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# Excimer laser treatment of ZE41 magnesium alloy for corrosion resistance and microhardness improvement

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ABSTRACT

A laser surface melting treatment (LSMT) was performed on a ZE41 Mg-alloy using an excimer KrF laser. The laser-melted layer depth depends on the laser scan speed. The morphology and the microstructure of the laser-melted surface were characterized, thanks to the scanning electron microscopy (SEM). The melted Mg-alloy presented a homogenous distribution of the alloying elements in the magnesium matrix. The laser surface melting treatment increased the microhardness of the ZE41 Mg-alloy and improved its corrosion resistance.



## 1. Introduction

Magnesium and its alloys, specially the ZE41, have a wide scope of applications in the fields of aerospace, automotive and many other industries where weight reduction is a concern, because of the low densities and high specific strength of these materials. In fact, magnesium alloys density is only two-thirds of that of aluminum alloys and a quarter of that of steels. Despite the versatility of these alloys, a relatively poor resistance to corrosion and fretting wear makes them less competitive than aluminum alloys [1]. The most common treatments used to improve these properties are chemical surface treatments such as anodization and mordanting process [2]. However these treatments temporarily protect magnesium alloys, they are harmful for the environment and expensive, and there is no doubt that much more efficient protection methods are still needed. Laser surface melting treatment is one of the most interesting materials processings which can enhance the corrosion and wear resistance of ZE41 alloy. LSMT has been reported to increase the wear and corrosion resistance of magnesium alloys [3–11]. Kalimullin et al. [3] reported that LSMT of MA21 alloy makes it possible to increase its corrosion resistance in a 3% NaCl solution in comparison with the untreated alloy by about 30 times with pulsed laser treatment and by more than 10 times with continuous laser radiation. According to Kalimullin et al., this corrosion resistance improvement is due to the refinement of MA21 grain structure. Koutsomichalis et al. [4] noted that an excimer-laser-treated AZ31B magnesium alloy exhibits higher corrosion resistance in a NaCl solution and lower microhardness in comparison with the untreated one. Majumdar et al. [6] indicates that LSMT significantly improves the pitting corrosion resistance of MEZ magnesium alloy in a 3.5% NaCl solution. It also enhances the microhardness of the alloy by 2–3 times. These improvements are attributed to the combined influence of grain refinement, dissolution of intermetallic phases and retention of alloying elements in an extended solid solution. Abbas et al. [7], Guo et al. [8] and Gao et al. [9] also observed a similar enhancement of corrosion resistance of laser-melted AZ31, AZ61, WE43 and AZ91 Mg-alloys. Jun et al. [10] and Zhang et al. [11] mentioned that both microhardness and wear resistance are improved by respectively Nd:YAG pulsed and $CO_2$ continuous Laser surface melting treatment of the AM50 and AZ91D magnesium alloys. However, Dubé et al. [5] reported no increase of the corrosion resistance of AZ91D and AM60B alloys in a sodium solution following the use of a pulsed Nd:YAG laser, although refinement of microstructure within the laser-melted layer had been achieved.

Our interest in excimer laser surface melting treatment stems from its ability to produce extremely high power densities ($>10^{12}\,\mathrm{W\,m^{-2}}$) and the possibility of applying them with precise spatial and temporal control to the processed surface. In addition, the high energy and short pulses of excimer laser associated with

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low reflectivity of metals in the ultraviolet range enable the modification of thin surface layers with a reduced thermal effect in the underlying bulk material. Moreover laser is a clean energy source which does not require a critical environment during processing.

## 2. Experimental procedure

ZE41 specimens with dimensions of $20\times20\times7\,mm^3$ were cut from the as-cast plate ($300\times140\times15\,mm^3$) which was subjected to a T6-heat treatment (Quench at 300 °C during 2 h, tempering at 200 °C during 16 h) and was protected by a HAE anodized coating. The chemical composition of a ZE41 alloy is presented in Table 1.

The magnesium specimens were irradiated in atmospheric conditions, without an assisting gas, using a Lambda Physik excimer laser using a KrF gas mixture. The wavelength of the laser was $\lambda=248$ nm and its pulse duration was $\tau=20$ ns. The energy of each pulse and the repetitive rate of pulses were fixed respectively at $E_p=100$ mJ and $F=100$ Hz. The laser beam has a rectangular shape with dimensions of $24\times10\,mm^2$. To perform laser surface melting treatment, the laser beam was focused thanks to a planoconvex lens with a focal distance of 130 mm. The LSTM was carried over a $1\times1\,cm^2$ area in a normal incidence by overlapping several melt tracks with a scan speed ($V_b$) varying between 250 and $50\,\mu m\,s^{-1}$ and with an overlapping of 50%. (See Fig. 1).

The general features of the melted surfaces were observed through macro photography and optical microscopy. Transverse sections of the laser-melted surfaces were mounted, polished to 1200 SiC and finally etched using a 4% nital solution before being observed by a scanning electron microscopy (SEM).

