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Surface oxidation by laser soft-melting treatment to change degradation behaviour of a magnesium alloy

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Abstract

The use of Mg and its alloys has been limited in engineering applications due to their low corrosion resistance. On the other hand, since a tuned degradation rate is attractive for biomedical applications, Mg and related alloys are considered a promising choice as bioresorbable metals. However, biomedical applications require a greater control of degradation behaviour and rate. Presence of O_2 and atmospheric moisture (H_2O) strictly affect degradation behaviour of magnesium alloys whose corrosion is accelerated in humid environment. Several authors studied the effect on Mg corrosion of different surface modification methods and environmental parameters. In this work, a laser treatment of an AZ31 Mg alloy is proposed as a surface treatment using a soft-melting approach. A ns pulsed fiber laser operating was used to promote different stages of surface oxidation, under two process conditions at different energy density applied in ambient atmosphere. Laser treatment directly generated a morphology change and a chemical modification of Mg substrates. Laser soft-melted surfaces at different conditions were tested and the laser effect on degradation behaviour of AZ31 was evaluated. Roughness measurement with an optical profilometer, surface morphology investigation using SEM analysis and chemistry evaluation by XPS technique were carried out. The relationship between laser action and changes in degradation behaviour of AZ31 Mg alloy was investigated. The studied conditions were compared to the untreated cold-rolled surface as reference.

Keywords: magnesium alloys, degradation, corrosion, laser melting, surface oxidation, morphology.

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1. Introduction

Magnesium and its alloys, despite their good mechanical and structural properties, are used in a limited manner because of their poor corrosion resistance in some specific conditions. Some biomedical applications are based on the bio-resorbability of the used material. For resorbable biometals, the degradation rate need to be carefully tuned to be adapted to the final need. Mg is an element naturally present in human body and it exhibits high biocompatibility. On the other hand, use of magnesium in biomedical applications requires a strict degradation rate control. As a matter of fact, extensive literature is available on the strategies proposed for degradation rate control and reduction.

Magnesium and Mg alloy degradation is affected by different aspects like surface treatments and operating environment. Concerning biomedical applications, surface modification methods such as heat-treatments, mechanical polishing, chemical and electrochemical treatments as well as coating deposition were investigated [1][2]. Intermetallic particles, surface roughness and impurities reduce dramatically degradation resistance[3]. On the other hand, Mg degradation can be significantly reduced by use of coating protection on the substrate. Magnesium oxide and hydroxide were used in applications, where high corrosion resistance is required [4][5]. Surface treatments and pre-treatments can be also realized using laser based techniques. Particularly, surface laser melting was studied in order to promote surface cleaning, grain refinement and surface oxidation improving

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magnesium corrosion behaviour [5]-[7]. Moreover, laser can be used to modify the surface topography and promote polymeric coating adhesion on magnesium substrate [8]. The degradation kinetics of Mg and its alloys have also been studied. Laboratory environment, condensation in atmospheric condition, humid air, tropical marine environment, different temperatures and different operating solutions were analysed to determine which factor influences to a greater extent magnesium corrosion patterns [9]-[14]. For this reason, more studies are required to assess and predict the surface performance in real applications.

In this work, a laser soft-melting approach was used in order to modify the morphology and the chemistry of AZ31 Mg alloy, for biodegradable implant applications. Treated surfaces can be used with or without the application of an additional biodegradable polymeric coating. In both cases, the contact with water is a crucial point to be assessed. Laser influence in degradation behaviour of magnesium alloy was determined thanks to a comparison with the untreated condition used as reference one.

2. Experimental details

2.1. Materials and methods

Cold rolled AZ31 Mg alloy sheets with 0.4 mm thickness were used in the present study. The maximum height of roughness profile R_z of the as received materials equal to 1.63 ± 0.41 μm. The material chemical composition is summarized in Table 1.

Table 1 Chemical composition of employed AZ31 magnesium alloy.

Element	Al	Zn	Mg
wt%	3.08	0.98	Bal.

