

PAPER • OPEN ACCESS

## Developing composites of zinc and hydroxyapatite for degradable orthopedic implant applications

To cite this article: P.V.S. Mahesh *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1116** 012002

View the [article online](#) for updates and enhancements.

You may also like

- [Biomimetic synthesis of novel polyvinyl alcohol/hydroxyapatite composite microspheres for biomedical applications](#)  
Ke Xue, Shu-Hua Teng, Niu Niu et al.
- [Hybrid core-shell scaffolds for bone tissue engineering](#)  
Muna M Kareem, Tom Hodgkinson, Manuel Salmeron Sanchez et al.
- [Preparation and biological properties of silk fibroin/nano-hydroxyapatite/hyaluronic acid composite scaffold](#)  
Lu Wang, Xiaoru Nan, Jiaxin Hou et al.

### ECS Toyota Young Investigator Fellowship



For young professionals and scholars pursuing research in batteries, fuel cells and hydrogen, and future sustainable technologies.

At least one \$50,000 fellowship is available annually.  
More than \$1.4 million awarded since 2015!



Application deadline: January 31, 2023

**Learn more. Apply today!**

# Developing composites of zinc and hydroxyapatite for degradable orthopedic implant applications

P.V.S. Mahesh<sup>1</sup>, S. Akhil<sup>1</sup>, P. Chiranjeevi<sup>1</sup>, Y. Sivaji<sup>1</sup>, V.V. Kondaiah<sup>1</sup>,  
M. Ananda Rao<sup>2</sup>, Ravikumar Dumpala<sup>3</sup>, B. Ratna Sunil<sup>1,\*</sup>,

<sup>1</sup> Department of Mechanical Engineering, Bapatla Engineering College, Bapatla  
522101, India

<sup>2</sup> CSIR-NML Chennai Centre, CSIR Madras Complex, Taramani, Chennai 600113,  
India

<sup>3</sup> Department of Mechanical Engineering, Visvesvaraya National Institute of  
Technology, Nagpur 440010, India

\* Corresponding author's e-mail address: bratnasunil@gmail.com

**Abstract.** In the present work, Zn-HA composites were developed by powder metallurgy route targeted for bone implant applications. Zn-HA powders with varying HA content (1, 2, and 4 wt.%) were ball milled for 1 hr and sintered to produce composite compacts. X-ray diffraction (XRD) studies were done for all the ball milled powders and sintered compacts. No impurities were observed in the ball milled powders. Microstructural observations revealed the formation of lamellar structure in the composites due to the plastic deformation of the Zn powders during ball milling. Grain size measurements revealed the decreased grain size with increase of addition of HA. Furthermore, aspect ratio (length to thickness ratio) of the grains was measured and found that the aspect ratio was also decreased with the increased HA content. Higher microhardness was measured for all the composites compared with pure Zn. However, composite with 1% has shown higher hardness compared with the remaining composites. From the preliminary observations, it can be concluded that Zn-HA composites can be successfully produced with lamellar morphology by ball milling followed by sintering for biomedical applications with increased hardness.

Key words: Zinc alloy, degradable implants, hydroxyapatite, sintering, micro-lemellar.

## 1. Introduction

Biodegradable implants are a class of materials which safely degrade in the physiological environment without causing any adverse health abnormalities. Generally, ceramics and polymers are used as biodegradable materials in the biomedical industry [1]. Recently, interest on developing metallic biodegradable implants has grown among the research teams across the globe. Magnesium (Mg), iron (Fe) and zinc (Zn) are the three metals can be well tolerated by the human body [2]. From the literature, it can be learned that the development of biodegradable implants for load bearing orthopedic



applications and cardiovascular stent applications based on Mg and iron degradation in biological environment has extensively studied [2, 3, 4, 5]. Research on developing Zn based implants is at the inferior state compared with Mg and iron.

