Combined effect of pulse electron beam treatment and thin hydroxyapatite film on mechanical features of biodegradable AZ31 magnesium alloy

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Abstract. The morphology, elemental, phase composition, nanohardness, and Young's modulus of the hydroxyapatite (HA) coating deposited via radio frequency (RF) magnetron sputtering onto the AZ31 surface were investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), and nanoindentationtechniques. The calcium phosphate (Ca/P) molar ratio of the HA coating deposited via RF-magnetron sputtering onto AZ31 substrates according to EDX was 1.57±0.03. The SEM experiments revealed significant differences in the morphology of the HA film deposited on untreated and treated with the pulsed electron beam (PEB) AZ31 substrate. Nanoindentation studies demonstrated significant differences in the mechanical responses of the HA film deposited on the initial and PEB-modified AZ31 substrates. The nanoindentation hardness and the Young's modulus of the HA film on the magnesium alloy modified using the PEB treatment were higher than that of the HA layer on the untreated substrate. Moreover, the HA film fabricated onto the PEB-treated surface was more resistant to plastic deformation than the same film on the untreated AZ31 surface.

Key words: *hydroxyapatite coating, magnesium alloy, RF-magnetron sputtering, pulsed electron beam treatment, nanohardness, Young's modulus*

1. Introduction

Magnesium and its alloys may potentially be applied as degradable metallic materials in surgical orthopedics and traumatology due to their degradability and resemblance to human cortical bone [1-4]. The control of biodegradation of the magnesium alloys has been the subject of research and development for decades [5]. In an attempt to improve the quality of the bone–implant interface and corrosion resistance, numerous implant surface treatments have been used [6]. The demand for new modifications of biodegradable magnesium alloys to control their degradation rate will continue to grow.The fabrication of hydroxyapatite (HA) coatings is a very popular approach to control the degradation rate of the magnesium alloys.

Electron beam treatment is a novel way for the modification of implant surfaces to produce a high degree of purity with enough roughness for good osseointegration [7]. Electron beam treatment can result in unique microstructures with increased hardness, corrosion resistance, or other useful surface properties of metallic materials. Moreover, recent study showed that electron beam irradiation is a new method of treating implant surfaces to produce a high degree of purity with improved corrosion resistance [7].

Combination of the electron beam treatment and the deposition of ceramic coatings onto the surface of magnesium alloys can open up new opportunities for the biodegradable composite developmentwith the improved mechanical features and corrosion resistance.

Since a nanostructure and high adhesion of the coating are necessary to maintain a healthy connection with the soft tissues, radio frequency (RF) magnetron sputter deposition of HA thin films was investigated [8]. Other important properties of the implant surface are its strength and elastic characteristics (hardness and the Young's modulus).

Therefore, the aim of the present study was to obtain results relating to mechanical features of the magnesium alloy AZ31 after the modifications, such as the pulsed electron beam (PEB) treatment and RF-magnetron sputter deposition of HA thin film.

2. Materials and methods

The AZ31 magnesium alloy substrates were purchased from GoodFellow (Germany). The size of the samples was set to 10 × 10 × 1 mm^3 (width × length × thickness). The surface of the magnesium alloys was treated by a high-energy PEB irradiation with a PEB generator "SOLO" (Institute of High Current Electronics SB RAS, Tomsk, Russia). The conditions of the PEB treatment were as follows: electron beam energy density: 14 J cm^{-2}, electron beam pulse duration: 50 μs, and number of pulses: 3. An average electron energy in the beam was 15 keV.

A pure HA target was prepared according to the previously described procedures [9]. A commercially available apparatus with an RF (13.56 MHz, COMDEL) magnetron source was used to deposit HA coatings. HA coatings with the thickness of 700±60 nm were deposited at an RF-power level of 500 W in pure Ar atmosphere onto the grounded substrate holder. Optical ellipsometry (Ellipse 1891-S AG, Institute of Semiconductor Physics, RAS, Siberian Branch) was used to evaluate the thickness of the thin HA film. The coating thickness was derived from the changes in ellipsometric parameters between the bare and the coated substrates using a three-phase model (substrate-layer-air).
Surface roughness examined by Atomic force microscope (AFM) Solver P47-PRO (NT-MDT, Moscow, Russia), operating in a tapping mode. The roughness parameters of the surface were calculated three times at different spots for each specimen from AFM scans over the surface areas of 5 × 5 μm^2 using Nova SPM software (NT-MDT).

