

PHASE TRANSFORMATION AND BIOMECHANICAL COMPATIBILITY OF CALCIUM-PHOSPHATE BIOCERAMICS^①

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ABSTRACT

TG-DTA and XRD were used to analyse the phase structure transformation of calcium-phosphate biomaterials fired and/or sintered at various temperatures, and animal tests were used to assess the biomechanical compatibility of the materials. The results demonstrate that proceeding parameters (pH value of sol-gel solution and firing or sintering temperature) exert a remarkable effect on phase transformation, and also that during a short time, biomechanical compatibility of β -TCP [$\text{Ca}_3(\text{PO}_4)_2$] is superior to that of HA [$\text{Ca}_5(\text{PO}_4)_6(\text{OH})_2$]; but with lasting implanting time, bio-mechanical compatibility of HA will surpass that of β -TCP.

Key words: biomaterials phase transformation bio-mechanical compatibility

1 INTRODUCTION

Calcium-phosphate minerals are particularly attractive biomaterials for bone and tooth substitution since they closely resemble vertebrate tooth and bone mineral and have proven to be biologically compatible with the hard and soft tissues of human bones^[1-4].

Among the various calcium-phosphate materials, there are three kinds of especially important biomaterials, HA, β -TCP, α -TCP with atom ratio of Ca to P being 1.67, 1.50 and 1.50 respectively. They have constructed the basic elements of biomaterial researches and applications for the past twenty years. However, those related researches are not successful for pervasive clinical application. Though HA, β -TCP and α -TCP materials mainly consist of Ca, P, OH atoms, which also mainly construct main compositions of human hard tissues, their biological effects are very discrepant, α -TCP is much bio-inert than HA and β -TCP, β -TCP is much easy for absorption (or biodegradation) in body liquids than HA and α -

TCP. Besides the biological characteristics, mechanical properties of these materials may be changed with the changing of phase structure, so that precisely controlling the phase transformation and composition will be able to control the biological characteristics and mechanical properties of calcium-phosphate bioceramics. Therefore understanding the phase transformation of calcium-phosphate materials and their bio-mechanical compatibility is the key to correctly use these biomaterials in clinic.

2 MATERIALS AND METHOD

The preparation of calcium-phosphate crystal powders was based on the sol-gel method described in Ref. [5] with some modifications. Reagent grade $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ raw materials were dispersed from concentrate stock solution doubly analysed from Ca^{2+} and PO_4^{3-} . The preparation of powder by sol-gel method was simply described as follows. A solution containing 1.0 mol Ca^{2+} which is dispersed in distilled water blended with a solution containing 0.6 mol PO_4^{3-} atom, accompa-

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nying the addition of ammonia liquid. During the sol-gel reaction, the blending solutions were heated at 90 °C for 1 h and the pH values changed from 9 to 12. Yielded white sol-gel precipitates were filtered and dried at 50 °C. Then phase structure and phase transformation were analysed by TG-DTA technique at various temperatures and the powders fired or sintered at various temperatures were scanned by XRD to confirm whether there is phase transformation. For comparison, analogous analyses have been made on human bone and dent which had been cut from died body sample and organic matters corroded by diluted HCl solution. Cu K_α radiation and a scan rate of 1.0(°)min⁻¹ were used. The recorded peaks were compared with ASTM diffraction files and the powder materials were judged as HA, β-TCP, α-TCP or compounds. Relative amounts of various phases in the powder samples were calculated from the integrated intensity *I* of selected reflection of the phase in a two-phase mixture^[6]:

$$\frac{I}{I_0} = \frac{WC_1}{W(C_1 - C_2) + C_2} \quad (1)$$

where *I*₀ is the integrated intensity from pure phase 1, *I* is from the sample being examined, *W* is the weight fraction of phase 1, and *C*₁ and *C*₂ are mass absorption coefficients. The mass absorption coefficients for HA and TCP are 85 and 95 respectively.

To appraise the biomechanical compatibility of above materials, the semi-cylinder dense sintered samples 6 mm × 8 mm were implanted in the Os femoris bone of New Zealand adult rabbit, and killed at interval times and cut the Os femoris in which the dense sample was implanted, tested the force to squeeze the implanted sample out of the Os femoris. The force is used to manifest the bio-mechanical compatibility of the materials.

