On the microstructure of biocomposites sintered from Ti, HA and bioactive glass

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Abstract

Sintering reactions and fine structures of the biocomposites prepared from powder mixtures of titanium (α-Ti), hydroxyapatite (HA) and bioactive glass (BG) (SiO₂-CaO-P₂O₅-B₂O₃-MgO-TiO₂-CaF₂) were investigated by X-ray diffraction and transmission electron microscopy. The results showed that complex reactions among the starting materials mainly depended on the initial Ti/HA ratios as well as the sintering temperatures. And the reaction could be expressed by the following illustrative equation:

\[ \text{Ti} + \text{Ca}_{10} \left( \text{PO}_4 \right)_{6} (\text{OH})_2 \rightarrow \text{CaTiO}_3 + \text{CaO} + \text{Ti}_x \text{P}_y + (\text{Ti}_2 \text{O}) + (\text{Ca}_4 \text{P}_2 \text{O}_9) + \text{H}_2 \text{O}. \]

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1. Introduction

It is well known that hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA) has a similar chemical and crystallographic structure to the bone mineral [1]. Extensive studies have indicated that HA is biocompatible with hard tissues of human beings and exhibits osteoconductive properties [1–3]. However, its poor mechanical properties are the most serious obstacles for applications of load-bearing implants [4].

On the other hand, mechanical properties of titanium and its alloys are good enough for load-bearing implants, but their biocompatibility is much worse than that of calcium phosphate ceramics [5,6]. Traditionally, hydroxyapatite was used as a coating material on titanium substrate by various techniques to increase the biocompatibility of titanium. Titanium and its alloys coated with plasma sprayed hydroxyapatite have been widely used in clinic [7]. But significant differences in physical and thermal properties between titanium and hydroxyapatite inevitably limit the use of this kind of materials [8]. In the present study, titanium/hydroxyapatite biocomposites were made from hydroxyapatite and titanium powders by powder metallurgy method to combine the bioactivity of hydroxyapatite and the mechanical properties of titanium.

Due to severe oxidation of titanium in air, hot-press sintering of titanium/hydroxyapatite (Ti/HA) composites has to be done in vacuum or under the protection of an inert atmosphere. However, under such sintering conditions, dehydration and decomposition temperatures of HA will decrease remarkably [9], which declines its bioactivity and mechanical properties. To decrease the sintering temperature and maintain the excellent properties of initial components, low melting point additives are usually used as a sintering aid to realize sintering densification. For the material used as an implant in human body, the sintering aid should be nontoxic, have good biocompatibility and provide sufficient mechanical strength to the sintered material. Some previous works indicated that the addition of bioglass to pure hydroxyapatite not only increased the mechanical properties of hydroxyapatite, but also improved its biological properties [10,11]. So bioglass may be a good candidate for the sintering of hydroxyapatite. In the present work, a system of SiO₂-CaO-P₂O₅-B₂O₃-MgO-TiO₂-CaF₂ bioactive glass (BG) was used as a sintering aid.

Our previous works [12] on a 50Ti/50HA (vol%) composite sintered from the mixture of Ti and HA...
powders showed that this material had an excellent in vitro bioactivity. And the preliminary work [13] showed that a 50Ti/40HA/10BG (vol%) composite sintered at 1200°C also had a good in vitro bioactivity. However, detailed examination of the effects of composition design and sintering temperatures on the micro-structure of these biocomposites has not been reported. In the present paper, the fine structures of the composites sintered from Ti, HA and BG powders were investigated, mainly through transmission electron microscopy (TEM).

2. Experimental procedure

Commercially pure titanium (α-Ti) and hydroxyapatite powders, with average diameters of 27.3 and 21.1 μm, respectively, were used as the starting materials. The chemical composition of the amorphous bioactive glass powder (with an average diameter of 23.4 μm) is shown in Table 1. Designed compositions for various composites are shown in Table 2. The composites as well as single-phase Ti and HA, were prepared by hot-press sintering in an argon atmosphere under a pressure of 20 MPa for 30 min. The sintering temperature ranged from 1000°C to 1200°C.

Densities and phase compositions of the sintered materials were examined by the Archimedes method and X-ray diffraction (XRD), respectively. Ion-thinned foils of the materials were investigated with transmission electron microscope (TEM, Philips CM-12) operated at an accelerating voltage of 120 KV. Energy-dispersive spectroscopy (EDS) of selected areas was simultaneously carried out during the TEM observations.

3. Results and discussions

For a better understanding of reactions occurred during the sintering of the Ti/HA/BG composites, we discuss several noteworthy sintering characteristics of the three initial components firstly, and then the microstructure of the Ti/HA/BG composites.