The surface morphology and surface composition of the deposited coatings were investigated using MERLIN field emission scanning electron microscope (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDX, Carl Zeiss).

The phase composition and structure of the surface were investigated using an X-ray diffractometer (XRD) (XRD-7000, Shimadzu, Japan) in Bragg-Brentano mode with a monochromatic CuK_α radiation source (a wavelength of 1.5406 Å) operated at 30 mA and 40 kV. The HA, magnesium XRD patterns (#9-0432 and #04-0770) from the ICDD database were used as references.

In order to fully investigate the indentation behaviour of HA films an investigation of the films was carried out by nanoindentation. Nanoindentation has been established as an important tool for measuring material hardness and elastic properties of thin films on the submicron scale [9-14].
Nanoindentation tests were performed using a Nanotriboindenter TI-950 (Hysitron Inc., USA) equipped with a Berkovich indenter with an angle between the opposite faces of 142.3° and tip radius of around 50 nm. A special software to calculate the nanohardness (H) and the reduced modulus (E) of

the coatings according to the analysis of Oliver and Pharr method was used [10]. Load–displacement curves with the load ranging from 0.1 mN to 10 mN were obtained in order to determine penetration depth (*h*), elastic modulus (*E*) and hardness (*H*) of the composites as a function of the applied load. Repeated indentations were performed on initial and modified AZ31 magnesium alloys and the values of *H* and *E* were calculated as an average of 10 indentations.

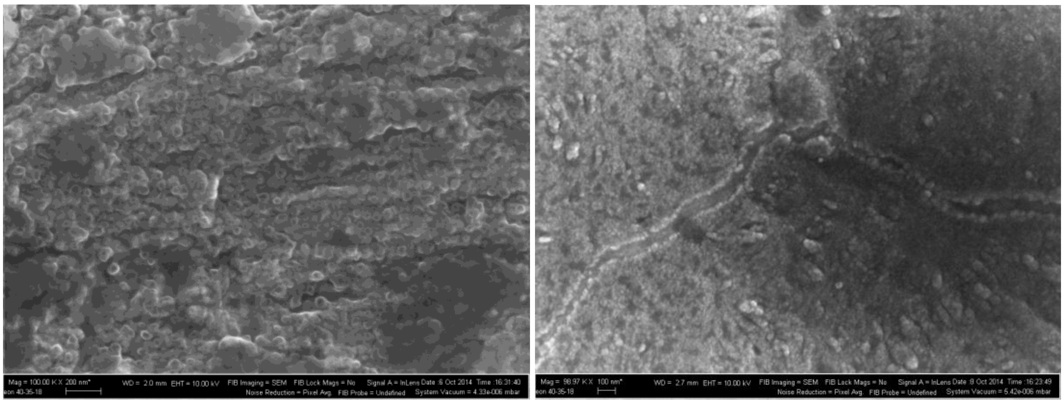
3. Results and discussion

Table 1 summarises the roughness parameters estimated by AFM for the uncoated initial substrates and AZ31 surface treated via PEB. All roughness parameters were measured for the scan areas of 5 × 5 μm^2. The initial substrate exhibited values higher than those measured for the AZ31 surface modified by PEB treatment.

Table 1. The surface roughness parameters of initial and PEB-treated AZ31 magnesium alloy substrate

Surface of AZ31	Roughness parameters			
	Sa, nm	*Sq*, nm	*Sz*, nm	*Smax*, nm
Initial surface	28.8	37.6	304	375
PEB treated surface	10.2	16.2	189	288

The typical SEM micrographs of the surface morphology of the initial and the HA-coated AZ31 substrates are shown in the figure 1.



