International Journal of Adhesion & Adhesives 40 (2013) 38–48

Contents lists available at SciVerse ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Effect of Na_2MoO_4 on bond strength of adhesive-bonded phosphate coated magnesium AZ31 sheets

Ting-Ting Wan [a], Zhong-Xia Liu [a,*], Ming-Zhe Bu [a], Pei-Chung Wang [b]

[a] School of Physics and Engineering, Key Lab of Materials Physics, Zhengzhou University, Zhengzhou 450052, PR China
[b] Manufacturing Systems Research Lab, General Motors Research and Development Center, 30500 Mound Road, Warren, MI 48090, USA

ARTICLE INFO

Article history:
Accepted 24 July 2012
Available online 4 August 2012

Keywords:
AZ31 magnesium sheets
Surface treatment by chemical solutions
X-ray photoelectron spectroscopy
Lap-shear
Durability

ABSTRACT

A pretreat phosphate solution having the formulation of $KMnO_4$, K_2HPO_4, Na_2SiO_3, NaF and Na_2MoO_4 was developed to improve the strength of adhesive-bonded magnesium AZ31 joints. The phosphate coating which has the magnesium phosphate, MgO, Mg $(OH)_2$, MgF_2 and minor Al_2O_3, $Al(OH)_3$ $Al_{0.35-0.55}Si_{0.10-0.48}P_{0.13-0.35}O_{2.1-2.2}$ and, $Al_{0.35}Si_{0.48}P_{0.18}O_{2.2}$, and $Al_{0.52}P_{0.48}O_{2.2}$ was formed on the surface of the magnesium AZ31 after treatment. The additives Na_2MoO_4 in a phosphate-permanganate solution mainly act as an accelerator to speed up the coating formation. The combination of Na_2MoO_4 and NaF improves significantly the corrosion resistance of the magnesium AZ31 and performance of adhesive bonded joints. The joint strength and durability of the bonded Mg AZ31 joints in hot-humid environmental condition are superior to that of the phosphate treated (RPT) and CrO_3 etching (CET) pretreated samples.

1. Introduction

Lightweight design using magnesium is in competition with lightweight design using aluminum, plastics and steel in the automotive industry due to magnesium and its alloys having high strength/weight ratio, low density, good cast and welding ability, high thermal conductivity and the fact that it is easily recycled [1,2]. An important opportunity for magnesium alloys is as structural components in the automotive industry. The application of joining technologies is a strategic aspect when considering broad application of magnesium alloys. Welding magnesium is difficult due to the oxide film on the magnesium which is naturally formed [3] while the serious corrosion of riveting magnesium alloys in corrosive environments is unavoidable and detrimental to service performance of structures [4]. Adhesive bonding is an alternative joining technology for magnesium alloys. It not only can bond the magnesium and other materials, but the bonded joints have high bond strength and excellent fatigue resistance.

The quality of the bonded joints is affected by various factors, such as the characteristics and curing technology of the adhesive, type of bonded joints and surface appearance of the adherends. In particular, the surface appearance of the adherends has a strong effect on the strength of the bonded joints. In a natural environment, the magnesium alloys are easily oxidized to form a loose oxide film on the surface. This film provides little protection for magnesium alloys which are easily corroded in corrosive environments in most cases. Most importantly, the loose oxide film results in poor mechanical performance of adhesively-bonded magnesium alloys. Therefore, a suitable surface pretreatment is necessary to improve the bond strength and corrosion resistance of the magnesium alloys. Emerging literature suggests exterior burnish, cold spray, micro arc oxidation [5,6] and chemical pretreatments [7–15] as means to improve the corrosion resistance of magnesium. Some effective chromium-free surface phosphate pretreatment processes developed recently are more environmentally friendly and have been shown to have the corrosion resistance comparable to chromate treatments and excellent paint adhesion [16–20]. Specifically, a phosphate-permanganate treatment using a bath containing potassium permanganate and sodium phosphate has been shown that a homogeneous, non-powdery and uniform coating can be achieved. Strictly controlling the pH value and phosphate concentration in potassium permanganate and sodium phosphate solution [19,20] and addition of sodium fluoride into phosphate solution [21,22] was found to be in favor of obtaining quality final coating and improving the corrosion resistance and paint adhesion of magnesium alloys. Unfortunately, most of the previous investigations focus on improving the corrosion resistance of magnesium alloys. Few studies were reported regarding its effect on the structural bonding of magnesium alloys.

* Corresponding author. Tel./fax: +86 3716 7767 776.
E-mail address: liuzhongxia@zzu.edu.cn (Z.-X. Liu).

