatibility and possibility of bonding strongly to new bone [1–6]. The applications, however, are limited because of its low mechanical strength and low toughness [7–11]. On the other hand, the implant materials generally need the complicated shape corresponding to each patient. From these reasons, it is important to develop a technique for coating the casted metal such as Co–Cr alloy with HAp ceramic.

In our recent investigation [12], it is found that the lithium phosphate, $Li_3PO_4$, is very effective at sintering HAp. By firing at 1050 °C, the relative density of HAp reaches more than 95% within a few minutes. This is a quite hopeful characteristic for coating the metal with HAp. The purpose of this investigation is to elucidate the sintering mechanism of HAp by addition of $Li_3PO_4$ in order to get the basic information for a coating technique.

Considering the densification rate, the liquid phase is expected to contribute to the sintering at the initial stage. From this point of view, the isothermal shrinkage is measured to confirm the appearance of liquid phase. Furthermore, it is suggested that, from the preliminary experiment, the HAp will decompose into β-tricalcium phosphate, β-$Ca_3(PO_4)_2$ (β-TCP), in the presence of $Li_3PO_4$. Therefore, the phase diagram of binary system β-TCP–$Li_3PO_4$ is also examined as the most possible system for supplying the liquid phase.

## 2. Experimental

### 2.1. Preparation of HAp and β-TCP

The HAp powder was synthesized by slowly dropping the solution (4 l) of 0.6 M $H_3PO_4$ into the suspension (4 l) of 1 M $Ca(OH)_2$ stirring at 100 °C [13]. The precipitated HAp was matured for 2 weeks at 100 °C and decanted off three times before filtering. The HAp cake, dried at 60 °C, was calcined at 800 °C for 3 h and reduced to powder. The X-ray powder diffraction indicated that a very small amount of β-TCP appeared when the synthesized HAp was fired for 1 h at 1200 °C.

The β-TCP was prepared by firing the amorphous calcium phosphate (ACP) at 900 °C for 1 h. The ACP was synthesized by mixing the two solutions (1 l each) of 0.08 M $Ca(NO_3)_2$ and 0.48 M $(NH_4)_2HPO_4$ at 0 °C [14]. The deposited ACP was freeze-dried after washing several times with the distilled water (0 °C).

### 2.2. Measurements of isothermal shrinkage

The isothermal shrinkage was measured in the case of both HAp and 0.6 wt % $Li_3PO_4$–HAp (Li–HAp). The commercially available $Li_3PO_4$ was used in this measurement. The HAp and Li–HAp powders were pulverized until all particles passed through the sieve of 37 μm. These powders were formed into rods by using the cylindrical die with an inner diameter of 5 mm and pressed at the hydrostatic pressure 196 MPa. These rods were cut into disks of 3 to 4 mm in thickness so that the opposed surfaces are parallel.

The disk specimen was just in contact with the alumel–chromel thermocouple and they were put into the furnace kept constant at 800, 900, 950, 1000 and 1050 °C. The temperature fluctuation in the furnace was about ± 3 °C. The firing time was defined as the elapsed time from when the temperature of thermocouple reached that of furnace within 3 °C, and was a few seconds to several hours. The changes in thickness of specimens were measured by using the micrometer.

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The measurements were repeated several times at the same firing temperature and time.

### 2.3. Phase diagram of binary system $\beta$-TCP–$Li_3PO_4$

The $(1 - \chi)$ $\beta$-TCP and $\chi Li_3PO_4$ were mixed, where $\chi$ is in intervals of 0.05. To determine the phase boundary by means of differential thermal analysis (DTA), a part of each mixture was previously reacted at 950 °C for 2 h. The DTA measurements were made at the heating rate of 5 °C/min up to 1300 °C. The identification of solid phases in this system were done with the X-ray powder diffraction method. The samples used in this examination were prepared by quenching in air after heating the above mixtures at the desired temperatures for 1 h.

