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Laser treatment of magnesium

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Magnesium alloy (AZ31 B) was irradiated in air using a pulsed KrF excimer laser. The surface of the irradiated magnesium exhibited a wavy topography and its surface roughness was found to depend on the laser power density. The corrosion behaviour of the laser-treated magnesium was studied and it was found to be slightly better than that of the untreated magnesium.

1. Introduction

The basis of the interest in lasers for materials processing stems from their ability to produce extremely high power densities (greater than 10^{14} W m^{-2}) and apply them with precise spatial and temporal control to the processed surface. Furthermore, lasers provide a totally clean energy source which can be located remote from the sample and which does not require a vacuum or critical environment during processing [1]. With the use of powerful lasers, several processing techniques have been applied for the surface treatment of various metallic materials, e.g. surface melting, transformation hardening, cladding and surface alloying, laser-assisted chemical and physical vapour deposition and welding [2].

The high energies and short pulses of excimer lasers, together with the low reflectivity of metals in the ultraviolet range enable the modification of thin surface layers without thermal loading of the underlying bulk material. The most recent research work, reported in the scientific literature, on the applications of excimer lasers in surface metallurgy is summarized below.

Panagopoulos and Michaelides [3] studied the effect of excimer laser radiation on thin sheets of pure copper. They found that the surface roughness of copper was found to depend on the laser power density. They also observed that the residual stress in the copper surface layers changed from tensile to compressive as a result of laser treatment. Tosto [4] observed and calculated the generation of shock waves in thin sheets of copper as a result of laser radiation. Ursu *et al.* [5] studied the change in the metallic surface microrelief as a result of multiple pulses of a powerful ultraviolet laser. They showed that the structure produced depends on the laser power density, the number of pulses and the ambient gas during the laser treatment. Badekas *et al.* [6] found that the laser surface treatment of an aluminium alloy changed the magnitude and the sign of the residual stress in the surface layers of the alloy from tensile to compressive. They also observed that the laser treatment of the alloy increased the microhardness in the top surface layers (30 μm).

2. Experimental procedure

The magnesium alloy used in this study was AZ31B H24 having the composition 3 wt % Al, 1 wt % Zn and 96 wt % Mg. Specimens with dimensions of 2.5 cm × 1.0 cm × 0.1 cm were cut from the magnesium alloy sheet. Before laser irradiation, the specimens were mechanically polished with SiC paper (240 M). The magnesium specimens were irradiated in atmospheric conditions with a Lambda Physik excimer laser using a KrF gas mixture. The wavelength of the laser was $\lambda = 248$ nm and the photon energy of each pulse was 300 mJ.

The specimen area which was irradiated by the excimer laser was 1.2 cm × 1.0 cm. The irradiation conditions of each magnesium specimen were determined by changing the following lasing parameters: (1) power density, (2) number of pulses per step, (3) number of successive passes of the laser beam over the same area of the specimen, (4) overlapping percentage of two successive laser pulses. The surface morphology of the irradiated specimens was examined using optical and scanning electron microscopy.

The surface roughness of laser-treated magnesium specimens was studied with a Perthometer M4P profilometer. The structure of the laser and non-laser-treated magnesium specimens was examined with a Philips diffractometer with CoK_a radiation ($\lambda = 0.791$ mm) and an iron filter. The microhardness of the laser-irradiated specimens, in various depths from the surface, was measured using a Vickers microhardness test instrument. The corrosion behaviour of the as-received and laser-treated magnesium was examined in 0.5 M NaCl solution at pH = 10 and 290 K.

The data presented in this study are the average values of six independent experiments.

