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PROPERTIES OF MAGNESIUM DOPED NANOCRYSTALLINE HYDROXYAPATITE SYNTHESIZE BY MECHANOCHEMICAL METHOD

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ABSTRACT

The sintering behaviour of Magnesium-doped nanocrystalline hydroxyapatite (MgHA) synthesized by mechanochemical method was investigated over the temperature range of 1000 ºC to 1300 ºC. The properties were investigated in terms of phase stability, bulk density and Vickers hardness. In the present research, a dry mechanochemical synthesis was successfully employed to synthesis a nanocrystalline MgHA powder without any secondary phases. Lower sintering temperature at 1000 ºC produced β-TCP phase in MgHA in all concentrations. Hence, doping Mg^{2+} into HA has induced the formation of brushite and α-TCP where these phases were averagely increased with Mg^{2+} concentration. Increasing Mg^{2+} concentrations have led to the decreased of HA phase and increased the secondary phases.Mg^{2+} did not significantly improved the density of HA as the density decreased with Mg^{2+} doping at 1200 ºC – 1250 ºC. However, Mg^{2+} increased the hardness of HA when sintered from 1000 ºC to 1300 ºC. The maximum hardness was obtained by 3% MgHA sintered at 1250 ºC with 5.47 GPa.

Keywords: magnesium, nanocrystalline, hydroxyapatite, mechanochemical, vickers hardness.

INTRODUCTION

Although Hydroxyapatite (HA) has a good osseo integration and osteo conductive properties, the low mechanical properties such as low strength and brittleness (Fu and Chen, 2005) have limited its use in load-bearing application. Other drawbacks such as design limitations (Simon *et al*., 2005) and high level of crystallinity could result the nondegradability of pure HA when implanted in an organ (Xiu *et al*., 2005). Before creating a device which has the ability to mimic human bone, different bone types and their mechanical properties like hardness, Young's modulus and fracture toughness etc. should be considered. Many researchers have tried to improve the mechanical properties of HA. One of the method is to dope HA with metal ions such as magnesium (Fadeev *et al*., 2003; Landi *et al*., 2008) manganese (Mayer *et al*., 2007), zinc (Laquerriere *et al.* 2006; Li *et al*., 2008), and strontium (Fu & Chen, 2005; Bigi *et al*., 2007). Those metals might affect the lattice parameters, the crystallinity, the dissolution kinetics and other physical properties of apatite (Li *et al*., 2008). Moreover, such metal ions play a significant role towards enhancing cell-material interactions of calcium phosphates and also upgrading its mechanical properties. The involvement of magnesium (Mg) ions into HA structure is of great interest for the growth of artificial bone substitutes. Mg^{2+} is one of the most important ions combined with biological calcium phosphates and plays significant role during spontaneous formation of *in vivo* calcium phosphate and bone bonding. Mg^{2+} is closely associated with mineralization of calcified tissues, and this ion indirectly influences mineral metabolism (adzila *et al*., 2012). The Mg^{2+} shortage has an adverse effect on all stages of the skeletal metabolism, as it causes the discontinuation of bone growth, the reduction of the activity of osteoblasts and osteoclasts, osteopaenia and bone fragility. Mechanochemical treatment is an example of non-conventional solid-state process, which can be applied for synthesis of new materials. Milling is very practical, convenient and rational tool to provide chemical reaction especially in solid-state without heating too much (Mochales *et al.,* 2004). In this study, dry mechanochemical method is used to synthesis HA and Mg-doped HA nanocrystalline powder. The synthesized powder is compacted and sintered at various temperatures ranging from 1000 ºC to 1300 ºC. The effect of Mg^{2+} doping from 1% MgHA - 9% MgHA concentration in nanocrystalline HA at various sintering temperature are characterized through the phase existence, density and hardness properties.

