Influence of Manganese Doping into HA Powders on the Properties of its Dense Bodies

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SUMMARY

The effect of Manganese (Mn) addition on the Vickers hardness and relative density of nanocrystalline hydroxyapatite (HA) dense bodies were studied. The starting Mn doped HA powders was synthesized via sol-gel method with Mn concentration varies from 2 mol% up to 15 mol% Mn. The Mn doped HA disc samples were prepared by uniaxial pressing at 200MPa and subsequently sintered at 1300°C. Characterization was carried out where appropriate to determine the phases present, bulk density, Vickers hardness of the various content of Mn doped HA dense bodies. The addition of Mn was observed to influence the color appearance of the powders and dense bodies as well. Higher Mn concentration resulted in dark grey powders. It was also found that the hardness and relative density of the material increased as the Mn content increased and influenced by the crystallinity of the prepared Mn doped HA powders.

INTRODUCTION

Manganese is one of the metallic elements which appear in biological apatite like bone and teeth. Its important effect on the growth and development of bone has been well known. Synthetic HA has raised much attention for application in bone bone augmentation and replacement programs. This is due to the fact that this biomaterial has close chemical resemblance with the mineral components and crystal structure to apatite in human skeletal system of natural bone and teeth[1]. Although HA is a stable phase, HA alone is not favored as it is a nonbiodegradable bone-replacement materials which would not be replaced by bone as it degraded. Moreover, its application is constrained to non load bearing region in clinical orthopedic and dental application due to its brittleness and low fracture toughness[1]. The pronounced importance of Mn in bone growth and development has been discovered first in 1936. In previous study, Mn in bone found to cause decreased in bone resorption[2]. It is also reported that Mn functioned as sintering additive of HA without producing other secondary phase like CaO. Hence, the incorporation of Mn into the apatite structure has been of great interest as it improves its bone like mechanical properties[3].

MATERIALS AND METHODS

The synthesis of Mn doped HA powder was carried out via sol-gel method by adding EDTA (Merck kGaA, Germany) into a heated ammonium solution (11% solution, R&M Chemicals, UK) while stirring until it dissolves. A calcium precursor, calcium nitrate tetrahydrate (Merck kGaA, Germany) was then poured into the mixture and followed by the dopant, manganese (II) nitrate tetrahydrate (Merck kGaA, Germany). Then a phosphorus precursor, di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (Merck kGaA, Germany) and urea (R & M Chemicals, UK) which act as gelling agent and ammonium donor agent are subsequently added. The mixture is then heated while stirring until white gel is obtained. The obtained gel is then dried at 340°C into a black gel and subsequently subjected to calcination at 900ºC.

The calcined powders were directly compacted into circular shape disks with diameter of 20mm at 200MPa via uniaxial pressing (Carver, 4350L). The green bodies were then sintered at 1300° with the rate of 2°C/min and 2 hours soaking time. Phase analysis by X-ray diffraction (XRD) (Shimadzu, XRD 6000) of the sintered samples was carried out. The density of the sintered compacts was measured by water immersion technique (Alfa Mirage, MD-300S) and the relative density was calculated by taking the theoretical density of HA as 3.156 g cm^{-3}. The hardness of the sintered samples was determined using the Vickers indentation method (Mitutoyo, MHV H-2). The particle sizes of the synthesized HA powders were measured vis Scherer's equation and Nanoparticle Sizer (Malvern Instruments, Zen 1600)

RESULTS AND DISCUSSION

The average powder particle size was measured via XRD analysis and found to be 58.7 nm, 40.3 nm, 46.2 nm and 56.0 nm for 2, 5, 10 and 15 mol% Mn doped HA powders respectively. Meanwhile the measurement of particles sizes via Nanoparticle Sizer analysis are 679.4 nm, 476.0 nm, 525.8 nm and 691.8 nm for the powders respectively. This difference is because Nanoparticle Sizer analysis was assumed to be measuring agglomerated particles instead of dispersed single particles. However, the particles are soft agglomerates which break easily during compaction which made it possible to be compacted without mixing with binder.

