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Heat treatment of cold spray coatings to form protective intermetallic layers

K. Spencer* and M.-X. Zhang

The University of Queensland, School of Engineering, Division of Materials, St Lucia, Qld 4072, Australia

A new technique for generating thick Mg/Al intermetallic coatings on Mg–Al–Zn alloys through post-spray annealing of aluminium cold spray coatings is discussed. Annealing at 400 °C, which is close to the solution treatment temperature for AZ91 alloy, results in the formation of thick $Mg_{17}Al_{12}$ and Al_3Mg_2 intermetallic layers. These layers have high hardness, and increase the corrosion resistance to a level similar to that of aluminium alloys.
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The low density of Mg alloys has led to increasing consideration for their use as structural materials in recent years [1,2]. However, the poor surface properties of cast alloys such as AZ91, including corrosion and wear resistance, means that they have limited wider application [1]. Design of new alloys is one possible route to achieving better surface properties, but thus far the Mg alloys that have the best corrosion resistance use expensive alloying elements [3], and wear resistance is not substantially improved. A less expensive route to improving the surface properties of Mg alloys is through surface modification; however, there is no single ideal technique available at present [4].

Surface alloying of Mg alloys with Al has been considered as an effective approach to improving both corrosion and wear resistance through the formation of Mg/Al intermetallic compounds. These compounds, including $Mg_{17}Al_{12}$ and Al_3Mg_2, not only have higher hardness than a Mg alloy substrate but also have good corrosion resistance in chloride solutions. Previous research [5,6] has indicated that the $Mg_{17}Al_{12}$ phase is inert in chloride solutions, and exhibits passive behaviour over a wider pH range than the surrounding Mg matrix. High volume fractions of the $Mg_{17}Al_{12}$ phase may act as an anodic barrier to inhibit the overall corrosion of the alloy [7]. For this reason, considerable research [8–16]

has been done trying to obtain an Al-enriched surface layer on Mg alloy substrates. Most of the previous work has used conventional diffusion coating techniques that produce alloyed surface layers containing a higher fraction of the $Mg_{17}Al_{12}$ phase compared to the as-cast structure. These layers show improved wear and corrosion resistance. However, in order to promote diffusion of Al into the Mg substrate, the diffusion coating has to be carried out at temperatures over 450 °C [8,10,11,13,14]. Such temperatures are too high to be of practical use because they result in surface melting and cracking. Through the addition of Zn into the diffusion process Zhang and Kelly [9] and Zhu and Song [16] were able to produce $Mg_{17}Al_{12}$-enriched layers on an AZ91 substrate at lower temperatures, 430 and 420 °C, respectively; however, the layers formed have extremely low homogeneity.

Recently, Zhang, Shi and co-workers [12,15] used a technique known as surface mechanical attrition treatment (SMAT) to form a nanocrystalline surface layer on AZ91 alloy, combined with surface alloying using Al powder. Short circuit grain boundary diffusion of the Al into the nanocrystalline layer lowers the diffusion coating temperature to 380 °C. Unfortunately, current SMAT techniques are not suited to components with complex shapes. Furthermore, all previously reported approaches only produce alloyed layers with a higher proportion of the $Mg_{17}Al_{12}$ phase than exists in the as-cast Mg matrix; none of them can generate continuous intermetallic coatings. Hence, the present work aims

* Corresponding author. Tel.: +61 7 3365 3580; fax: +61 7 3365 3888; e-mail: k.spencer@uq.edu.au

to develop a novel process to produce continuous Mg–Al intermetallic coatings on AZ91 substrate and to investigate the potential wear and corrosion resistance of the coatings.

Our previous work has shown that cold spray deposition of Al on AZ91 Mg substrates and subsequent heat treatment at 400 °C produces a layer of $Mg_{17}Al_{12}$ at the coating/substrate interface [17]. This is considered a useful starting point because cold spray coatings can be produced quickly and are inexpensive [18]. In the present work this process is further extended to produce thick intermetallic layers, and their structure, hardness and corrosion resistance are investigated.

