Laser Forming of Zr-Based Coatings on AZ91D Magnesium Alloy Substrates for Wear and Corrosion Resistance Improvement

T. M. Yue and K. J. Huang

The Hong Kong Polytechnic University, Hung Hom, Hong Kong, P.R.China

To improve the wear and corrosion resistance of AZ91D magnesium alloy, Zr-based coatings were fabricated on the alloy substrate using laser forming. They were prepared from (i) Zr+Mg powders (5 : 1 mass%), and (ii) an undercoating of Zr+Mg powders (5 : 1 mass%) with a top layer of Zr powder. The Zr+Mg powder coating was found to consist primarily of Zr particles with some Zr-based intermetallic compounds in a Mg-Al matrix, while that with an extra top coating of Zr powder had an outer layer composed of Zr oxides and Zr aluminides. With regard to wear and corrosion resistance, the highest improvement was obtained for the specimen that was clad with a top layer of Zr powder. Compared to the AZ91D specimen without a laser formed coating, a fivefold decrease in weight loss and around three orders of magnitude decrease in corrosion current density respectively were obtained. [doi:10.2320/matertrans.M2010274]

Keywords: laser processing, magnesium, biomaterial, zirconium coating, wear, corrosion

1. Introduction

It is well established that ceramics, metals, polymers and their composites can serve as biomaterials. Among these, metals such as stainless steels, titanium alloys and cobalt-based alloys are suitable for load-bearing applications due to a combination of high mechanical strength and excellent fracture toughness. However, conventional metallic biomaterials have a risk of releasing toxic metallic ions and/or fracture toughness. However, conventional metallic biomaterials have a risk of releasing toxic metallic ions and/or particles through corrosion or during the wear process, and the elastic moduli are not well matched with natural bone tissue. The latter often causes stress shielding which can lead to reduced stimulation of new bone growth and remodeling, and as a result decreases implant stability.

Searching among the existing commercially available metals and alloys, it is not difficult to recognize that Mg is probably the most appropriate metal that can best fulfill the density and stiffness requirements. Indeed, as early as 1907, magnesium was reported to have been used as having been secured to fracture of a human leg. Although the attempt failed as the metal corroded too rapidly in vivo, interest in using Mg for orthopedic implants has not faded but still remains strong. Indeed, recently, a considerable number of research activities have generated much interest in developing Mg and its alloys as degradable biomaterials. This is largely due to research results which found that the corrosion rate of Mg and its alloys, when tested in physiological environments, can be modulated through the use of high purity Mg or new alloying systems and surface treatments. It is considered that if the corrosion problem of Mg can be resolved, Mg or its alloys could become good materials for implantation applications.

In the present study, an attempt has been made to fabricate Zr-based coatings on AZ91D magnesium alloy substrates using laser forming. Zr was employed because the metal and its oxides display excellent electrochemical properties and biocompatibility. Although other surface coating techniques, such as PVD, thermal and plasma sprayings can also be used to fabricate corrosion resistant coatings on Mg, they have their own disadvantages. The drawbacks of thermal spraying and plasma spraying are the presence of excessive defects such as pores in the coating and weak bonding between the coating and the substrate. While PVD is a line of sight technique so there are limitations on workpiece geometry, also the coating does not form a metallurgical bond with the substrate. The advantages of laser forming are that porosity free products with a strong metallurgically bonded coating interface can be obtained. Moreover, multiple powder compositions can be fed simultaneously or sequentially to form the desired properties at specific locations.

2. Experimental Methods

Laser cladding of Zr and Mg mixed powders was undertaken on AZ91D (Mg-8.9Al-0.6Zn) magnesium alloy substrates. These powders were premixed in a mass ratio of 5 : 1 using a ball mill. The size of the powders was less than 75 μm and the purity was 99 mass%. The powders were delivered into the laser melted pool with a lateral powder feeder driven by a flow of Ar gas. Laser processing was performed using a high power CO₂ continuous wave laser. The laser spot diameter and laser power were kept constant at 3 mm and 1000 W, respectively. A track overlap condition of 30% was used. Specimen 1, which has a Zr-based coating was fabricated from Zr+Mg powders (5 : 1 mass%), while Specimen 2, has a top coating formed by laser cladding of Zr powder on Specimen 1. The thickness of the Zr+Mg undercoating was aimed at approximately 1 mm, while that of the Zr top coating was targeted at about 200 μm. The microstructure of the coatings was examined using a JSM-6490 scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS). A micro-hardness tester using a test load of 100 g and a load-dwell time of 15 s was employed to measure the hardness of the coatings.