In the current work, it was observed that Mn addition has also greatly influence the appearance of the white HA powder and dense samples as well. Transformation from light gray at 2 mol% Mn to brown at 5 mol% Mn and finally dark gray at 15 mol% Mn content was observed. This might be influenced by the natural appearance of the Mn itself as blackish or brown solid. In this work also, 0.01 mol% Mn doped HA has been synthesized via sol gel method, and it was observed that

Table I: Phases present and intensity of the synthesized powders and the sintered dense bodies

Mn (mol %)	Mn doped HA powders		Phases present (Sintered dense bodies)
	Phases present	Intensity (counts)	
2	HA, β-TCP	605	HA
5	HA, β-TCP	357	HA
10	HA, β-TCP	404	HA
15	HA, β-TCP	554	HA

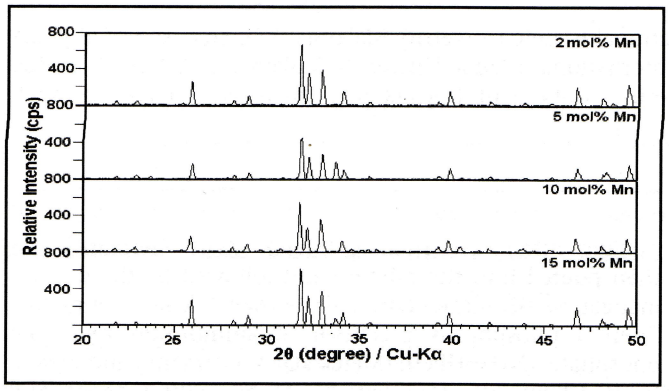

Fig. 1: The XRD patterns of the Mn doped HA dense bodies after sintering at 1300°C.

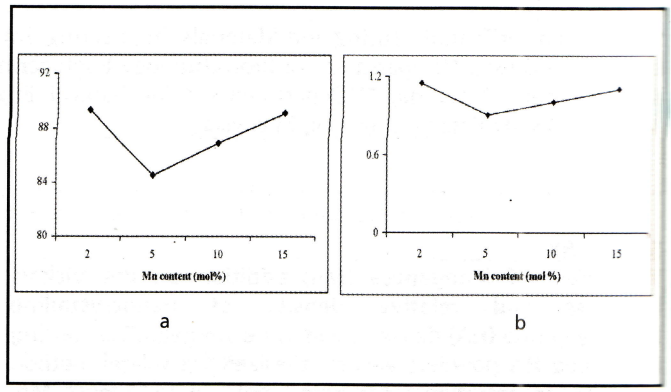

Fig. 2: The influence of Mn addition on the properties of HA compacts: (a) relative density and (b) Vickers hardness.

powders appeared in bluish white color. This confirmed that addition of Mn influenced the HA powder appearance even at small concentration of Mn.

The crystalline phases that were detected in the as prepared powder and sintered samples are presented in Table I. It was found that the BCP ceramics powder is converted to Pure HA ceramic when sintered at 1300°C. From this study also, it was observed that the increased amount of Mn being doped into HA powders has decreased the intensity of β-TCP peak. This can be associated with the substitution of the Mn ion with Ca ion in the β-TCP phase [2, 4]. This preference was supported by the atomic radii consideration, as Mn atom is smaller than Ca atom. Fig. 1 is showing the XRD pattern of the sintered dense bodies which consisting of only the HA phase which is in agreement with the standard JCPDS file No. 9-432 for HA.

The effect of Mn doping on the densification and Vickers hardness of HA compacts is shown in Fig. 2. In general, the bulk density variation of the HA samples increased with increasing in Mn content from 5 – 15 mol% Mn. The ceramics exhibited 84-89% of theoretical density when sintered at 1300°C. It can also be deduced that the density increased as the crystallinity of the powder increased (Table I). This is proven by the result observed for 2 mol% of Mn dopant, where highest relative density of 89.3% obtained. This result derived due to the highest crystallinity of its prepared powder. As reported, the crystallinity of the powder will determine the effectiveness of the powder in its application [5].

From Fig. 2(b)., the change in Vickers hardness with Mn content for samples sintered at 1300°C was observed. It was found that samples with highest Mn content exhibited the highest hardness of 1.15GPa. It can be deduced here that hardness of the samples is increased with Mn content. The same pattern for 2 mol% Mn doped HA samples in its relative density measurement was also observed here where it gave the highest hardness value. This once again conform to the effect of powder crystallinity has on the properties of sintered dense samples. Hence, it can be concluded that this hardness trend correlates well with the change in relative density where hardness increases steadily with relative density of the samples.

CONCLUSION

The influence of Mn doping into HA had been observed with its effect on the appearance, phases present, density and hardness of the samples when sintered at 1300°C. It was found that Mn doping has greatly influenced the appearance of the HA powders and dense samples as well, where the highest Mn doping gave the darkest shade of dense bodies. XRD analysis of the synthesized powders showing the appearance of β-TCP peak but the increased in Mn content has decreased the β-TCP peak. However, mere HA phase present in the sintered ceramic. Generally, increase in Mn content has increased both the relative density and the Vickers hardness of the samples. Despite of that, the hardness trend correlates well with the change in relative density where hardness increases steadily with relative density of the samples. The slight deviation observed for 2 mol% Mn doped HA ceramic where it gave highest value for both measurements above all. This could be attributed to the highest crystallinity of its prepared powders which influenced its dense samples properties.

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