Thermochimica Acta, 218 (1993) 465–475
Elsevier Science Publishers B.V., Amsterdam

Thermal expansion application to assess calcination of bovine hydroxyapatite

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Keywords: Biological apatite, calcination, thermal expansion, phase analysis, microstructure.

ABSTRACT

The thermal behaviour of hydroxyapatite prepared from bovine tibia was followed. Combined differential thermal analysis and thermogravimetric analysis were carried out for this biological apatite. The stability range was followed through thermal expansion measurements of the calcines and supplemented by X-ray diffraction analysis and scanning electron microscopy.

The existing structure of the hydroxyapatite persisted up to and above 1000 °C with the development of high crystallinity as proved by their diffractograms and surface topography of the samples heated between 700 and 1000 °C.

The flattened turning points of dilatometric curves for samples calcined above 800 °C along with reduced expansion values prove completed calcination.

Detailed knowledge of the thermal behaviour is helpful for well balanced calcination process involving, therefore, minimal fuel consumption. The importance of hydroxyapatites of various origins lie on their compatibility as bone substitute. Complete structural characterization of such potential graft material needs to be carried out to assess its biocompatibility.

INTRODUCTION

Recent work conducted on the reconstruction of resected mandible of rabbits classified the present veterinary hydroxyapatite (VHAP) as a bioactive material (Abdel-Fattah et al., 1989). Its natural porosity enhanced cellular ingrowth and guaranteed close adhesion which prevented infection from the implant. Also its use in the closure of oro-nasal defects in dogs was found well tolerated by soft and hard tissue (Soliman, 1990). On the other hand, its catalytic activity was found to vary with the calcination temperature of the derived hydroxyapatite (Abdel-Fattah et al., 1992). Moreover, the traditional bone china with its attractive aesthetics is composed of 30 to 60% of bone ash along with Kaolin and cornish stone (Kingrey et al., 1967) an application which needs controlled calcination processes.

Bone is a heterogeneous material composed 65% hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and 35% of protein. About 40% of the bone mineral is amorphous calcium phosphate. Therefore, the production of ash necessitates chemical and thermal treatment to remove the organic matter. This processing is intended to prevent the possible antigenic response to organic compounds and reduces the risk of rejection and toxicity when the ashed bone is used as an allogenic implant. It is equally important for the whiteness and translucent parameters of bone china. The surface texture has a dual role for both applications.

Thermoanalytical methods are utilized to optimize firing curves (Sladek, 1985) as well as the respective kiln construction (Sladek, 1989) for the sintering of various ceramic products. Others identified clay minerals on the same bases (Sikalidis, 1980). However, the literature pertaining to the optimum calcination temperature for producing bone ash in relation to its textural and structural properties are very limited.

The present article deals with optimizing the calcination process through thermodilatometric analysis of pre- and post-heated bovine bone. Accompanying, morphological changes were followed and supplemented by X-ray diffraction analysis as well as thermal ones.

EXPERIMENTAL

The bovine tibia bone (VHAP) was mechanically cleaned, crushed and boiled for several hours in a solution of sodium carbonate (0.5 N) to extract the organic matter and washed with hot water several times. The bone fragments were calcined in an electrical tubular furnace up to 600 , 800 , 900 and 1000 °C at a heating rate of 5 °C/minute and mild stream of air 3.5 L/min. At each step, temperature was maintained for three hours to ensure reaction completion.

Thermal expansion

A horizontal vitreous silica dilatometer (J. Malkin and Co. Ltd, England) was used at heating rate of 4 ± 1 °C/minute (ASTM C824-76)Results obtained are the mean of duplicates. A fused silica rod (N.B.S. No. 739, Kirby et al., 1974), was used for instrumental calibration. Thermal runs were performed for the original bovine bone and the calcination products obtained at the above mentioned temperature.

Simultaneous DTA, TGA and DTG

Thermal analyzer with differential scanning colorimeter cell was used up to 1000 °C with a heating rate of 5 °C/minute (Netzsch Gerateban Gmbt sub, Bestell-Nr 348-172 C) for the washed precalcined bone sample.

X-ray diffraction analysis

Crystalline structure of the VHAP before and after calcination at various temperatures was followed using Phillips (PW 1390) X-ray Diffractometer. Continuous scans were performed between 19° and 50° 2θ using CuK_α and CoK_α radiation at a rate of 2θ = 2 °/minute. A scan of calcitite (bone grafting hydroxyapatite, San Diago) was performed for comparison.

