View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Electronic Sumy State University Institutional Repository

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **1** No 2, 02NNBM05(3pp) (2012)

Effect of Sintering Atmosphere on Phase Evolution of Hydroxyapatite Nanocomposite Powders

Mohsen Ebrahimi *, Touradj Ebadzadeh †, Esmail Salahi ‡

Department of Ceramic, Materials & Energy Rresearch Center (MERC), P.O. Box 31787-316, Alborz, Iran

(Received 30 April 2012; published online 17 August 2012)

In the present work, pure hydroxyapatite, hydroxyapatite-20 wt% alumina and hydroxyapatite-20 wt% titanium mixtures were pressed and sintered in air, moist, and reduction atmospheres at 1200°C for 2 h. XRD investigations of sintered samples showed that, pure hydroxyapatite is stable in all three atmospheres. But, moist and reduction atmospheres were preferred to suppress the hydroxyapatite decomposition in hydroxyapatite -alumina and hydroxyapatite – titanium nanocomposites, respectively.

Keywords: Hydroxyapatite, Decomposition, Nanocomposite, Atmosphere, Phase transformation.

PACS number: 64.70.Nd

1. INTRODUCTION

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is very similar to the mineral part of bone and is highly bioactive and biocompatible and because of that it is the most appropriate material for hard tissue replacement implants [1,2]. The application of HA involves heat treatment at elevated temperatures in order to prepare useful shapes for biological and medical purposes. However, it was found that hydroxyapatite starts to decompose in the oxidizing atmosphere from about 700°C [3]. On the other hand, the second phases promote the HA decomposition during pressureless sintering giving rise to tricalcium phosphate (TCP), $Ca_3(PO_4)_2$, and other deleterious phases that results in poor sintering characteristics and mechanical properties of HA ceramic. Sintering temperature, type and fraction of second phases, and sintering atmosphere are the most important factors affecting the degree of decomposition of hydroxyapatite [1,4]. Alumina is one of the most widely investigated materials as reinforcement. When fine Al_2O_3 powder was used as reinforcement, the strength increased steadily with increasing the amount of Al_2O_3. In this case, however, further improvements in mechanical properties were hindered because of the incomplete mixing and excessive reaction between HA and Al_2O_3 [5-7].

Therefore, to improve the mechanical properties of HA-based composite, it is necessary to suppress the reaction between the HA and Al_2O_3 as well as improving the mixing process. Titanium (Ti) and its alloys, on the other hand, are among the most successful metallic biomaterials for orthopaedic and dental applications due to their high specific strength, excellent corrosion resistance and good biocompatibility [8, 9]. The purpose of the present investigation is to survey the effect of sintering atmosphere on decomposition of hydroxyapatite in pure hydroxyapatite, hydroxyapatite-20 wt% alumina and hydroxyapatite-20 wt% titanium nanocomposites.

2. MATERIALS AND METHOD

Hydroxyapatite (MERCK 2196), nanosize alpha alumina (PlasmaChem 12489), and titanium (MERCK 1.12379) were used as starting materials. The phase composition and morphology of samples were investigated using X-ray diffractometer (Siemens, 30 kV and 25 mA) with Cu Kα radiation (l = 1.5405 A °) and scanning electron microscope (SEM: Cambridge S360) operating at 15 kV, respectively.

The powders consisting of HA, HA-20 wt% Al_2O_3, and HA-20 wt% Ti were mechanically mixed using a ball mill for 4 h. Mixed powders were sieved through a 20 mesh sieve. The obtained powders were uniaxially pressed at 50 MPa, followed by cold-isostatic pressing at 180 MPa. The green compacts were subsequently pressureless sintered in air, moist, and reduction (using carbon black) atmospheres at 1200°C for 2 h using a heating rate of 5°C/min.

3. RESULTS AND DISCUSSION

The SEM images of starting powders are illustrated in Fig. 1. It shows that hydroxyapatite and alumina grains are nearly spherical and their sizes are below 100 nm. The average particle size of Ti was measured about 100 μm. The XRD results of three powders (Fig. 2) show that all starting materials are single phase.