3.1. Sintering stability of the initial components

3.1.1. Ti and its sintering characteristics

Compared with initial titanium powders, the titanium sintered at 1200°C remained an h.c.p. structure (α-Ti). Its relative density reached as high as 99.4%. As shown in Fig. 1, two kinds of typical martensitic structures could be found in the sintered titanium. One was a lamellar structure with large quantity of dislocations and dislocation walls (Fig. 1a), which showed a similarity in morphology to the reorientation bonds reported by Moskalenko [14]. The other was an N-shape structure having an inclination angle of about 30° (Fig. 1b). The formation of the above martensitic
structures could be explained as follows. It has been established that at temperatures around 882.5°C allotropie transformations between α-Ti and β-Ti (with b.c.c. structure) could occur [15]. Thus, during the cooling process of the sintered titanium from 1200°C to room temperature, a diffusionless martensitic phase transformation from β-Ti to α-Ti inevitably occurred following the Burgers crystallography relations of (1 1 0)ₜ//(0 0 0 1)ₐ and [1 1 1]ₜ//[1 1 2 0]ₐ.

### 3.1.2. HA and its sintering characteristics

Decomposition of HA may have negative effect on its mechanical and biological properties [16]. Thus, it is necessary to investigate the structural stability of HA, which can be influenced by many factors such as powder preparation, impurities and their contents, sintering atmosphere, Ca/P atomic ratio and so on [9]. Many researches on the structural stability of HA at elevated temperatures have been reported. Corresponding results, however, are not always the same due to different experimental conditions. The decomposition of sol–gel HA at 800°C to Ca₃(PO₄)₂ [17,18], dehydration of HA at 900°C and further decomposition at 1350–1500°C to other forms of phosphate [19,20] have been reported.

XRD pattern of the hydroxyapatite sintered at 1200°C showed a similarity to that of the initial hydroxyapatite powders (PDF 9-432), except for an increased sharpness for these diffraction peaks due to an increased grain size after the sintering process. However, such agreement in XRD pattern was not sufficient to prove that the hydroxy function (OH) in hydroxyapatite still existed, because oxyapatite could have quite similar crystal parameters and X-ray diffraction pattern to those of hydroxyapatite [21]. For this reason we also performed FT-IR analyses of the sintered hydroxyapatite. It indicated that the sintered hydroxyapatite had a similar spectrum to that of the initial hydroxyapatite powders; the bands at 3571 and 630 cm⁻¹, corresponding to OH stretching vibration mode were very obvious. Thus, it could be concluded that hydroxyapatite was stable at 1200°C in an argon atmosphere, which coincided with the results of Ruys [22].

TEM microstructure of the sintered hydroxyapatite (Fig. 2) revealed that many equiaxed grains, with a grain size ranging from 0.1 to 1 μm, formed a dense structure nearly without sintering micropores. A measured relative density of 99.6% for the sintered hydroxyapatite also confirmed its high densification. Some literatures reported that hydroxyapatite could have a monoclinic crystalline structure depending on the kinds of impurities [9]. In this study, typical selected area diffraction (SAD) patterns of the sintered hydroxyapatite (Fig. 3) suggested that it had a h.c.p. (P6₃/m) structure, instead of a monoclinic (P2₁/b) structure.

### 3.1.3. BG and its sintering characteristics

Precipitated phases in the bioactive glass and its corresponding composites, during the sintering at elevated temperatures, have an important effect on the biological properties of the final materials. Our previous work [23] showed that phase precipitation in the amorphous bioactive glass occurred at a temperature about 600°C. Fig. 4 showed an XRD pattern of the bioactive glass heat-treated at 800°C for 2 h. It was found that all of the diffraction peaks for the precipitated phase were identical to those of hydroxyapatite. The existence of HA could be also confirmed by FT-IR analyses. Therefore, it was expected that the precipitation of hydroxyapatite in the bioactive glass, at sintering temperatures higher than 800°C, could improve the sintering of Ti/HA composites and would not have negative effects on their biological properties.
3.2. Microstructures of the sintered composites

The influence of initial Ti content on the phase components of the Ti/HA composites could be found from XRD patterns (Fig. 5). It suggested that sintering reactions among the starting materials occurred during the sintering process. For the 3T6HB composite with a lower Ti content, the reaction was so severe that diffraction peaks of both Ti and HA disappeared, whereas, only those of CaTiO$_3$, CaO and Ti$_x$P$_y$ phases (determined by EDS analyses during TEM observations) could be detected. With an increase of initial Ti content, diffraction peaks of Ti$_2$O and $\alpha$-Ti appeared, besides those of CaTiO$_3$, CaO and Ti$_x$P$_y$ phases. Further increasing the Ti content to 70%, the main crystalline phase of the composite was nearly $\alpha$-Ti phase. It was reported that a presence of Ti and/or its oxides could contribute to the decomposition of HA. Weng et al. [24] argued that in vacuum the presence of Ti reduced the decomposition temperature of the HA to 800°C, but no titanium compounds were found in his results. And it was also shown that, at temperatures higher than 800°C, HA decomposed to Ca$_4$P$_2$O$_9$, Ca$_3$(PO$_4$)$_2$ and H$_2$O. But for the present Ti/HA/BG composites sintered at 1200°C, we only found CaTiO$_3$, CaO and Ti$_x$P$_y$ compounds but no Ca$_4$P$_2$O$_9$ and Ca$_3$(PO$_4$)$_2$. The densities of the 3T6HB, 5T4HB and 7T2HB were 3.812, 4.229 and 4.380 g/cm$^3$, respectively, which were between those of HA (3.15 g/cm$^3$) and Ti (4.51 g/cm$^3$). As the initial HA and Ti have reacted each other, it is hard to obtain relative densities of the Ti/HA composites.