Grain morphology SEM

A Scanning electron microscope (Jeol JSM-T 20) was used to examine the morphological transitions of the calcines, VHAP and calcitite. The powder was ground and the range of 300-600 mm size suitable for bone grafting was chosen for the studies.

RESULTS AND DISCUSSION

Thermal expansion

The dilatometer plot of VHAP has a very characteristic expansion-contraction course during calcination as shown in Figure 1. The initial

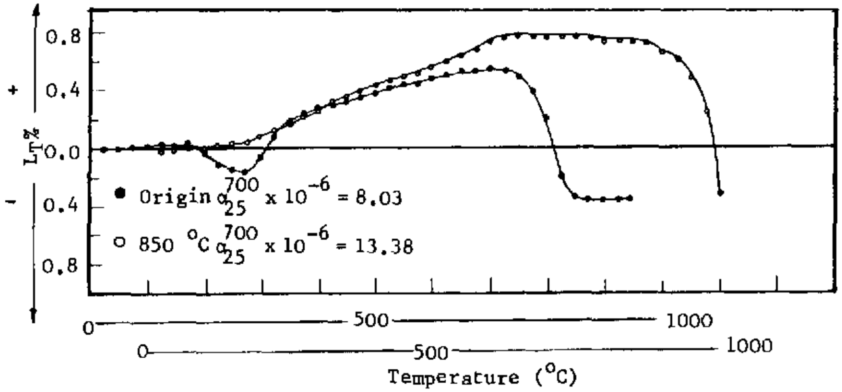

Fig. 1. Thermodilatometric curves for bovine bone (VHAP) and when calcined at 850 °C.

phase of slight expansibility occurs from room temperature up to approximately 175 °C, (± 0.03%) and is followed by a period of contractility which extends up to 275 °C (-0.16%). Thenafter, a steady increase in expansibility extends up to 700 °C (+0.54%). Here follows a period of rapid contractility which lasts up to 850 °C with stable values upwards. Dilatometric curves of the calcines, Figure 2, display common feature of characteristic turning points of contraction after a period of expansion. The temperature recorded for the turning points increase with increasing the calcination temperature and acquired a flattened shape. The calcines obtained at 800 and 900 °C have similar behaviour. The wider flattened end (700-1000 °C) of the dilatation plots of the calcines obtained at 900 and 1000 °C and having reduced expansion coefficient values prove completion of the transitional steps.

Simultaneous DTA, TGA and DTG

Figure 3 shows the combined weight loss TG and its rate DTG as well as differential thermal analysis DTA of the original bone where three transitions are recorded. The transitions are interpreted as water desorption, an oxidation reaction(s) and possible crystal phase transitions. The first endo-reaction with its maximum at 120 °C extends up to 250 °C and is accompanied by a 0.25% loss in weight. This endotherm corresponds to the first contraction observed in the dilatation, Figure 1. Both of these measurements are consistent with the assumption that water is being eliminate from the specimen. The second reaction occurs

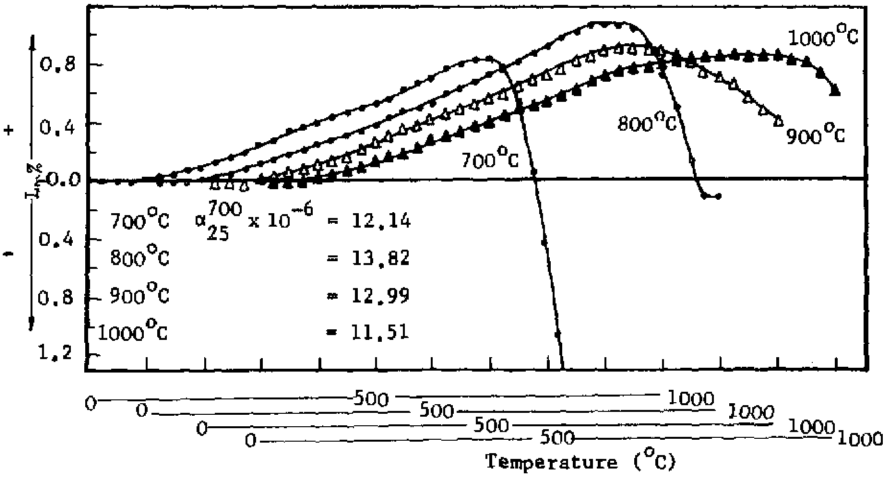

Fig. 2. Thermodilatometric curves for bovine bone (VHAP) and when calcined at 700, 800, 900 and 1000 °C.

