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Research Paper

# Enhancement of the mechanical properties of AZ31 magnesium alloy via nanostructured hydroxyapatite thin films fabricated via radio-frequency magnetron sputtering

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ABSTRACT

The structure, composition and morphology of a radio-frequency (RF) magnetron sputter-deposited dense nano-hydroxyapatite (HA) coating that was deposited on the surface of an AZ31 magnesium alloy were characterized using AFM, SEM, EDX and XRD. The results obtained from SEM and XRD experiments revealed that the bias applied during the deposition of the HA coating resulted in a decrease in the grain and crystallite size of the film having a crucial role in enhancing the mechanical properties of the fabricated biocomposites. A maximum hardness of 9.04 GPa was found for the HA coating, which was prepared using a bias of −50 V. The hardness of the HA film deposited on the grounded substrate (GS) was found to be 4.9 GPa. The elastic strain to failure ($H/E$) and the plastic deformation resistance ($H^3/E^2$) for an indentation depth of 50 nm for the HA coating fabricated at a bias of −50 V was found to increase by ~30% and ~74%, respectively, compared with the coating deposited at the GS holder. The nanoindentation tests demonstrated that all of the HA coatings increased the surface hardness on both the microscale and the nanoscale. Therefore, the results revealed that the films deposited on the surface of the AZ31 magnesium alloy at a negative substrate bias can significantly enhance the wear resistance of this resorbable alloy.

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## 1. Introduction

The successful application of different magnesium alloys as biodegradable biomaterials is critically dependent on the control of their degradation rate (Witte et al., 2005). The fabrication of different coatings on the surface of different magnesium alloys (Mg, AZ31, AZ91, AZ91D, Mg4Y, Mg–Ca etc.) to prevent contact with their environment is the best way to avoid corrosion and has attracted the most interest (Phani et al., 2005; Kannan Mathan and Liyanaarachchi, 2013; Seyfoori et al., 2013; Zhang et al., 2014). Most studies are focused on investigating the influence of ceramic and organic films on the corrosion properties of magnesium alloys (Phani et al., 2005; Gray-Munro et al., 2009; Thomann et al., 2010; Cui et al., 2013; Kannan Mathan and Liyanaarachchi, 2013). The most frequently used techniques to prepare protective CaP-based coatings on the surface of Mg alloys are biomimetic techniques (Yang et al., 2012; Lorenz et al., 2009; Kannan and Orr, 2011; Hornberger et al., 2012), plasma electrolytic oxidation (Yao et al., 2009; Bala Srinivasan et al., 2010; Hornberger et al., 2012), electrodeposition (Song et al., 2008; Wen et al., 2009), sol–gel ( Roy et al., 2011) etc. It should be mentioned that the prepared CaP coatings possess a thicknesses that is typically greater than several microns or even tens of microns (Hornberger et al., 2012). However, the most important limitation of these techniques is that the CaP coating adhesion strength is not sufficient for their practical applications. RF magnetron sputtering is an extremely useful technique to obtain wear-resistant CaP coatings; moreover, a good biological response, both *in vitro* and *in vivo*, was found (Long et al., 2002; Coelho and Suzuki, 2005; Coelho et al., 2009). To the best of our knowledge, there are no studies available that address dense nanostructured nanometre-thick RF magnetron sputter-deposited HA coatings on Mg alloys (Dorozhkin, 2014; Surmenev et al., 2014; Surmeneva et al., 2014). Much of recent research includes studies on magnetron HA films deposited onto the surface of titanium, titanium alloys, NiTi, and silicon plates (Pichugin et al., 2008; Surmenev et al., 2011). Generally HA thin films deposited on titanium and its alloys using RF magnetron sputtering consist of a dense and nanocomposite structure, which provide a good biological response *in vivo* and *in vitro* and enhanced hardness of load-bearing surfaces (Surmenev, 2012). HA-coated NiTi has previously been shown to significantly decrease Ni release in a 0.9% NaCl solution compared with the uncoated substrate. The thickness of the RF magnetron sputter deposited coating usually does not exceed 1 μm (Surmenev et al., 2011, 2013a, 2013b).

The average ion energy can be increased by applying a negative bias to the substrate to accelerate the ions from the plasma towards the substrate (Surmenev et al., 2011). The kinetic energy of the ions is then converted to sputtering energy, thermal energy, implantation energy, and migration energy on the substrate surface for nucleation (Martin, 1986; Surmeneva et al., 2013a). Additionally, ions with very low energies may still influence coating nucleation and growth and enhance the chemical reactivity. In our previous studies, we have reported changes in the morphological properties and stoichiometry of HA coatings deposited on titanium as a function of the negative substrate bias (Surmenev et al., 2011, 2013a). Therefore, additional substrate bias was used to vary the coating properties.

The hardness of Mg alloys (Mg, AZ91D) is reported to be in the range of 0.5–0.75 GPa (Witte et al., 2007; Zeng et al., 2008). It is also reported that the biodegradation and mechanical properties of the magnesium alloy were an especially attractive combination for orthopaedic applications due having elastic modulus of 40–50 GPa as compared to natural bone, which is in the range of 3–20 GPa (Staiger et al., 2006). These mechanical and biodegradation properties are an important issue in evaluating the wear resistance of a surface for a long-term success of an implant. Moreover, enhancement of the $H/E$ ratio (and thus the resistance of the material to plastic deformation $H^3/E^2$) of the implant surface may offer advantages, such as less potential for surface damage and increased durability. The term $H/E$ can be considered to be a useful indicator of a good wear resistance of the coating (Leyland and Matthews, 2000). According to this study a coating with a high $H/E$ ratio exhibited increased durability. The coatings with a high plastic resistance ratio $H^3/E^2$ are more likely to resist plastic deformation during low load contact events and exhibit higher yield strength (Musil, 2000; Roy et al., 2010; Surmeneva et al., 2014). Few studies have been conducted that have focused on the influence of the surface substrate composition and the microstructure on the mechanical properties of HA thin films surfaces on titanium. The important parameters that are lacking are the hardness, Young's modulus and the resistance to plastic deformation (Dey et al., 2013). The mechanical properties of the HA coating have been reported to be strongly affected by the film growth mechanism and the substrate microstructure. There is a lack of in-depth understanding of the mechanical properties as well as the wear resistance at the local nano- and micro-structural length scale of a HA coating obtained by RF magnetron sputtering on magnesium alloy.

Therefore, the aim of this study is to evaluate the potential of a HA coating deposited by RF magnetron sputtering to enhance the hardness and resistance to plastic deformation of an AZ31 magnesium alloy. First, we will discuss the results of the influence of the applied substrate bias on the structure and morphology of the HA coating fabricated on the magnesium alloy. Subsequently, we will present results from nanoindentation tests and from the analysis of the correlation between the surface properties (roughness and microstructure) and obtained mechanical parameters (hardness, $H$, Young's modulus, $E$, elastic recovery, plastic resistance parameter ($H/E$) and a resistance of the material to plastic deformation ($H^3/E^2$)), which provide information about the wear resistance of the HA-coated magnesium alloy.

## 2. Materials and methods

AZ31 magnesium alloy substrates with the nominal mass composition of 96% Mg, 3% Al and 1% Zn were bought from GoodFellow (Germany). The size of the samples used in the experiments was set to $20 \times 20 \times 1\ \mathrm{mm}^3$ (width × length × thickness). The substrates were cleaned ultrasonically in a diluted acetone bath for 30 min at 100 °C. The substrates were ultrasonically cleaned a second time in ethanol followed by rinsing in distilled water. Pure HA target was prepared according