Being a vital micronutrient, Zn essentially required for human metabolic activities. Kubasek et al., [6] produced Zn – Mg alloys with 0.5 to 3 wt.% Mg for biomedical applications. The produced Zn-Mg alloys have shown excellent mechanical properties and lower corrosion rate in NaCl solution and simulated body fluid (SBF) compared with pure Mg and pure Zn. Furthermore, they suggested to carryout secondary mechanical or thermal treatments to enhance the mechanical and corrosion performance. Vojtech et al., [7] also developed Zn-Mg (3 wt.%) alloy for biomedical applications and the performance of the alloy was compared with pure Mg, AZ91 Mg alloy and Zn-Al-Cu alloys. The corrosion behavior of the developed alloy was measured as significantly lower compared with pure Mg and AZ91 Mg alloy. Further, the concentration of Zn in the degraded solution was measured and found that the values were lower than the required daily intake of Zn which strongly suggests the nontoxicity due to the lower levels of Zn resulted during the degradation. These findings demonstrate the potential of Zn based materials for degradable implants applications without causing any toxicity issues. Similarly, Xiao et al., [8] developed Zn-0.05 wt.% Mg alloy and enhanced mechanical strength due to alloying. Additionally, excellent biocompatibility was observed for the alloy from the in vitro and in vivo studies. Yang et. al., [9] also reported increased osseointegration for Zn-Mg alloy due to the release of Zn ions during the degradation. Murni et al., [10] demonstrated better mechanical properties of Zn-3 wt.% Mg alloy and excellent cell interactions between the alloy and human osteoblast cells was observed. Very recently, Yang et al., [11] carried out a detailed study on the effect of alloying elements Ca, Mg, Li, Sr, Mn, Cu, Fe and Ag on mechanical behavior, corrosion properties and tissue response by using animal models. From the results, it was clearly demonstrated that the addition of Li has shown profound effect on improving the strength and addition of Sr, Mg, Ca and Li enhanced the biocompatibility of the Zn alloy. On the other hand, hydroxyapatite (HA) is bioceramic material that has the chemical composition of the bone mineral phase and widely used in the medical industry [12]. Information on Zn based composites for biomedical applications is insufficient in the literature, particularly, using HA as the dispersing phase. Therefore, in the present work, Zn-HA composites were prepared by powder metallurgy route and characterized. The role of ball milling on the grain morphology has been investigated and presented.

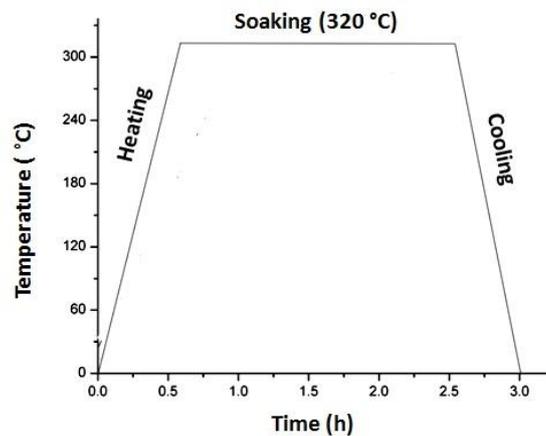
## 2. Experimental details

Pure zinc (Zn) powder (Himedia, India) and in-house laboratory synthesized hydroxyapatite powder was used in the present work to develop Zn-HA composites. Table 1 lists the selected compositions used to produce the composites. The powders were ball milled (Fritsch, Germany) for 1 hr at 200 rpm. Ball milling was carried using WC vials of 80 ml by using WC balls (10 mm dia) with 1: 20 powder to balls weight ratio. Ball milling was carried out in ethanol medium to avoid any oxidation. Ethanol was filled in the vial up to a level to completely submerge the balls and the powder. After ball milling the powders were collected from the vial and dried in the open air. Then the powders were compacted (25 mm dia) by using a set of die and punch in a hydraulic press by applying 200 kN. The green compacts were then sintered in a box furnace by heating up to 320 °C. The sintering cycle is shown in Figure 1. After sintering, the compacts were polished with different grades of polishing papers followed by polishing with alumina paste and diamond paste as per the standard metallographic procedure. Then the polished samples were cleaned with ethanol and dried. Chemical etching was carried out in a solution of distilled water and sodium hydroxide (100 ml and 10 g respectively) for 60 s. The etched samples were dried and optical microscope (Leica, Germany) observations were carried out at different locations.