## 3. Results

Figs 1 and 2 show the relationship between $\ln(\Delta L/L_o)$ and $\ln t$ on HAp and Li–HAp, respectively, where $L_o$ is the thickness of specimen before firing, $\Delta L$ is the shrinkage value and $t$ is the firing time. The figures near the lines are the values of slope calculated by the least squares method. The slopes of HAp at the initial stage are almost same. On the contrary, at the same stage those of Li–HAp increase with increasing temperature above 900 °C and the value at 1050 °C is 1.29.

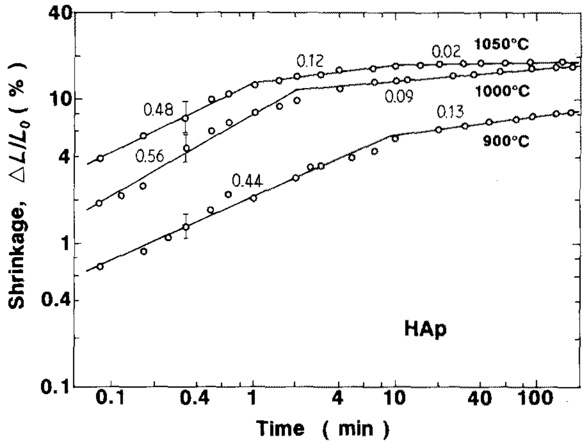

*Figure 1* The relationship between isothermal shrinkage and firing time on HAp. The figures near the line indicates the value of slope calculated by least squares method.

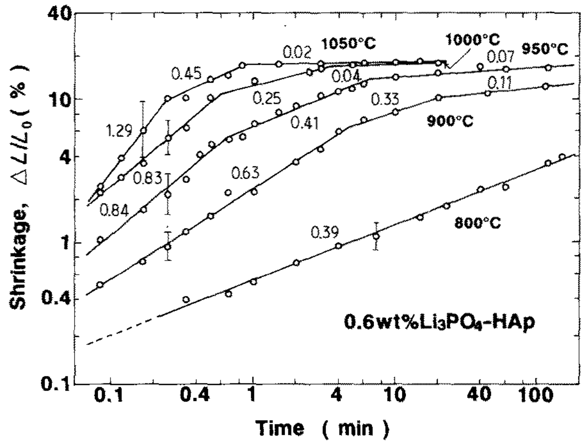

*Figure 2* The relationship between isothermal shrinkage and firing time on Li–HAp. The figures near the line indicates the value of slope calculated by least squares method.

Fig. 3 shows the phase diagram of the binary system $\beta$-TCP–$Li_3PO_4$ in the range of composition from 30 to 100 wt % $Li_3PO_4$. An eutectic point appears at 1010 °C in the composition 60 wt% $Li_3PO_4$. The important result is that the liquid phase appears in the wide range of composition at a temperature above 1010 °C. In the range below 30 wt% $Li_3PO_4$, no liquid phase is observed in the present temperature range examined.

## 4. Discussion

### 4.1. Sintering of Li–HAp

At the initial stage of sintering in the presence of liquid phase, Kingery [15] has expected that the rate of densification follows a relation,

$$\Delta L/L_o \sim t^{1+y},$$

corresponding approximately to viscous flow, where the value of $y$ is 0.3 to 0.4 according to Kingery and Narasimhan [16]. In the present measurement, $y$ of Li-HAp is 0.29 at 1050 °C and is quite close to the value stated above. Therefore, we would be able to conclude that the initial stage of sintering Li–HAp at 1050 °C is promoted by the liquid phase. The resultant liquid will dissolve the intergranular materials and the capillary pressure will allow the HAp particles to get maximum packing. As a result, the rearrangement of HAp particles would lead to the sudden densification of Li–HAp. However, considering that $1 + y$ decreases rapidly with increasing firing time as indicated in Fig.