EXPERIMENTAL METHOD

The starting precursors for Mg-doped HA powder were commercially available calcium hydroxide, $Ca(OH)_2$ (98%, R and M Chemicals), di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (98%, Systerm) and magnesium hydroxide, $Mg(OH)_2$ (95% - 100%, Systerm) (Adzila *et al*., 2011).The reaction equation for Mg-doped HA from the three precursors is described in Equation.(1):

$$(10 - X)\ Ca(OH)_2 + XMg(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10-x}Mg_x(PO_4)_6(OH)_2 + 12NH_3 + (18-X)H_2O \quad (1)$$

Where X = 0, 0.1, 0.5, 0.6, 0.7, 0.8, 0.9, denoted as Mg precursor. The milling process was carried out in

zirconia vial with zirconia balls in Retsch planetary ball mill. The mixed precursors with molar ratio of 1.67 (Ca+Mg)/P weremilled at 370 rpm for 15 hours (where 15 minutes were set as an interval pause for every 1 hour milling. 1g of the synthesized HA and Mg-doped HA powders were compacted at 2.5 MPa load into disc shape (10.3 mm diameter x 5.3 mm thickness) using a hardened steel mould and die set. The mould should be cleaned first by using oil (e.g. WD40) or silicon spray to remove any impurities and to remove the sample easily after compaction. Basically the density variation in the green product will caused differential shrinkage and crack initiation upon sintering (Satapathy, 1997). Due to this matter, the green compacts were packed into rubber gloves and subsequently vacuumed to remove the air and cold isostatically pressed (CIP) for 5 minutes at 200 MPa. The samples then were sintered at different temperatures; 1000 ºC, 1100 ºC, 1200 ºC, 1250 ºC and 1300 ºC in a pressure less conventional heating furnace. The heating and cooling rates were set at 5 ºC/min in 2 hours holding time. The bulk densities of sintered compacts were obtained by using water immersion technique based on Archimedes principle by a standard Mettler Toledo Balance Densitometer. The sintered disc samples were ground on SiC paper (600 - 1000 grit) and polished with 1µm diamond suspension (Mecapol, P260) to yield an optical reflective surface prior to Vickers hardness test. 10 indentations were made by using pyramidal diamond indenter (HMV, Shimadzu) for 10-15 seconds under 200 gf load (HV 0.2). The phase existed in the sintered samples were analyzed using X-Ray diffraction (XRD, Bruker, USA and Rigaku, Japan) with Copper Kα radiation (λ = 1.5406 Å) operated at 40 kV and 40 mA with diffraction angles (2θ) between 25º and 55ºwith a step size of 0.02º per sec. All the peaks obtained were compared to the standards of the Joint Committee of Powder Diffraction Standard - International Centre for Diffraction Data (JCPDS-ICCD) files for HA (PDF No. 74-566 for $Ca_{10}(PO_4)_6(OH)_2$ or PDF No. 9-432 for $Ca_5(PO_4)_3OH$), β-TCP (PDF No. 9-169), α-TCP (PDF No. 37-1497), TTCP (PDF No. 25-1137).

RESULTS AND DISCUSSIONS

Figure-1 shows the XRD pattern of Mg–free HA and Mg–doped HA (1% MgHA - 9% MgHA) compacts sintered at 1000 ºC. All the samples do not only contain a monophase of HA but existed with secondary phases. Doping Mg^{2+} into HA has induced the formation of brushite (calcium phosphate hydroxide hydrate, $CaPO_3(OH).2H_2O$) and this phase averagely increased with Mg^{2+} concentration. The HA peaks in 7% MgHA were more intense compared to Mg-free HA and other Mg-doped HA. Thus, the intensity of β-TCP and brushite were smaller than the other compacts. This can be deduced that 7% NaHA prevent the increment of the secondary phases by reducing the water release during heat treatment or sintering. The existence of secondary phase such as brushite in Mg-doped HA could be associated with the smaller ionic radius of Mg^{2+} that has influenced the stabilization of HA since its incorporation in HA has decreased the temperature onset of thermal decomposition (Cacciotti *et al*., 2009). Brushitebioceramics have been tested *in vivo*, *in vitro* and clinically for a series of orthopaedic and dental applications, as well as for other biotechnology uses, such as drug delivery, cancer therapy and the development of biosensors (Tamimi *et al*., 2012). The present result is also supported by (Ren *et al*., 2010) where the destabilization was due to the substitution of much smaller ions. This leads to severe lattice strain and results more defects which may cause HA decomposition. The structures of defect in HA ceramic are important as it can cause bone apposition on bioactive materials. The decomposition of HA and Mg-doped HA were also existed in the compacts sintered at 1100 ºC – 1300 ºC.