Commercial as-cast AZ91E was used as a substrate material. Spherical, atomized Al powder with an average diameter of 15 μm was cold sprayed onto the substrate. In the cold spray process, the powder is entrained in an inert gas stream and accelerated to velocities of 500–1000 m s^{-1}. The impact of the powder on the substrate results in a dense coating that is well-bonded with the substrate, in a process analogous to explosive cladding [19]. The cold spray was done using a kinetic metallization (KM) system, which is a commercially available cold spray variant (Inovati, Santa Barbara, CA, USA). Whereas a conventional cold spray system uses a convergent–divergent nozzle to accelerate the process gas to supersonic speeds [20], KM uses a convergent nozzle to accelerate the process gas to ⩽Mach 1 [18]. Helium was used as the process gas, with a stagnation temperature and pressure of 200 °C and 620 kPa respectively. The mass flow rate of the Al powder was 15 g min^{-1}. The nozzle standoff distance was 12 mm and the traverse speed was 50 mm min^{-1}.

Post-spray heat treatments were carried out at 400 °C for 20 h in a controlled atmosphere furnace with a flow-through of argon, followed by air cooling. This heat treatment temperature and time is similar to the typical solution treatment process used prior to artificially ageing AZ91 alloy to its T6 condition. After the heat treatment, unreacted Al power was removed and the exposed intermetallic surface was polished to a 0.05 μm finish with colloidal silica for corrosion testing. X-ray diffraction (XRD) with Cu K_α radiation was used to identify the phases formed at the coating/substrate interface.

Corrosion resistance of the coatings was assessed using two techniques. The first was to immerse the samples in a neutral solution of 5% NaCl for 48 h with only the polished Al_3Mg_2 intermetallic coating surface exposed, and the substrate masked off with lacquer. The second approach was to measure the electrochemical response of the intermetallic coatings subject to linear potentiodynamic polarization, using a neutral 5% NaCl solution as an electrolyte and a scan rate of 0.166 mV s^{-1}. A cell with a round O-ring opening was used in order to expose only the polished surface of the intermetallic coatings. The Al_3Mg_2 layer was exposed and prepared as for the XRD measurements; the $Mg_{17}Al_{12}$ layer was exposed by polishing away the Al_3Mg_2 phase carefully until only the $Mg_{17}Al_{12}$ phase remained, as verified using XRD. For comparison polarization experiments were also performed on as-cast commercial purity Al, a cast 601 Al–Si–Mg alloy, peak aged AZ91E alloy, and

commercial purity Mg. Microhardness testing was done using a load of 200 g.

The as-deposited Al coatings are almost fully dense, and the amount of porosity was measured by image analysis to be less than 1% by volume. Post-spray heat treatment of the coated samples at 400 °C for as little as 2 h results in a discontinuous $Mg_{17}Al_{12}$ intermetallic layer at the coating substrate interface. In order to produce thicker and continuous intermetallic layers the heat treatments were carried out for 20 h, with a typical result shown in Figure 1. The intermetallic layers are continuous and have a uniform thickness. Energy dispersive X-ray analysis (not shown here), and XRD analysis of samples with the unreacted Al polished away (Fig. 2) confirm the two diffusion layers as Al_3Mg_2 and $Mg_{17}Al_{12}$, with a small amount of solid solution Zn (<1 wt.%). The thickness of the Al_3Mg_2 layer is about 150 μm and the $Al_{12}Mg_{17}$ layer is 50 μm. The thickness of the two diffusion layers in the present work is similar to that reported by Funamizu and Watanabe [21] for pure Al–Mg diffusion couples heated to 425 °C for ~20 h.

Funamizu and Watanabe's data show that the growth rate of the Al_3Mg_2 and $Mg_{17}Al_{12}$ phases follows a parabolic relationship typical of pseudo steady-state diffusion processes [22], at least for heat treatment times up to 36 h. Increasing the heat treatment temperature from 340 to 425 °C for 20 h increases the thickness of the Al_3Mg_2 layer by a factor of ~13, and the $Mg_{17}Al_{12}$ layer by a factor of ~1.7. This suggests that to obtain fast layer growth it is important to perform the heat treatments at temperatures between 400 °C and the practical upper limit of 436 °C, beyond which melting can occur.

