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IMPROVED MECHANICAL AND IMMERSION CHARACTERISTICS OF MG-B-TRICALCIUM PHOSPHATE COMPOSITES TARGETING ORTHOPAEDIC APPLICATIONS

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ABSTRACT

Magnesium-based materials owing to their biodegradable nature are modern materials suitable for orthopaedic implant applications. Design of such materials with controlled degradation rate coupled with superior mechanical properties is a niche field of research to meet the ever-increasing demands of the medical community. Development of novel magnesium based materials with suitable alloying elements and bio-ceramic reinforcements can act as a possible solution to this demand. In the current study, the influence of addition of 2 vol. % β-tricalcium phosphate (β-TCP) on the mechanical, damping and immersion characteristics of pure magnesium are studied. The addition of β-TCP enhanced the yield strength and ultimate strength of pure magnesium without adversely affecting the ductility. Also, Mg 2 vol. % β-TCP composite resulted in ~115 % enhancement in the damping characteristics compared to pure magnesium. Addition of β-TCP particles also assisted in controlling the corrosion rate of pure magnesium.

KEYWORDS: Magnesium, β-Tricalcium Phosphate, Compression, Corrosion.

Bone is a natural composite made up of type I collagen and hydroxyapatite [1]. The collagen prevents brittle failure of the bones and makes it elastic whereas hydroxyapatite provides the necessary mechanical strength. In the past decade, significant progress has been made in the research community to keep introducing novel materials targeting various biomedical applications to the market. Ceramic and polymer based biomaterials have superior biocompatibility and bioactivity thereby finding applications in tissue regeneration and drug delivery [2]. However, insufficient strength and non-biodegradability hinder their application in fixation devices like pins, screws and plates targeting load bearing orthopaedic applications. Metal based biomaterials like 316L stainless steel, Ti6Al4V alloy and Co-Cr biomedical alloy amongst others have been long used as commercial orthopaedic implants. Although these implant materials perform the suitable function of assisting in bone remodelling and resorption, a mismatch in elastic modulus between these materials and the bone induces several stress-shielding effects on the bone/implant interface inducing severe pains to the patient [1]. Either these implants materials are in the human body throughout leading to apparent toxicity at later stages or may require a secondary surgery to remove the implant adding to the long facing trauma of the patient. In order to solve this issue, the need is to design and develop a biodegradable metal based orthopaedic implant with superior strengths and optimum degradation rates to serve the purpose of bone remodelling and disintegration into the human body without causing any ill-effects to the patient.

Magnesium (Mg), being the lightest structural element, biodegradable, non-toxic, abundant and therefore can be a solution for the ongoing problem. However, low room temperature ductility and reduced corrosion resistance in biological environments are the reasons why it is not already extensively used in the biomedical sectors [3]. Degradation occurs faster than the bone remodelling process and hence there is minimum retention of mechanical integrity in the bone chips. Therefore, the addition of biocompatible reinforcements using the composite technology to control the degradation rates without adversely affecting the strength properties is the key. Mg has prime importance in the metabolism process being the second most abundant cation in the human body and helps in the the formation of antibodies maintaining required wall tension in blood vessels and aids in muscle contraction regulation [4]. Any sort of deficiency in Mg may lead to the change in bone structure, the reduction in osteoblast/osteoclast activity and may also result in cardiovascular issue leading to death.

Incorporation of bioceramics like hydroxyapatite (HA) and tricalcium phosphates (TCP) into the Mg matrix seems very promising in the field of bone regeneration. Not only they exhibit superior biocompatibility and no visible signs of systemic and local toxicity, their crystal structure and chemical composition are close to the mineral parts of bone which may help in tailoring desired biological properties. β-tricalcium phosphate (β-TCP) is an excellent bioceramic with superior biocompatibility, chemical

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stability, and osteointegration behaviour in body environment with the resorption rate better than HA ceramics thereby finding numerous applications in skeletal and dental prosthetics [5]. β-TCP has already been investigated as a coating material for surface modification of Mg alloys with positive results [6]. However, its influence as a reinforcement in the Mg matrix synthesized using solid state blend-press-sinter powder metallurgy technique is not available in the public domain which is the novelty of this study.

EXPERIMENTAL

Synthesis Methodology

Pure Mg and Mg 2 vol. % β-tricalcium phosphate (β-TCP) composite was synthesized using powder metallurgy technique followed by hybrid microwave sintering technique [7]. The homogenized billets were soaked at 400 °C for 1 h and then hot extruded at 350 °C to obtain cylindrical rods of 8 mm diameter. Samples cut from the rods were then characterized for physical and mechanical properties.

