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High-Temperature Hydroxyapatite–Titanium Interaction

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Abstract—Hydroxyapatite–titanium interaction has been studied in the temperature range 700 to 1200°C with a view to designing biocompatible dispersion-hardened hydroxyapatite-matrix materials for bone implants. The sequence of phase transformations in hydroxyapatite–titanium powder mixtures during heating in air has been identified using IR spectroscopy, differential thermal analysis, and X-ray diffraction. It is shown that hydroxyapatite decomposition can be inhibited via heat treatment in an atmosphere containing carbon monoxide.

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INTRODUCTION

Hydroxyapatite (HA) based materials are analogs of the mineral component of bone tissue and are thought to have the greatest potential for the fabrication of bone graft substitutes [1, 2]. Unfortunately, the use of ceramics as materials for load-bearing implants is limited by their inherent brittleness and low strength. The mechanical properties of ceramics can be improved by introducing various reinforcing agents provided that such agents will not affect the biocompatibility of the material [2]. HA-based composites reinforced with fine Al_2O_3, SiO_2, TiO_2, and ZrO_2 particles have been the subject of many studies [3–9]. Fine oxide particles slightly raise the compressive strength of HA, to 50–70 (Al_2O_3, SiO_2 and ZrO_2) or even 105 MPa (TiO_2), but this is by far insufficient for structural applications. Reinforcement with soft metal particles is more effective in improving the mechanical properties of ceramics. The bending strength, compressive strength, and fracture toughness of HA-cement-based materials containing fine titanium particles reach 28 MPa, 140 MPa, and 0.8 MPa $m^{1/2}$, respectively (the fracture toughness of titanium-free analogs is just 0.2 MPa $m^{1/2}$) [10]. Titanium is a bioinert, corrosion-resistant, light metal, widely used in medicine. HA/Ti composites can be produced by hot pressing at high temperatures. The sintering temperature of HA exceeds 1200°C. Titanium rapidly oxidizes at temperatures above 450°C [11], whereas HA decomposes starting above 900°C to form tricalcium phosphate and calcium oxide. This imposes certain limitations on the thermal conditions for the fabrication of HA/Ti composites. Sintering aids, which ensure liquid-phase sintering, enable a slight reduction in the sintering temperature of HA. HA–titanium interaction processes have not yet been studied in sufficient detail. The objective of this work was to study HA–titanium interaction at temperatures from 700 to 1200°C in air and carbon oxide (CO and CO_2) atmospheres.

EXPERIMENTAL

HA powder with an average particle size of 40–60 nm, prepared via precipitation from aqueous solutions of calcium nitrate and ammonium hydrogen phosphate using aqueous ammonia as the precipitant, was mixed with titanium powder (average particle size, 5 μm) in the weight ratio 1 : 1 by grinding in a planetary mill using Teflon vials and alumina balls. The powder-to-ball weight ratio was 1 : 5, and the mixing time was 20 min. The resultant mixtures were heat-treated in air at temperatures from 700 to 1200°C in a compartment furnace with Silit heaters. The mixtures were heated at a rate of 10°C/min and held at the highest temperature for 1.5 h. In a number of preparations, the mixtures were heat-treated in a carbon oxide atmosphere, which was generated by reacting a carbon powder charge with atmospheric oxygen. To this end, the samples were placed in alumina crucibles, packed with carbon powder, and covered with a tightly fitting lid. During heating to above 600°C, the carbon reacted with atmospheric oxygen to form CO and CO_2.

Differential thermal analysis (DTA) and thermogravimetry (TG) were conducted in a MOM Q-1500D thermoanalytical system during continuous heating. The phases present were identified by X-ray diffraction (XRD) on a Shimadzu XRD-6000 diffractometer (CuK_α radiation, JCPDS data, quantitative phase analysis with external standards). IR spectra were measured on a Nicolet Avatar 330 IR spectrometer in the range 400–4000 cm^{-1}, using samples pressed with KBr.

RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of the starting mixture and the samples heat-treated in air at different temperatures. The XRD pattern of the starting mixture shows peaks characteristic of titanium and a broad halo in the range 31–34°, due to nanocrystalline HA. After heat treatment of the HA–titanium mixture at 700°C, the

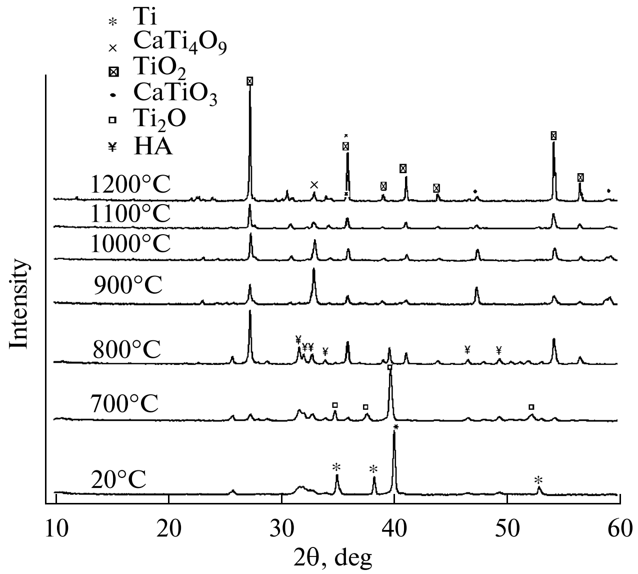

Fig. 1. XRD patterns of the titanium–HA powder mixture heat-treated in air.

main peak of Ti near 2θ 40° was missing, and the XRD pattern showed a peak characteristic of Ti_2O, shifted to lower angles. In addition, a weak reflection from TiO_2 emerged near 27°. Heat treatment at 800°C led to further oxidation, as evidenced by the increase in the intensity of the TiO_2 peaks. The halo at 31°–34° transformed into a quadruplet characteristic of crystalline HA. At 900°C, the titanium almost completely oxidized, and the reflections from Ti_2O disappeared. This is indirectly supported by the DTA and TG data in Fig. 2. The exothermic peak is due to the oxidation of the titanium to Ti_2O and then to TiO_2 in the range 700–800°C, accompanied by an oxidation-related weight gain. At 900°C, the HA and TiO_2 react to form calcium titanate, $CaTiO_3$, and the reflections from HA disappear. A destabilizing effect of titanium on HA was also reported by Ye et al. [11]. Raising the temperature from 900 to 1200°C increases the intensity of the reflections from rutile and reduces that of the reflections from calcium titanate, which may be due to the thermal decomposition of the latter. The samples heat-treated at 1200°C consisted of only two crystalline phases: TiO_2 and $CaTiO_3$.

According to the IR spectroscopy data in Fig. 3, the starting powder consisted of carbonate-containing HA. The features in the range 1300–1540 cm^{-1} are characteristic of the ν_3 mode of the CO_3 group [2]. At temperatures above 900°C, the bending band of the OH group at 3571 cm^{-1} disappears. Heat treatment at 900°C leads to significant changes in the bands related to the ν_4 vibrational mode of the PO_4 group in the range 520–660 cm^{-1} and to its ν_3 mode at 1030–1080 cm^{-1} This may be interpreted as evidence for at least partial thermal decomposition of the HA as a result of the reaction with titanium, because the temperatures 800–900°C are too low for the thermal decomposition of HA without titanium [2].

In the range 900–1200°C, the percentage of $CaTiO_3$ decreases with increasing heat-treatment temperature: 60, 50, 35, and 10 wt % after heat treatment at 900, 1000, 1100, and 1200°C, respectively. It is reasonable to assume that heat treatment is accompanied by the formation of liquid glass phase, which dissolves the calcium titanate and HA as the temperature is raised. The XRD patterns of our samples showed no reflections from other possible HA–Ti reaction products: Ti_xP_y, CaO, or other calcium phosphates (in particular, no reflections from $Ca_4P_2O_9$ [3]). Figure 4 illustrates the microstructure of the sample prepared by uniaxial pressing of the Ti–HA mixture at 100 MPa, followed by sintering in air at 1200°C. There are two characteristic microstructural constituents: dense rutile particles embedded in finer particle, porous matrix material.

Yang et al. [12] and Berezhnaya et al. [13] reported that the heat treatment environment had a significant effect on

