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Excimer laser surface treatment of magnesium alloy WE43 for corrosion resistance improvement

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Magnesium alloys are of paramount interest to the aerospace and automotive industries because their density is only two-third of aluminum alloys. Among the many magnesium alloys, WE43 is an yttrium-containing cast and wrought alloy with excellent retention of properties at elevated temperatures up to 300 °C [1]. Comparative studies have shown that when subjected to immersion tests in NaCl solution or salt spray tests, the corrosion resistance of WE43 is measurably better than many of the current magnesium alloys [2, 3]. Notwithstanding the relatively good corrosion resistance of WE43 alloy, there is no doubt that prevention measures, such as surface treatments and/or coatings are still needed, if the alloy is to be widely used for engineering applications. Laser surface melting (LSM) is a versatile and promising technique which has been used to improve the corrosion resistance of light alloys [4–6]. In the present study, an excimer laser was used, which is unique for surface modification thanks to the laser emission in the ultraviolet (UV) range and the extremely short pulse duration in the range of nanoseconds. It is envisaged that the inherently high cooling rate of the process would result in a shallow melted zone which is largely free from constituent particles. This should improve the resistance of pitting corrosion of the alloy.

The WE43 alloy (4.1%Y-2.3%Nd-1.0%HRE-0.5Zr) was heat-treated to the peak-aged condition. The laser treatment was conducted using an excimer laser which was operated at an irradiation wavelength of 248 nm. The laser pulse duration and frequency were fixed at 25 ns and 50 Hz, respectively; while the laser energy (E) was set at a constant of 6 J/cm^2. The laser scanning speeds (V) employed were 2 mm/s and 10 mm/s. Laser surface treatment was performed under a flow of nitrogen gas at a rate of 35 L/min. Potentiodynamic electrochemical corrosion measurements were made with a scan rate of 1 mV/s. The electrolyte was a solution of 3.5% NaCl with an initial pH value of 6.8. The microstructure of the WE43 alloy consists of a recrystallized grain structure with a dispersion of second phase particles. The EDAX analysis revealed that the particles are the $Mg_{12}Nd$ phase, which agrees with the results suggested by Valente [3]. To reveal the effect of second phase particles on the corrosion behaviour of the material, a droplet of 3.5% NaCl solution was applied to the surface of an untreated specimen. An observation under the optical microscope shows that hydrogen bubbles were initiated immediately at second phase particles. This illustrated that the particles served as cathodes with respect to the matrix. Fig. 1 shows that after 10 min of immersion in a 3.5% NaCl solution, localized dissolution of the matrix had occurred around the particles, indicating that micro-cells have been established between the particles and the adjacent matrix. No apparent attack was found at the particle-free areas.

Within the range of laser parameters employed in this study, a melt-layer in the range of 1.5–2 μm thick was obtained. The cross-sections of the specimens that were treated using a pulse laser energy density of 6 J/cm^2 with scanning speeds of 2 mm/s and 10 mm/s, are shown in Fig. 2a and 2b, respectively. It is apparent from Fig. 2a that under the condition of a relatively low scanning speed, the portion of $Mg_{12}Nd$ particle that lay within the laser-melted layer had been virtually dissolved away. On the other hand, for the specimen that was treated at a high scanning speed of 10 mm/s, only partial melting of the particle occurred.

A comparison of the typical potentiodynamic polarization curves of the untreated and laser-treated specimens are presented in Fig. 3. The curves of the laser-treated specimens were displayed to the left to that of the untreated specimen. Compared to the untreated specimen, all the laser-treated specimens have considerable lower anodic and cathodic reaction currents, indicating an improvement in corrosion resistance was obtained. Previous studies have shown that when magnesium-based materials were irradiated by excimer lasers in a nitrogen atmosphere, fine particles of magnesium oxides and nitrides could be formed [7, 8]. The reduction in anodic current is considered to be attributed to the presence of fine magnesium oxides and nitrides at the surface of the laser-melted layer, while the decrease in cathodic activities is believed to be due the reduction of cathodic particles in the laser-modified layer. The corrosion current of the laser-treated specimens was found to be much lower than that of the untreated specimen. The lowest corrosion current was obtained for the specimen treated using a low scanning speed of 2 mm/s. In this case, the current was some one order of magnitude lower than that of the untreated specimen. As the scanning speed was increased