The parabolic layer growth is limited in practice by the Kirkendall effect, indicated by the layer of porosity in Figure 1. Inert marker experiments by Funamizu and Watanabe [21] showed that Al diffuses into the intermetallic layers faster than Mg. The excess vacancies on the Al side of the interface condense as a dense layer of pores. Once the density of the pores reaches a sufficient level the layer growth will be arrested due to insufficient flux of material across the interface. While this places practical limits on the maximum possible thickness of the diffusion layers, the presence of a dense layer
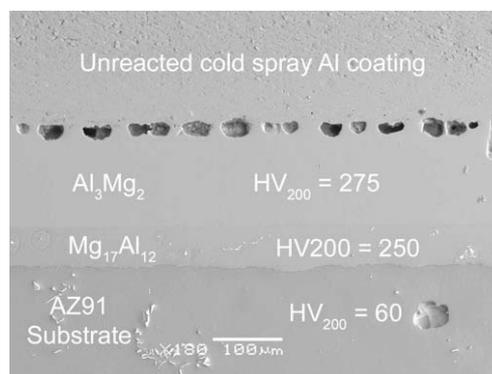

Figure 1. Backscatter SEM image of a cold sprayed Al diffusion coating on an AZ91E substrate, heat treated at 400 °C for 20 h; HV$_{200}$ indicates Vickers microhardness with a 200 g load.
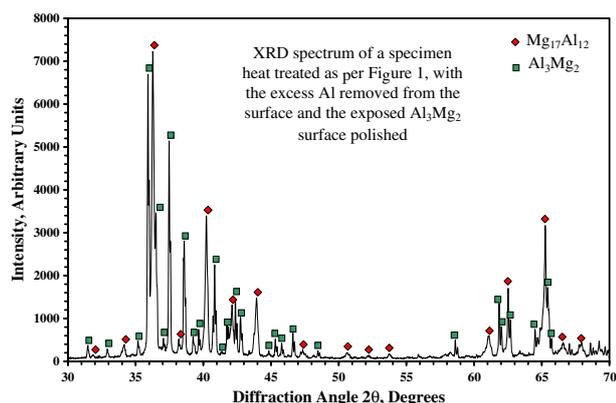
Figure 2. XRD spectrum of a cold sprayed Al diffusion coating on an AZ91E substrate, heat treated at 400 °C for 20 h.

Figure 3. AZ91E sample with Al_3Mg_2 coating on top (left) and AZ91E (right) after 48 h immersion test in 5% NaCl.

of pores has the advantage of making the unreacted Al easy to remove. It was possible to remove the excess Al by hand. While the present work treats only the case of Al coatings on an AZ91 substrate, it should be possible to extend this method of surface intermetallic layer growth to any coating/substrate system where (a) intermediate phases are present and will grow at temperatures below the melting points of both the substrate and coating, and (b) the coating material diffuses into the intermediate phases at a higher rate than the substrate material, so that the condensation of vacancies arising from the Kirkendall effect occurs between the outer intermetallic layer and the unreacted coating material, as in the present case.

In the condition shown in Figure 1, the Vickers hardness of the $Mg_{17}Al_{12}$ and Al_3Mg_2 layers was 250 and 275, respectively. Comparing these hardness values to the hardness of the AZ91 substrate in the as-cast and peak aged condition respectively (60 and $\sim$90), the intermetallic layers result in a significant increase in hardness. Although wear resistance does not always scale directly with hardness due to the variety of possible wear mechanisms, it is nonetheless a useful indicator of wear resistance. The large increase in hardness of the intermetallic layers over peak aged AZ91 alloy should result in significantly increased wear resistance in service. Since the bond between the intermetallic layers and the substrate is a diffusion bond, it will have high strength and should provide sufficient adhesion to resist pull-off when subject to normal and shear abrasive loading.

Samples immersed in a neutral 5% NaCl solution with the polished Al_3Mg_2 surface exposed were compared with peak aged AZ91 samples under the same conditions. This is considered a relevant electrolyte when considering materials for ground transportation applications where road salt exposure may occur during winter months. Figure 3 shows an example of an AZ91 sample with an Al_3Mg_2 coating compared to an AZ91E sample after a 48 h immersion. The AZ91 sample shows extensive and deep pitting while the Al_3Mg_2 surface showed only minor discolouration from the salt. The good performance of the intermetallic layer suggests that it would perform well under conditions of real use. It has been suggested that continuous immersion or salt spray tests are overly conservative when predict-

ing corrosion resistance of exposed parts in service in automobiles, for example [23].