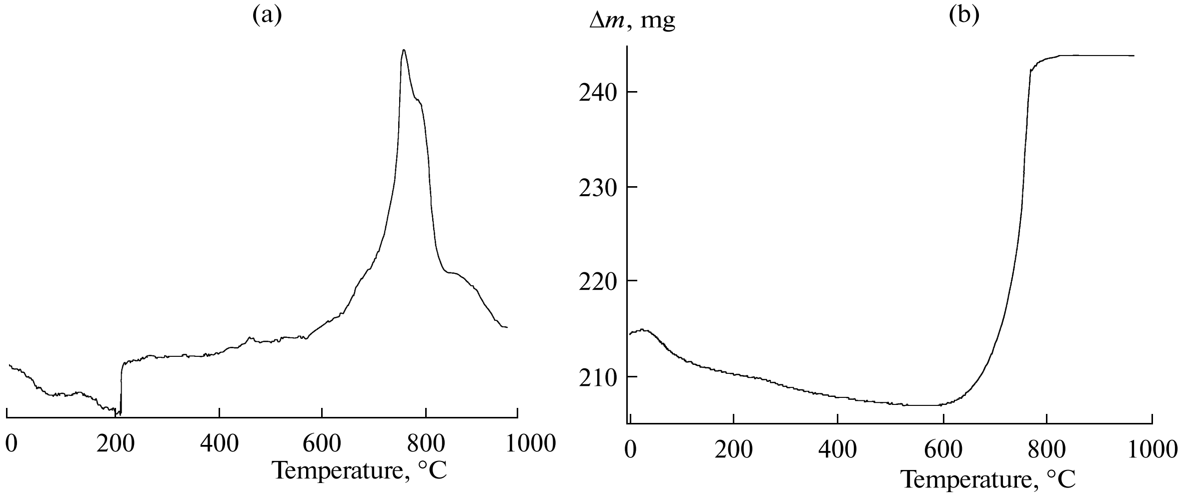

Fig. 2. (a) DTA and (b) TG curves of the titanium–HA powder mixture during continuous heating in air.

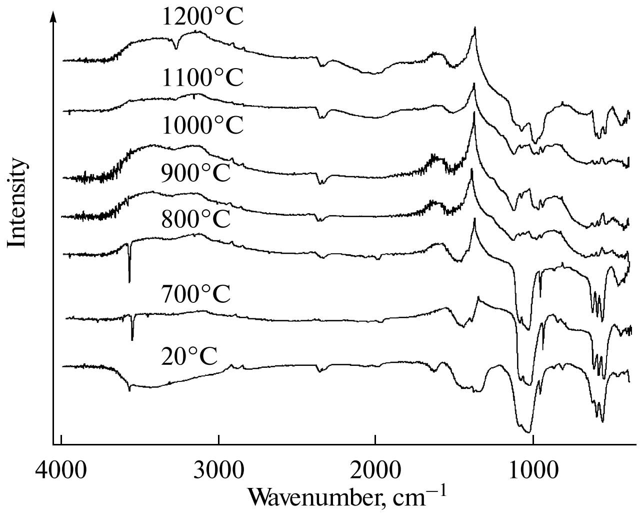

Fig. 3. IR spectra of the powder mixture heat-treated in air.

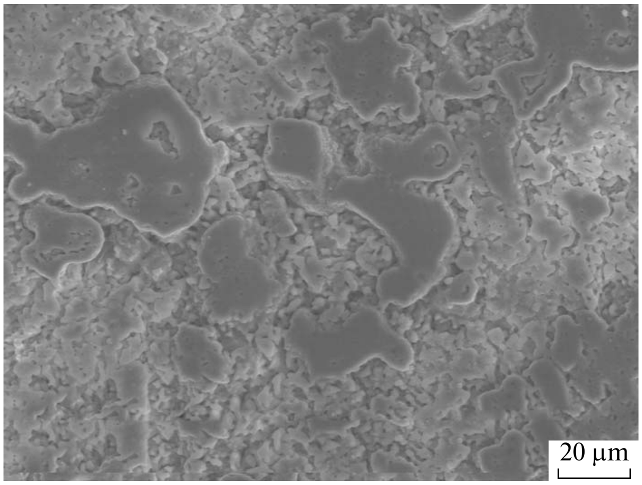

Fig. 4. Microstructure of the sample heat-treated at 1200°C in air.