A nanosecond pulsed fiber laser was used for surface structuring (YLP-1/100/50/50 by IPG Photonics, Oxford, MA, USA). Beam handling was controlled using a scanner head (TSH 8310 by Sunny Technology, Beijing, China) equipped with an f-theta lens characterized by 100 mm of focal length (SL-1064-70-100 from Wavelength Opto-Eletronic, Ronar-Smith, Singapore). Laser system specifications are summarized in Table 2.

Table 2 Specifications of employed laser system

Wavelength	λ	1064 nm
Maximum average power	P_{max}	50 W
Pulse duration	τ	250 ns
Pulse repetition rate	PRR	20-80 kHz
Beam quality factor	M^2	1.7
Collimated beam diameter	d_c	5.9 mm
Focal length	f	100 mm
Focused beam diameter	d_0	39 μm

Laser treatment was realized using a soft-melting technique. AZ31 sheets were laser textured with two energetic levels to obtain different morphologies conditions. Texture 1 was characterized by a low average fluence level (40.2 J/cm^2) and Texture 2 by a higher average fluence level (140.8 J/cm^2). Laser treatments were performed in atmosphere and without any controlled atmosphere. Textures were obtained by overlapping of scanning lines with two different strategies. Texture 1 was realized by a single pass in the same direction of surface lamination (0°). Texture 2 was realized in 4 consecutive laser passes; each pass with different scan angle (0°, 45°, 90°, 135°). In both surface treatments lines pitch was fixed at 10 μm. Laser texturing was achieved 2 mm above focal position obtaining a spot diameter of 124 μm on the substrate. Laser parameters, used in this work are listed in Table 3.

Table 3 Laser texturing parameters

	Texture 1	Texture 2
Pulse Energy, E (mJ)	0.25	0.25
Pulse repetition rate, PRR (kHz)	20	70
Scanning speed, v (mm/s)	100	100
Number of pass, S	1	4

2.2. Surface qualification

Laser treated surfaces were analyzed in terms of roughness and morphology. The comparison between treated conditions was performed using base material as control state. Laser treated substrates were studied using an optical profilometer (InfiniteFocus from Alicona Imaging GmbH, Graz, Austria) and SEM. Chemistry evaluation was performed with XPS. The study was focalized on water effect on laser treatments when compared with reference condition. Reference and laser treated surfaces were immersed in distilled water for 5 seconds, then extracted, dried and stocked in atmosphere. Degradation behavior was investigated by surface analysis before water immersion and 30 days after immersion.

3. Results and discussion

In Figure 1, 3D surface profiles of reference and textured surfaces are shown. Textured surfaces showed a morphology whose roughness can be related to the amount of increased roughness as a function of energetic level (Table 4). Texture 2, which was characterized by higher fluence value, showed also the higher value of R_z. Texture 2 presented an inhomogeneous distribution of fractal features. Stochastic nucleation of cauliflower elements is typical of magnesium reaction, with oxygen, at elevate temperatures where a vapor phase occurs [15]. These discontinuities in substrate features dispersion was responsible of the high standard deviation value of the surface roughness parameter.

Table 4 R_z values of reference and textured surfaces, before and after water immersion

		R_z [μm]	
	Fluence value [J/cm^2]	**Before water immersion**	**After 30 days from water immersion**
Reference surface	-	1.63±0.41	2.96±1.79
Texture 1	40.2	7.53±0.45	7.98±0.74
Texture 2	140.8	20.41±6.31	24.47±2.72

On the contrary, Texture 1, which was associated to a low fluence level, presented a random surface texture, where soft material remelting generated a more uniform surface topography.

All conditions reveled an increase of roughness values after water immersion. Particularly, reference surface showed a considerable increase in R_z and standard deviation value after interaction with distilled water (Table 4). This behavior underlines an increased inhomogeneity on the substrate, where degradation products radically change surface morphology.