3 RESULTS AND DISCUSSION

3.1 Phase Structure and Phase Transformation

XRD patterns of calcium-phosphates dried at 50 °C and human bone as well as human dent were given in Fig. 1. Powder A which came from the sol-gel solution with pH value being equal to 12

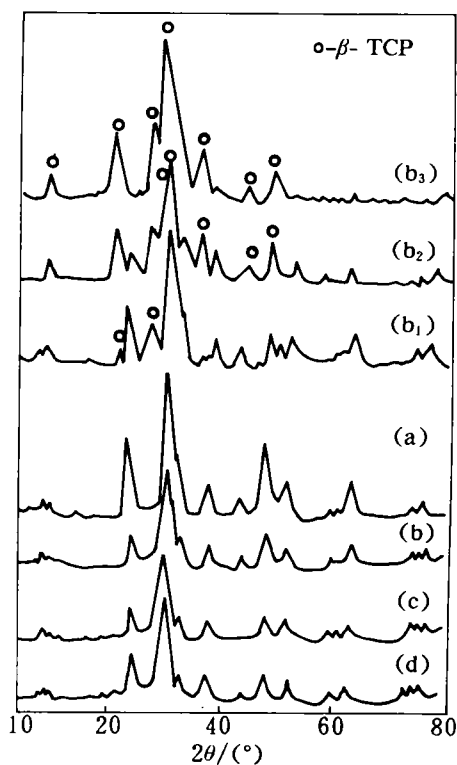


Fig. 1 XRD patterns of calcium-phosphates and human bone as well as dent

- (a)—powder A; (b)—powder B dried at 50 °C;
- (c)—human iliac; (d)—dent;
- (b₁)—powder B, fired at 790 °C;
- (b₂)—powder B, fired at 1100 °C;
- (b₃)—powder B, fired at 1200 °C

shows the HA hexagonal structure, with the ratio of Ca to P being equal to 1.67. All the peaks correlated closely with ASTM diffraction files. There is phase structure some what similar to powder A in powder B which came from the sol-gel solution with pH value being equal to 9 and so as in human iliac as well as human dent. It should be paid attention to that the phase structure of powder B is very close to that of human bone before heat treatment. Partial amorphous phase is included in powder B and human bone and dent. The above X-ray diffraction identified that HA hexagonal structure constructs the main part of human bone and dent. Fig. 2 shows the TG-DTA analysis curves of sol-gel powders and human iliac and dent at the temperature span of 0 °C to 1000 °C. In powder A

there is no phase transformation during the test and only an endothermic peak could be found at 67 °C, which is a de-water reaction, seeing curve (a). Besides the de-water reaction in powder B, there is another endothermic reaction that would be found at about 789 °C, which means that a crystal phase structure transformation took place at 789 °C, seeing curve (b). Like powder A, there are not changes during the test in human bone and dent, seeing curve (c) and (d). X-ray diffraction also shows that after fired at 790 °C, phase transformation is absent in powder A, but β -TCP phase becomes very clear in powder B, which means that the HA structure of powder B is partially changed into β -TCP structure, and OH^- ions also partially lost. Accompanying the annihilation of amorphous phase in powder B, the crystallization degree has been largely improved. According to equation 1, the relative amounts of HA and β -TCP in powder B fired at 790 °C are 68~73 weight percent and 32~27 weight percent respectively. After fired at 1100 °C for 2h, XRD shows that there is more β -TCP phase transformed from HA phase in powder B than the powder fired at 789 °C, and β -TCP increased to 71~76 weight percent. After fired at 1200 °C, there is no longer HA phase and only β -TCP presented in powder B, seeing Fig. 1 (b₃). A new phase, α -TCP could be found in powder B fired at 1300 °C for 2h, and their relative amount are 45~49 per cent and 52~55 per cent respectively. For powder A, XRD results asserted that no phase transformation presented in powders fired at 790 °C and 1100 °C for 2h and crystallization degree is excellent integrity. However, after fired at 1200 °C, like the situation of powder B fired at 790 °C, partial HA changed into β -TCP. The relative amounts of HA and β -TCP have been given in Table 1. After fired at 1300 °C, three kinds of phase structures HA, β -TCP, α -TCP presented in powder A simultaneously. By this time the relative amount of phases is unable to be calculated via equation 1. XRD results confirmed that no phase transformation took place in human iliaica and dent and some small peaks for the carbide salts, such as $\text{Ca}(\text{CO}_3)_2$ could be found in human bone and dent fired at various temperatures.