Physical Characterization

Density measurements were performed on both monolithic and composite samples using the Archimedes principle. Four samples were cut from different parts of the extruded rods and tested for conformance. The samples were weighed separately in air and water using an A&D ER-182A electronic balance with an accuracy of ± 0.0001 g. The theoretical density was calculated using the densities and weight percentages of the constituents by means of the rule of mixtures. From the experimental and theoretical densities, porosity values of the samples were determined.

Coefficient of thermal expansion (CTE) of pure Mg and composite was measured using a LINSEIS TMA PT 1000LT thermomechanical analyser for a 5°C/min heating rate at 0.1 lpm argon flow rate. The displacement that the samples underwent was measured as a function of temperature (30°C – 350°C), with the help of an alumina probe.

Microstructural Characterization

Cylindrical samples having a diameter of 8mm and length of 5mm were ground, finely polished and etched according to the conventional techniques of metallography to obtain a clear distinction between the grain boundaries with the help of a LEICA-DM 2500M metallographic light microscope. The images were captured at different magnifications using a standard bright field illumination technique. Four representative micrographs were analyzed for each composition to obtain accurate grain sizes. The grain sizes were measured using standard ASTM technique. The OLYMPUS metallographic microscope and JEOL JSM-5800 LV Scanning Electron Microscope (SEM) was used for the microstructural characterization studies.

Mechanical Properties

Microhardness measurements were performed on the as-polished samples using Vickers microhardness tester Matsuzawa MXT 50 (indenter phase angle ~136º; in conformance with ASTM standard E384-11-1 [8]. Fifteen readings were taken to arrive at an average representative value.

Compression testing in the quasi-static mode was performed on cylindrical samples having 8 mm diameter and 8 mm length, utilizing a fully automated servo-hydraulic mechanical testing machine (Model-MTS 810; in conformance with ASTM test method E9-09) at a strain rate $8.33\times10\text{-}5\ s^{-1}$ [9]. Four specimens each for both the compositions were tested to ensure reproducibility.

Damping characteristics and elastic modulus of the cylindrical samples (7 mm diameter and 60 mm length) were analysed using the resonant frequency and damping analyser (RFDA) equipment from IMCE, Belgium. Recordings of the vibration signal were obtained in terms of amplitude vs. time. Damping capacity, loss rate and elastic modulus values for both pure Mg and Mg 2 vol. % β-TCP composite sample was recorded.

Immersion studies

Cylindrical samples of (5mm diameter and 5 mm length) were immersed in Hanks balanced salt solution (HBSS) for 96h. The setup was immersed in a water bath maintained at 37 °C to simulate the temperature of the human blood. The sample to solution ratio was maintained at 20 ml:1 cm^2.

Weight and pH measurements are measured after every 24h. Corrosion rates were calculated for the samples at the end of 96h.

RESULTS AND DISCUSSION

Density and Porosity

Density and porosity levels of pure Mg and Mg 2 vol. % β-TCP reinforced magnesium composite are shown in Table 1. The experimental density of Pure Mg was found to increase with the addition β-TCP and Mg 2

vol. % β-TCP composite exhibited an experimental density value of 1.7398 g·cm^{-3}. The slight increase (0.2 %) in the density can be imputed to the fact that there is a density difference between the matrix (1.74 g·cm^{-3}) and reinforcement (3.14 g·cm^{-3}). Porosity levels have also increased with the addition of the β-TCP and a porosity value of ~0.29 % was observed for Mg 2 vol. % β-TCP composite. Since less than 1 % porosity was measured, it indicates the suitability of processing methodology to generate near dense composites [3].

Table 1: Density and porosity of pure magnesium and Mg-β-TCP composites

Composition	Experimental Density (g·cm^{-3})	Theoretical Density (g·cm^{-3})	Porosity (%)
Mg	1.7363±0.0003	1.74	0.2126±0.009
Mg2.0 β-TCP	1.7398±0.0007	1.7449	0.2906±0.018

Microstructure

Table 2 and Figure 1 (a) shows the grain size of pure Mg and Mg 2 vol. % β-TCP reinforced magnesium composite. The grain size of pure Mg was found to decrease with the addition of β-TCP particles. The refinement in grain size was ~53 % for Mg 2 vol. % β-TCP composite when compared to the grain size of pure Mg (~34 µm). Near equiaxed grain, morphology was observed with the addition of β-TCP particles which may be attributed to the ability of the β-TCP particles to uniformly pin the grain boundaries [10].