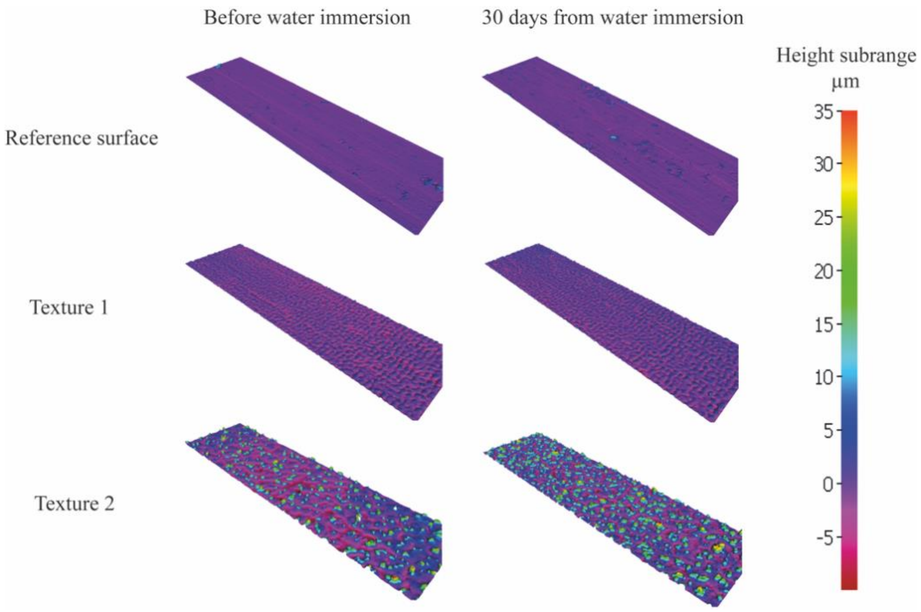

Figure 1. 3D surfaces profiles before and after water immersion

In

Figure 2-a, the reference surface appears smooth and grooves aligned along the rolling direction are clearly visible. Thirty days after water immersion, the same surface showed an increased roughness and the substrate was characterized by an inhomogeneous distribution of cavities and degradation products, probably the result of an accelerated corrosion phenomenon (**Errore. L'origine riferimento non è stata trovata.**-d). The effect of a high corrosion rate upon very limited time of contact with water is visible also in the case of laser treated surfaces. Texture 1, reveled a different degradation phenomenon. In this case, corrosion propagation followed the laser generated micro-structures geometries in a conformal manner. A great number of cracks are visible in

Figure 2-e, and remelted material seems to be more sharply divided in peaks and valleys. The result was a little increased value of R_z. Texture 2 sample presented different features. Surface topography in **Errore. L'origine riferimento non è stata trovata.**-c and