3.2 Biomechanical Compatibility

Table 1 Compositions (wt.-%) and phase structures of fired powders

Powder No.	Composition	Phase structure	Firing temp.	pH value
A ₁	100 HA	Hexa HA	50	12
B ₁		Hexa HA	50	9
A ₂	>98 HA	Hexa HA	790	12
B ₂	68~73 HA 32~27 TCP	Hexa HA β -TCP	790	9
A ₃	>96 HA	Hexa HA	1100	12
B ₃	24~29 HA 71~76 β -TCP	Hexa HA β -TCP	1100	9
A ₄	74~77 HA 23~26 β -TCP	Hexa HA β -TCP	1200	12
B ₄	>97 TCP	β -TCP	1200	9
A ₅		Hexa HA β -TCP, α -TCP	1300	12

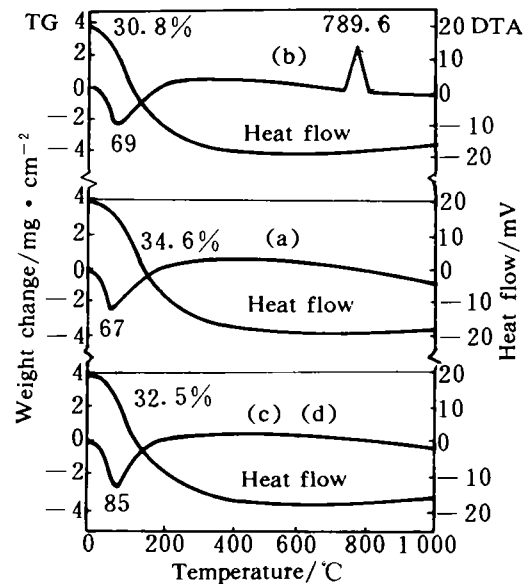


Fig. 2 TG-DTA curves of calcium-phosphates and human bone as well as dent
(a)—powder A; (b)—powder B;
(c)—human iliaica; (d)—dent

Implanting samples made by powder A and B via compacting and sintering respectively at 1100 °C and 1200 °C were implanted into adult rabbit bone to measure the biomechanical compatibility. The research results are shown in Fig. 3. Observing these testing curves, it can be found that the force to squeeze the implants out of rabbit bone increased with increasing implanting time. During the time interval of 8 weeks and 12 weeks, the

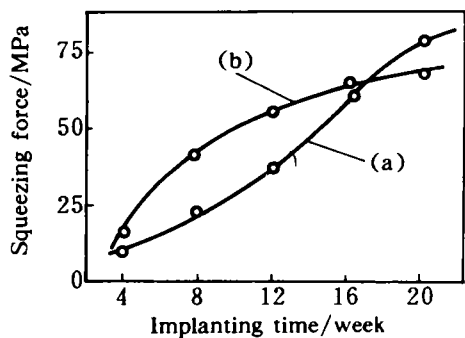


Fig. 3 Bio-mechanical compatibility of calcium-phosphates

(a)—sample A (1100 C, 2h)
 (b)—sample B (1200 C, 2h)

squeezing force of sample B (made from powder B, fully consisted of β -TCP) is about twice that of sample A (made from powder A, fully consisted of HA). And until 16th week the squeezing force of sample A did not equal that of sample B. However, at the time of 20th week, the former surpassed the latter.

3.3 Discussion

HA and TCP are understood as pervasively potential biomaterial used for clinical application. The present research confirmed that the analogous phase structure is presented between HA, TCP materials and hard tissue of human bone, especially before firing and/or sintering, seeing Fig. 1. This analogue will provide the guarantee on the microscopic level for the special combination between material and human bone.

The effect of pH value of sol-gel solution on crystal forming and phase structure is remarkable. Adding excessive ammonia is beneficial to form HA crystal and remain HA phase till elevated temperature. Like pH value, firing and/or sintering temperature will also decide phase structures of calcium-phosphates. The sequence of phase transformation with increasing firing and/or sintering temperature is HA(hexa) \rightarrow β -TCP(hexa) \rightarrow α -TCP(orthorhombic), which is identical with phase diagram^[7], seeing Fig. 4.

