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A systemic study on key parameters affecting nanocomposite coatings on magnesium substrates



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ABSTRACT

Nanocomposite coatings offer multiple functions simultaneously to improve the interfacial properties of magnesium (Mg) alloys for skeletal implant applications, e.g., controlling the degradation rate of Mg substrates, improving bone cell functions, and providing drug delivery capability. However, the effective service time of nanocomposite coatings may be limited due to their early delamination from the Mg-based substrates. Therefore, the objective of this study was to address the delamination issue of nanocomposite coatings, improve the coating properties for reducing the degradation of Mg-based substrates, and thus improve their cytocompatibility with bone marrow derived mesenchymal stem cells (BMSCs). The surface conditions of the substrates, polymer component type of the nanocomposite coatings, and post-deposition processing are the key parameters that contribute to the efficacy of the nanocomposite coatings in regulating substrate degradation and bone cell responses. Specifically, the effects of metallic surface versus alkaline heat-treated hydroxide surface of the substrates on coating quality were investigated. For the nanocomposite coatings, nanophase hydroxyapatite (nHA) was dispersed in three types of biodegradable polymers, i.e., poly(lactic-co-glycolic acid) (PLGA), poly(L-lactic acid) (PLLA), or poly(ε-caprolactone) (PCL) to determine which polymer component could provide integrated properties for slowest Mg degradation. The nanocomposite coatings with or without post-deposition processing, i.e., melting, annealing, were compared to determine which processing route improved the properties of the nanocomposite coatings most significantly. The results showed that optimizing the coating processes addressed the delamination issue. The melted then annealed nHA/PCL coating on the metallic Mg substrates showed the slowest degradation and the best coating adhesion, among all the combinations of conditions studied; and, it improved the adhesion density of BMSCs. This study elucidated the key parameters for optimizing nanocomposite coatings on Mg-based substrates for skeletal implant applications, and provided rational design guidelines for the nanocomposite coatings on Mg alloys for potential clinical translation of biodegradable Mg-based implants.

Statement of Significance

This manuscript describes the systemic optimization of nanocomposite coatings to control the degradation and bioactivity of magnesium for skeletal implant applications. The key parameters influencing the integrity and functions of the nanocomposite coatings on magnesium were identified, guidelines for the optimization of the coatings were established, and the benefits of coating optimization were demonstrated through reduced magnesium degradation and increased bone marrow derived mesenchymal stem cell (BMSC) adhesion *in vitro*. The guidelines developed in this manuscript are valuable for the bio-metal field to improve the design of bioresorbable implants and devices, which will advance the clinical translation of magnesium-based implants.

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1. Introduction

1.1. Magnesium for biodegradable implant applications – promise and challenge

Biodegradable materials such as magnesium (Mg) [1–3] provide an attractive alternative to non-degradable materials for skeletal implant applications when the implants (e.g., internal fixation devices) only need to serve their functions in the body for a set period. Mg implants naturally degrade in the body and thus do not require surgical removal. In addition, Mg has excellent mechanical [2,4,5] and biological [6–8] properties, and can bond strongly to bone tissue *in vivo* [1].

One of the major challenges for clinical translation of Mg alloys is that they degrade faster than the typical clinical requirement for bone repair [9,10] due to the abundant aggressive ions such as chloride (Cl^-) [11,12]. The degradation rate of Mg-based implants may be controlled by adjusting alloy composition and processing, or by modifying the surface properties through coatings and surface treatments. This article focuses on the coating approach for controlling the degradation of Mg-based substrates.

1.2. Surface coatings for controlling magnesium degradation – promise and challenge

Surface coatings have many advantages as a means of controlling Mg degradation, because coatings can be combined with other degradation control mechanisms such as alloy composition and processing [13,14]. As the Mg substrates support the load-bearing requirements, we designed nanocomposite coatings for the dual purposes of reducing Mg degradation and improving interfacial bioactivity.

Hydroxyapatite [HA; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is the predominant mineral component in natural bone and has excellent osteoconductivity [15–17], especially when it is in the form of nanophase HA (nHA) [18]. HA or its derivative phases, when used alone, may not be ideal for load-bearing applications due to their inherent brittleness. Thus, HA-based calcium phosphates are often used as coating materials on metallic implant substrates, such as Ti or Mg [19,20]. However, the brittleness of HA and its mismatch with metallic substrates in thermal expansion coefficient often lead to cracking in HA coatings [20]. Moreover, when the HA coatings have weak adhesion to the substrates, the implant stability becomes a serious concern [21]. These drawbacks of using HA alone may be mitigated by compositing HA with a polymer of complementary properties.