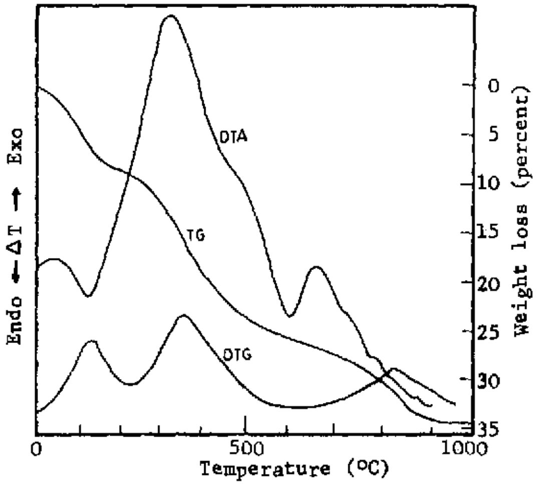

Fig. 3. Simultaneous differential thermal analysis DTA, thermogravimetric analysis TGA and derivative thermogravimetric analysis DTG.

between 250 and 550 °C having its maximum at 320 °C. This exo-reaction is attributable to combustion of organic matter and its accompanied by high expansibility. A final weight loss of 6.75% which extends up to 900 °C is accompanied by endothermic reaction and consequently is ascribed to $CaCO_3$ dissociation. This is reflected as sharp contractility in dilatation courses. The rate of the first two reactions is very high compared to that of carbonate dissociation. Thus an appropriate period of time must be provided for completion of those processes and to avoid carbon fixation.

X-ray diffraction (XRD)

The X-ray tracings of the preheated washed powder and when heat treated at 600 and 700 °C as depicted in Figure 4 reveal the minimal crystallinity of mineral hydroxyapatite. Diffraction lines corresponding to c-axis (002), i.e. 3.34 Å and a-axis (300), i.e. 2.71 Å are very broad and with low intensity. Calcination as early as 600 °C developed highly crystalline hydroxyapatite. The intensity of the diffraction lines obtained at 700 °C grew sharper and were comparable to that of calcitite as represented in Figure 5.

As bone is composed of 65% hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and 35% of protein (Tiselius et al., 1956), the first contractility is ascribed to interfacial water evaporation (Wafa and Selim, 1991) This is followed by organic matter decomposition up to 600 °C, then came the carbonate ion dissociation along with minor crystallization. It is reported that the carbonate ion constitutes 5% of the total weight of ashed bone. The first two transitions are quite observable in the plot of the variation of coefficient of thermal expansion as a function of temperature, Figure 6.

The above mentioned changes are expected to be accompanied by densification. The values of powder density of the original bone is very low compared to that of hydroxyapatite (3.14 g/cm^3) due to the presence of moisture, organic compounds, and carbonate ions. Density values increase with calcination temperature to reach its maximum at 1000 °C as samples calcined at 1200 °C possess similar powder density.

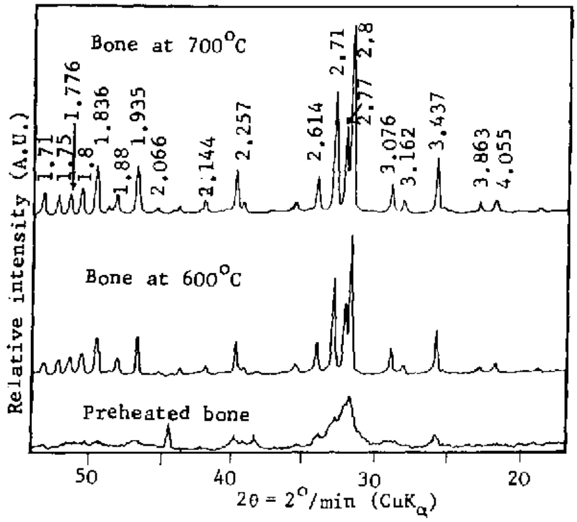

Fig. 4. X-ray diffraction tracings of the bovine bone (VHAP) and bone calcined at 600 and at 700 °C. (CuK$_\alpha$) radiation.