The microhardness of the laser-treated and the as-received magnesium alloy was measured using a Leika VMHT Vickers microhardness tester using a load and indentation time respectively equal to 0.49 N and 15 s.

The corrosion behavior of the as-received and laser-treated magnesium alloy was examined by two methods: the first one consisting in recording the open circuit potentials continuously for 24 h in 0.5 M NaCl solution at pH=10 and 293 K and the second method being the salt-spray test performed as prescribed in the ASTM B 117-97 standard.

**Table 1**
Chemical composition of ZE41.

| Alloying elements | Zn | TR | Zr | Mn | Si | Cu | Mg |
|---|---|---|---|---|---|---|---|
| % Weight | 3.21 | 1.23 | 0.83 | 0.013 | 0.009 | 0.04 | 94.668 |

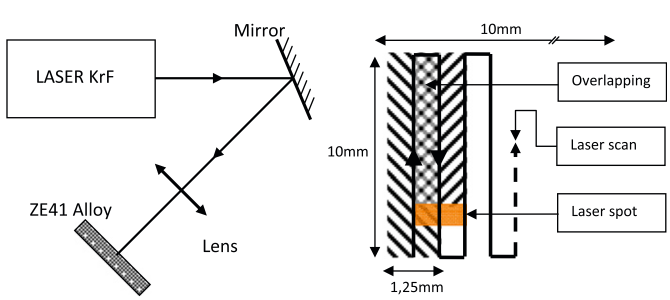


**Fig. 1.** Schematic diagram of the experimental set-up for laser surface melting of ZE41.

## 3. Results and discussion

The laser surface melting treatments presented below were performed under 100 mJ pulse energy, 100 Hz repetitive pulse rate and a scan speed ($V_b$) varying between 250 and $50\,\mu m\,s^{-1}$. Laser surface melting treatments were carried out ten times to ensure their repeatability and to provide enough samples for corrosion and microhardness tests. Fig. 2 shows the transverse section of the ZE41 specimen irradiated respectively at 250, 100 and $50\,\mu m\,s^{-1}$ scan speeds. The pictures show two zones: the lower one representing the granular structure of the as-received ZE41 specimen. The higher zone is the melted layer. Several measurements of laser-melted layer depth by image processing prove that the layer depth is uniform for each specimen and it is inversely proportional to scan speed. Fig. 3 shows the evolution of the laser-melted layer depth as function of the scan speed.

### 3.1. Morphology and microstructure of the laser-melted surfaces

After the laser surface melting treatment, the ZE41 displayed a complex rippled surface morphology. Fig. 4 shows a wavy morphology: a succession of hollows and hills can be seen on the irradiated surface of the ZE41 specimen. Each hollow corresponds to a laser beam track. Such morphology is due to several causes. The first one is loss of material by evaporation caused by the high power density ($160\,MW\,cm^{-2}$) of the laser beam. This power density is not homogenous within the laser spot; it reaches the maximum at the centre of the beam and decreases whenever we approach the beam border. Therefore evaporation is emphasized at the centre and a hollow is created. In addition, the high power density brought by the laser pulse creates a temperature gradient around the irradiated zone. This temperature gradient induces a gradient of surface-shear stress, which increases with the distance from the irradiated surface. Consequently, the molten material is pushed away from the irradiation centre towards the beam periphery where the surface-shear stress is the highest. During laser surface melting treatment, we noticed a creation of plasma on the magnesium alloy surface. The plasma vapours' pressure drives shock waves and compresses the molten material beneath the incident laser beam, enhancing formation of the wavy topography. The irradiated surface is dark and covered with a white powder which can be wiped off. This white powder comes from ionized gas and metal from the plasma which reacts together and form solid products deposited on the magnesium surface as an extremely thin film. The dark thin layer on the irradiated surface is formed by the oxidation of the very hot laser-melted surface.

Fig. 5 shows the transverse section of a ZE41 specimen treated with $E_p=100$ mJ, $F=100$ Hz and $V_b=50\,\mu m\,s^{-1}$. This section was observed by a scanning electron microscope (SEM) after being mounted, ground to 1200 SiC, polished with diamond suspensions to 0.05 μm and finally etched using a 4% nital solution.

As mentioned before, pictures present two zones, the higher one being the laser-melted layer. It has a uniform depth of 70 μm (Max=73 μm, Min=69 μm). The lower zone represents the structure of the as-received ZE41 specimen. This structure is composed of magnesium grains having an average size of 70 μm and surrounded by intermetallic compounds, where alloying elements were held. In the laser-melted layer, we cannot observe a crystalline structure because the crystallites are extremely small. We can notice also that there is no intermediary zone between the laser-melted layer and the granular structure because of the rapid heat exchanges during heating and cooling processes. In fact, a small surface of the magnesium alloy absorbs a quantity of the laser energy in an extremely short