3. Results and discussion

After laser treatment, the magnesium alloy specimens exhibited a complex rippled surface morphology. Figs 1 and 2 show the surface appearance of magnesium laser-treated with 200 and 300 MW cm^{-2} power density, respectively. From these figures, a rough,

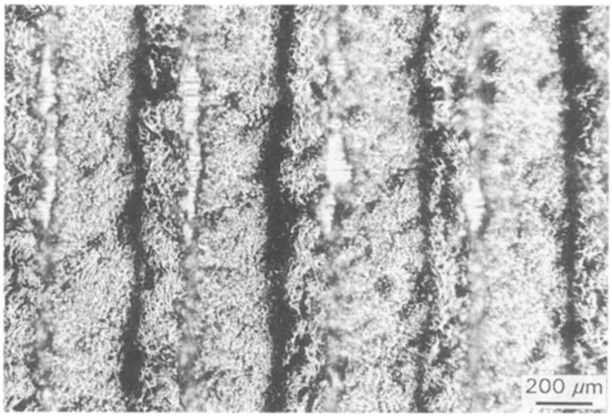

Figure 1 Plan view of the magnesium alloy laser treated with 200 MW cm^2 power density and three scans.

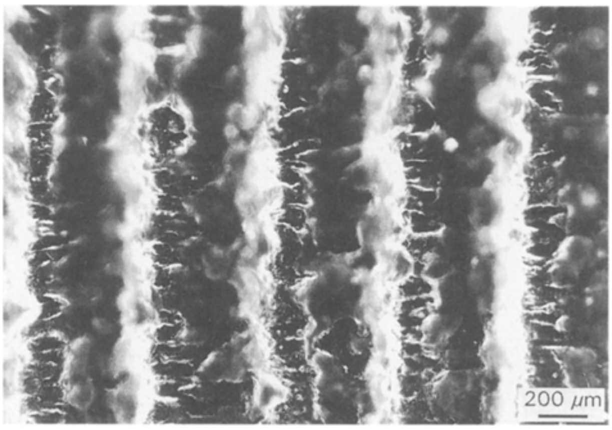

Figure 2 Plan view of the magnesium alloy irradiated with 300 MW cm^2 power density and three scans.

wave-like morphology can be seen on the surface of the laser-treated magnesium. A succession of "valleys" and "hills" can be noticed on the surface of the laser-irradiated specimens. The "valleys" (light areas) correspond to the maximum power of the incident laser pulse and the "hills" (dark areas) correspond to the overlapping area of two successive laser pulses as shown in Fig. 3. The formation of the wavy topography on the surface of the irradiated specimens may be attributed to the temperature gradient around an incident laser pulse. During laser surface remelting of the magnesium alloy, the temperature of the melt pool at the centre of an incident pulse reaches the maximum value and decreases gradually in proportion to the distance from the centre of the irradiation. On the other hand, the surface shear stress increases with the distance from the centre of the incident pulse [7].

Therefore, a gradient of surface shear stress is developed causing a flow of the molten material away from the irradiation centre towards the area of high shear stresses. The result of this phenomenon is the formation of a "valley" at the centre of an incident pulse and the elevation of the melt at the adjacent area (Fig. 3b). The formed surface topography is frozen due to rapid solidification, resulting in a rippled structure. The formation of the wavy topography is enhanced by

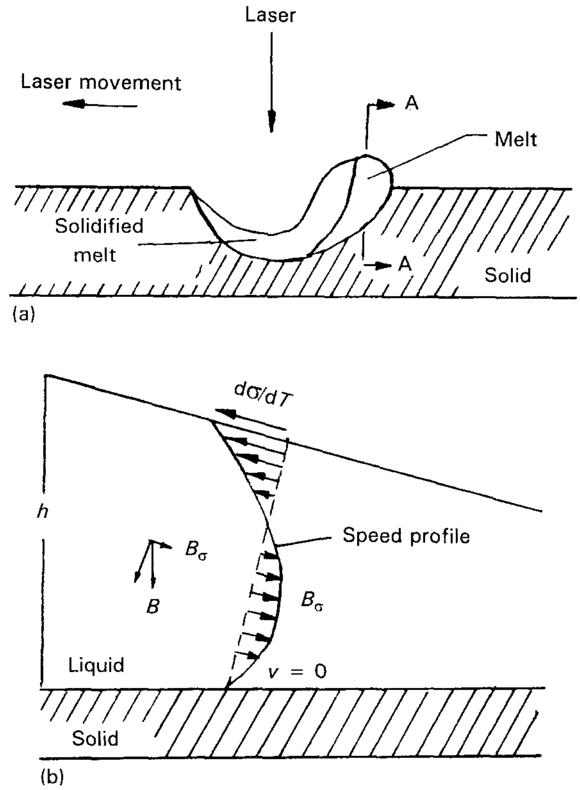

Figure 3 Schematic drawing showing the formation of the wavy topography during laser treatment of the magnesium specimen.

the creation of plasma on the magnesium alloy surface during excimer laser irradiation. In particular, the plasma vapours pressure-drive shock waves and compress the molten material beneath the incident laser beam, enhancing the mechanism described earlier [8]. The creation of plasma was observed to occur for laser power densities higher than 250 MW cm^{-2}.