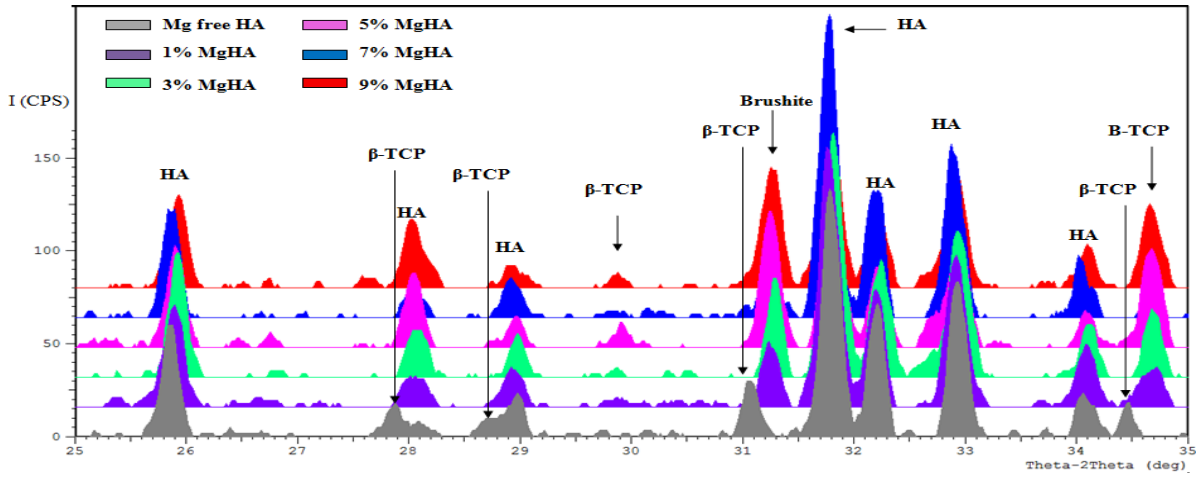

Figure-1. XRD pattern of Mg–free HA and Mg–doped HA compacts sintered at 1000 ºC.

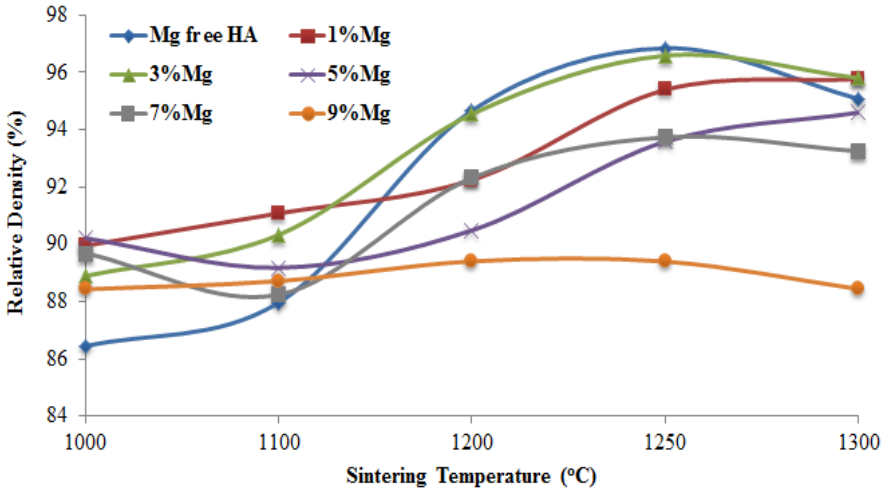

Figure-2. Relative densities of Mg-free HA and Mg doped HA as a function of sintering temperature.