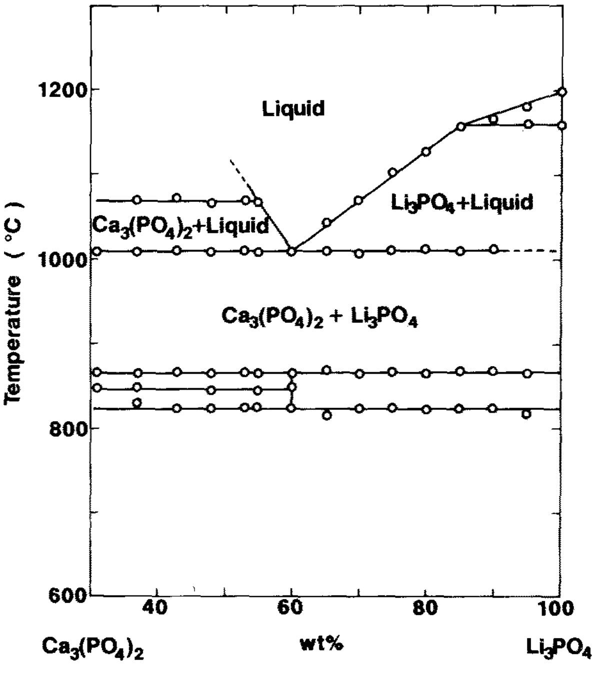

*Figure 3* Phase diagram of binary system $\beta$-TCP–$Li_3PO_4$ in the composition range of 30 to 100 wt % $Li_3PO_4$. In the $\beta$-TCP rich region (less than 30 wt % $Li_3PO_4$), the liquid phase did not appear in the temperature range examined.

2, the rearrangement process at 1050 °C will be completed within a short time. The next stage, at which the slope is 0.45, could be regarded as a solution precipitation process described by Kingery [15]. These two processes have finished within 1 min and the density has almost approached the maximum value which Li–HAp could reach. The final stage is a very slow densification process. This stage might be regarded to be a coalescence process [15], but it would be better to use the idea of solid–solid reaction process after the liquid phase disappeared as discussed below.

The remaining questions are the composition of liquid phase and the temperature at which the liquid phase forms. Fig. 4 shows the changes in the X-ray diffraction pattern by heating the HAp with various amounts of $Li_3PO_4$ at 900 and 1050 °C. Compared with Li–HAp, these very large amounts of $Li_3PO_4$ were added, but we would see the same situation in Li–HAp if we study the small region of grain size level, because $Li_3PO_4$ is added in the form of powder. From this measurement, we find that the HAp decomposes into β-TCP above 900 °C and that the degree of decomposition increases with increasing amount of $Li_3PO_4$. Fig. 5 indicates the changes in the DTA curves on the mixtures of HAp and $Li_3PO_4$ (20 and 40 wt %) by repeating the measurements without exchanging the specimen. In the first run in which HAp and $Li_3PO_4$ react together, both specimens have endothermic peaks at 1010 °C. This temperature is good agreement with the eutectic temperature of the system β-TCP–$Li_3PO_4$ as shown in Fig. 3.

From these results, it is reasonable that β-TCP, produced by the decomposition of HAp, forms the liquid phase together with $Li_3PO_4$ above 1010 °C. After the second run in 20 wt % $Li_3PO_4$, however, the endothermic peak at 1010 °C disappears. This is because much more β-TCP is produced and the relative amount of $Li_3PO_4$ becomes smaller than 30 wt %. Therefore, in Li–HAp, with small amounts of $Li_3PO_4$, the composition of liquid phase would move to the β-TCP rich region and the liquid phase would disappear at the early stage of sintering, probably before the starting time of the final stage at 1050 °C.

