Rapid Coating of AZ31 Magnesium Alloy with Calcium Deficient Hydroxyapatite Using Microwave Energy

Yufu Ren, Huan Zhou, Sarit B Bhaduri.
University of Toledo, Toledo, OH 43606

Statement of Purpose: Recently, magnesium and its biodegradable alloys have been extensively studied as revolutionary implant materials due to their unique properties such as high strength/weight ratio, comparable mechanical properties with natural bones and excellent biocompatibility. However, the extremely high degradation rate of magnesium alloys in physiological environment has restricted its clinical application. To successfully employ these alloys, some kind of protective coating is desirable. Among the coatings produced on mg alloys, calcium phosphate coatings especially Hydroxyapatite /Calcium Deficient Hydroxyapatite (HA/CDHA, $Ca_{10}(PO_4)_6(OH)_2$) coatings present good corrosion resistance as well as outstanding biocompatibility and bioactivity. This paper reports the use of a novel microwave assisted coating technology to improve the in vitro corrosion resistance and biocompatibility of Mg alloy. Our results indicate a dense and crystallized CDHA layer was uniformly deposited on AZ31 substrate in less than 10 minutes. The corrosion resistance, biocompatibility and bioactivity of AZ31 alloy were significantly promoted by the CDHA coating.

Methods: AZ31 disks were firstly polished and ultrasonically cleaned to achieve the homogeneous roughness. Two sets of CaP coating solution were prepared by following compositions as shown in Table 1. AZ31 samples were placed in one 200 ml beaker, filled with 100 ml coating solution The top of the beaker was covered by an alumina fiberboard. Afterwards, the entire set up was moved into a 1200 W microwave oven and irradiated at maximum power for 4 minutes. The above steps were repeated once more to ensure the uniformity of the coatings. Finally, the coated samples were dried in a 100 °C oven.

Table 1 Compositions of coating solutions.

	H_2O	$Ca(NO_3)_2$ •$4H_2O$	NaH_2PO_4	$NaHCO_3$	Ca/P
CS-1	200ml	0.6612g	0.2016g	0.0672g	1.67
CS-2	200ml	0.6612g	0.1344g	0.0672g	2.50

CDHA coatings were characterized using XRD, FTIR, SEM and EDS. CDHA coated and bare AZ31 samples were immersed in SBF for 7 days to evaluate the degradation rate and bioactivity of the samples. Finally, cytotoxicity test of CDHA coated AZ31 samples were carried out by indirect assays.

Results: Both the XRD and FTIR spectra (Figure 1.) confirmed the formation of HA coatings on the AZ31 substrate through novel microwave assisted coating treatment with various initial Ca/P ratios. Fig. 2 presents the surface morphology and elemental composition of the as-deposited coatings on AZ31 specimens. As shown in Fig. 2 (a) and (c), the CS1-treated sample is densely covered with irregular rod-like crystals. The CS2 coating (Fig. 2b and 2d) showed a tabular structure comprised of flake-like crystals measuring approximately 2-4 microns in length. The EDS spectra revealed Ca, P and O were main elements present in both coatings. Additionally, the Ca/P ratios were calculated to be 1.30 for the CS1 coating and 1.46 for the CS2 coating indicating the formation of Calcium Deficient Hydroxyapatite (CDHA), as opposed to Stoichiometric Hydroxyapatite (Ca/P 1.67).

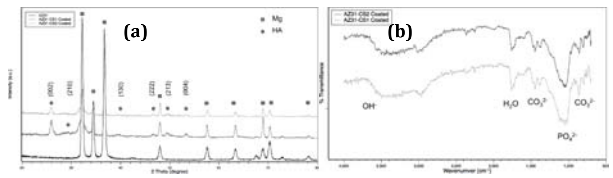

Figure 1. a) XRD patterns of CDHA coated samples and AZ31 substrate, b) FTIR spectra of the coated samples

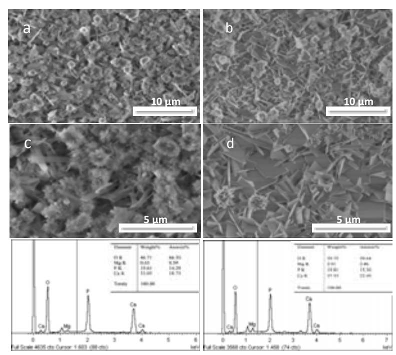

Figure 2. SEM images of (a,c) CS1 coating, (b,d) CS2 coating and associated EDS spectra

In comparision of un-coated AZ31 sample corrosion rate of CDHA coated AZ31 samples decreased significantly at each time point as shown in fig 3 (a). In addition, CDHA coated samples presented excellent cytocompatibilty.

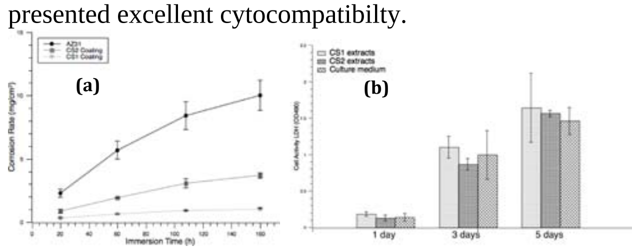

Figure 3. a) Variance of weight loss of coated sample and non-coated sample with immersion time in t-SBF solution b) O.D. values of MC3T3-E1 cells seeded in extracts of coatings and culture medium for 1, 3 and 5 days

Conclusions: Biodegradable CDHA coating was fabricated onto AZ31 substrates using a novel microwave assisted coating technique in minutes. CDHA coatings produced in aqueous solutions with various Ca/P ratios showed different microstructures. Results of in vitro immersion assessment revealed that CDHA coated samples showed significantly improved corrosion resistance. Cell culture assays demonstrated that the CDHA coated samples possessed good cytocompatibility and promoted cellular proliferation after 5 days incubation. This study suggested that microwave assisted coating treatment could rapidly induce the deposition of a uniform protective CDHA layer on the AZ31 surface to improve the biological response of the magnesium alloy.