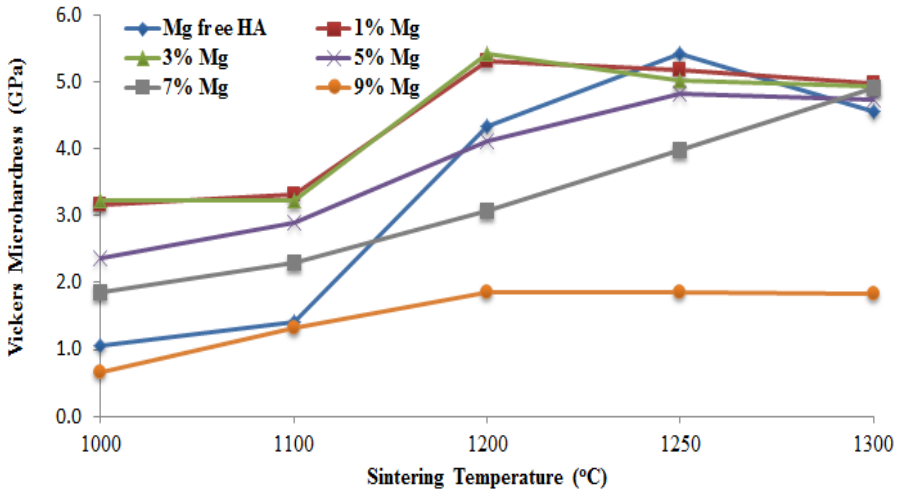

Figure-3. Vickers hardness of Mg-free HA and Mg-doped HA as a function of sintering temperature.

Figure-2 shows that increasing the sintering temperature generally cause the increase of relative densities of Mg–free HA and Mg-doped HA. All the sintered compacts showed the increase of densities until 1250 °C except 1% MgHA and 5% MgHA which rise continuously until 1300 °C. Mg^{2+} increased the density of HA when sintered at 1000 °C to 1100 °C with the maximum value was recorded in 5% MgHA (90.2%) and 1% MgHA (91.1%) respectively. However, when sintered at 1200 °C – 1300 °C, Mg^{2+} does not give any improvement in density of HA as the density decreases with Mg^{2+} doping. Similar to the present study, Cacciotti *et al*. (2009) also found that the increase of Mg^{2+} (2.5% - 10% MgHA) has reduced the relative densities of HA from 92% to 85% when sintered at 1250 °C due to residual porosity, which linearly increase with the Mg^{2+} content.

Figure-3 presents the Vickers hardness of Mg–free HA and Mg–doped HA in various concentrations. The hardness of Mg–free HA, 5% MgHA and 9% MgHA increased until 1250 °C and then decreased at 1300 °C. This trend is in agreement with the relative densities obtained. Thus, 1% MgHA and 3% MgHA showed that the Vickers hardness increased until 1200 °C and start to decrease at 1250 °C.

However, the continuous increase of hardness was observed in 7% MgHA. In general, Mg^{2+} doping improved the hardness of HA when sintered from 1000 °C to 1300 °C. The maximum hardness was recorded in 3% MgHA with 5.42 GPa compared to HA (4.34 GPa) when sintered at 1200 °C. However, sintering at only 1250 °C resulted in a decrease of hardness with increasing Mg^{2+} concentration. This result is also in agreement with the relative densities measured at 1250 °C where the densities decreased from Mg–free HA (97%) to a minimum value of 89% in 9% MgHA. Another factor such as the existence of secondary phase, α-TCP which increased with the sintering temperature and Mg^{2+} concentration, might reduce the strength of the HA. The decreasing of hardness

could be explained through the existence of closed porosity and/or the increased grain size in the sintered compacts (Thangamani *et al*., 2002).

CONCLUSIONS

Lower sintering temperature at 1000 ºC produced β-TCP phase in Mg-doped HA in all concentrations. Hence, doping Mg^{2+} into HA has induced the formation of brushite and α-TCP where these phases were averagely increased with Mg^{2+} concentration. Increasing Mg^{2+} concentrations have led to the decreased of HA phase and increased the secondary phases. Mg^{2+} did not significantly enhance the density of HA as the density decreased with Mg^{2+} doping at 1200 ºC – 1250 ºC. Mg^{2+} dopanthas also averagely increased the hardness of HA when sintered from 1000 ºC to 1300 ºC. The maximum hardness was obtained by 3% MgHA, 5.42 GPa when sintered at 1200 ºC. The 9% MgHA merely deteriorated the HA properties as the hardness was lower than 2.00 GPa.

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