ENHANCING CORROSION PROTECTION OF AZ91D SURFACE VIA DIFFUSION, PA-PVD AND DUPLEX TECHNIQUE: A COMPARISON STUDY

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Article History: Received 10 September 2018; Revised 20 July 2019;
Accepted 15 October 2020

ABSTRACT: Magnesium and its alloys are widely known metal due to its excellent properties such as low density, high specific strength, and high recyclability. However, its corrosion resistance is low compare to other metals. Thus, in this paper, three techniques known as diffusion, plasma-assist physical vapor deposition (PA-PVD) and duplex were selectively applied onto AZ91D surface as an attempt to enhance its corrosion resistance. For the diffusion, AZ91D was exposed to oxygen gas at a constant rate of 5 scfh at 400°C for 2 hours in a tube furnace. For the PA-PVD, AZ91D surface was deposited with CrO hard coating of 1 to 2 microns in thickness using RF magnetron sputtering. For the duplex, AZ91D surface was treated with a sequential step of diffusion followed by PA-PVD technique. The morphology and elemental composition of AZ91D was analysed using SEM-EDX. The case-depth was evaluated using microhardness tester and its corrosion rate were calculated from the Tafel plot. Results showed that the corrosion rate of AZ91D surface was found to perform best with the diffusion treatment followed by the duplex and the PA-PVD. However, for the duplex, a slightly lower performance of the corrosion rate was notice due to the reduction of the oxide zone thickness underneath the CrO coating caused by the erosion process of ion bombardment during the PA-PVD sputtering process.

KEYWORDS: *AZ91D; Corrosion; Diffusion; Duplex; PA-PVD*

1.0 INTRODUCTION

Magnesium alloy, especially AZ91D is widely applied in the electronic and telecommunication industries due to its low densities, excellent strength to the weight ratio, easier to cast with a thin wall, and good electromagnetic shielding [1]. Among the available materials, such as aluminum alloy, magnesium alloy, and titanium alloy, AZ91D is the best candidate as it can shield electromagnetic emissions because the magnesium alloys that have been utilized in the development of electronic products can absorb electromagnetic waves. Therefore, the material is suitable to be used as chassis in many electronics and telecommunication product such as the walkie-talkie. Furthermore, its high dimensional stability, good machinability, and easy to recycle allow AZ91D to be formed into complex shape [2]. Unfortunately, its poor performance either in wear or corrosion resistance has limited its potential to be used in a more severe application [3-5]. Surface modification has been proved can offer a better solution to Mg and its alloys in enhancing its surface from corrosion [6]. There are many types of surface modification to prevent corrosion such as coating, diffusion, electroplating [7] and the others.

Magnesium AZ91D has many applications, therefore it is subjected to heavy environments and their corrosion behaviour is a major concern. Magnesium is a reactive metal, and its alloys are not corrosion resistant below several aqueous or environmental conditions. The use of magnesium alloys in the telecommunications and automotive industry nowadays is currently limited to the interior components due to poor corrosion behaviour [8]. Improving the corrosion behaviour of magnesium and its alloys is essential for increasing their prospective applications.

One of the many methods that still applicable to enhance its surface corrosion resistance is the diffusion process. It is a process of diffusing gas molecules interstitially at the substrate’s surface to modify the surface properties. Oxygen can diffuse into magnesium surface to form oxidation. In fact, most metals tend to form oxides in oxidizing atmospheres and this tendency will increase with the increasing of temperature [9]. Magnesium surface can easily oxidize in an ambient atmosphere, but the rate of reaction differs depending on the temperature. At elevated temperature, the rate of reaction will increase and more oxide layer will growth to form MgO. This oxide layer then, act as a protective layer in reducing corrosion to growth further [10-11].

During oxidation, the diffusion temperature need to be controlled to preserve the bulk properties of magnesium and it alloys. Most magnesium alloys were oxidized at a temperature lower than 6000°C. Above this temperature, magnesium can transform to a vapour state. Therefore, the oxidation process must be kept below this temperature to avoid extremely changes on their mechanical properties as well as their microstructures [12].