Biomechanical compatibility tests displayed

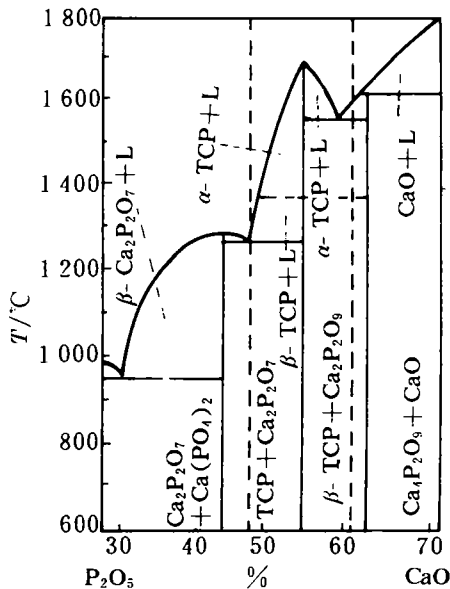


Fig. 4 CaO-P₂O₅ phase diagram

that HA and TCP can be combined with animal bone in a short time, constructing bone-bond between implanting material and natural bone. β -TCP has good bio-activity and a rapid combination has been formed between implant and rabbit bone in 12 weeks. It should be understood as if biomechanical compatibility of β -TCP may be superior to that of HA in a shorter time than 12 weeks, the biodegradation function of β -TCP may destroy the mechanical properties which will result in mismatch in load bearing parts of the skeleton. May be the biodegrading action, biomechanical compatibility of β -TCP no longer increased after 16 weeks, seeing Fig. 3. Therefore while using TCP as prosthesis, it must be considered that the biodegrading velocity should match the growth velocity of the new forming bone. Too fast degradation may result in forming large cavity which is difficult to cure over.

The author's prior research^[8] testified that the correct control of phase structure of calcium-phosphates is critical for clinical application. Materials with different performances should be required to adapt for the different parts of human skeleton. Making an example, the non-resorbed and good bio-mechanical compatibility materials will be used for institution of dent and load bearing parts of the

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texture corresponds with that of the primary recrystallization texture, the primary recrystallization texture inherits the unsymmetry in deformation texture. This fact illustrates that the primary recrystallization almost produces in every layer at same time. Otherwise, the unsymmetry will not exist. It is deduced that nucleation occupies a dominant position in the primary recrystallization.

5 CONCLUSIONS

(1) The main texture in every layer in primary recrystallization texture of 70-30 brass rolled by cross shear rolling in single direction is $\{236\}$ $\langle 385 \rangle$ yet, but the intensities of every texture in $\{236\}$ $\langle 385 \rangle$ are not the same, namely there is a macroscopic statistical unsymmetry.

(2) The primary recrystallization in every lay-

er inherits the unsymmetry of deformation texture in corresponding layer.

(3) Nucleation occupies a dominant position in the primary recrystallization.

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(From page 104) skeleton. The materials with biodegradating function and introducing bone formation function will be used to fill the vacancies in which cancers have been scraped over. The author recommends that the composites of HA and TCP which have atom ratio of Ca to P being equal to 1.50~1.67, seeing the dotted line part in Fig. 4, are good for some other surgical situations attributing to both their biodegradation and bio-mechanical compatibility. The author's works^[9] have confirmed the above views.

4 CONCLUSIONS

Calcium-phosphate biomaterials with phase structure closely similar to that of hard tissue of human bone and dent can be yielded by sol-gel method. The present research has testified that the effects of the pH values of sol-gel solutions and firing and/or sintering temperature on phase transformation are remarkable. XRD and TG-DTA show that phase transformation takes place at 789 °C in powder B which comes from the sol-gel solution with lower level pH value, and more HA structure transforms into TCP structure in powder B while fired at 1100 °C. There is no phase transformation in powder A which comes from the sol-gel solution

with higher level pH value until 1100 °C. Usually the higher the firing (sintering) temperature, the more the TCP structure in both powder A and powder B.

Animal implanting tests expressed that a firm bone-bond can be formed between HA, TCP and natural hard tissues in a short time and biomechanical compatibility of HA material is superior to that of TCP with lasting implanting time.

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