Representative XRD patterns of the pure HA and HA-based composites are shown in Figs. 3-5. In pure HA sintered in different atmospheres (Fig. 3(b-d)), as expected, only peaks corresponding to HA were detected, since the decomposition temperature of pure HA is generally found above 1300°C [10].

Several researches indicated that HA decomposes at elevated temperatures or in presence of second phases, to form TCP as follows [8]:

$$Ca_{10}(PO_4)_6(OH)_2 \leftrightarrow 3Ca_3(PO4)_2 + CaO + H_2O \qquad (1)$$

* Ebrahimi186@yahoo.com
† ebadzadehtouradj@yahoo.co.uk
‡ E-salahi@merc.ac.ir

 © 2012 Sumy State University

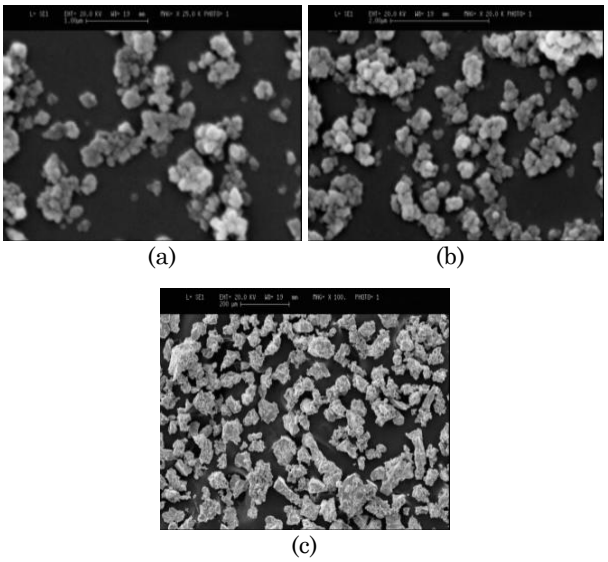

Fig. 1 – SEM images of starting powders HA (a), Al_2O_3 (b), Ti (c)

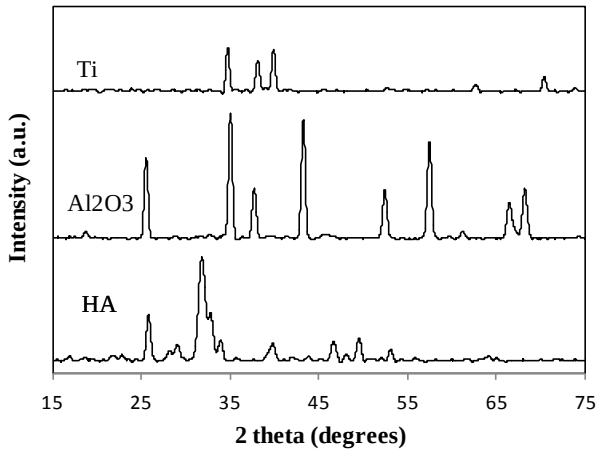

Fig. 2 – XRD patterns of starting powders

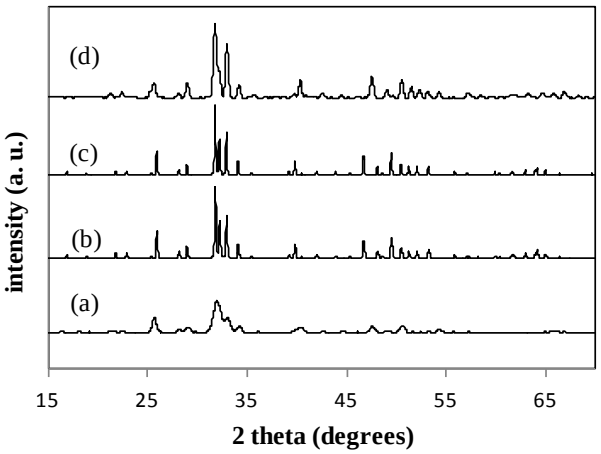

Fig. 3 – XRD patterns of HA powder sintered at 1200 °C in (a) air (b), moist (c), and reduction (d) atmosphere