PVD coating is another well-known process that can be applied to protect surface of magnesium and its alloy from corrosion [13-14]. Chromate coating, for an example, is one of the most conventional coating available in surface treatment industries due to its excellent corrosion resistance [15]. This chromate coating therefore, act as a barrier between material surface and its corrosion environment. In this study, the work is focused on comparing the corrosion performance of AZ91D surface among three different available process known as the diffusion, the plasma assist physical vapor deposition (PA-PVD) and the duplex.

Duplex is a combination of two surface treatment process in a sequential step which are, in this case, the diffusion and the PA-PVD.

2.0 METHODOLOGY

2.1 Sample Preparation

Prior to surface treatment process, AZ91D samples were ground with SiC paper to 1200 grit and followed by polishing with 0.05 µm Al_2O_3 paste. Samples were then ultrasonically clean with distilled water in an ultrasonic bath for 5 minutes before dried.

2.2 Diffusion Process

The samples of AZ91D were subjected to the diffusion process, using a Tube Furnace with the following specifications: Model TF70-1600 with 3 kW power, with the tube size of 70mm OD X 60mm ID X 1000mm L. The samples of AZ91D were placed in the tube. Prior to the oxidation process, the tube furnace was cleaned to avoid any contamination to the samples that could interfere with the final results. First, the AZ91D samples were inserted into the tube and special cotton were placed at the inlet and outlet of the tube to avoid temperature leakage during the diffusion process. Then, the tube was closed using a cap with an O ring to avoid gas and temperature leakage. The temperature was set at 400°C and the sample was soaked for 2 hours.

2.3 PA-PVD Coating

The AZ91D surface was deposited with CrO coating using rf-magnetron sputtering equipment. A pure Cr disc of 5 mm in diameter was used as target. The substrate to target distance was kept at 15 cm. prior to deposition; sputter cleaning was carried out with Argon gas for 1 min to avoid contamination [16]. The CrO coating was deposited using the following process parameters: argon gas 50 SCCM, pressure 7.5×10^{-3} Pa. The coating duration was 60 min.

2.4 Duplex Coating

Duplex coating was done by combining the diffusion and the PA-PVD process. Initially, the AZ91D sample was diffused in a tube furnace with a temperature of 400°C for 2 hours. Then, the diffused AZ91D was coated with CrO in the PA-PVD chamber.

2.5 Characterization

The SEM cross-section and the EDX analyses were obtained with JEOL JSM-6010PLUS/LV. Case depth analysis were done using the Mitutoyo microhardness tester with diamond indenter using 5gf as indentation load. The corrosion rate was analyzing using PG STAT 101 corrosion test for all the substrates and the result from the corrosion rate was analyze from the Tafel plot.

3.0 RESULTS AND DISCUSSION

3.1 SEM Cross-Section and EDX Elemental Analysis

Figure 1 shows the comparison on the cross-section and the EDX of untreated AZ91D with the treated AZ91D before corrosion test.