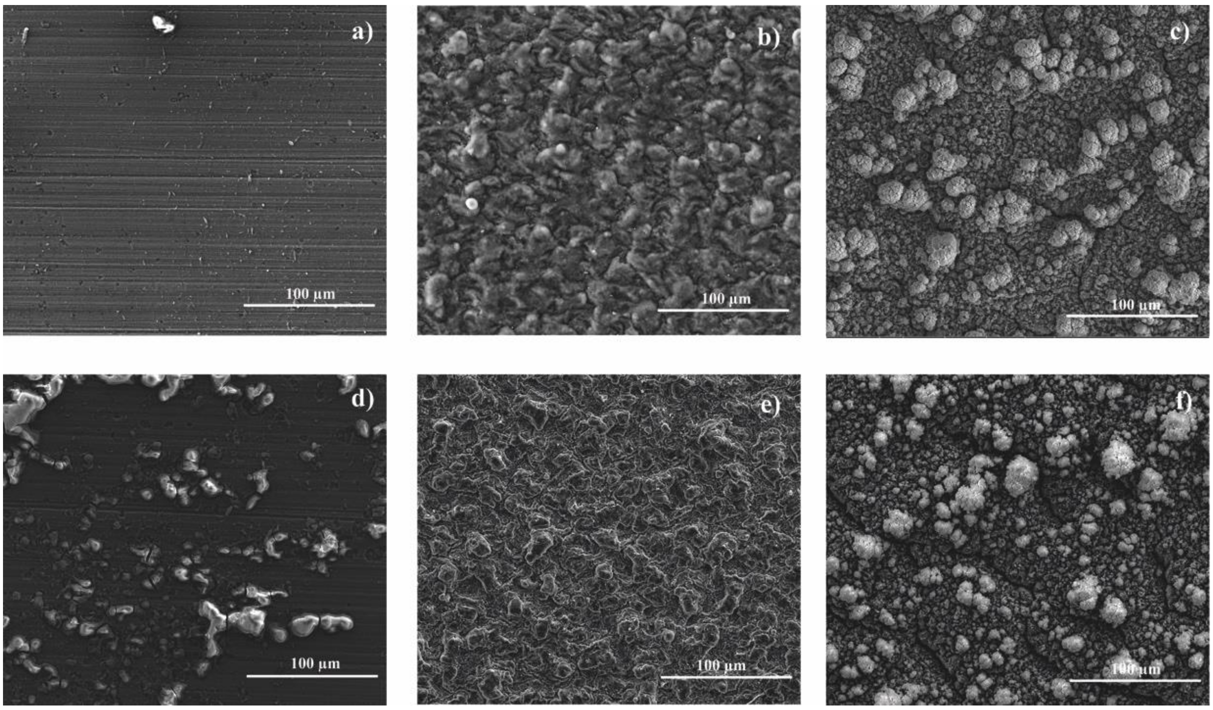

Figure 2-f seems rather similar. Nonetheless, also for Texture 2, after water immersion, R_z value increased slightly, testifying that the initial laser structured topography was maintained.

Figure 2 SEM analysis: a) reference surface before water immersion, b) Texture 1, before water immersion, c) Texture 2, before water immersion, d) reference surface after 30 days from water immersion, e) Texture 1, after 30 days from water immersion and f) Texture 2, after 30 days from water immersion.

Table 5 XPS survey analysis of reference and textured surfaces, before and after water immersion

		Before water immersion			After 30 days from water immersion		
		Reference surface	Texture 1	Texture 2	Reference surface	Texture 1	Texture 2
At. %	C1s	54.1±2	25.7±1	22.9±1.6	50.7±9	22.9±2.2	21.9±2.5
	O1s	34.9±1.1	48.7±0.8	45.3±1	36.8±6.2	57.1±2.4	55.9±1.5
	Mg2p	6.7±2.3	19.5±0.4	22.8±1.6	9.4±3.1	16.9±0.3	18.4±1.5
	Ca2p	2.7±0.2	3.3±0.3	5.3±0.2	1.4±0.6	0.8±0.5	1.3±0.5
	Ar2p	0.9±0.2	2.2±0.1	2.4±0.2	1.1±0.1	1.5±0.2	1.5±0.2
	Zn2p3	0.6±0.2	0.3±0.2	0.9±0.2	0.4±0.2	0.5±0.2	0.5±0.2
	Fe2p3	0.1±0.2	0.4±0.3	0.4±0.2	0.2±0.2	0.4±0.2	0.5±0.4

Surface chemistry was performed by XPS technique. Results of XPS survey were reported in Table 5. Laser treatments seems to modify the chemical composition of the reference surface reducing the carbon content from 54% to 26-23%. Oxygen content was present in all conditions. Particularly, reference surface suggested the presence of a thin natural oxide layer, due to the high reactivity of magnesium, also in atmosphere environment. Laser treatment increased oxygen content, promoting magnesium-oxygen bond. Texture 1 and Texture 2 were characterized by a thicker oxide layer as suggested also by a previous work with XRD and cross section analysis [16]. On the other hand, water interaction further increased oxygen contents in all conditions, suggesting bonds between MgO and H_2O producing magnesium hydroxide $Mg(OH)_2$ [17].

4. Conclusions

Two different strategies of laser texturing, using soft-melting approach were realized on AZ31 magnesium alloy substrate. Laser treatment increased surface roughness modifying the substrate morphology. On the other hand, laser treatments promoted the formation of a thicker oxide layer and the reduction of surface carbon content. Tests in distilled water confirmed the high reactivity of magnesium alloy: relevant morphology changing was observed; corrosion phenomena and degradation products were clearly visible on reference surface and Texture 1. XPS surfaces analysis. The modification of surface topography before or after water immersion can be attributed to the formation of new phases, such as Mg oxides and hydroxides as degradation products. Moreover, morphological analyses suggest that the corrosion pattern is influenced by the preexisting surface morphology induced by the laser treatment in a conformal way. This factor can be highly beneficial for achieving more homogenous degradation in biomedical implants.

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