Fig. 4 shows the transverse section of a laser-treated magnesium alloy specimen. The presence of the laser-affected zone near the surface is noticeable in this picture. The layer of the laser-affected zone has an average depth of 30 μm and consists of finer grains in comparison with the deeper layers. The depth of the laser-affected zone is not uniform; this may be attributed to the non-uniform heat transfer from the top layers to the deeper ones during the laser irradiation caused by various defects on the surface of magnesium alloy specimens.

Using X-ray diffraction (XRD) technique, spectra of laser-treated and non-laser-treated magnesium specimens were taken and examined. The peaks in the spectrum of the laser-treated specimens were wider than the same peaks in the spectrum of the non-laser-treated specimen, as shown in Fig. 5a and b. This is direct evidence, according to the Scherrer formula [9], that the crystallites of the laser-treated specimen are smaller than those of the as-received specimen. Additionally, the peaks in the XRD spectrum of the laser-treated specimen were shifted to lower diffracting angles in comparison with the same peaks of the non-laser-treated specimen. This observation might be indirect evidence that the surface layers of the laser-treated specimen are under lower residual tensile

Figure 4 Transverse section of excimer laser-treated magnesium alloy with 100 MW cm^2.

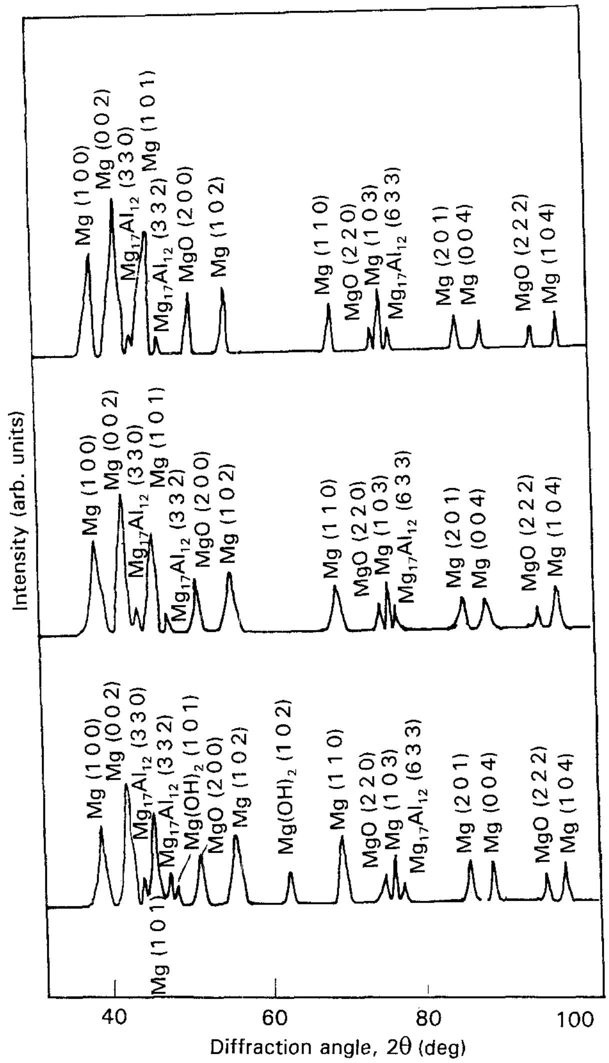

Figure 5 XRD spectra of (a) as-received magnesium alloy, (b) laser-treated magnesium alloy, and (c) the laser-treated alloy after corrosion.

stress than the surface layers of the as-received specimen, as a result of excimer laser treatment of magnesium.