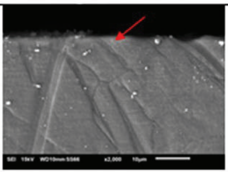
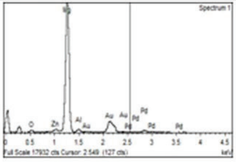
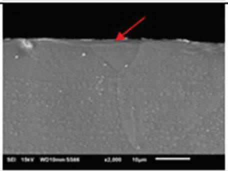
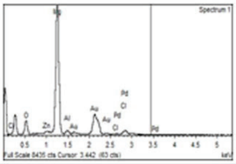
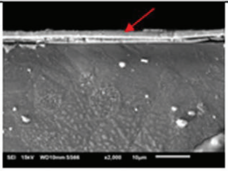
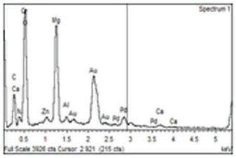
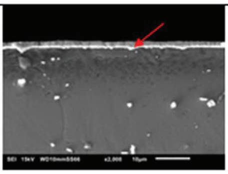
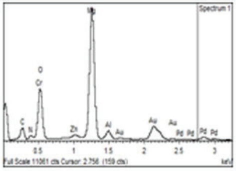
<table>
<tr><th>Surface Treatment Process</th><th>SEM Cross Section Images</th><th>EDX Spectrum</th><th>EDX Elemental</th></tr>
<tr><td>Untreated AZ91D</td><td></td><td></td><td><table><tr><th>Element</th><th>Weight%</th><th>Atomic%</th></tr><tr><td>O</td><td>3.97</td><td>8.36</td></tr><tr><td>Mg</td><td>59.12</td><td>82.01</td></tr><tr><td>Al</td><td>1.81</td><td>2.27</td></tr><tr><td>Zn</td><td>1.61</td><td>0.83</td></tr></table></td></tr>
<tr><td>Diffusion</td><td></td><td></td><td><table><tr><th>Element</th><th>Weight%</th><th>Atomic%</th></tr><tr><td>O</td><td>15.6</td><td>32.59</td></tr><tr><td>Mg</td><td>41.36</td><td>56.85</td></tr><tr><td>Al</td><td>1.47</td><td>1.82</td></tr><tr><td>Cl</td><td>0.58</td><td>0.55</td></tr><tr><td>Zn</td><td>0.84</td><td>0.43</td></tr></table></td></tr>
<tr><td>PA-PVD</td><td></td><td></td><td><table><tr><th>Element</th><th>Weight%</th><th>Atomic%</th></tr><tr><td>C</td><td>0.00</td><td>0.00</td></tr><tr><td>N</td><td>6.51</td><td>12.74</td></tr><tr><td>O</td><td>34.11</td><td>58.40</td></tr><tr><td>Mg</td><td>11.48</td><td>12.93</td></tr><tr><td>Al</td><td>0.61</td><td>0.62</td></tr><tr><td>Ca</td><td>0.49</td><td>0.33</td></tr><tr><td>Cr</td><td>19.56</td><td>10.30</td></tr><tr><td>Zn</td><td>1.33</td><td>0.56</td></tr></table></td></tr>
<tr><td>Duplex Coating</td><td></td><td></td><td><table><tr><th>Element</th><th>Weight%</th><th>Atomic%</th></tr><tr><td>C</td><td>6.55</td><td>11.85</td></tr><tr><td>N</td><td>7.67</td><td>11.90</td></tr><tr><td>O</td><td>33.06</td><td>44.91</td></tr><tr><td>Mg</td><td>27.65</td><td>24.71</td></tr><tr><td>Al</td><td>1.93</td><td>1.55</td></tr><tr><td>Cr</td><td>6.53</td><td>2.73</td></tr><tr><td>Zn</td><td>1.21</td><td>0.40</td></tr></table></td></tr>
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Figure 1: SEM cross section with its EDX analysis of treated and untreated AZ91D

As for the untreated AZ91D, the oxygen content on the surface was as expected to be low (~ 4 wt.%). For the diffusion process, the oxygen level at the surface was successfully increased to 16 wt.% without noticeable formation of compound layer. The formation of MgO phase occurred when oxygen gas was introduced inside the tube furnace with temperature. The high temperature of 400°C was applied to help the oxygen diffuse into the surface of AZ91D. At 400 ºC, AZ91D reached the thermal stability, and the reaction rate was increased due to the high energy collisions for activation energy. In this work, the 400°C is the most suitable temperature to apply as to ensure the lattice diffusion to form MgO.

It is clearly seen that a CrO coating layer of 1 μm in thickness was successfully deposited on the AZ91D surface via PA-PVD process. However, evidence of coating delamination was spotted at the coating-substrate interface which signify poor adhesion. In contrast to PA-PVD, the duplex process imparts better adhesion with a more uniform of 1 μm CrO coating deposited on the AZ91D surface. These observations implies that, diffusion prior to coating had successfully enhanced the substrate-coating interface and thus, lead to better adhesion.

3.2 Case Depth Analysis

Figure 2 shows the comparison profile of surface hardness and case depth values of the untreated versus the treated AZ91D samples.