а) б)

Figure 1. SEM images of AZ31 magnesium alloy substrates before (a) and after (b) PEB treatment.
The initial surface of AZ31 magnesium alloy was homogenous and revealed well-refined granular features

The typical XRD patterns of the untreated and treated via PEB AZ31magnesium alloy are shown in Fig. 2. XRD patterns showed that PEB treatment affected the preferential orientation of magnesium alloy substrates. The change in preferential orientation of the AZ31 was observed after the irradiation. Peaks located at 2θ=32.2°, 34.4°, 36.6°, 47.8°, 57.4° and 63.1° are assigned to the (100), (002), (101), (102), (110), and (103) planes of hexagonal magnesium (04-0770), respectively. It was interesting that the most intense peak (002), occurring at 2θ=34.4°, was found for the initial sample. When the substrate surface was modified by PEB the peaks at 2θ=32.2° and 36.6°, were more intense than the XRD reflexes for the initial Mg sample.

The evolution of the mechanical properties of the initial AZ31 sample as a function of the penetration depth revealed that the elastic modulus and hardness remain unchanged. The obtained increase in hardness and modulus at very low indentation depths is generally related to various effects like tip surface roughness and morphology.

The average values of *E* and *H* obtained for the penetration depths of 50 and 100 nm for the treated and untreated samples are presented in Table 2. The values of the elastic strain to failure ratio (*H/E*), and the parameter H^3/E^2 for the initial and modified substrates are also summarized in table 2. The initial magnesium alloy substrate revealed a nanohardness of 1.19 ± 0.32 GPa and a Young's modulus of 44.24 ± 3.40 GPa for a penetration depth of 100 nm.

The term *H/E* can be considered to be a useful indicator of a good wear resistance of the material [15, 16]. The material 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 [17, 18]. 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.