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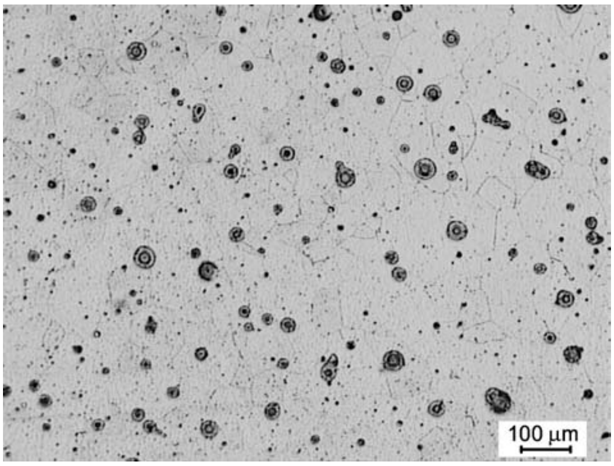
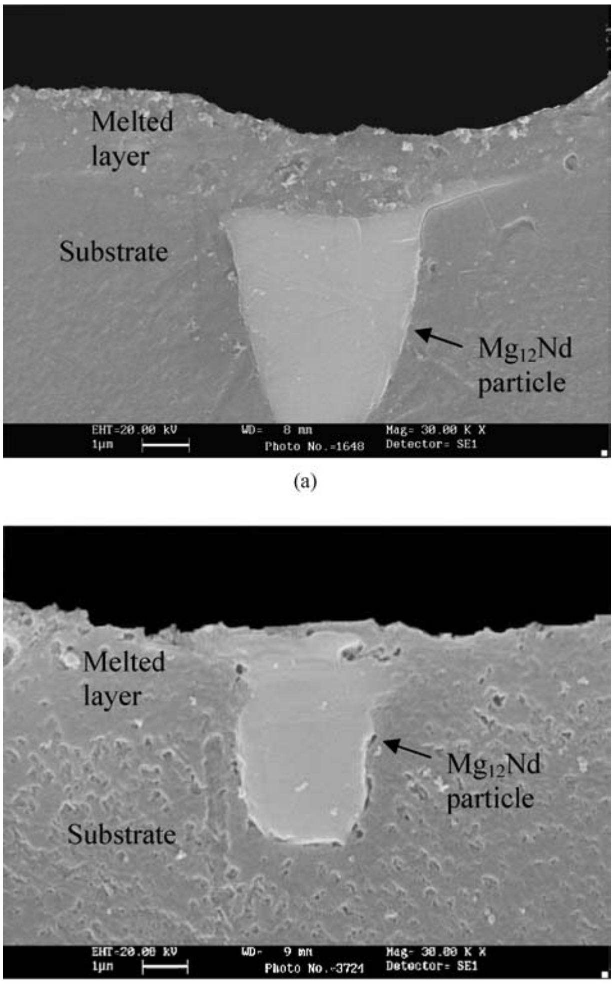


Figure 1 Pitting corrosion was evident at sites of second phase particles after 10 min of immersion in 3.5% NaCl solution.



(a)

(b)

Figure 2 Cross-sections of the laser-treated specimens produced using different processing parameters (a) $E = 6$ J/cm^2, $V = 2$ mm/s; (b) $E = 6$ J/cm^2, $V = 10$ mm/s.

to 10 mm/s, the corrosion current was also increased, but it was still two times less than that of the untreated specimen. The results thus show that laser scanning speed has a significant effect on corrosion current when a relatively low pulse energy density was used. This suggests that accumulative melting of the second phase particles resulting from a low scanning speed can reduce the corrosion current of the alloy. The superior