### 4.2. Activation energy for sintering

Fig. 6 shows the Arrhenius plot of the isothermal shrinkage rate at the initial stage of sintering. Below 900 °C, HAp and Li–HAp have the same activation energy, 161 kJ $mol^{-1}$ (38.4 kcal $mol^{-1}$). Above 900 °C, that of Li–HAp is 246 kJ $mol^{-1}$ (58.7 kcal $mol^{-1}$). The difference between Li–HAp and HAp above 900 °C is 85 kJ $mol^{-1}$ (20.3 kcal $mol^{-1}$). As shown in Fig. 4, the decomposition of HAp by $Li_3PO_4$ begins at about 900 °C. Moreover, the sintering rate of Li–HAp increases above 900 °C as indicated in Fig. 2. Taking these facts into account, we can assume that the decomposition process of HAp in Li–HAp greatly promotes the sintering. Namely, both HAp and Li–HAp will sinter by the same mechanism at the temperature up to 900 °C, but in Li–HAp, above 900 °C, the atomic diffusion accompanied with the decomposition of HAp will take place vigorously. This will help to sinter and will cause the increase of activation energy. On the other hand, although the liquid phase in Li–HAp appears above 1010 °C, there is no change in activation energy. This is probably because the energy is

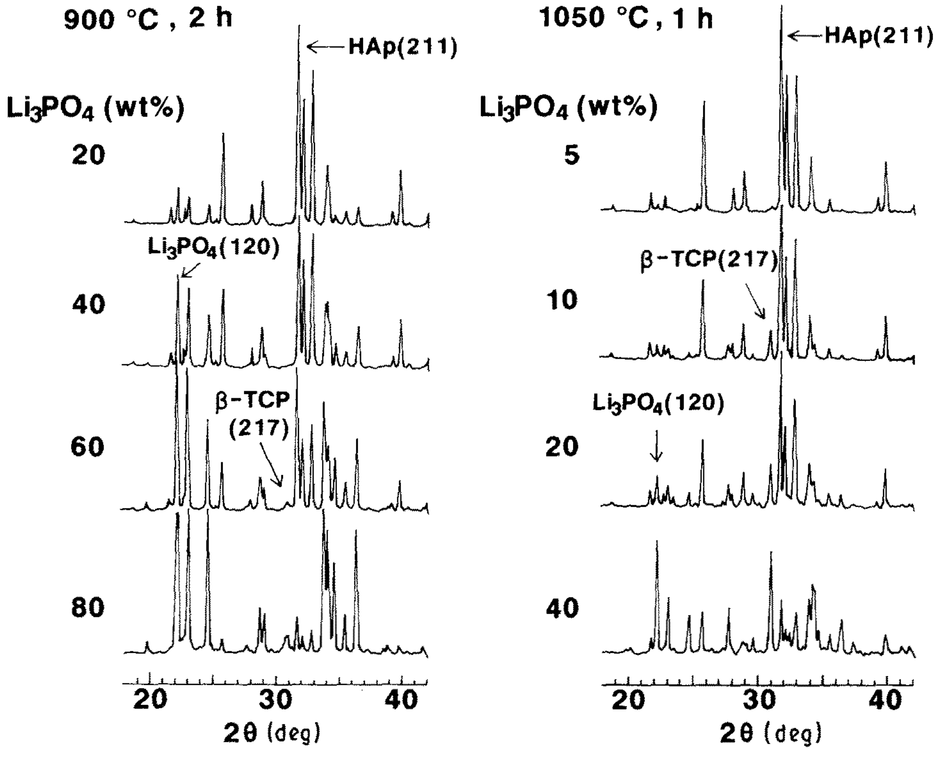

*Figure 4* The change of X-ray diffraction patterns on HAp after heating at 900 and 1050 °C by adding various amounts of $Li_3PO_4$. The decomposition of HAp into β-TCP was observed at the $Li_3PO_4$ composition of 60 wt % at 900 °C.