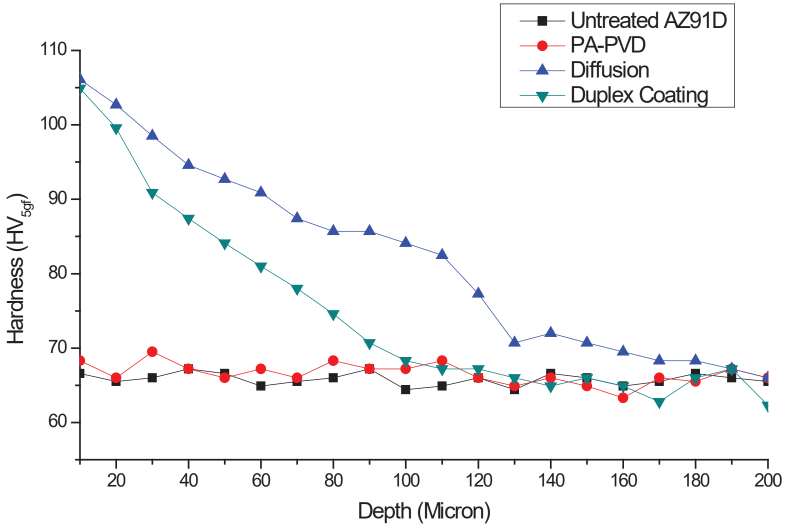

Figure 2: SEM Case-depth profile of the untreated AZ91D and the treated AZ91D

Obviously, AZ91D sample treated with a diffusion process display the highest surface hardness and deepest case depth values of about 105 HV and 180 μm respectively as compared to other samples. MgO phase was formed during the oxidation process helped to enhance the hardness of the substrates on the diffusion area. The ionic bonding between magnesium and oxygen became stronger due to greater charge on the ions, where the Mg lost two electrons and O received two electrons that form the cubic structure. With the higher depth of diffusion, the corrosion protection and delayed the corrosion initiation on the AZ91D surface were enhanced.

Meanwhile, the AZ91D sample treated only with the PA-PVD process, exhibit similar case-depth with the untreated AZ91D. The similarity in both case-depth was not surprise since only thin CrO coating was developed on the treated AZ91D surface without any other significant modification underneath the surface that can act as a second support layer. Therefore, such a poor case depth result of AZ91D treated with PA-PVD was expected. A slight increase on its hardness was observed and can be related to the development of very thin oxide zone underneath the CrO coating generated from diffused oxygen due to the ions bombardment activities during the PA-PVD treatment. This slight increased, however, is small and insignificant.

Despite of showing high surface hardness, the case-depth of the duplex treated AZ91D was only 90 μm. This phenomenon can be related to the reduction in the thickness of the diffused oxide zone due to the erosion process caused by the ions bombardment activities during the deposition of CrO coating. Besides, the sputter cleaning process also known can contribute to the thinning of the diffused oxide zone [17].

3.3 Corrosion Rate

Figure 3 shows the corrosion rate of the untreated and the treated AZ91D for comparison.