According to Le Chatelier's principle, dehydration and the associated decomposition of hydroxyapatite to biodegradable unhydrated calcium phosphates during sintering may be suppressed under a moist sintering atmosphere [8]. This is the reason that, when 20 wt% nano-Al_2O_3 powder was added and sintered under the same atmospheres, only HA and alumina peaks were detected for specimen sintered in moist atmosphere (Fig. 4b). TCP peaks were detected along with alumina and HA peaks for specimens sintered in air and reduction atmospheres (Fig. 4).

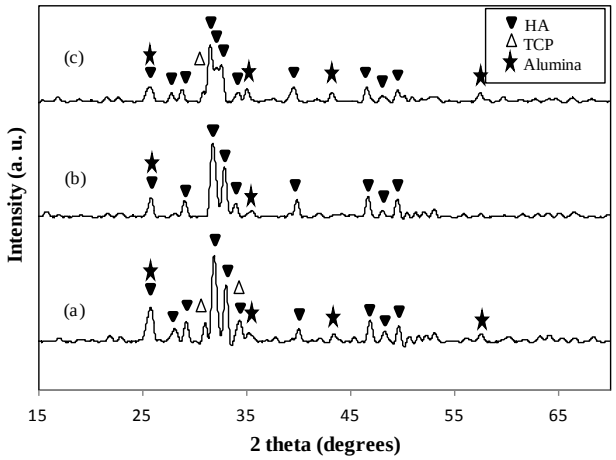

Fig. 4 – XRD patterns of HA-20 wt% Alumina composites sintered at 1200 °C in (a) air, (b) moist, and (c) reduction atmosphere

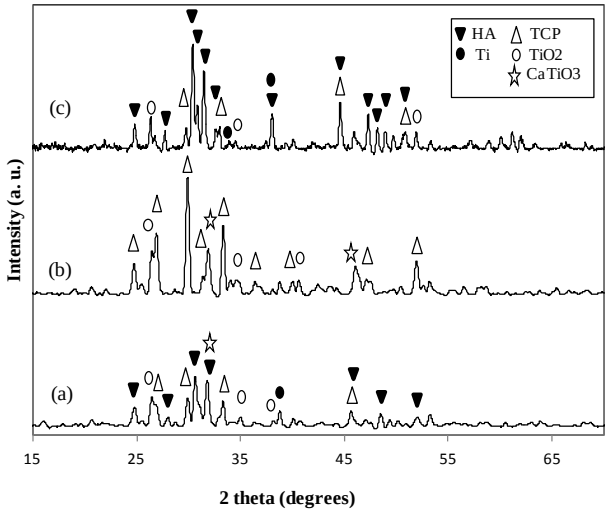

Fig. 5 – XRD patterns of HA-20 wt% Ti composites sintered at 1200oC in (a) air, (b), moist, and (c) reduction atmospheres

In case of HA-20 wt % Ti composite, moist atmosphere caused extensive oxidation of Ti, and as a consequence of CaO tendency to react with TiO_2 to form calcium titanate, HA was decomposed completely to TCP. But, for specimens sintered in air, oxidation of Ti and resulting decomposition of HA was much lower (Fig. 5).

On the other hand, the partially oxidation of Ti, as a result of dehydration of HA, can be responsible for partially decomposition of HA in reduction atmosphere. As can be seen in Fig. 5(c), no $CaTiO_3$ related peaks were detected for specimen sintered in reduction atmosphere. Fig. 6 shows the increase of dehydration and decomposition of hydroxyapatite as a result of increasing temperature. This is in agreement with previous works on pure hydroxyapatite and different hydroxyapatite composites [1-4].