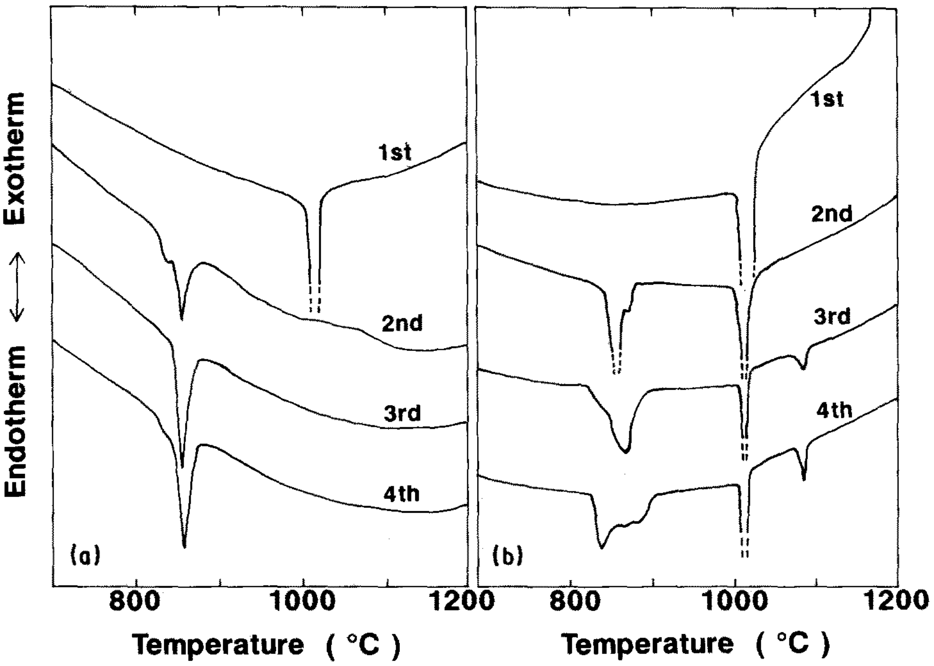

*Figure 5* The change of DTA curve on HAp with: (a) 20 and (b) 40 wt % added $Li_3PO_4$. The measurement was repeated without changing the specimen. The endothermic peak observed at 1010 °C in the first run did not appear in 20 wt % $Li_3PO_4$ after the second run.

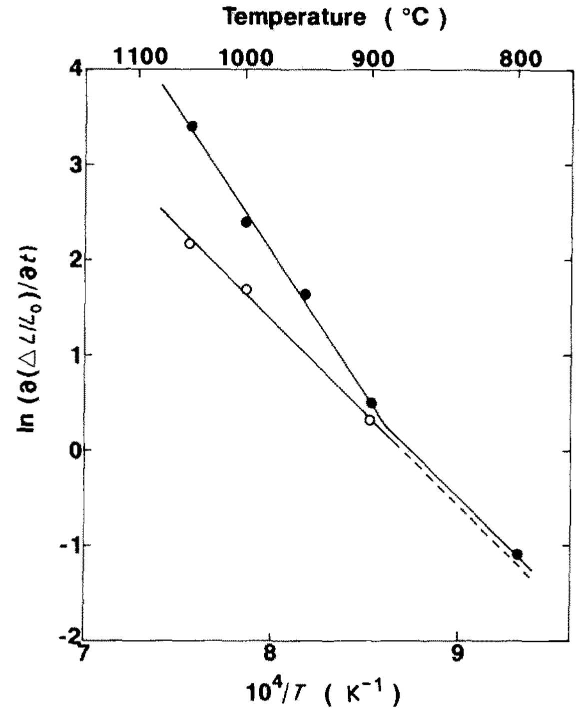

*Figure 6* Arrhenius plots of sintering rate on both HAp (161 kJ $mol^{-1}$) and 0.6 wt % Li–HAp (246 kJ $mol^{-1}$). The activation energy of Li–HAp increases above 900 °C.

quite low for the rearrangement of HAp particles in the presence of liquid phase.

## 5. Conclusion

The hydroxyapatite (HAp) containing $Li_3PO_4$ decomposes into β-$Ca_3(PO_4)_2$ above 900 °C. At the same time, the sintering rate of HAp by diffusion process increases because the decomposition of HAp promotes additional atomic diffusion. Furthermore, above 1010 °C, the liquid phase is formed from the binary system β-$Ca_3(PO_4)_2$–$Li_3PO_4$. This liquid phase causes the sudden densification through the rearrangement process of HAp particles.

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*Received 25 May
and accepted 27 June 1990*