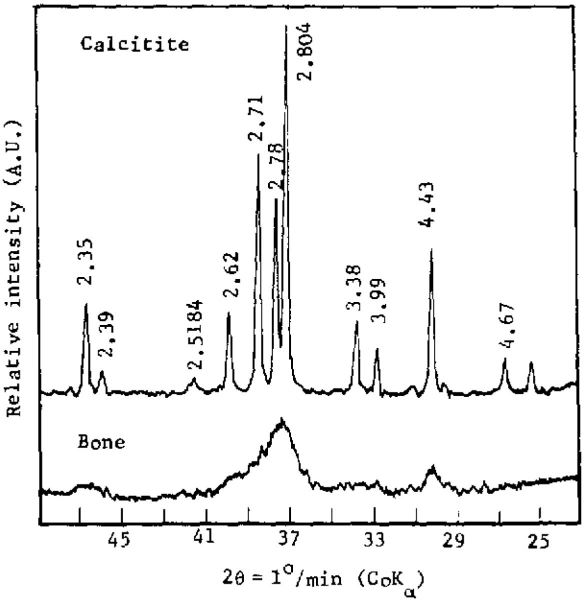

Fig. 5. X-ray diffraction tracings of the bovine bone (VHAP) and bone calcitite (bone grafting). (CoK$_\alpha$) radiation.

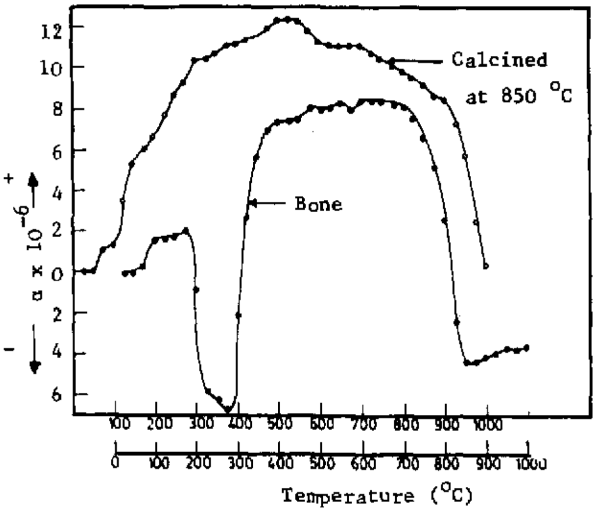

Fig. 6. Variation of expansion-contraction thermal coefficient of precalcined bovine bone (VHAP) and bone bovine at 850 °C.

TABLE 1

Variation of powder density with calcination temperatures

Calcination Temperature (°C)	Precalcination	600	800	900	1000	1200
Powder density (g/cm^3)	2.094	2.90	2.988	3.051	3.058	3.056

The results prove thermal stability at and above 900 °C. To confirm, bone was calcined at 850 °C and its thermal expansion was measured and compared to that of the original bone as in Figure 1. The dilatation course show close similarity to those of calcines obtained at 900° and 1000 °C, Figure 2.

Surface texture (SEM)

The photomicrographs of bone (VHAP) exhibit angular grains with patches of finer particles within the grain, Figure 7 a,b. Upon calcination at