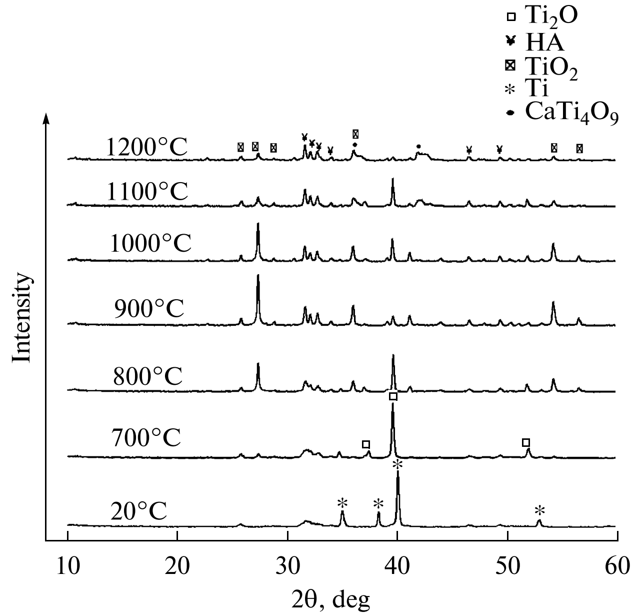

Fig. 5. XRD patterns of the powder mixture heat-treated in carbon powder.

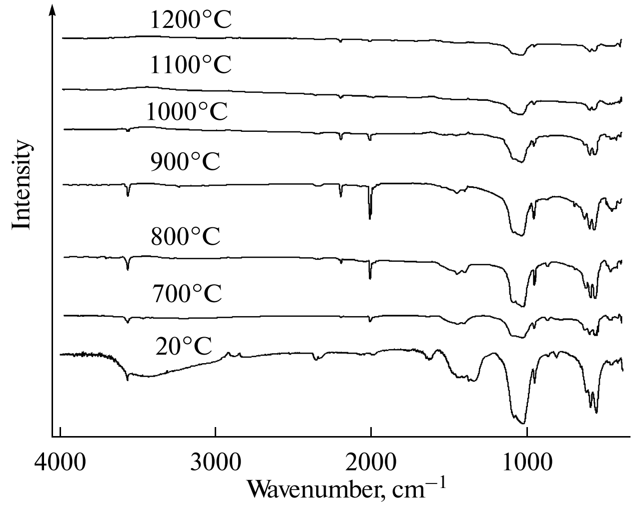

Fig. 6. IR spectra of the powder mixture heat-treated in carbon powder.

phase changes in the Ti–HA system. During firing at 1100°C in vacuum, all of the titanium reacted with HA to form calcium titanate [12]. $CaTiO_3$ was found to form as a result of the reaction between HA and titanium (HA coatings on titanium) during heat treatment at 1050°C both in air and in an argon atmosphere [13]. In our experiments, the carbon powder the samples were embedded in did not prevent the oxidation of the titanium particles (Fig. 5), which indicates that the oxidation process was due to solid-state reactions between the components of the starting mixture. The XRD patterns of the samples heat-treated in air and in a carbon oxide atmosphere differed most significantly at heat-treatment temperatures above 800°C: sintering in carbon powder prevented HA decomposition at temperatures of up to 1200°C (quadruplet at 31°–34°). During firing of the mixture in carbon powder, Ti oxidized starting at 700°C to form Ti_2O and a small amount of TiO_2. When the samples were packed with carbon powder, the intensity of the reflections from TiO_2 decreased and that of the reflections from Ti_2O increased as the heat-treatment temperature was raised from 800 to 1100°C. The reason for this is that, at temperatures above 900°C, the CO resulting from the combustion of the carbon powder in an oxygen-deficient environment reacted with titanium dioxide to form Ti_2O by the reaction [14]

$$2TiO_2 + 3CO = Ti_2O + 3CO_2.$$

Note that, after heat treatment at 1100–1200°C, the XRD pattern showed a broad line around 43°, corresponding to calcium tetratitanate, $CaTi_4O_9$, with the lowest possible calcium content.

In the case of firing in carbon powder, the absorption due to the OH group persisted up to 1000°C (Fig. 6), and the structural changes in HA above 800°C were weaker than those in the mixture fired in air (Fig. 3). Thus, packing in carbon powder prevents HA decomposition at firing temperatures of up to 1100°C and does not lead to titanium carbide formation.

CONCLUSIONS

The present results demonstrate that air firing of HA–titanium powder mixtures at temperatures from 700 to 1200°C leads to active oxidation of titanium starting at 700°C. At 800°C, the oxidation process results in TiO_2 formation. At higher heat-treatment temperatures, the mixture consists of only two crystalline phases, TiO_2 and $CaTiO_3$, and the content of the latter decreases as the temperature is raised from 900 to 1200°C because it dissolves in an amorphous phase. Packing in carbon powder inhibits HA decomposition and reduces the TiO_2 content as a result of the partial reduction of titania to lower titanium oxides. Thus, packing in carbon powder is a simple way to stabilize HA at high heat-treatment temperatures.

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