To show the influence of the BG addition on the phase components of the Ti/HA composites, 5T5H composite without the BG was also prepared through a sintering at 1200°C. It could be found that XRD pattern of this 5T5H composite [12] was similar to that of the 5T4HB composite (Fig. 5b). The addition of the BG to the Ti/HA composite could hardly affect the final phases of the composite. The density analysis showed this composite also had a similar density (4.234 g/cm$^3$) as that of the 5T4HB composite. Thus, it can be inferred that HA precipitated from the bioactive glass in the composites during the sintering process behaved the same way as the initial HA powders did.

To investigate the influence of sintering temperatures on the phase components of the Ti/HA composites, 5T4HB composites sintered at 1000°C and 1100°C were also prepared. These two composites had similar XRD...
patterns, which showed that the main crystalline phases of these two composites are α-Ti, CaTiO$_3$, CaO, Ti$_x$P$_y$ and Ca$_4$P$_2$O$_9$ (PDF 11-232). It indicated that, at elevated temperatures, reactions between HA and Ti were accompanied with the decomposition of hydroxyapatite. The complete disappearance of hydroxyapatite suggested that the existence of titanium reduced the decomposition temperature of hydroxyapatite to temperatures lower than 1000°C. However, no α-Ca$_3$(PO$_4$)$_2$ or β-Ca$_3$(PO$_4$)$_2$ was found in our study. The above facts implied that the decomposition mechanism for hydroxyapatite here is different. Because the composites sintered at 1100°C and 1000°C is not compact, it is hard to get their density values by Archimedes method. But the electron probe microscopy analysis (EPMA) results showed that the relative densities of the Ti/HA composites decreased with the decrease of sintering temperature.

Fig. 6 presents TEM microstructure of the 3T6HB composite sintered at 1200°C. Most of the reaction products (CaTiO$_3$, Ti$_x$P$_y$ and CaO) could be observed. And it should be noted that Ti$_x$P$_y$ grains always were surrounded by CaTiO$_3$ ones. EDS analyses revealed that the $x/y$ ratio for Ti$_x$P$_y$ compounds mainly had two values, 0.96 and 1.66 (Fig. 7). The amount of the former was much larger than that of the latter. Although these two Ti$_x$P$_y$ compounds showed similar chemical compositions to those of TiP and Ti$_{17}$P$_{10}$, their SAD and XRD patterns did not agree with those of TiP and Ti$_{17}$P$_{10}$. As shown in Fig. 6, these Ti$_x$P$_y$ phases exhibited equiaxed grains with a grain size of 0.2–0.8 μm. Very few defects were observed in Ti$_x$P$_y$ grains; only twins were found occasionally (Fig. 8). At present, the complexity of the
Ti–P compounds (shown in the binary phase diagram of Ti–P) [25] makes it difficult to definitely identify these Ti$_x$P$_y$ phases. The formation of these Ti–P phases could be affected by several factors such as local chemical composition, defect density and local thermal condition. In the present study, these Ti$_x$P$_y$ compounds may be a consecutive solid solution.

TEM image and SAD pattern of the CaTiO$_3$ products are shown in Fig. 9. The grain size of CaTiO$_3$ was obviously larger than that of Ti$_x$P$_y$. Large quantity of dislocation loops and stacking faults were observed in the equiaxed CaTiO$_3$ grains. The dislocation loop either existed in the grain separately (Fig. 9a) or coexisted with the stacking fault (Fig. 9b). The dislocation loop always showed a similar morphology to secondary precipitations. But the difference was that the dislocation loop would gradually disappeared when it was irradiated with electron beam. The above dislocation loop should be Frank-type, which were caused by thermal mismatch stresses due to the different crystal structures between CaTiO$_3$ and the initial components. It is well known that CaTiO$_3$ has an orthogonal lattice with crystal parameters of $a = 0.5440$, $b = 0.7644$, and $c = 0.5381$ nm (PDF card No. 22-153). Whereas, both $\alpha$-Ti and HA have a h.c.p. structure, while $\beta$-Ti has a b.c.c. structure. Thus, during the cooling process of the composite from sintering temperature to room temperature, the lattice mismatch between CaTiO$_3$ and the above three phases could produce high mismatch stress around the CaTiO$_3$ grain. To decrease the lattice mismatch, large quantity of defects such as vacancies, dislocations and stacking faults will appear. When sufficient supersaturated vacancies are formed in the CaTiO$_3$ grain, they would coalesce along a preferred crystal plane, with a natural tendency to lower the energy, and thus a vacancy plate is formed. Once the external forces make the vacancy plate collapse Frank-type dislocation loop is then formed [26].