Table 2: Grain size, microhardness and coefficient of thermal expansion of pure magnesium and Mg-β-TCP composites

Composition	Grain Size (µm)	Microhardness (H_V)	CTE (x 10^{-6} K^{-1})
Mg	34±2	46 ± 3	25.28
Mg2.0 β-TCP	16±2 (↓ 53 %)	52.5 ± 1.9 (↑ 14 %)	24.29

The superior grain refinement also aids in the strengthening of the composites by means of Hall-Petch mechanism activation. Also, near uniform distribution of β-TCP was observed in the pure magnesium matrix as shown in Figure 1 (b). The near-uniform distribution of β-TCP throughout the Mg matrix can be attributed to the suitable blending, compaction and extrusion parameters used for the synthesis of Mg- β-TCP composites.

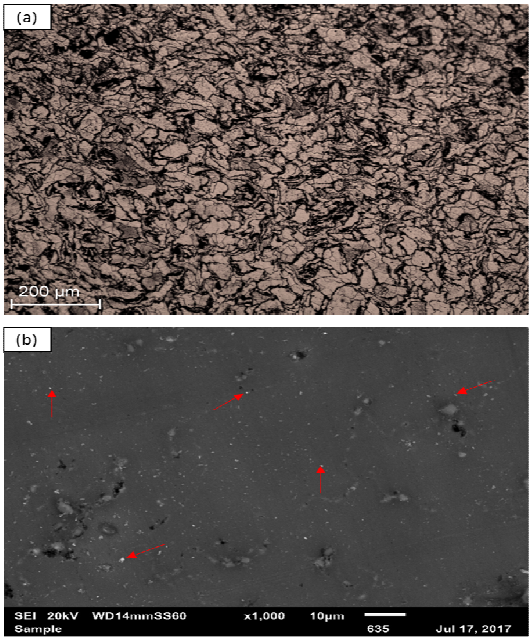

Figure 1: (a) Grain morphology; (b) particle distribution within the Mg matrix of Mg 2 vol. % β-TCP composites

Microhardness

The results of the microhardness tests performed on pure Mg and Mg 2 vol. % β-TCP composite is presented in Table 2. The microhardness results of Mg 2 vol. % β-TCP composite reveal the improvement of ~14 % when compared to pure Mg hereby indicating the increased resistance to indentation. This increase in the hardness value can be attributed to the nearly uniform distribution of β-TCP particles throughout the Mg matrix and the reduced grain size of the Mg 2 vol. % β-TCP composite leading to the increased resistance to localized plastic deformation [11].

Coefficient of Thermal Expansion (CTE)

The results of CTE measurement are summarized in Table 2. Mg 2 vol. % β-TCP composite exhibited a CTE value of 24.29 x 10^{-6} K^{-1} which is a minor decrease of ~4 % when compared to the CTE value of pure Mg (25.28 x 10^{-6} K^{-1}). This decrease in the coefficient of thermal expansion can be attributed to the lower value of CTE for β-TCP (14.2 x 10^{-6} K^{-1}) when compared to that of pure Mg [12]. The decreased CTE value reveals that the addition of β-TCP particles to pure Mg contributes positively to its dimensional and thermal stability. The mismatch in CTE values also contributes to the strengthening further enhancing the yield strength of the developed composite.

Damping and Elastic Modulus

The damping test measurements and elastic modulus are tabulated in Table 3. The results show an overall enhancement in the damping characteristics of the Mg 2 vol. % β-TCP composite when compared to that of pure Mg. This improvement in the characteristics can be attributed to the well-dispersed β-TCP particles throughout the composite. The increased porosity values of the composite when compared to pure Mg are major contributing factors for the enhancement of the damping capacity of the composite [13]. It can be observed that the ability of the composite to absorb or stop vibration (damping loss rate) is 17.9 which is ~100 % enhancement when compared to pure Mg. Further, since the porosity of the composite is higher than that of pure Mg and the reinforcement (β-TCP) being uniformly distributed throughout the pure magnesium matrix, the damping capacity also turns out to be higher in the case of the Mg 2 vol. % β-TCP composite by ~14 %. As shown in Figure 2, the time taken by the system to cease the vibrations also decreased with the addition of β-TCP reinforcement to pure Mg. The time taken for vibrations to cease for pure Mg was ~0.6 s whereas Mg 2 vol. % β-TCP composite took ~0.4 s to bring the impulse action to rest.