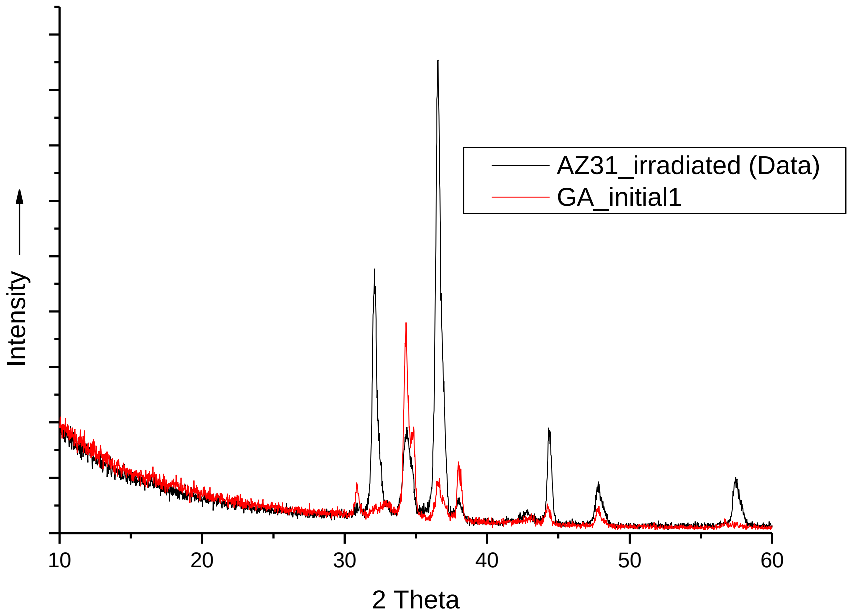
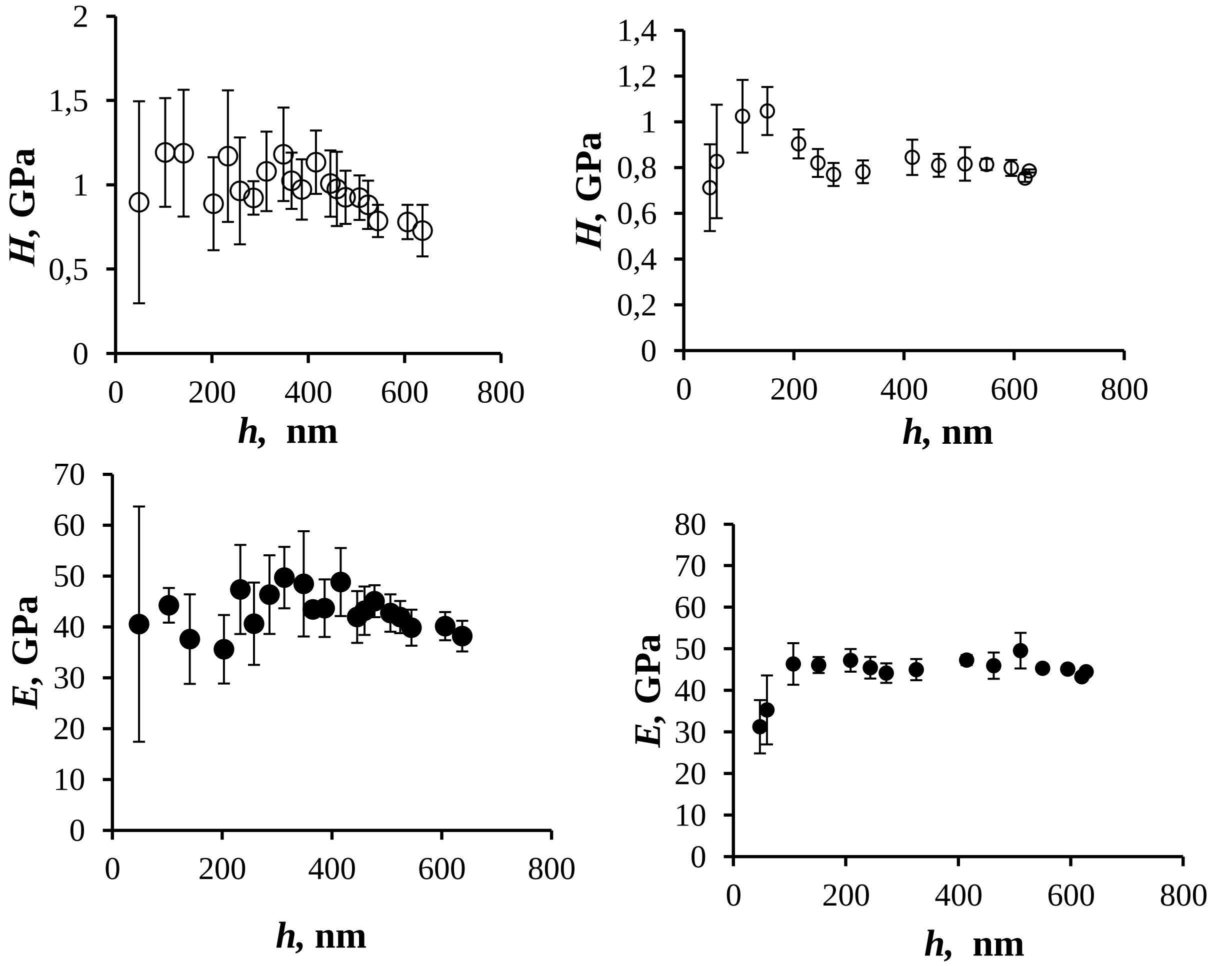


Figure 2. The typical XRD patterns of the AZ31 samples after (a) and before (b) PEB treatment

It could be seen that the magnesium alloy AZ31 treated with PEB demonstrated the heterogeneous elastic mechanical properties. However, the variation of values in that case was reducedsignificantly compared to the initial substrate. When the penetration depth was reduced to around 300 nm, the hardness decreased to 0.8 GPa, and the modulus increased to 45 GPa. These values of the hardness and Young's modulus were found to be slightly reduced compared to that of the initial substrate.
Therefore, according to XRD analysis the PEB treatment affected the preferential orientation of magnesium alloy substrates. The nanoindentation test revealed the decrease of the average values of the hardness and Young's modulus on the nano- and microscale for the magnesium alloy treated with PEB. However, the parameters *H/E*иH^3/E^2 of the AZ31 surface remained unchangedafter the irradiation.

Examination of the coating microstructure by SEM revealed that the modification of the surface via the PEB irradiation has an influence on surface morphology. Fig. 4 showed the SEM images of the HA films fabricated on untreated and treated AZ31 magnesium alloy. All of the HA coatings deposited on untreated alloy revealed a regular grain-like morphology. However, the surface topography of HA film deposited onto the AZ31 substrate treated with PEB was smoother on the nano- and microscale level. Moreover, it can be observed that the coating on the treated substrate exhibited well-refined granular features. Therefore, the surface morphology of thin HA film is sensitive to the initial substrate topography.