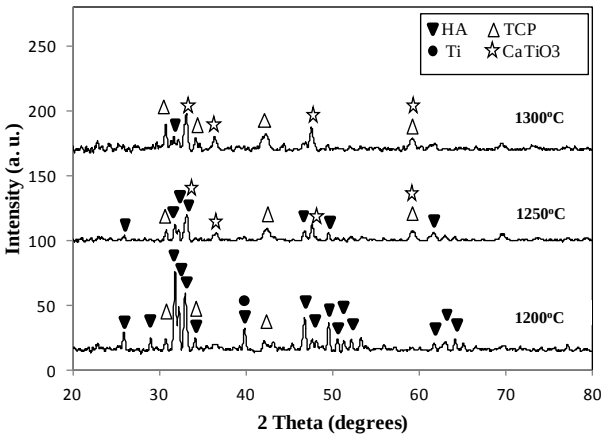

Fig. 6 – XRD patterns of HA-20 wt% titanium nanocomposites sintered at different temperatures for 1 hr in reduction atmosphere

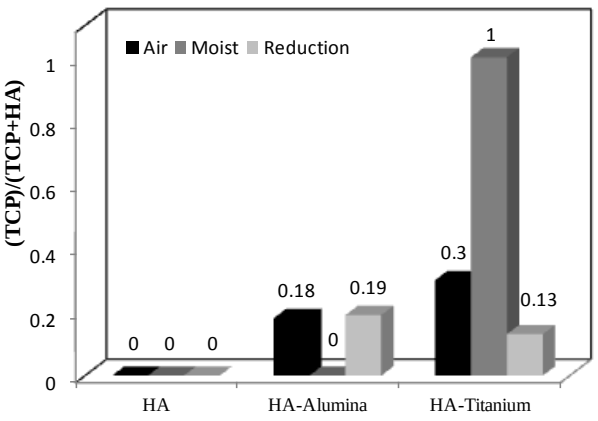

Fig. 7 – Relative amounts of TCP to HA deduced from the XRD patterns, indicating the degree of decomposition of HA and HA composites sintered at different atmospheres

The relative amount of TCP to HA was deduced from the intensities of HA and TCP peaks and shown in Fig. 7. By XRD analyses alone, it is hard to determine the precise amounts of phases present in a specimen.

But, it is useful to distinguish the relative differences between the specimens processed under the same conditions.

From Fig. 7, it is clear that moist and reduction atmospheres are preferred sintering atmospheres for HA- Al_2O_3 and HA-Ti composites, respectively.

4. CONCLUSION

The effect of different sintering atmospheres on phase decomposition of pure HA, HA-Al_2O_3, and HA-Ti nanocomposites was investigated. Results suggested the following optimal conditions for each system.

Sintering of pure nano-HA at 1200°C, results no phase decomposition, regardless of sintering atmosphere.

For HA-Al_2O_3 nanocomposite the moist atmosphere completely suppressed the decomposition of HA.

In HA-Ti nanocomposite, HA completely decomposed in moist atmosphere. But, reduction atmosphere can considerably impede the HA decomposition.

REFERENCES

1. M.A. Monge et al., *J. Ceram. Int.* **35**, 2373 (2009).
2. Zafer Evis, Robert H. Doremus, *J. Mater. Lett.* **59**, 3824 (2005).
3. K. Haberko et al, *J. Ceram. Int.* **35**, 2537 (2009).
4. I. Mobasherpour, M. Solati Hashjin, S.S. Razavi Toosi, R. Darvishi Kamachali, *J. Ceram. Int.* **35**, 1569 (2009).
5. J. Li, B. Fatash, L. Hermansson, *J. Biomat.* **16**, 417 (1995).
6. Huaxia Ji, P.M. Marquis, *J. Mater. Sci..*, **28**, 1941 (1993).
7. Huaxia Ji, P.M. Marquis, *J. Biomat.* **13**, 744 (1992).
8. R.V. Noort, *J. Mater. Science* **22**, 3801 (1987).
9. M. Long, H.J. Rack, *J. Wear* **205**, 130 (1997).
10. M.R. Dickson et al., *J. Mater. Science: Mater. Medicine* **6**, 297 (1995).
11. E. Champion, S. Gautier, D. Bernache-Assollant, *J. Mater. Science: Mater. Medicine.* **7**, 125 (1996).