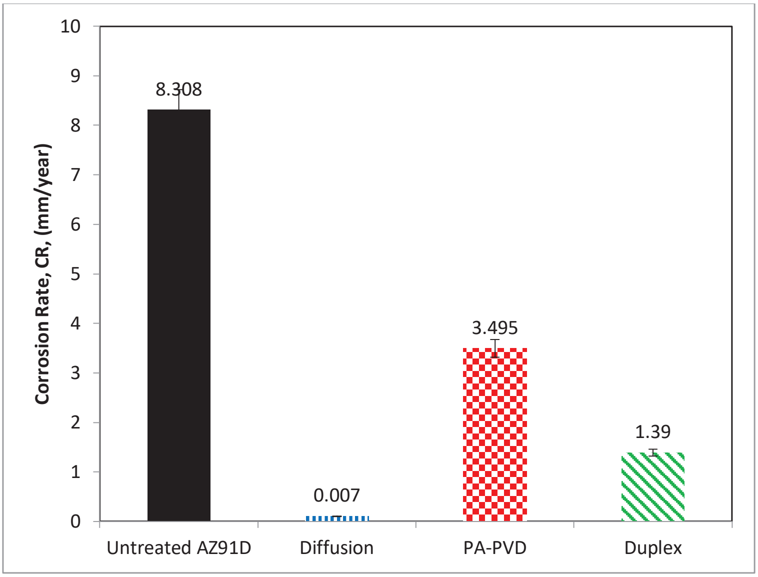

Figure 3: SEM Corrosion rate of the untreated AZ91D and the treated AZ91D

As expected, the untreated AZ91D demonstrated the weakest corrosion resistance among others with a corrosion rate value of 8.308 mm/year. The best corrosion rate with a value of almost 0 mm/year was shown by the diffused AZ91D. Obviously, its corrosion rate protection performance is enhanced due to the establishment of the deeper oxide diffusion zone with a case-depth of almost 180 μm as explained in the previous section. The oxide diffusion zone successfully enhanced the AZ91D surface from corrosion reaction.

Meanwhile, the corrosion performance of the PA-PVD treated AZ91D was not as good as the AZ91D treated with the diffusion but still far better than the untreated samples. The corrosion rate value was 3.495 mm/year. This inferior performance than the diffused sample could be due to the spallation of coating area resulted from the poor adhesion possess by the coating-substrate interface. Since, the layer underneath the coating is similar with the untreated AZ91D therefore, any uncoated area that expose directly to the corrosive medium can corroded instantly.

In contrast, the corrosion rate for the duplex process is far better than the untreated AZ91D and the PA-PVD treated AZ91D. The corrosion rate value is 1.39 mm/yr. Not only the duplex AZ91D has the diffuse oxide zone underneath, the adhesion of the coating-substrate interface also better compares to the PA-PVD treated AZ91D. However, the corrosion performance of the duplex is still slightly poor compared to the diffused AZ91D. This observation could be related to the shallow case-depth established by the duplex AZ91D caused by the erosion of ion bombardment process during the PA-PVD treatment. The thin CrO coating together with shallow case-depth make it less effective in protecting the substrate from corrosion environment as compare to the diffused AZ91D.

4.0 CONCLUSION

In summary, the corrosion protection of the AZ91D surface was enhanced throughout all surface treatment. The best corrosion rate was obtained with the diffusion treatment followed by the duplex and then the PA-PVD treatment. The best corrosion performance obtained from the diffused process can be related to the establishment of the deeper oxide zone with a case-depth of almost 180 µm. This oxide zone acted as a barrier to enhance the AZ91D surface from corrosion. From the diffusion process, the formation of an oxide layer such MgO has observed for the oxidized AZ91D through the tube furnace at the high process temperature 400°C. The formation of the oxide layer has proved by the SEM and EDX analysis for the cross section images where there are the presences of increasing oxygen element on the cross section of oxidized AZ91D. However, the corrosion rate of the duplex is slightly poor than the diffused sample even though the duplex consists of a combination of CrO coating and a diffuse oxide zone. It was due to the very thin CrO coating produced together with a very shallow case depth. The poor CrO coating together with shallow case-depth make it less effective in protecting the substrate from corrosion environment as compare to the diffused AZ91D. PA-PVD process and duplex treatment also suitable for the corrosion resistance for AZ91D, but, it involves the coating properties that need to concern especially the coating adhesion where the coating adhesion plays a major role in the surface corrosion protection. Different for the diffusion process, where the process involves is the diffusion on the AZ91D surfaces and there is a non-issue for the coating adhesion that will disturb the corrosion protection, and it will give the maximum protection for corrosion suitability.

ACKNOWLEDGMENTS

The authors would like to thank the financial support from the Ministry of Higher Education and Universiti Teknikal Malaysia Melaka for the RAGS/1/2014/TK01/FTK/B00086 grant and the SM4GT group members under Advanced Manufacturing Centre, UTeM for the support given during this research.

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