Microstructural analysis was carried out by using ImageJ software (Netherlands). Grain size measurements were carried out by linear intercept method. Powders were characterized by X-ray diffraction (XRD, D8 Advanced, Bruker, USA) analysis before and after ball milling. The sintered compacts were also analyzed by XRD method. Scanning was carried out by using  $\text{CuK}\alpha$  radiation from 20 to 80 ° range with a step size of 0.1°. Microhardness measurements were done by Vicker's indentation method (Onmitech, India) across the samples by applying 100 g load for 15 s dwell time.

**Table 1.** Composition of the samples used to develop Zn-HA composites in the present work

S.No	Sample	Zn (wt. %)	HA (wt. %)
1	Pure Zn	100	0
2	Zn-1HA	99	1
3	Zn-2HA	98	2
4	Zn-4HA	96	4



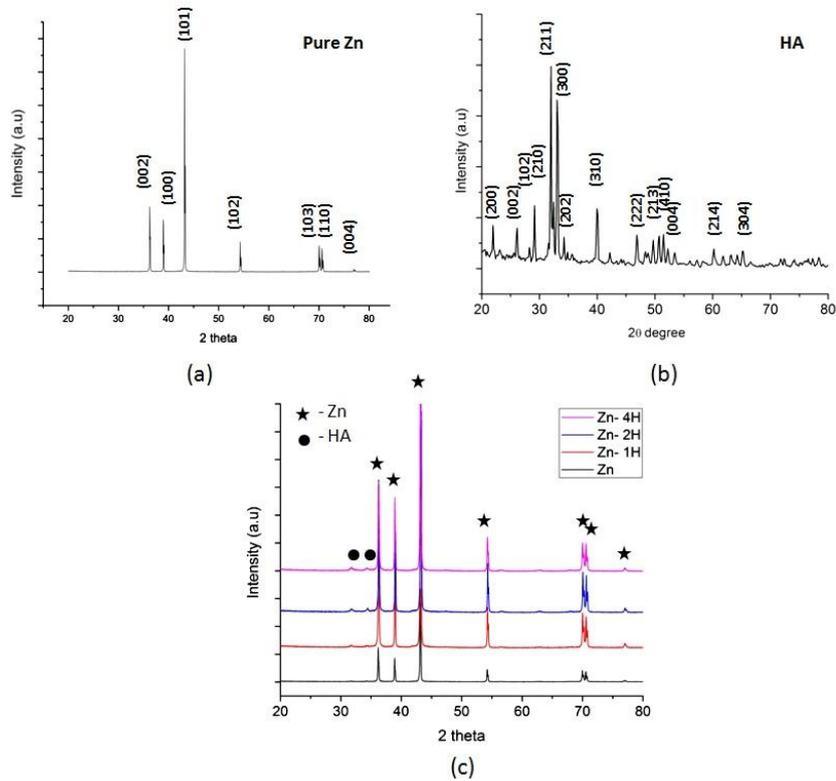
**Figure 1.** Sintering cycle adopted in the present work.

### 3. Results and discussion

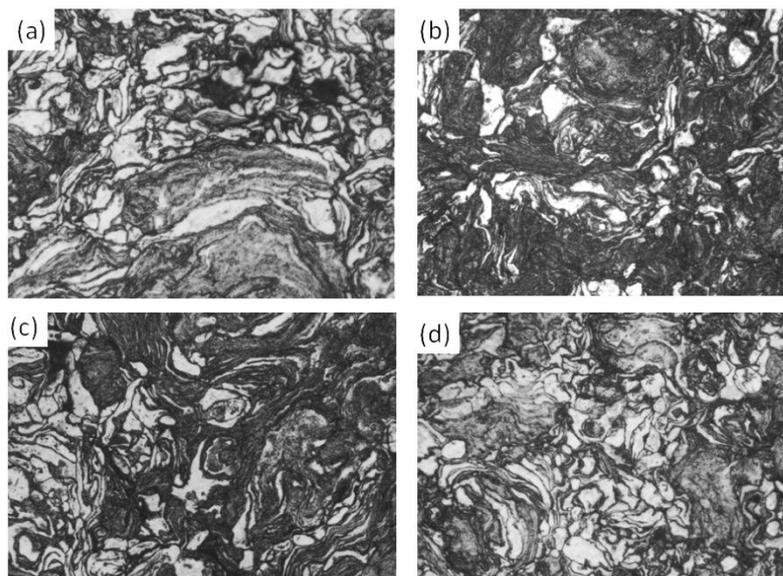
From the XRD analysis as shown in Figure 2, no impurities were identified from the as received powders. All the peaks were identified and indexed as per the international Centre for Diffraction Data (ICDD). No new phases were observed in all the composites after sintering. The results suggest that the phases were stable and presence of HA in Zn did not cause development of any new phase. In the present work, the sintering temperature was lower (320 °C); at which HA is stable and does not transform to any other phase. Stability of HA is a prime concern while developing metal matrix composites by using HA as the reinforcement for biomedical applications. Able to produce the composite at lower temperature is advantage if Zn is used as the matrix where the sintering can be completed relatively at lower temperatures compared with other metals such as Mg, Ti and Fe.