On addition of the β-TCP reinforcement, an increase in the matrix defects at an atomic level occurs leading to a localized crystal distortion considering the presence of two-dimensional defects at the matrix/reinforcement interface causing an atom slip up at the interface [3]. This results in a flexible dislocation movement and hence improves the damping capacity of the composite [14]. The marginal change in elastic modulus of the composite when compared to that of pure Mg provides a wider scope for application. Mg has a lower elastic modulus when compared to other commercial orthopaedic materials like steel and titanium which helps in mitigating stress-shielding effects and elimination of secondary surgeries [15]. This minimal increase in the elastic modulus of pure Mg with the addition of β-TCP particles is a favourable response to replace existing materials for orthopaedic applications.

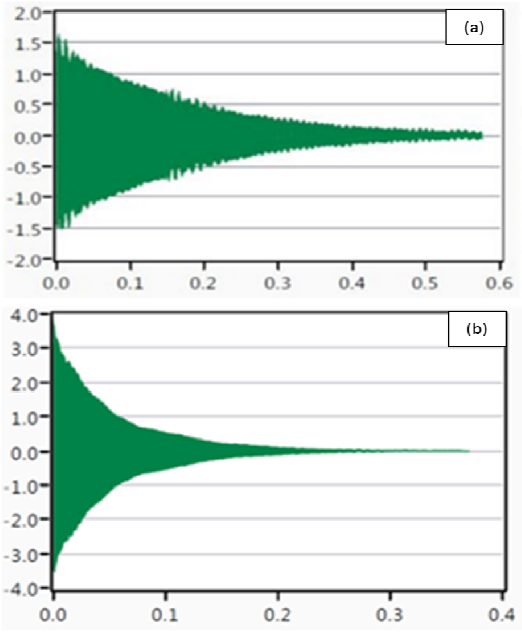

Figure 2: Damping characteristics of (a) pure Mg; (b) Mg 2 vol. % β-TCP composites

Table 3: Damping characteristics of pure magnesium and Mg-β-TCP composites

Composition	Damping Capacity	Damping Loss Rate	Elastic Modulus (GPa)
Mg	0.000564 ± 0.00003	8.3 ± 0.2	44.7 ± 0.20
Mg2.0 β-TCP	0.000656 ± 0.00002 (↑ 14 %)	17.9 ± 0.8 (↑ 116 %)	42.9 ± 0.6 (↓ 4 %)

Compression Properties

Table 4 shows the compressive properties for pure magnesium and Mg 2 vol. % β- TCP reinforced magnesium composite. Addition of β- TCP enhances the compressive properties of pure magnesium. The compressive yield strength, 0.2% CYS and ultimate compressive strength, UCS exhibit a value of ~96 MPa and ~240 MPa which is a ~25 % and ~54 % enhancement. The significant increase in the strengths of Mg 2 vol. % β-TCP composite may be due to [16]: (a) superior grain refinement leading to Hall-Petch strengthening (b) presence of uniformly distributed β-TCP particulates leading to Orowan strengthening (c) sufficient transfer of load from Mg matrix to β-TCP reinforcements owing to high wettability between Mg and β-TCP and (d) mismatch in the coefficient of thermal expansion values between the matrix and reinforcement

leading to forest strengthening of the composite [17]. Mg 2 vol. % β-TCP composite also showed the maximum value for fracture strain (~20 %) which is ~25.9 % greater than pure magnesium (~16 %). The energy absorbed until the failure is also superior for Mg 2 vol. % β-TCP which is 64.9 % greater than pure Mg.

Table 4: Room temperature compressive properties of pure magnesium and Mg-β-TCP composites

Composition	0.2 CYS (MPa)	UCS (MPa)	Fracture Strain (%)	Energy Absorbed ($MJ \cdot m^{-3}$)
Mg	77 ± 5	156 ± 7	15.8 ± 1.5	17.7 ± 1.7
Mg2.0 β-TCP	96 ± 11 (↑ 25 %)	240 ± 12 (↑ 54 %)	19.9 ± 0.8 (↑ 26 %)	29.2 ± 2.4 (↑ 65 %)