The dry sliding wear resistance of the Zr-based coatings as well as the as-received AZ91D material was evaluated using a block-on-ring wear tester. They were made to slide against a rotating ring made of hardened bearing steel AISI52100
with a hardness of 60HRC. The test load used was 98 N, and the relative sliding speed was 0.4187 m/s. The wear test cycle lasted for 4500 s and the corresponding total wear sliding distance was 1884 m. Each test was repeated three times.

Potentiodynamic polarization testing was employed to evaluate the corrosion behavior of the Zr-based coatings. The specimen surface area for the corrosion test was $1.0 \times 10^{-4}$ m$^2$, and testing was conducted in a simulated body fluid, namely Ringer’s solution (8.5 g/L NaCl, 0.25 g/L KCl, 0.22 g/L CaCl$_2$, 0.15 g/L NaHCO$_3$) at pH = 7.4. The test employed a saturated calomel electrode (SCE) as the reference electrode and a platinum counter electrode. Polarization was carried out at a scan rate of 1 mV/s. Before the polarization test, the specimens were kept in the Ringer’s solution for 600 s at 37°C.

3. Results and Discussion

3.1 Microstructure and hardness

Figures 1 and 2 show the microstructure of the coatings of Specimen 1 and Specimen 2, respectively. These figures reveal that dense Zr-based coatings free from major defects can be formed on AZ91D substrates with a metallurgically bonded interface (Fig. 1(a) and Fig. 2(c)). Figure 3 shows a TEM image of an area in the coating of Specimen 1 with the SAED pattern of a Zr particle. Table 1 summarizes the results of the EDS analysis of the Zr-based coatings of both Specimens 1 and 2. The EDS results together with the TEM study suggest that the microstructure of the coating of Specimen 1 mainly consists of Zr particles (Fig. 1(b), position 1) in an Mg-Al matrix (Fig. 1(b), position 2). Although the EDS analysis of a Zr particle shown in Fig. 1(b) reveals the element oxygen, it is considered that it was caused by the oxidation effect of the specimen surface. This is supported by the SAED pattern (Fig. 3) of those particles embedded in the Mg matrix that they are Zr particles and not Zr oxide particles. The Zr particles in Specimen 1 were largely unmelted, and still exhibited the originally angular morphology, except that a small amount of relatively small round shaped particles were found (Fig. 1(b), position 3). The result of the EDS analysis of these round shaped particles showed the presence of both aluminum and oxygen. Therefore it is considered that they were formed when a small quantity of Al reacted with the partially melted Zr powders resulting in some Zr-Al intermetallic compounds with a small quantity of oxygen in the solid solution state. Moving closer to the substrate, the coating contains less Zr powders, and a fine dendritic structure was revealed (Fig. 1(c)). Figure 4(a) shows the hardness values measured across the coatings of Specimen 1. Due to negligible solubility of Zr in Mg, and according to the Zr-Mg phase diagram, no major reaction between these two elements should occur. Since the Zr powder did not, to any significant degree react with Mg and the quantity of Zr-Al intermetallics formed was small, the hardness of the coating was not high and has an average value of 112 HV. This is reasonable because the hardness of the Zr powder was 193 HV while that of the Mg substrate was 64 HV, and a calculation using simple rule of mixture will give the coating a hardness of 102 HV, which is close to that of the measured value. Nonetheless, slightly higher hardness values were obtained between 0.5 mm and 1 mm, this is considered to be due to a refined Mg dendritic and eutectic structure was obtained after laser forming. However, it was noticed that there was a relatively large fluctuation in hardness across the coating. This is believed to be due to the uneven distribution of Zr particles in the coating.