Polymers have also been studied as coating materials for controlling Mg degradation, especially biodegradable poly(lactic-co-glycolic acid) (PLGA) [22–24], poly(L-lactic acid) (PLLA) [25–27], and poly(caprolactone) (PCL) [25,26,28–30]. These polymers are biocompatible and their degradation products are naturally occurring metabolites, e.g., lactic acid, glycolic acid, and 6-hydroxyl caproic acid [31]. The microstructure and properties of polymers can be further tailored during post-deposition processing. Heat treatments, such as annealing or melting, can reduce the permeability of the polymers by increasing their crystallinity and sealing pores [32–34]. However, PLGA, PLLA, and PCL have low mechanical properties [35] and bioactivity [36–39]. Skeletal implants with low bioactivity may have little bone tissue ingrowth [40–42] and likely leave an empty socket in the bone after the implants degrade [36,41,43]. Thus, the biodegradable polymers should be combined with bioactive ceramics to achieve desirable mechanical properties and bioactivity for implant applications.

The integration of nHA, biodegradable polymers, and Mg-based biodegradable metals addresses the key challenges encountered

when using each material alone and provides synergistic properties for skeletal implant applications. The presence of a flexible polymer phase could prevent crack propagation through HA coatings [30]. Three types of biodegradable polymers, i.e., PLGA (85:15), PLLA, and PCL, were investigated in this study to elucidate the effects of a broad spectrum of polymer properties on nanocomposite coatings. The nHA particles were dispersed into the polymer matrix because they increased the mechanical properties and bioactivity of polymers *in vitro* [44,45], and improved bone ingrowth *in vivo* [37]. The ratio of 30 wt% nHA and 70 wt% polymer was used in the nanocomposites because it provides a balanced mechanical and biological properties for bone regeneration [44,46–48]. The nHA/polymer coatings can increase the surface osteoconductivity and reduce the degradation rate of Mg substrates, while the Mg substrates provide mechanical properties similar to cortical bone for load bearing. The synergistic properties of these three components (nHA, polymer, Mg) are ideal for skeletal implant applications.

1.3. Optimization of nanocomposite coatings on mg substrates – objectives of this study

The objective of this study was to optimize the design and processing of nanocomposite coatings to maximize the synergy between the three components (i.e., nHA, polymer, Mg). To achieve this, we first screened different combinations of the coating parameters for surface hydrophobicity and the lowest corrosion rates using potentiodynamic polarization (PDP) curves. Secondly, we characterized the slowest degrading samples using immersion degradation and coating adhesion strength tests. Lastly, we investigated *in vitro* responses of bone marrow derived mesenchymal stem cells (BMSCs) to the samples with the slowest immersion degradation rate. This study elucidated the interactions among different parameters of nanocomposite coatings (i.e., substrate surface conditions, polymer types, and post-deposition processing) and their effects on the degradation of Mg substrates, thus providing valuable design guidelines for polymeric and nanocomposite coatings on Mg-based substrates for skeletal implant applications.

2. Materials and methods

2.1. Preparation of magnesium substrates

Mg-based bars (97% Mg, 3% Al, 1 mm thick; Miniscience, Cat# MGFLAT) were ground with 600 grit silicon carbide paper (SiC; Ted Pella) while using ethanol (EtOH; Koptec) as a lubricant. The grinded Mg bars were then cut into 10×10 mm squares using a notcher (No. 100, Whitney Metal Tool Co). The Mg substrates were degreased in acetone (Sigma Aldrich) in an ultrasonic bath (VWR Symphony) for 30 min, and then cleaned in ethanol in the same ultrasonic bath for another 30 min. These Mg substrates had a metallic surface and were designated as M_Mg.

A separate group of M_Mg substrates had their surface modified using an alkaline heat treatment procedure to create a surface rich in $\text{Mg}(\text{OH})_2$ [19]. The alkaline heat treatment was performed by immersing the M_Mg substrates in 1 M NaOH (Strem Chemicals) at 80 °C for 2 h. After immersion, the substrates were gently rinsed with deionized (DI) water (Millipore Milli-Q® Biocel System) for three times and dried in air at room temperature. These alkaline-heat-treated substrates were named as A_Mg.

Before the coating deposition, the M_Mg or A_Mg substrates were cold mounted into epoxy resin (MG Chemicals, Cat # 832HT) with a diameter of 18 mm and a thickness of 2 mm. Only a single face of 10×10 mm of the Mg substrates was exposed for coating. Prior to mounting, a copper wire was secured

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