No formation of magnesium oxides or nitrides was detected using X-ray diffractometry. The surface colour of the irradiated zone was dark for the magnesium alloy. This is an indication that some phases were produced on the surface of the magnesium alloy. However, these products were too thin to be identified by X-ray diffractometry. Assuming that the surface temperature of the magnesium alloy exceeds its boiling point (700 °C), for the laser power densities used, the surface layers of the magnesium alloy evaporate and are ionized instantaneously. In such a case, magnesium nitrides and oxides (Mg_3N_2 and MgO) are formed indiscriminately by a reaction of ionized metal and ionized gas elements; then, the products are deposited on the magnesium alloy surface as an extremely thin film which colours the alloy surface.

Fig. 6 shows the microhardness as a function of depth for the laser-treated and non-laser-treated specimens. From this figure it can be observed that the microhardness of the laser-treated magnesium alloy is lower than that of the as-received specimen in the first 30 μm below the surface. At greater depths the values of microhardness are approximately the same for both specimens. The lower microhardness found at the laser-treated alloy surface may be attributed to the following reasons:

(a) the stress relief (e.g. the lowering of the tensile residual stress in the surface) caused by the laser irradiation;

(b) the laser treatment of the alloy allows a fast quench and may cause inhomogeneity of the $Mg_{17}Al_{12}$ precipitates in the surface layers, forming regions of lower concentration of the precipitates and therefore softer surface layers.

Fig. 7 shows the roughness of laser-treated magnesium alloy as a function of the laser power density for one and three scans, respectively. For power densities lower than 100 MW cm^{-2} the surface roughness of the laser-treated magnesium alloy is observed to be independent of the power density and the number of scans. The surface roughness of magnesium alloy irradiated with three scans is always higher than the surface roughness of magnesium specimen irradiated with

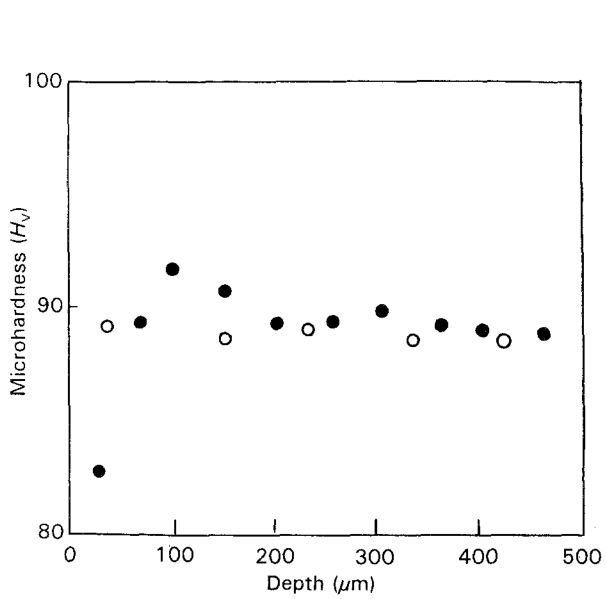

Figure 6 Microhardness as a function of the depth for the (○) as-received and (●) laser-treated magnesium alloy. KrF laser, 20 Hz, 1 scan, 10 pulses/step.

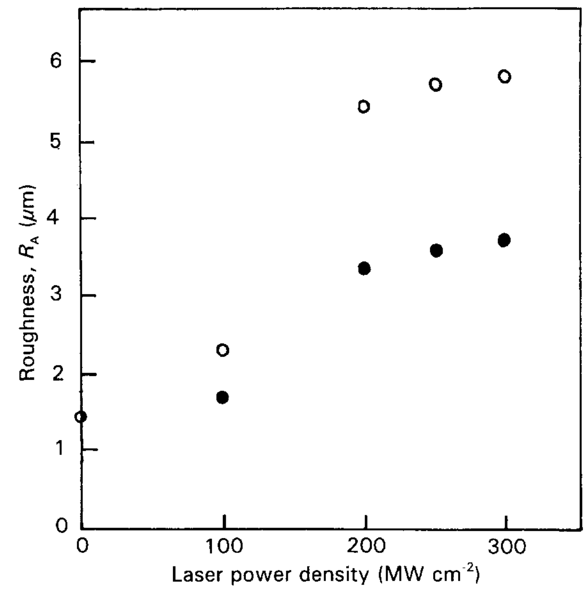

Figure 7 Surface roughness of KrF laser-treated (20 Hz) magnesium as a function of the incident laser power density for 10 pulses and (●) 1 scan and (○) 3 scans.