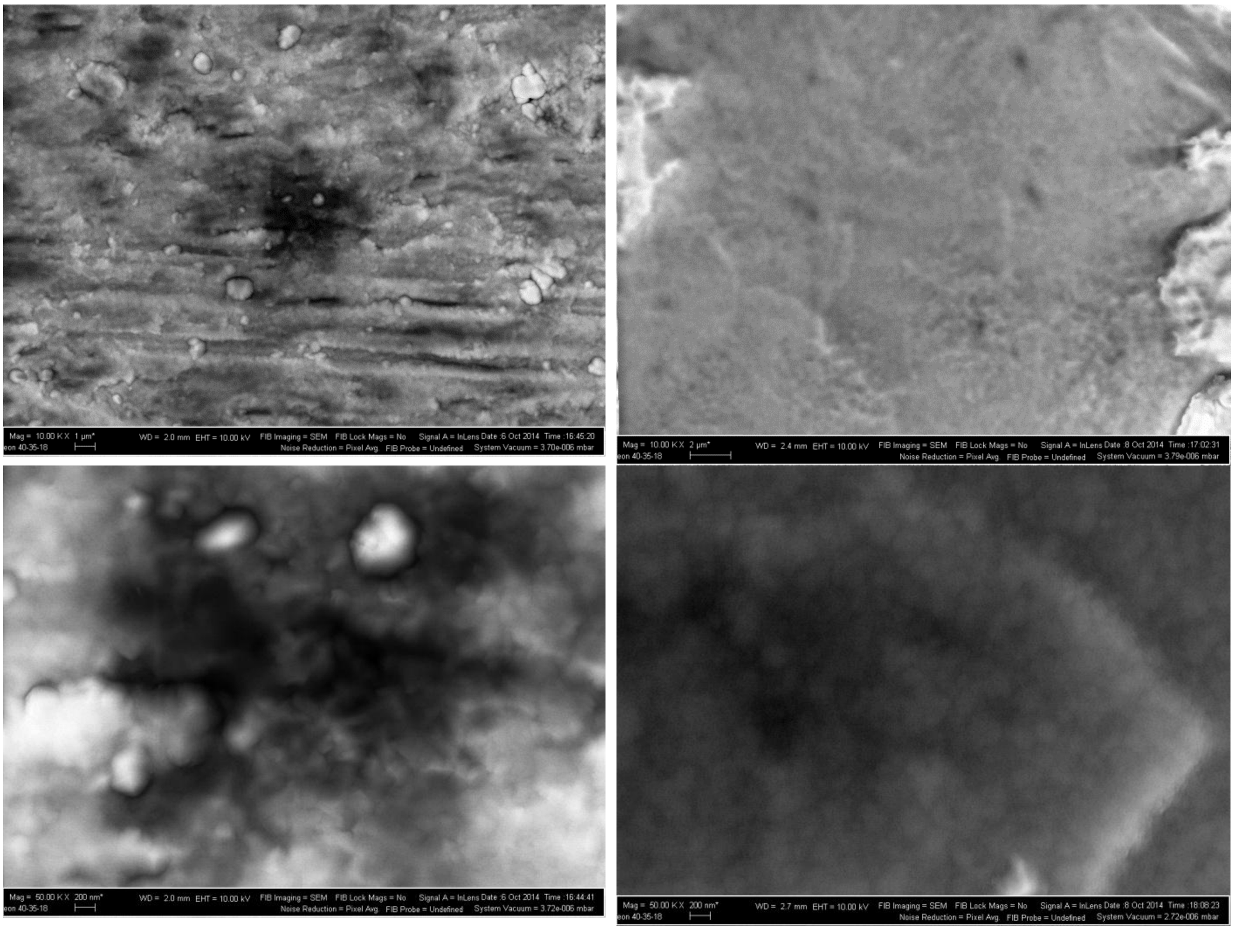
a) b)

Figure 3. The hardness *H* and Young's modulus *E* values plotted as a function of the indentation depth for AZ31 magnesium alloy before (a) and after PEB treatment (b)

RF-magnetron sputter deposited HA coatings on the magnesium alloy have been described as dense, uniform, non-porous films [19] and improved corrosion resistance compared to uncoated substrate.

