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Improved corrosion and wear resistance of Mg alloys via laser surface modification of Al on AZ31B

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ABSTRACT

A highly intense laser beam from a continuous wave diode-pumped ytterbium laser source was used to synthesize a corrosion and wear resistant aluminum coating rich in $Al_{12}Mg_{17}$ intermetallic phase by direct melting of aluminum precursor powders on AZ31B Mg alloy substrates. The coating composition and microstructure were studied by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and high resolution energy diffraction spectroscopy in a transmission electron microscope. From X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy diffraction spectroscopy analysis it was confirmed that laser processing resulted in uniform distribution of a highly corrosion resistance $Al_{12}Mg_{17}$ intermetallic phase within the coating. The effect of this type of coating on the corrosion and wear resistance of the Mg alloy is investigated in the current study. Under the set of laser processing parameters employed in the current work, no significant change in microstructural and phase evolution and thereby corrosion and wear performance was observed for the laser processed samples. In general improved corrosion resistance was observed for the laser processed samples as compared to the untreated AZ31B. Also, as the precipitation of an intermetallic phase is expected to strain harden the matrix, an improvement in dry sliding wear was observed for the laser processed samples.

1. Introduction

Magnesium alloys are the lightest structural materials with a number of desirable properties such as low density, high specific strength, excellent castability, machinability and damping characteristic [1]. Moreover, these alloys are non-magnetic, have good thermal and electrical conductivity and good vibration and shock adsorption ability [2]. As a result, magnesium alloys are finding a wide range of applications as structural material in the aerospace, electronics and automobile industries.

However, magnesium is highly reactive and is prone to atmospheric and galvanic corrosion. The poor corrosion resistance of Mg is due to the lack of formation of self-healing passive surface film, as a result of the misfit between the hydroxide lattice [$Mg(OH)_2$] in the surface region and the lattice of the bulk material [3]. Apart from its poor corrosion resistance Mg alloys are also known to have a low wear resistance [4–6]. Hence, this poses a concern for the safe use of magnesium and its alloys for practical applications. Protective surface treatments of magnesium alloys such as chemical conversion coatings, metal coating and paint coating, anodizing and plating have been investigated for improving the corrosion resistance of these alloys [7]. Anodizing with chromate solution has been shown to be effective for improving the corrosion properties but is hazardous to the environment [8–10]. Non-chromate coatings, though nontoxic, have proved to be less reliable as compared to chromate coatings. Further, various other surface modification techniques have also been tried to improve both the wear and corrosion properties of these alloys as reviewed by Gray et al. [11]. Among these techniques, laser surface modification was considered as a promising surface engineering tool for corrosion and wear resistance applications, owing to the advantageous features listed below [12,13]:

1. Localized heating from the laser beam results in reduced thermal distortion and size of the heat affected zone and thereby do not alter the bulk properties of the material;
2. Refinement and homogenization of microstructure in the laser processed regime leads to improved mechanical properties and corrosion resistance;
3. Controlled levels of dilution within the coating and metallurgical bonding at the interface;
4. The ability to synthesize novel corrosion and wear resistance phases due to the non-equilibrium nature of the process.

Hong Ye and coauthors [14] deposited a layer of Al on AZ31 Mg alloys by thermal spray technique and then laser melted the Al-rich layer using a CO_2 laser to synthesize a highly corrosion and wear

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resistant surface. The authors attributed the improved corrosion resistance to the presence of $Al_{12}Mg_{17}$ intermetallic phase formed within the coating. Another similar work by Ignat et al. [15] demonstrates a side injection laser cladding and alloying of Al powders on Mg alloy substrates to improve their surface properties. The authors reported an increased hardness in the modified region owing to the presence of Al_3Mg_2 and $Al_{12}Mg_{17}$ intermetallic phases within the coatings. Because of the above advantageous features associated with laser surface modification, in the present study, an attempt was made to improve the corrosion and wear properties of AZ31B (an all-purpose wrought Mg alloy with good strength and ductility) by employing a laser direct melting technique. Here a highly intense laser beam was used to melt the pre-sprayed Al precursor powder on AZ31B Mg alloy and thereby synthesize a highly corrosion and wear resistant surface. One of the major advantages associated with the laser direct melting technique is the control over the laser processing parameters to precisely mitigate the laser material interaction and thereby synthesize a surface having uniform composition and morphology. Unlike, laser cladding where the surface morphology or uniformity of the coating surface largely depends on the powder flow rate and agglomeration of the precursor, here by having pre-sprayed surface such factors can be completely avoidable.