0143-7496/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijadhadh.2012.07.011

Nomenclature

RPT reference phosphate treatment
CET CrO_3 etching treatment
MPPT phosphate-permanganate treatment with additive Na_2MoO_4
SEM scanning electron microscope
EDS energy dispersive X-ray spectroscopy
XPS X-ray photoelectron spectroscopy
CCD charge-coupled device
R.H. relative humidity

To apply adhesive-bonding of magnesium alloys for automotive applications, a practical surface pretreatment is needed to ensure the joint strength and desired corrosion resistance to maintain excellent durability in a hot-humid environment. Our investigation on adhesive bonded AZ31 magnesium alloys showed that the phosphate pretreatment with phosphate-permanganate solution makes AZ31 alloys have excellent adhesive performance and durability in a hot-humid environment [23]. But the decrease in the strength of the bonded joints in a hot-humid environment indicated the phosphate coating needs to be further modified to enhance the adhesive performance and corrosion resistance.

Molybdates have similar chemical properties to chromium (groups VI and VII of the periodic table) and can serve as oxidizing alternative species to chromium in zinc galvanized steel surface treatment [24,25]. Molybdate coatings have been applied on Zn, Al alloy, steel substrates [26–28] and magnesium alloy [29,30] to improve the corrosion resistance of those substrates. More recently, molybdate/phosphate composite conversion coatings have been developed to obtain further improvement of corrosion protection for magnesium alloys [31–33]. In addition to that, Gorecki et al. [34] found that addition of a compound containing MoO_4^{2-} ions as an accelerator can avoid hydrogen evolution and accelerate the phosphating and obtain uniform bluish phosphate coatings. Despite that, the problem that may arise is whether the addition of molybdate would show similar improvement on the bond performance of magnesium alloys.

To investigate the effect of Na_2MoO_4 on the bond performance of the magnesium alloys, Na_2MoO_4 as an additive was added into a permanganate-phosphate pretreatment solution in the present study. The permanganate-phosphate treatment solution with Na_2MoO_4 (MPPT process) was used to phosphate 2 mm thick magnesium AZ31.There are three main parts in this report; the first presents the experimental procedure including material, surface pretreatment methods, surface characterization, sample fabrication, mechanical testing, environmental chamber, mechanical testing and corrosion resistance assessment. The next section shows the surface characteristic of phosphate coating and the acceleration effect of Na_2MoO_4 on formation of phosphate coating. The characteristics and chemical composition of the phosphate coating were analyzed with scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) technology. Finally, we discuss the effect of Na_2MoO_4 on the strength and durability of bonded magnesium AZ31 in hot-humid exposure. The strength of adhesive-bonded joints was evaluated using lap-shear joints. Optimum bonded joint was fabricated and exposed for various times in a hot-humid environment. The strengths of the bonded joints before and after exposure were measured and compared with that of CrO_3 etching (CET) pretreated joints. The corrosion resistance of the phosphate coating was evaluated by polarization test. The pretreated magnesium alloys were shown to enhance the corrosion resistance and bond strength when using this phosphate coating as pretreatment coating of bonded magnesium alloys.

2. Experimental procedure

2.1. Material

2.0 mm thick magnesium AZ31 alloy was used in this study. The chemical composition and mechanical properties per our experimental measurements are listed in Tables 1 and 2, respectively. The adhesive used in this study was Henkel 5089, a proprietary one-part toughened epoxy with a 39.2 MPa of tensile strength and 1.5 GPa of elastic modulus.

2.2. Surface pretreatment

The magnesium AZ31 sheets were pretreated using a phosphate-permanganate treatment solution with molybdate additive Na_2MoO_4 (MPPT) prior to adhesive bonding. The constituent content of MPPT solution is listed in Table 3. As shown, K_2HPO_4, $KMnO_4$, NaF and Na_2SiO_3 are the base constituents of the solution used for forming the phosphate coating. The Na_2MoO_4 is the additives used for modifying the quality of the phosphate coating, which is used to investigate the effect of addition of Na_2MoO_4 on the strength of bonded magnesium AZ31. For the purpose of comparison, two kinds of reference pretreatment processes were used. Reference phosphate process (RPT) is a process that the samples were treated with a phosphate solution without additive Na_2MoO_4, which was developed by our previous investigation [23]. CrO_3 solution etching treatment (CET) is an ASTM D 2651-01 standard. The details of each process are shown in Table 4.

Table 1
Nominal chemical composition of magnesium AZ31.

Element	Al	Zn	Mn	Si	Fe	Cu	Ni	Ca
Wt%	2.5–3.5	0.6–1.4	0.2–1.0	0.08	0.003	0.01	0.01	0.04

Table 2
Mechanical properties of Mg alloy AZ31.

Modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)
34,414	162	251	15.3

Table 3
Concentration of phosphate-permanganate solution (g/L).

	NaF	Na_2MoO_4	$KMnO_4$	K_2HPO_4	Na_2SiO_3
MPPT 1	0.5	0.3	40	150	6
MPPT 2		0.5			
MPPT 3		0.8			
MPPT 4	0.8	0.3			
MPPT 5		0.5			
MPPT 6		0.8			