Figure 3 shows the optical microscope images of the produced composites. From the images, it can be seen that the Zn powder has undergone significant plastic deformation during the ball milling as reflected from the elongated grain structure. The particles have turned into flakes due to the high impact loads encountered during the milling. This is similar to earlier studies in which Mg particles became flakes after ball milling and micro-lamellar structure was observed in the sintered composites [13]. In the present work, similar morphology has been noticed in the sintered compact as shown in Figure 3. Representing the grain size as a linear dimension is inappropriate for this kind of microstructure. Hence, the length and the width of the grains were measured and the grain size with

aspect ratio is compared in Table 2. From the microstructural observations, aspect ratio of the composites was marginally decreased compared with the pure Zn sample. This can be understood by considering the role of HA in the composites which decreased the effect of impact load resulted during the collusion of the balls on the plastic deformation of Zn particles.



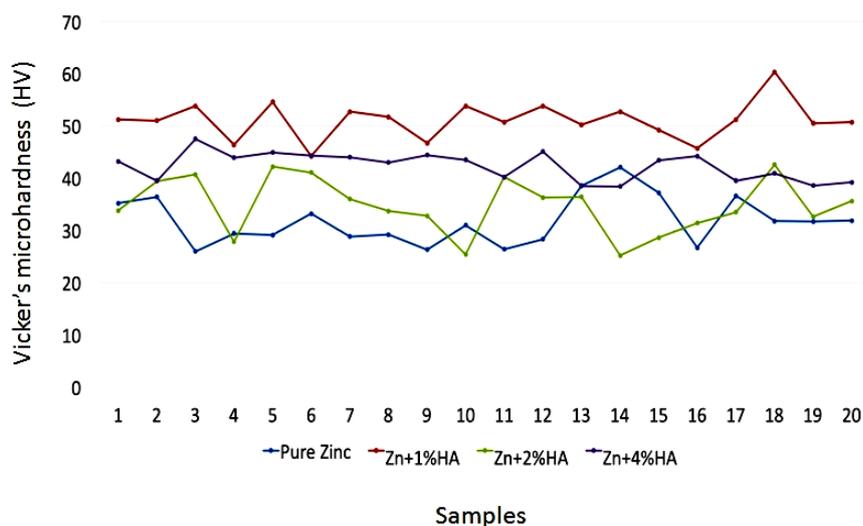
**Figure 2.** XRD plots of the samples: a) pure Zn, b) HA and c) Zn-HA composites produced from sintering



**Figure 3.** Optical microscope images of the samples: a) Zn, b) Zn-1HA, c) Zn-2HA d) Zn-3HA and e) Zn-4HA.

**Table 2.** Grain size measurements of the samples

S.No.	Sample	Average length ( $\mu\text{m}$ )	Average thickness ( $\mu\text{m}$ )	Aspect ratio (length: thickness)
1	Pure Zn	34.9	10.8	3.22:1
2	Zn-1HA	24.04	7.9	3.04:1
3	Zn-2HA	32.6	11.37	2.87:1
4	Zn-4HA	29.5	19.59	2.76:1