Fig. 10 showed CaO phases in the composite were nanocrystals with an average grain size around 30–40 nm. High magnification images of these nanocrystals also revealed that, as a matter of fact, each nanocrystal was composed of many smaller subgrains. As phosphorus in the initial bioactive glass diffused away at elevated temperatures to form Ti$_x$P$_y$ phases with Ti, the residual exhibited an amorphous matrix with several kinds of precipitations (Fig. 11).

Fig. 10. CaO in the composite: (a) TEM image, and (b) SAD pattern.
Previous XRD analyses indicated that with the increase of initial Ti content, residual Ti could be found in the sintered composite. Different from those in pure Ti sintered at 1200°C (Fig. 1), the defects in the residual Ti were mainly stacking faults (Fig. 12) and a few of dislocations. Ti2O has a similar crystal structure and lattice parameters to those of α-Ti, so it was hard to distinguish α-Ti from Ti2O with TEM. The same phenomenon was also shown by the EPMA analyses of α-Ti and Ti2O. Under TEM observation, it was found that TiₙPₚ layers often distributed around these α-Ti or Ti₂O phases (Fig. 13). For the composites with high-Ti content sintered at 1200°C (5T4HB, 7T2HB and 5T5H), they not only had the same phase components as those in the 3T6HB composite but also had some additional TiₙPₚ phases with Ti/P ratios of 2–4, which is mainly due to the increase of local Ti concentration. The thickness of the TiₙPₚ layer decreased with the increase of initial Ti content.

Due to different atomic diffusion rates at elevated temperatures, the formation of TiₙPₚ compounds remarkably depended on the sintering temperature. Under TEM observations, it was found that in the composite sintered at lower temperatures, the quantity of TiₙPₚ compounds with a higher Ti/P ratio tended to increase. The TiₙPₚ compounds close to the Ti particle had a higher Ti/P ratio, whereas, the TiₙPₚ compounds far away from the Ti particle had a smaller Ti/P ratio. It also showed that there were clear boundaries among different TiₙPₚ compounds. This could be reflected by the TEM images and SAD pattern of the TiₙPₚ in the 5T4HB composite sintered at 1000°C (Fig. 14). The TiₙPₚ layer close to the α-Ti had a Ti/P ratio of 2.77, whereas, the upper TiₙPₚ layer with a stripe image had a Ti/P ratio of 1.93. In addition, Ca and P could also lead to the formation of a Ca₄P₂O₉ phase (Fig. 15) in the composites sintered at 1100°C and 1000°C, which was confirmed by XRD and EDS analyses.

4. Conclusions

(1) Complex reactions between Ti and hydroxyapatite occurred during the sintering of Ti/HA/BG composites. The phase components of the composite varied
with the initial Ti content and the sintering temperature. After sintered at 1200°C, the composite with a lower initial Ti content had main crystalline phases of CaTiO₃, CaO and TiₓPᵧ. Increasing the initial Ti content to 50 vol%, Ti₂O and residual α-Ti also observed. Further increase of the initial Ti content resulted in a composite with only α-Ti as its main crystalline phase. Moreover, the addition of bioactive glass to the Ti/HA showed little effect on the main phase components of the composites.

(2) The reaction degree decreased with a decrease of the sintering temperature. When the composites were sintered at lower temperatures, Ca₄P₂O₉ phase was also formed in the reaction system.

(3) Defect density in the TiₓPᵧ phase was very low, whereas, a large quantity of defects (mainly in the form of stacking faults and dislocation loops) could form in the CaTiO₃ phase. The CaO phase existed in the form of nanocrystals. The defects of the α-Ti phase in the composites mainly were stacking faults, which was quite different from the high-density dislocation observed in the sintered pure α-Ti.

(4) The sintering reaction could be expressed by the following illustrative equation:

\[
\text{Ti} + \text{Ca}_{10} (\text{PO}_4)_{6} (\text{OH})_2 \rightarrow \text{CaTiO}_3 + \text{CaO} + \text{Ti}_x \text{P}_y + (\text{Ti}_2 \text{O}) + (\text{Ca}_4 \text{P}_2 \text{O}_9) + \text{H}_2 \text{O}.
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References


