Preparation of Bioresorbable Magnesium-substituted Tricalcium Phosphate Ceramics

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Introduction:

β-tricalcium phosphate [$Ca_3(PO_4)_2$, β-TCP] ceramics have been widely used in dental and skeletal prosthetic applications, due to their good biocompatibility, osteointegration and bioresorbability. However, the poor mechanical properties of β-TCP ceramics, caused by the brittleness and insufficient compaction after sintering below the β- to α- transformation temperature ~1125°C, limit the applications. To increase the transition temperature and improve the sintering properties, Mg-substituted tricalcium phosphate [β-TCMP, $(Ca,Mg)_3(PO_4)_2$] has been produced. With 3 mol% Mg, β-TCMP has the transition temperature above 1300°C. Dense β-TCMP ceramics (~99% dense) were produced by sintering this β-TCMP grenn body at 1250°C for 2 hours. In addition, macroporous β-TCMP ceramics were created with sucrose as the porogen.

Methods:

β-TCP powders were prepared by a two-step process. Apatitic tricalcium phosphate [$Ca_9(HPO_4)(PO_4)_5(OH)$] was first prepared through a precipitation method. $Ca(NO_3)_2$ solution was slowly titrated into $(NH_4)_2HPO_4$ solution (pH~10) at room temperature. The precipitates were aged for 1 hour, harvested and dried at 80°C for 12 hours. This β-TCP 'precursor' was then heated at 800°C for 3 hours to produce β-TCP. To prepare β-TCMP, varying amounts of $Mg(NO_3)_2{\cdot}6H_2O$ were added into $Ca(NO_3)_2$ solution as the Mg source. For dense ceramics, β-TCMP powder was grinded with addition of drops of 5wt.% polyvinyl alcohol (PVA) solution. The powder was then uniaxially pressed in a stainless steel die on a load frame at different pressures. The green bodies were further sintered in air at 1250°C for 2 hours. For macroporous β-TCMP ceramics, sucrose was mixed with β-TCMP powder as the porogen to make a green body. The green body was then slowly heated up to burn off sucrose and further sintered at 1250°C to improve structural integrity of the porous body. The samples were characterized by XRD, TG/DTA, SEM, EDS and FT-IR techniques. The relative density of the compacted ceramics was measured following Archimedes' method. Quasi-static compression tests were conducted at a strain rate of 10^{-3}/s.

Results:

β-TCMP precursor was prepared by the precipitation method at room temperature (Fig. 1a). Pure β-TCMP can be prepared by heating this precursor at 800°C for 3 hours (Fig. 1b). With increase of the amount of Mg, the β- to α-transition temperature increases. β-TCMP with 3mol%Mg has a transition temperature above 1300°C (Fig. 1c).

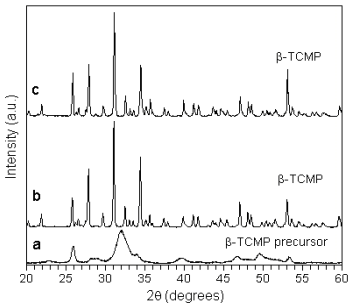

Fig. 1. XRD pattern of (a) β-TCMP (3mol%Mg) precursor, (b) β-TCMP produced by heating the precursor at 800°C for 3 hours and (c) heated at 1300°C for 2 hours.

The ceramic density is affected by the loading pressure for the green body. With a loading pressure of 60MPa and 150MPa, the relative density of β-TCMP ceramics after sintered at 1250°C are ~93% and 99%, respectively (Table 1). The average compressive strength of ~99% relative dense β-TCMP ceramics is ~190MPa.

Table 1. The effect of loading pressure to the density of β-TCMP ceramics (3mol%Mg) sintered at 1250°C for 2h.

Sample	Loading pressure	Relative density
1	60MPa	93%
2	100MPa	97%
3	150MPa	99%

Macroporous β-TCMP ceramics (pore size ~100-300μm) can be produced from β-TCMP or 'precursor' powder with sucrose as the porogen (Fig. 2). The ceramics were heated up at 2°C/min and sintered at 1250°C for 2h in air.

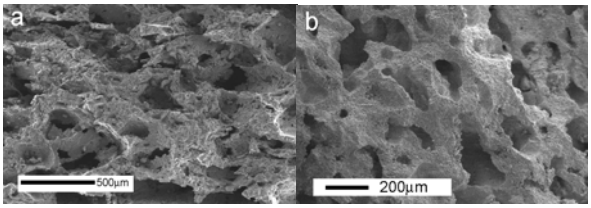

Fig. 2. SEM images of macroporous β-TCMP ceramics created from (a) β-TCMP (3 mol% Mg) precursor, (b) β-TCMP (5 mol% Mg) powder with sucrose as the porogen.

Conclusions:

β-TCMP was produced by a two-step process: precipitation and further heating of β-TCMP precursor. With the increase of the amount of Mg, β- to α- transition temperature increases. β-TCMP with 3mol%Mg has a transition temperature above 1300°C. 99% relative dense β-TCMP (3mol%Mg) can be produced with a compaction pressure of 150MPa and further sintering at 1250°C for 2 hours. The average compressive strength of 99% dense β-TCMP is ~190MPa. Macroporous β-TCMP ceramics can be created with sucrose as a porogen.