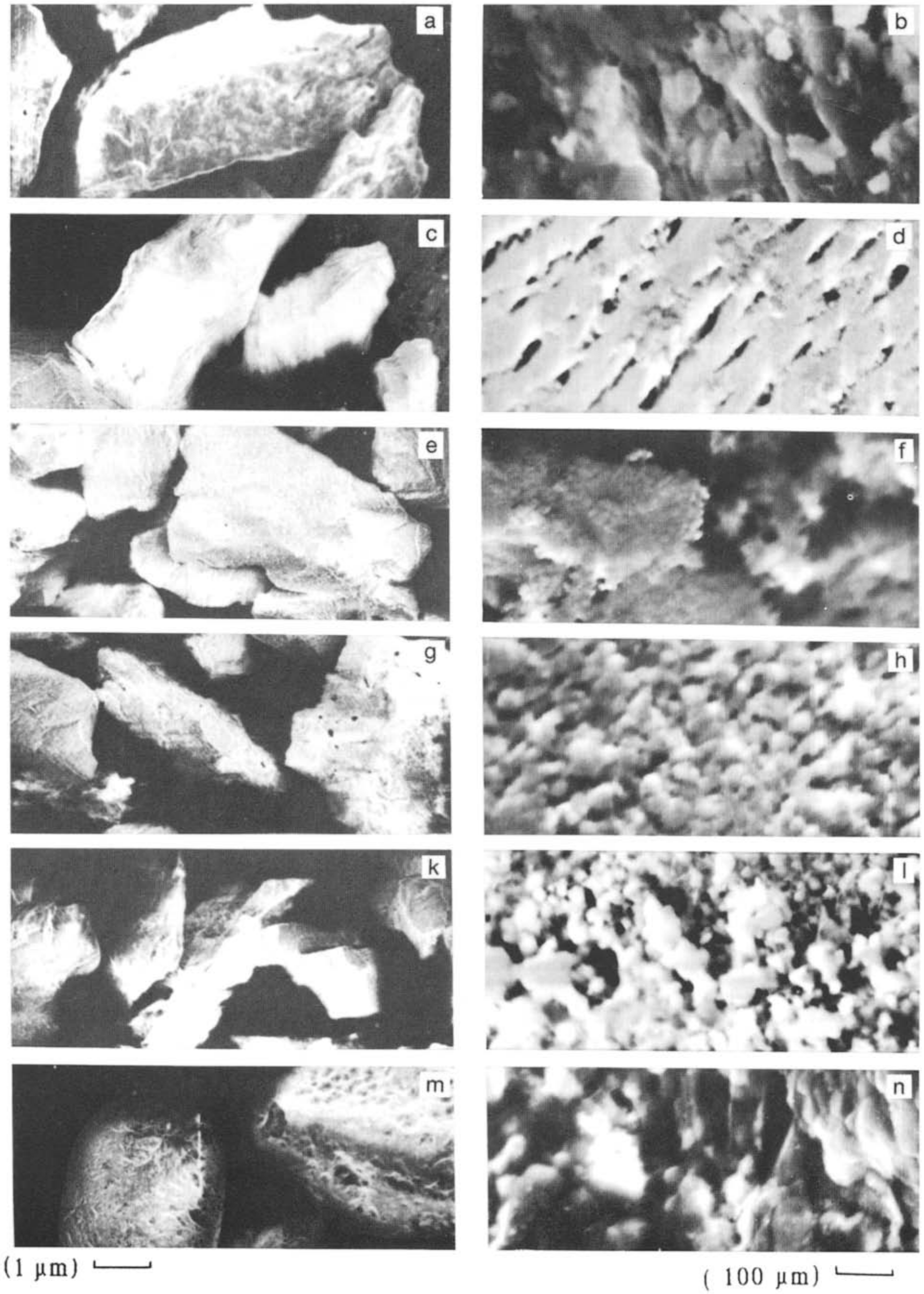

Fig. 7 SEM of (a,b) VHAP, (c,d) calcine at 600 °C, (e,f) calcine at 700 °C, (g,h) calcine at 800 °C, (k,l) calcine at 1000 °C and (m,n) calcitite bone grafting

600 °C, the crystallites constituting the grains with diagonal filaments and pores quite observable in various parts of the sample, Figure 7 c,d. The bone calcined at 700 °C has more porous structure with patches and a network of bony tissue, Figure 7 e,f. Grain growth is clearly observed upon calcination at 800 °C with numerous angular and rounded particles, Figure 7 g,h. The formation obtained is very similar to Tiselius (1956) hydroxyapatite. Higher calcination temperature (1000 °C) produced similar texture but with more porosity, Figure 7 k,l. The texture of calcitite, Figure 7 m,n, could be compared with bone obtained at 800 °C, Figure 7 g,h.

Therefore, a calcination temperatures of 800° and 850 °C would be sufficient and could be selected for bone ash production whereby lower energy consumption is achieved through:

a. lower calcination temperature than previously reported, and
b. fine grinding low temperature calcined powders is achieved at half time needed for powders obtained at high calcination temperature as a consequence of their higher crystallinity.

Bone ash production was reported by Raymond (1980) to be at 1000 °C while Ismatov et al. (1983) reported temperatures between 1173 and 1673 °C with boron flux for same purpose.

CONCLUSIONS

1. The initial and final dilatometric contractions are paralleled with the endothermic and weight loss observations interpreted as evaporation of interfacial water and carbonate decomposition, respectively. Expansion accompanied the combustion of organic matter with its exothermic reaction is accompanied by weight loss.
2. Calcination of bovine bone is accompanied by crystallization and grain growth of hydroxyapatite which is completed at and above 850 °C with the development of highly porous structure.
3. Dilatometric studies are sensitive to reactions involving expansion-contraction and are indispensably required for optimizing the calcination process aiming at reducing energy consumptions.
4. It is necessary to supplement results of dilatometric studies with data obtained from XRD, DTA and SEM as well.

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