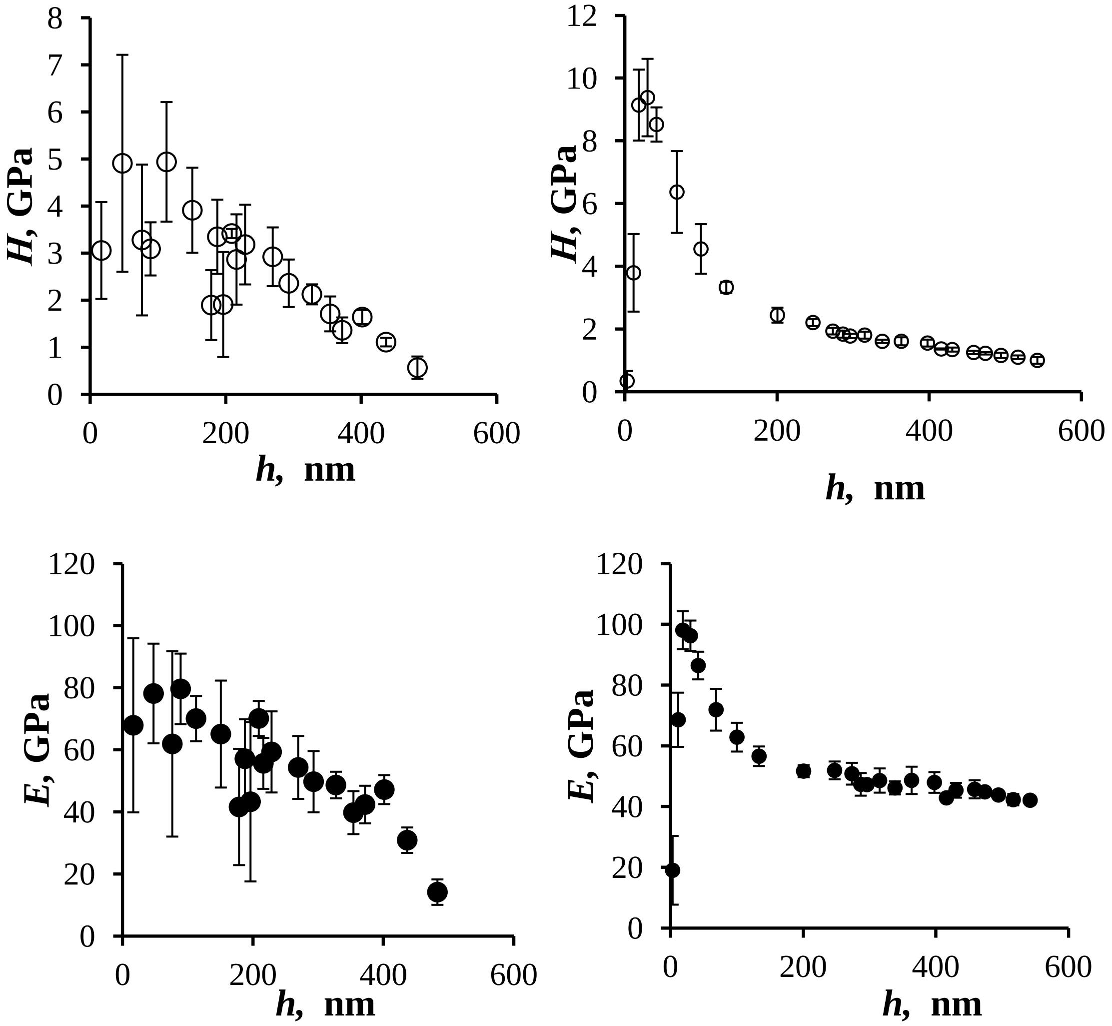
The most important parameters are the molar n(Ca)/n(P) ratio and the solubility [20]. The lower the Ca/P molar ratio is, the more soluble the calcium phosphate. The chemical formula of HA is $Ca_{10}(PO_4)_6(OH)_2$, and the stoichiometric Ca/P atomic ratio of 1.67 is close to that of natural bone. The Ca/P ratios of the HA films fabricated via RF magnetron sputtering onto the AZ31 substrate according to EDX were 1.57±0.03, which are slightly lower than the 1.67 Ca/P ratio of stoichiometric HA.