Immersion Characteristics

Weight loss and pH measurements of pure Mg and Mg 2 vol. % β-TCP composite is recorded for 4 days at every 24h interval. The recorded pH values after every time interval are recorded in Table 5 to understand the effect of the addition of β-TCP on the immersion characteristics of pure Mg. The samples were weighed after every 24h to compute the weight loss/gain due to immersion. The corrosion rate was calculated after every 24h and is recorded in Table 5. Equation (1) is used to calculate the corrosion rate

$$CR = \frac{(K \times W)}{(A \times T \times D)} \quad (1)$$

where, time conversion coefficient, K = 8.76 x 10^4, W is the weight difference before and after immersion (g), A is the sample area exposed to solution (cm^2), T is the exposure time (h) and D is the density of the material ($g \cdot cm^{-3}$). Due to high immediate activity post immersion into the Hanks' solution, higher corrosion rates are observed for both pure Mg and Mg 2 vol. % β-TCP composites. Although, with increased immersion times, the rate of corrosion decreases for the composite sample. It can also be observed from Table 5 that the pH values of pure Mg were higher than that of the composite.

Table 5: pH measurements and corrosion rates of pure magnesium and Mg-β-TCP composites

Time of immersion (hrs)	Composition			
	Pure Mg		Mg2.0 β-TCP	
	CR ($mm \cdot year^{-1}$)	pH	CR ($mm \cdot year^{-1}$)	pH
0	0	7.4	0	7.4
24	0.623	10.1	0.493	9.58
48	0.51	10.51	0.393	9.65
72	0.42	10.83	0.261	9.72
96	0.296	10.86	0.1964	9.92

This decreased pH values and the decrease in corrosion rates behaviour suggests that the amount of hydrogen evolved leading to an increase in pH is lesser for the Mg 2 vol. % β-TCP composite when compared to pure Mg. It is well known in Mg-biomaterial community that the maximum hydrogen evolution happens in the first 12h of immersion in salt solutions and biofluids. Hence, the presence of β-TCP in the magnesium matrix helps in faster pH stabilization thereby a controlled degradation can be achieved.

The cumulative effect of enhanced damping, compression and corrosion properties is key to qualify a certain material to be a potential orthopaedic implant. In addition to the mitigation of stress-shielding effects and bioresorbable nature of magnesium, enhanced structural properties are also equally important considering that Mg-based implants and stents may witness a 15-20% decrease in strength and ductility when immersed in a physiological environment [18]. The compressive properties of the Mg- β-TCP composite is compared with hard and soft tissues of the human body in Table 6. With bone remodelling process taking 10-12 weeks for an average human being, incorporating novel biocompatible reinforcements in the magnesium matrix which can protect pure Mg from expedited degradation. Further, to understand and critically evaluate the possibility of using Mg- β-TCP composites in orthopaedic applications, advanced immersion and corrosion analysis in stimulated biofluids followed by cytotoxicity evaluations must be performed.

Table 6: Comparison between the biomechanical properties of Mg-β-TCP composites with hard and soft tissues of the human body [3]

Material	0.2 CYS (MPa)	UCS (MPa)	Fracture Strain (%)	Young's Modulus (GPa)
Mg	77 ± 5	156 ± 7	15.8	44.7
Mg2.0 β-TCP	96 ± 11	240 ± 12	19.9	42.9
Cortical bone	-	131-224	2-12	15-30
Dentin	-	193	12	11
Cancellous bone	-	2-5	5-7	0.4
Articular cartilage	-	15-50	-	10.5
Ti6Al4V [19]	-	970	-	113.8
Co-Cr alloy [20]	-	283-313	-	222-240

CONCLUSION

Following conclusions were drawn from this innovative attempt to synthesize Mg 2 vol. % β-TCP composite.

1. Pure Mg and Mg 2 vol. % β-TCP composite were successfully synthesized using the blend-press-sinter powder metallurgy technique.
2. Reinforcing pure Mg with β-TCP particles resulted in a superior refinement in grain size.
3. Mg 2 vol. % β-TCP composite exhibited enhanced microhardness value when compared to pure Mg highlighting the resistance to localized plastic deformation.
4. Mg 2 vol. % β-TCP composite exhibits decreased CTE value suggesting superior thermal and dimensional stability.
5. Superior enhancement in the 0.2 CYS, UCS and fracture strain of the Mg 2 vol. % β-TCP composite was observed when compared to the pure Mg.
6. The damping loss rate and damping capacity of pure Mg enhanced with the addition of β-TCP particles with a minimal increase in elastic modulus.

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