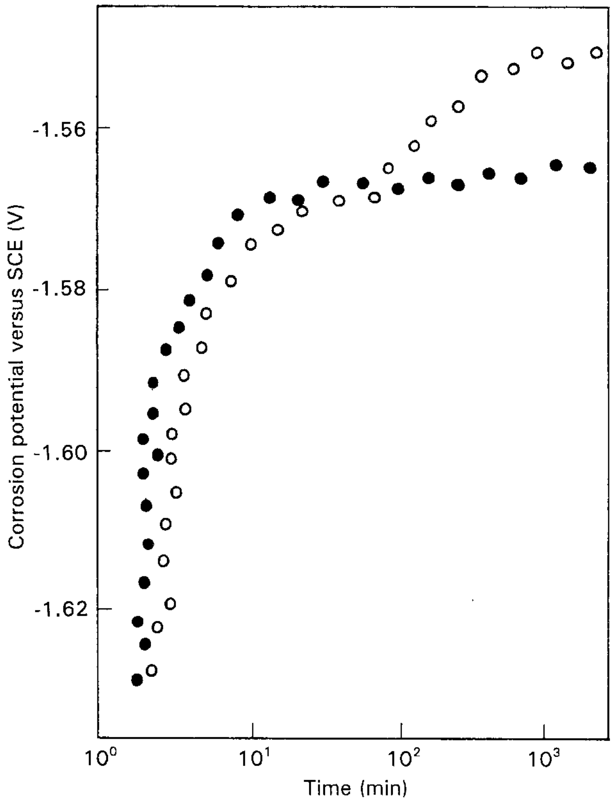

Figure 8 Plot of corrosion potential versus time for the (○) as-received magnesium alloy specimen, and (●) laser-treated magnesium specimen, with 200 MW cm^2 power density, in 0.5 M NaCl.

only one scan. This increase of surface roughness may be attributed to the fact that each laser scan causes a pretreatment of the surface for the following laser scans. In particular, the initial laser scans roughen the specimen surface and therefore significantly decrease the magnesium reflectivity resulting in a higher absorption of the incident laser energy. A controlled surface roughness can be obtained by adjusting the overlap of the steps during laser irradiation. An increase of the overlap percentage reduces the surface roughness of the laser-treated magnesium alloy. This observation may be attributed to the higher homogeneity in irradiation achieved by appropriate adjustment of the overlap of the steps during laser scanning.

The corrosion of the laser and non-laser-treated specimens was examined in a 0.5 M NaCl solution of pH = 10 at 290 K. The specimens were immersed in the solution and the corrosion potential of the immersed specimen was monitored as a function of immersion time; the corrosion potentials were measured with a high impedance acquisition system. The equilibrium (steady-state) corrosion potentials were read from the horizontal portion of the corrosion potential curve.

Fig. 8 shows open-circuit corrosion potentials for the magnesium alloy and its laser-modified surface. The potential curve of the non-laser-treated magnesium is moving towards more positive values which means that passivation of this specimen occurs with increasing corrosion time. The corrosion potential of AZ31B alloy against SCE is 1.55 V. A similar corrosion behaviour was observed for the magnesium alloy laser-treated with 200 MW cm^{-2}. The corrosion potential of the laser-treated specimen became more noble than the potential of the untreated specimen after 80 min testing. The equilibrium potential of the laser-treated alloy against SCE was found to be 1.57 V or approximately 20 mV nobler than that of the conventional alloy.

Magnesium forms a protective hydroxide film in aqueous environments according to the following reaction

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2 \qquad (1)$$

The magnesium hydroxide film is extremely protective, but is quite responsive to electrochemical and environmental changes [10]. Where this protective scale is broken off from the magnesium surface, hydrogen evolves vigorously because fresh metal reacts with the water according to Reaction 1. Hydrogen evolution was observed during the corrosion testing.