The evolution of *H* and *E* as a function of the penetration depth, determined from nanoindentation tests for the HA coating deposited on the untreated and treated AZ31 substrate, are shown in Fig. 5. The dispersion of *H* and *E* values in the case of the HA film on the AZ31 treated via the PEB were much smaller compared to that of *H* and *E* values obtained for the coating deposited on the untreated substrate. These results clearly indicated that the surface of the modified substrate with HA film exhibited more homogeneous properties. The evolution of the elastic modulus and hardness wasvery similar. The hardness as well as Young’s modulus values decrease with increasing indentation depth independently of the HA film thickness. Saha and Nix observed a reduced hardness with increasing penetration depth in the case of a hard film on a soft substrate [21].



a) b)

Figure 4. SEM micrographs of HA coatings on the surface of AZ31 substrate before (a) and after PEB treatment (b)



a) b)

Figure 5. The hardness *H* and Young's modulus *E* values plotted as a function of the indentation depth for HA-coated AZ31 magnesium alloy before (a) and after PEB treatment (b)

Table 2. The values of the penetration depth *h*, nanohardness*H* and Young's modulus *E*, *H*/*E* ratio, parameter H^3/E^2 for the HA-coated AZ31 magnesium alloy before and after PEB treatment

Sample	*h*, nm	*H*, GPa	*E*, GPa	*H/E*	H^3/E^2,GPa
Initial AZ31 surface	100	1.19 ± 0.32	44.24 ± 3.40	0.027	0.0009
	50	0.90 ± 0.80	37.01 ± 22.30	0.024	0.0005
HA coated AZ31 surface	100	3.08 ± 2.00	79.03 ± 11.00	0.039	0.0047
	50	4.90 ± 2.50	78.04 ± 16.00	0.063	0.0193
AZ31 surface after PEB treatment	100	1.02 ± 0.16	46.35 ± 5.00	0.022	0.0005
	50	0.71 ± 0.24	31.25 ± 6.41	0.023	0.0004
PEB treated and HA coated surface	100	4.55 ± 0.79	62.8 ± 4.7	0.072	0.0239
	50	8.52 ± 1.4	86.38 ± 4.6	0.099	0.0829

In the table 2 the results of nanoindentation of the HA coating deposited on the treated and precursor samples are summarized. Large differences are observed, which can be attributed to the surface structure of magnesium alloy treated differently. The HA coating on the AZ31 substrate processed by the PEB treatment was much harder (*H* = 8.52 ± 1.4 GPa, table 2) than the HA film on the rough initial substrate (*H* = 4.90 ± 2.50GPa, Table 2). Moreover, the Young's modulus of HA coating on the treated substrate was observed to be higher at the depth of 50 nm than HA film prepared by sputtering onto the initial AZ31 substrate (Table 2). The pre-treatment of the AZ31 substrates resulted in an increase in the *H/E* ratio and the plastic resistance ratio H^3/E^2. The same effect of the pre-treatment was observed for the HA coating deposited on the acid etched and pulse electron beam treated surfaces [9].

4. Conclusion

The morphology, elemental, phase composition, nanohardness, and Young's modulus of the HA coating deposited viaRF-magnetron sputtering were investigated by SEM, EDX, XRD, and nanoindentationtechniques. The Ca/P ratio of the HA coating deposited via RF-magnetron sputtering onto AZ31 substrates according to EDX was 1.57±0.03. The SEM experiments revealed significant differences in the morphology of the HA films deposited onto the initial AZ31 substrate and the PEB-treated substrate.

Nanoindentation studies demonstrated significant differences in the mechanical responses of the HA films deposited onto the initial and PEB-modified AZ31 substrates. The nanoindentation hardness and the Young's modulus of the HA films on the PEB-treated magnesium alloy are higher than that of the HA layer on the initial substrate. Moreover, the HA filmfabricated onto the treated surface is more resistant to plastic deformation than the same film deposited on the untreated AZ31 surface.

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