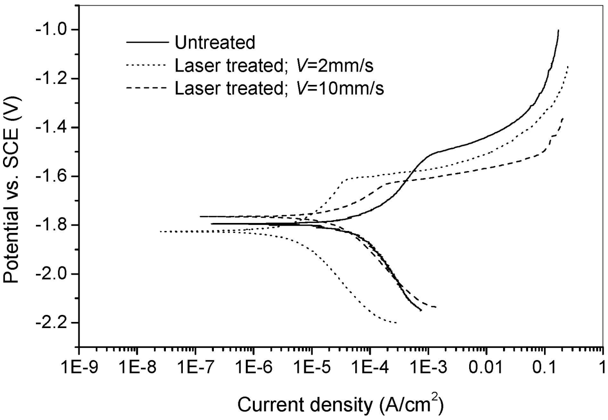
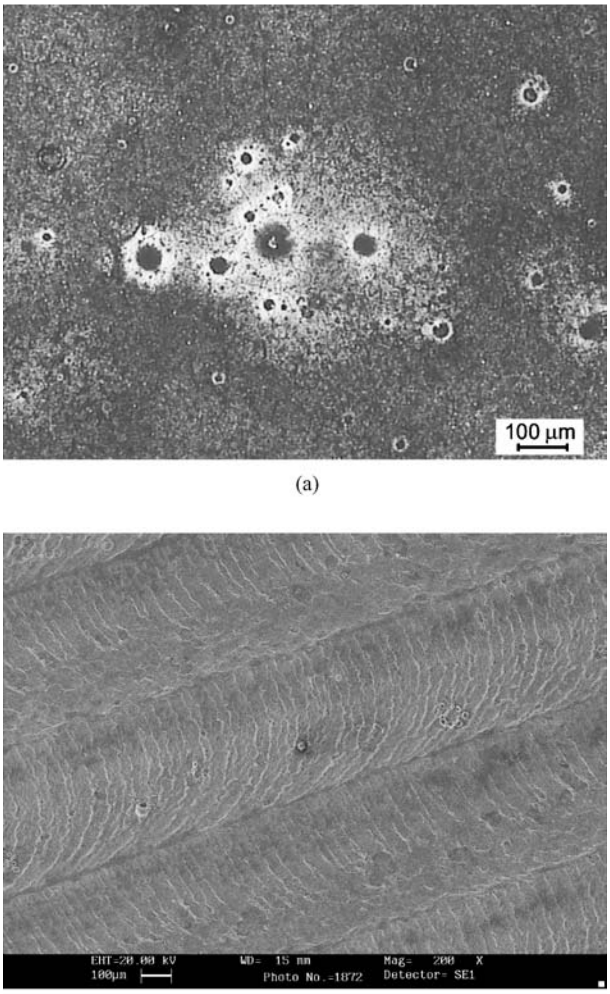


Figure 3 Potentiodynamic polarization curves of the untreated specimen and laser-treated specimens ($E = 6$ J/cm^2).



(a)

(b)

Figure 4 After 4 h immersion in 3.5% NaCl solution (a) the untreated specimen, (b) the laser-treated specimen ($E = 6$ J/cm^2).

corrosion properties of the laser-treated specimens can be demonstrated by the results of the immersion test, where both the untreated and laser-treated specimens were immersed in a 3.5% NaCl solution for 4 hr. Fig. 4 clearly shows that severe corrosion pitting attacks had occurred to the untreated sample, and magnesium hydroxides were formed around the second phase particles, while only few small pits developed in the laser-treated specimen.

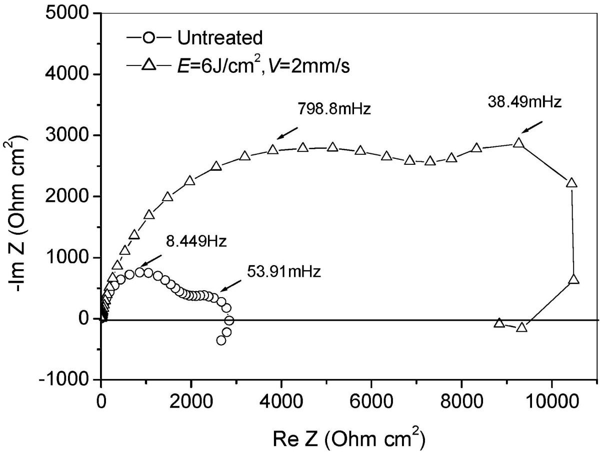


Figure 5 Nyquist plots for the untreated specimen and the laser-treated specimen ($E = 6$ J/cm^2, $V = 2$ mm/s).

The corrosion behavior of the specimens was also studied by means of electrochemical impedance spectroscopy (EIS). The measurement of impedance was made under the condition of open-circuit potential with the application of a small sinusoidal perturbation signal of 5 mV; the frequency used was ranging from 10^5–10^{-2} Hz. Fig. 5 shows the Nyquist plots for the untreated and the laser-treated specimen. Both plots consist of two capacitive loops, one at the high-frequency range and the other at the medium-frequency range. In addition, an inductive loop appears at low frequencies. The high-frequency loop is the contribution of both the charge transfer process and the film effect, while the medium frequency loop is due to mass transport in the solid phase, i.e. the diffusion of Mg^{2+} through the corrosion product. The inductive loop is believed caused by the relaxation processes of adsorbed species [9]. An equivalent circuit was used to fit the EIS data of the high-frequency loop; the high-frequency resistances calculated for the untreated and laser-treated specimens were 1817 (Ω cm^2) and 7608 (Ω cm^2), respectively. The increase in corrosion resistance of the laser-treated specimen at high frequencies can be explained by an increase in charge transfer resistance. This could well be related to the dissolution of cathodic particles, i.e. $Mg_{12}Nd$ as a result of the laser treatment, and as such a homogenized microstructure was obtained. This is consistent with the results of the potentiodynamic test.

Acknowledgments

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