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Microstructures and properties in surface layers of Mg−6Zn−1Ca magnesium alloy laser-clad with Al−Si powders

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Abstract: Laser surface cladding with Al−Si powders was applied to a Mg−6Zn−1Ca magnesium alloy to improve its surface properties. The microstructure, phase components and chemical compositions of the laser-clad layer were analyzed by using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). The results show that the clad layer mainly consists of α-Mg, Mg_2Si dendrites, $Mg_{17}Al_{12}$ and Al_3Mg_2 phases. Owing to the formation of Mg_2Si, $Mg_{17}Al_{12}$ and Al_3Mg_2 intermetallic compounds in the melted region and grain refinement, the microhardness of the clad layer ($HV_{0.025}$ 310) is about 5 times higher than that of the substrate ($HV_{0.025}$ 54). Besides, corrosion tests in the NaCl (3.5%, mass fraction) water solution show that the corrosion potential is increased from −1574.6 mV for the untreated sample to −128.7 mV for the laser-clad sample, while the corrosion current density is reduced from 170.1 to 6.7 μA/cm^2. These results reveal that improved corrosion resistance and increased hardness of the Mg−6Zn−1Ca alloy can be both achieved after laser cladding with Al−Si powders.
Key words: laser cladding; Mg−6Zn−1Ca alloy; microstructure; hardness; corrosion resistance

1 Introduction

As promising lightweight materials, magnesium alloys have been widely used in many fields, such electronic, automotive and aerospace industries, due to their high specific strength and low density [1,2]. Besides, magnesium alloys have many other advantages, such as excellent machinability, good castability, hot formability and recyclability. However, magnesium alloys also suffer from some disadvantages. For example, magnesium alloys have low hardness, poor wear and corrosion resistance, which greatly limit their further applications in industries [3,4]. Considering that these shortcomings are always related to the surface states, different surface treatment methods, such as physical and chemical depositions, micro-arc oxidation, laser cladding, painting, and ion implantation, have been applied to magnesium alloys in order to improve their surface properties [5−11].

As one of the efficient surface treated techniques, laser treatment has been widely utilized to process many kinds of metals and alloys [12−15]. The advantages of laser surface treatment include thick treated layer, fine microstructure, good metallurgical bonding with substrate, etc. In particular, fiber laser shows better application performances than CO_2 laser with high output power, high conversion efficiency, high beam quality and stable power. HAZRA and MONDAL [14] revealed that the wear resistance of the MRI 153M magnesium alloy was improved by an order of magnitude after laser cladding with Al+Al_2O_3. However, the corrosion resistance of the alloy was deteriorated owing to the presence of cracks and pores in the clad layer. TAN et al [16] have investigated the laser cladding of an AZ80 Mg alloy with Al−Cu−Zn powders under water cooling conditions. The results showed that the laser-clad layer had higher microhardness and wear/corrosion resistances of the alloy were significantly improved as a result of the formation of Al-based amorphous−nanocrystalline composite coatings. WANG and LI [17] reported that wear and corrosion resistances

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of the AZ91HP magnesium alloy were improved by laser surface cladding with eutectic-based Ti−Ni−Al alloy. These results showed the high potential of laser surface treatments on improving surface properties of Mg alloys.

Mg−Zn−Ca ternary alloys are considered as good heat-resistance materials and bio-medical materials. Previous investigations on Mg−Zn−Ca ternary alloys mainly focused on microstructural characterizations, aging behaviors [2] and corrosion behaviors in Hank's solution [18,19]. However, the effects of surface modifications on microstructure and properties of Mg−Zn−Ca ternary alloys were not well studied. In this work, the laser surface cladding was firstly applied to a Mg−6Zn−1Ca magnesium alloy by using a fiber laser apparatus. In previous works, laser cladding with Al−Si powders was proven to be able to improve significantly the surface properties of Mg-based alloys and composites [20,21]. By considering this, the effects of the scanning speed on the microstructure, microhardness and corrosion resistance of a Mg−6Zn−1Ca alloy laser-clad with Al−Si powders were carefully investigated.

2 Experimental

2.1 Sample preparation

In the present work, the selected substrate material is the Mg−6Zn−1Ca Mg alloy, which contains about 6% Zn and 1% Ca (mass fraction). The thickness and diameter of the cylinder specimens are 10 and 35 mm, respectively. In order to obtain a clean and smooth surface, these specimens were all ground with 800-grit SiC sand paper and washed with ethanol before laser cladding. For the laser cladding treatments, the powders used in this work are commercial pure aluminum (≥99% purity) and silicon (≥99% purity) powders. Their average particle size is 75 μm. The two kinds of powders were mixed through ball-milling for 6 h with an Al to Si mass ratio of 3:1 [22]. In the end, the mixed powder was put on the substrate surface and compressed to a thickness of about 0.5 mm.

The laser cladding treatments were carried out using an IPG−YLS−5000W fiber laser (wavelength of (1075±5) nm) with the maximum output power of 5000 W. The beam is quadrate with a size of 5 mm × 5 mm and the laser cladding process was done under an argon shielding gas of 20 L/min. The scanning rate ranges from 4 to 6 mm/s with a fixed output power of 2500 W.

2.2 Microstructure analyses

In order to observe the morphology and the microstructure of the laser-clad layer from top surface to the bottom of the clad layers, the treated specimens were cut perpendicular to the scanning direction. After that, the cross sections of the specimens were ground and polished with diamond paste down to 2.5 μm. Then, the samples were cleaned with pure ethanol. In the end, the cleaned specimens were etched by an alcohol + nitric acid (volume ratio of 96:4) solution and completely dried in air. An AS−3400 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS) was used to examine the microstructure and compositions of the laser-clad layers. X-ray diffraction (XRD) measurements were carried out using a Shimadzu D−6000 goniometer equipped with a Cu K_α radiation source to detect the phase components in the surface of the laser-clad layers.

2.3 Surface properties

A HXD−1000 microhardness tester with Vickers indenter was used to measure the microhardness of the laser-clad specimens from the cross sections. The measurements were done with a load of 0.25 N and the loading time was set to be 15 s ($HV_{0.025}$/15). The cross section microhardness profiles were obtained by doing at least five parallel measurements at certain depth and getting the average value.

The potentiodynamic polarization measurements were performed in a standard three-electrode cell using a saturated calomel electrode as a reference electrode. Before the corrosion test, the surfaces of specimens were ground and polished with diamond paste to 2.5 μm and cleaned in pure ethanol. The corrosion tests were carried out in a 3.5% NaCl (mass fraction) water solution. The exposed area for the corrosion measurements was about 0.25 cm^2. The temperature of the solution was kept at room temperature. The potentiodynamic polarization curves were measured with a scanning rate of 0.001 mV/s. The cathodic polarization scanning started from −1872 mV (vs SCE) for the Mg−6Zn−1Ca magnesium alloy and from −500 mV (vs SCE) for the laser-clad specimens. The samples were dipped into the NaCl solution until a steady corrosion potential was achieved, and then the anodic polarization scanning was started. Afterward, the polarization curves were used to evaluate the corrosion current density (J_{corr}) and the corrosion potential (φ_{corr}) by Tafel extrapolation.

3 Results and discussion

3.1 XRD analysis

Figure 1 shows the X-ray diffraction patterns of the untreated sample and the laser-clad samples with different scanning speeds. The untreated Mg−6Zn−1Ca alloy contains α-Mg as the majority phase and Mg_2Zn and $Ca_2Mg_6Zn_3$ as the minority phases, as shown in Fig. 1. The XRD results also indicate that the clad layers are mainly composed of α-Mg and some intermetallic