**Figure 4.** Microhardness distribution of the samples.

Microhardness measurements (Figure 4) revealed higher hardness for all the composites. Among the composites, Zn-1% has shown marginally higher average hardness ( $51 \pm 3.1$  HV) compared with all other samples. It was reported that the lamellar structure improves the hardness and fracture toughness in Mg-hydroxyapatite composites [13]. Similarly, incorporating nano-hydroxyapatite into Mg and AZ31 Mg alloys also promoted higher hardness in the composites developed by solid state processing routes [14, 15]. In the present work, the increased hardness can be attributed to the combined effect of microlamellar morphology of the composites and dispersed nano-HA. Hence, from the preliminary observations, it can be summarized that the micro-lamellar composites of Zn-hydroxyapatite can be successfully produced by ball milling followed by sintering without affecting the HA stability. Additionally, improved hardness also can be achieved in the composites. The presence of HA promotes bioactivity and enhances the tissue implant interactions [16]. Therefore, the produced Zn-HA composites can be a viable alternative for producing biodegradable implants for orthopedic applications. Additional studies to investigate the role of microlamellar structure and presence of HA on degradation mechanisms are needed to be carried out.

#### 4. Conclusions

In the present work, zinc-nanohydroxyapatite composites were produced through ball milling followed by sintering with varying HA content (1, 2 and 4 wt. %). XRD studies indicated no impurities of formation of new phases after sintering. From the microstructural studies, the morphology of the composites was observed as micro-lamellar with decreasing length to thickness ratio with the increased HA content in the composites. Microhardness was observed as increased for the composite

due to the microlamellar morphology and also presence of HA. The observations confirm the possibility of producing Zn-HA microlemellar composites for biomedical applications. Further investigations to evaluate these novel composites in the context of degradation and tissues interactions to make them suitable for biodegradable implant applications.

## References

- [1] Park J, Lakes R S, 2007 *Biomaterials An Introduction* Springer, New York, USA.
- [2] Kirkland N T, Birbilis N 2014 *Magnesium Biomaterials Design, Testing, and Best Practice*. Springer, New York, USA.
- [3] Hermawan H, Dubé D, Mantovani D, 2010 *Acta Biomater.* **6** 1693.
- [4] Witte F, Hort N, Vogt C, et al., 2008 *Curr. Opin. Solid State Mater. Sci.* **12** 63.
- [5] Ratna Sunil B, Sampath Kumar T S, Uday Chakkingal 2012 *Mater. Sci. Forum.* **710** 264.
- [6] Jiří Kubásek, Dalibor Vojtěch, 2012 *Metal*, **23** 6.
- [7] D. Vojtěch, J. Kubásek, J. Šerák, P. Novák, 2011 *Acta Biomater.* **7** 3515.
- [8] Xiao C, et al., 2018 *J. Mater. Sci. Technol.* **34** 1618.
- [9] Yang H, et al., 2018 *ACS Biomater. Sci. Eng.* **5** 453.
- [10] Murni N, Dambatta M, Yeap S, Froemming G R A, Hermawan H, 2015 *Mater. Sci. Eng. C* **49** 560.
- [11] Hongtao Yang, Bo Jia, Zechuan Zhang, Xinhua Qu, Guannan Li, Wenjiao Lin, Donghui Zhu, Kerong Dai, Yufeng Zheng, 2020 *Nat. Commun.* **11** 401.
- [12] Ratna Sunil B, Jagannatham M, 2016 *Mater. Let.* **185** 411.
- [13] Ratna Sunil B, Ganapathy C, Sampath Kumar T S, Uday Chakkingal, 2014 *J. Mech. Behav. Biomed. Mater.* **40** 178.
- [14] Ratna Sunil B, Sampath Kumar T S, Uday Chakkingal, Nandakumar V, Mukesh Doble, 2014 *J. Mater. Sci. Mater. Med.* **25** 975.
- [15] Ratna Sunil B, Sampath Kumar T S, Uday Chakkingal, Nandakumar V, Mukesh Doble, 2014 *Mater Sci Eng C* **39** 315.
- [16] Witte F, Feyerabend F, Maier P, et al. 2007 *Biomaterials* **28** 2163.