For Specimen 2, the coating was formed by laser cladding of Zr powder on Specimen 1. The results of the EDS analysis (Table 1) together with the coating microstructure presented in Fig. 2(b) suggest that the microstructure of the top coating mainly consists of a two-phase dendritic structure of Zr oxide and Zr$_2$Al. The dendritic structure of the Zr oxide phase suggests that during laser forming of the top layer, the Zr powder would have melted. It was found that no Mg, but Al was detected in this two-phase structure. The explanation is that during laser forming of the top Zr...
higher than that of the Zr\textsubscript{a} dendritic structure because its melting temperature is oxygen enriched liquid will form, which will solidify first as a pool to react with Zr. Now, since oxygen in the surrounding Mg would be vaporized leaving Al in the melt (2740 K). Under such a condition, when Zr was melted, the boiling point of Mg (1380 K), but lower than that of Al melting point of Zr (2125 K), which is higher than the light shallow scoring marks. These marks, as indicated by the untreated AZ91D specimen suffered from abrasive wear with specimens. Figure 6 shows that the worn surface of the material without a coating, i.e. untreated, under dry wear conditions. The weight loss decreased in the sequence of Specimen 1 and Specimen 2, were affected by particles at the surface. It is considered that the majority of these particles are oxides of Zr and Mg, formed as a result of oxidation of Zr particles and the matrix during the sliding action. This wear oxide debris present on the wear tracks could lead to three-body abrasion and as such, could reduce wear rate. Regarding Specimen 2, the wear mode was considered to be mainly of a crack-nucleation type, controlled by the brittleness of the hard two-phase structure which cannot tolerate high plastic strain. The worn surface of Specimen 2 (Fig. 8) shows that the surface contains a fair amount of broken particles; most of these are believed to be wear debris of the two-phase dendritic structure.

Figure 9 shows the potentiodynamic polarization curves of different specimens tested in Ringer’s solution. These test results show that the corresponding free corrosion potentials of Specimen 1 and Specimen 2 are $-1.422\, \text{V}$ and $-1.544\, \text{V}$, which are 161 mV and 39 mV respectively, more positive than that of the untreated AZ91D substrate. While the corrosion current densities of the untreated AZ91D specimen, Specimen 1 and Specimen 2, were $6.079 \times 10^{-2}\, \text{A}\cdot\text{m}^{-2}$, $2.446 \times 10^{-1}\, \text{A}\cdot\text{m}^{-2}$, and $2.004 \times 10^{-3}\, \text{A}\cdot\text{m}^{-2}$, respectively. These results clearly indicate that the corrosion resistance of Specimen 2 is significantly higher than that of the untreated AZ91D material. The corrosion current density of Specimen 2 was more than 3000 times lower than that of the untreated AZ91D material. This can be attributed to the high corrosion resistance of Zr oxides and the Zr\textsubscript{2}Al phase of the coating.\textsuperscript{14,15} Regarding Specimen 1, its corrosion resistance, in terms of corrosion current density, was found to be inferior to the untreated AZ91D material: the corrosion current density of Specimen 1 was about four times higher than that of the untreated AZ91D material. The corrosion current density of Specimen 2 is significantly higher than that of the untreated AZ91D substrate. When the corrosion current densities of the untreated AZ91D specimen, Specimen 1 and Specimen 2, were $6.079 \times 10^{-2}\, \text{A}\cdot\text{m}^{-2}$, $2.446 \times 10^{-1}\, \text{A}\cdot\text{m}^{-2}$, and $2.004 \times 10^{-3}\, \text{A}\cdot\text{m}^{-2}$, respectively. These results clearly indicate that the corrosion resistance of Specimen 2 is significantly higher than that of the untreated AZ91D material. The corrosion current density of Specimen 2 was more than 3000 times lower than that of the untreated AZ91D material. This can be attributed to the high corrosion resistance of Zr oxides and the Zr\textsubscript{2}Al phase of the coating.\textsuperscript{14,15} Regarding Specimen 1, its corrosion resistance, in terms of corrosion current density, was found to be inferior to the untreated AZ91D material: the corrosion current density of Specimen 1 was about four times higher than that of the untreated specimen. This is considered to be due to the presence of some noble Zr particles being embedded in a matrix of Mg-Al. In this situation, galvanic

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Table 1 Results of the EDS analysis of the Zr-based coatings.
corrosion can occur with the dissolution of the matrix. Figure 10 shows the corroded surface of Specimen 1, which reveals that the Mg matrix has been preferentially dissolved.

4. Conclusions

(1) A high wear and corrosion resistant Zr-based graded coating can be fabricated on AZ91D magnesium alloy by laser forming of an undercoating produced from Zr+X%Mg powders with a top layer formed from Zr powder.

(2) The Zr-based coating is mainly composed of Zr oxides and Al-Zr intermetallics.

(3) Under the dry sliding wear condition, the wear resistance of the coating was considerably higher than that of the untreated AZ91D material, and the weight loss of the former was about five times higher than that of the coating.

(4) The coating has superior corrosion resistance when compared to the untreated AZ91D material. The corrosion current density measured for the coating was three orders of magnitude lower than that of the untreated AZ91D material.

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