2. Materials and methods

2.1. Sample preparation and Al coatings on AZ31B Mg alloy

The material selected for this study was magnesium alloy AZ31B. The chemical composition of this alloy is listed in Table 1. Substrate coupons of AZ31B (50 mm × 50 mm × 7 mm) were cut from the rolled and heat treated sheets using a low speed diamond saw. The cut coupons were prepared for coating by initially polishing using 30 μm grit silicon carbide emery followed by ultrasonic rinsing with acetone. Aluminum (Al) powder of 99.5% purity and −325 mesh obtained from Cerac specialty inorganics (Milwaukee, Wisconsin, USA) were used as the precursor material. The Al precursor powder was mixed in a water-based organic solvent LISI W 15853 obtained from Warren Paint and Color Company (Nashville, TN, USA). The mixed slurry of ~99.0 vol.% precursor powder was then sprayed onto the substrate coupons using an air-pressurized spray gun. The sprayed coupons were air dried for 24 h to remove the moisture and a uniform thickness of approximately 200 μm was maintained for the pre-coating deposits. The coating thickness was measured by scratching of the preplaced precursor at one corner and measuring the change in depth of focus using an optical microscope. The pre-deposited sample surfaces were then processed using a 3 kW IPG Photonics continuous wave (CW) diode-pumped ytterbium laser operated in the infrared region with a wavelength of 1070 nm. The laser beam from the laser system was transferred to the sprayed coupons using a fiber optic beam delivery cable interfaced with a Scanlab X–Y scanning mirrors. The spot diameter of the circular laser beam at the surface of the work piece was maintained at 1 mm and the safe working distance (distance between the work piece and lens assembly) was kept at 509 mm. The processing parameters used for the coating process are illustrated in Table 2.

2.2. Phase, microstructural, and elemental characterization

Phase evolution in the laser processed samples, and the phase constitution in untreated Mg alloy and Al powder were studied using a Rigaku III Ultima X-ray diffractometer (XRD) with Cu Kα radiation of wavelength 0.15418 nm. The XRD system was operated at 40 kV and 44 mA in a 2θ range of 20–90° using a step size of 0.025° and a scan speed of 4°/min. Subsequent to background correction carried out using standard software (JADE), the phases present were identified by comparing the XRD pattern with standard ICDD (International center for diffraction data) files obtained from the joint committee of powder diffraction standards (JCPDS).

Table 1
Chemical composition of the material (wt.%).

Al	Zn	Mn	Fe	Ni	Cu	Si	Ca	Mg
2.98	0.97	0.004	0.007	0.005	0.002	0.02	0.05	Bal

Table 2
Laser parameters used for the study.

Average power (Watts)	600, 700 and 800
Laser scan speed (mm/s)	20
Working distance (mm)	509
Spot diameter on the surface (mm)	1000 μm
Input power density (W/m^2)	7.6×10^8, 8.9×10^8, 1.02×10^9
Lateral track overlap/hatching distance (mm)	0.5

For microstructural observation in the cross-section of laser processed samples, the samples were initially sectioned perpendicular to the laser track using a low speed diamond saw. The sectioned samples and an unprocessed Mg alloy were then polished with emery papers of different grits ranging from 200 to 1000 μm in succession, followed by disk polishing with colloidal silica of 0.3 μm and 0.05 μm to get a mirror-finished surface. The polished samples were then cleaned with acetone and etched with an etchant constituting of a mixture of 59 vol.% $C_2H_6O_2$, 20 vol.% CH_3COOH, 20 vol.% H_2O and 1 vol.% HNO_3 for approximately 15 s by immersion etching to reveal the microstructural features. The microstructural analysis was then carried out using a FEI Quanta 200 environmental scanning electron microscope (ESEM) under low vacuum. The semi-quantitative elemental analysis of the laser processed samples was conducted using an Energy-Dispersive X-ray Spectroscopy (EDS) detector attached to the SEM instrument.

The coatings from selected laser fluences were also characterized using a FEI Tecnai field emission gun transmission electron microscope (TEM) for high resolution EDS analysis and bright field images, and thereby precisely understand the distribution of elements and formation of phases within the coatings. The TEM analysis in the current work was performed at an accelerating voltage of 200 kV. The sample preparation for TEM analysis was carried out using a lift out technique from a desired location in a FEI Nova 200 Dual Beam FIB (Focused Ion Beam) source. The samples were finally polished using 5 kV Gallium ion source to minimize the effects of beam damage.

2.3. Electrochemical tests

For electrochemical studies, circular samples measuring 1 cm in diameter were cut from the laser treated samples and from the base (untreated) AZ31B sheets. The samples were cleaned with acetone before testing. Potentiodynamic polarization tests were conducted to study the anodic polarization behavior of the aluminum coated AZ31B and untreated AZ31B samples in 3.5% NaCl solution. In order to see the environmental parameters of the sample in the NaCl solution, the pH of the solution was measured prior to the tests and was found to be 6.8. Electrochemical experiments were carried out using the computer controlled VersaStatII, Potentiostat/Galvanostat (EG&G, Princeton Applied Research). The reference electrode used for these tests was a saturated calomel electrode (SCE) whereas graphite rod was used as a counter electrode. Initially the open circuit potential was measured for each sample, after which the anodic polarization scan was started at a potential 250 mV below the corrosion potential measured. The potential scan rate for all the potentiodynamic polarization tests were 1 mV s^{-1}. All the electrochemical