In the presence of chloride anions, a soluble magnesium salt is formed at the metal–solution interface as follows

$$Mg_{(c)} + 2Cl^-_{aq} \longrightarrow MgCl_{2(c)} + 2e^- \qquad (2)$$

This soluble magnesium salt damages the protective $Mg(OH)_2$ film and the exposed metal reacts with the electrolyte (self-dissolution) at sites where the protective scale is broken off, thus increasing the corrosion rate [11]. However, it has been reported that at low chloride levels, similar to those of our solution, the above mechanism is negligible and, consequently, ennoblement of the metal is still observed [12].

In the case of the AZ31B magnesium alloy the bulk matrix, which has a small aluminium content, is anodically more active than the $Mg_{17}Al_{12}$ (β-phase). Beck and Chan [12] have found that magnesium passivates also as a result of $MgCl_2$ precipitation. The improved corrosion behaviour of the laser-treated magnesium alloy may be attributed to the microstructural refinement due to rapid solidification caused by the laser

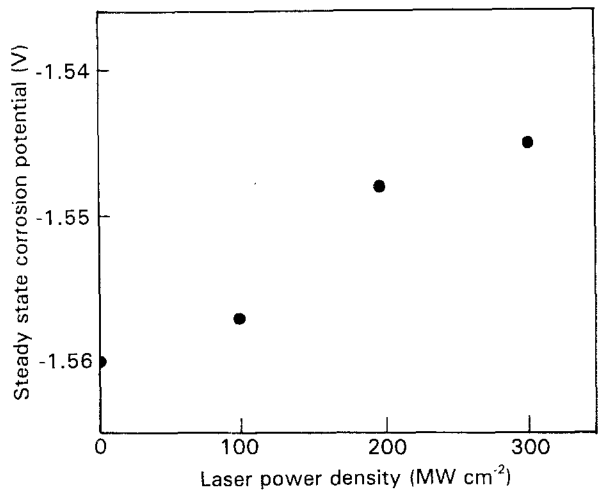

Figure 9 Plot of steady-state corrosion potential versus laser pulse power density. KrF laser, 20 Hz, 1 scan.

treatment. Similar observations are reported elsewhere in the literature for magnesium alloys irradiated with CO_2 lasers [13, 14].

The steady-state corrosion potentials become considerably nobler with increasing laser power densities, as shown in Fig. 9. This observation indicates that the increase of laser power density enhances rapid solidification phenomena and, consequently, the microstructure is expected to be refined at greater depths, resulting in raising of the corrosion resistance of the irradiated alloy.

Consequently, the improved corrosion resistance caused by the laser irradiation may be attributed to the following reasons:

(a) the inherent rapid solidification involved in laser processing results in microstructural refinement which is reported to improve the corrosion resistance of magnesium alloy specimens [12];

(b) the increased cooling rates related to the laser treatment, help the β-phase ($Mg_{17}Al_{12}$) to precipitate forming a discontinuous network enveloping patches of the matrix alloy. The corrosion behaviour of magnesium alloys is basically controlled by the electrochemical properties of $Mg_{17}Al_{12}$ intermetallics relative to the electrochemical behaviour of the matrix alloy. Therefore, the distribution of β-phase has a beneficial effect on the corrosion resistance of the alloy.

4. Conclusions

1. The surface of laser-treated magnesium alloy showed a wavy topography consisting of successive "valleys" and "hills".
2. The surface roughness of the irradiated magnesium alloy was found to depend on the laser power density and the overlapping of successive laser pulses.
3. The surface layers of the irradiated specimens were observed to be under lower tensile stress than the surface layer of the non-laser-treated specimens.
4. The microhardness of the laser-treated alloy was found to be lower in the first 30 μm below the surface (laser-affected zone), being approximately constant at greater depths.
5. The laser-treated magnesium alloy exhibited higher corrosion resistance in comparison with the untreated one. The corrosion behaviour of the irradiated specimens was found to be related to the power density of the incident laser pulses.

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