A more quantitative assessment of the corrosion resistance of the intermetallic layers was made using potentiodynamic electrochemical measurements in the same 5% NaCl electrolyte, shown in Figure 4. Commercial purity Mg and peak aged AZ91 alloy both show the most active behaviour, while the electrochemical performance of the $Mg_{17}Al_{12}$ and Al_3Mg_2 layers is similar to that of commercially pure Al and 601 Al alloy. Both layers are passive over a wide potential range. This suggests that either of these intermetallic layers would have significantly better corrosion resistance in an aggressive NaCl environment than AZ91 alloy or pure Mg.

The results of the present work are consistent with the little data available in the literature on the electrochemical behaviour of Mg–Al intermetallic compounds. Song and co-workers have measured the polarization curves for the $Mg_{17}Al_{12}$ phase in a similar NaCl solution to the present work [7,24], and observed a passive region stable over a similar potential range. The present work confirms that both the $Mg_{17}Al_{12}$ and Al_3Mg_2 phases show similar passive behaviour to pure Al and Al alloys. There has been some disagreement in the literature on how to characterize the electrochemical behaviour of the Al_3Mg_2 phase [25–27]. It has been characterized as
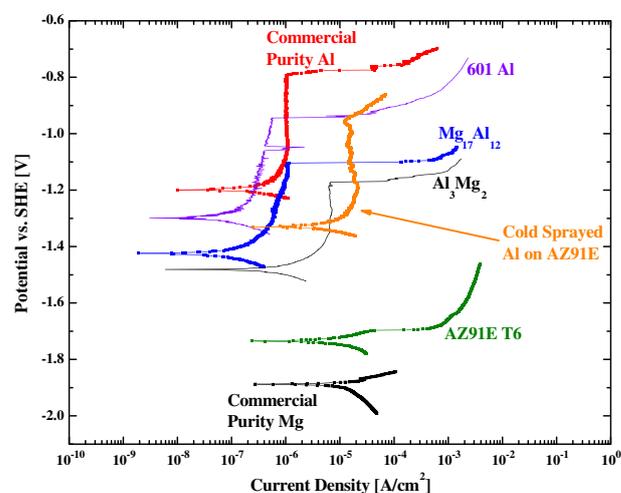

Figure 4. Comparison of the electrochemical response of the Mg–Al intermetallic coatings with other materials, subject to linear potentiodynamic polarization in 5% NaCl; data is plotted relative to a standard hydrogen electrode potential (SHE).

"active" in terms of its low corrosion and breakdown/pitting potential relative to Al–Mg alloys that contain Al_3Mg_2 precipitates [25,26]; however, its breakdown potential is relatively insensitive to pH and the compound does exhibit spontaneous passivation [25–27]. The results of the present electrochemical and immersion tests suggest both the $Mg_{17}Al_{12}$ and Al_3Mg_2 compounds have significantly better corrosion resistance than AZ91 alloy, and they offer a similar level of corrosion resistance to Al alloys.

In summary, using a simple Al cold spray coating process coupled with a standard AZ91 solutionizing heat treatment, it is possible to reproducibly grow continuous intermetallic layers that are 150–200 μm thick on an AZ91 alloy substrate. A finishing operation to remove the excess Al coating exposes an Al_3Mg_2 or $Mg_{17}Al_{12}$ intermetallic layer that is significantly harder than peak aged AZ91 alloy, and offers corrosion resistance similar to that of Al alloys. This approach takes advantage of the good metallurgical bonding produced by cold spray coating to enable a diffusion treatment that is much simpler than a conventional packed powder surface diffusion treatment. Furthermore, it should be possible to extend this approach to forming protective intermetallic layers to other systems where asymmetry of diffusion coefficients ensures the formation of a vacancy layer between the intermetallic layer and the unreacted coating material.

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