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Phosphonate-functionalized ORMOSIL coatings for magnesium alloys

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ABSTRACT

Hybrid organically modified silicates, or ORMOSIL materials, with covalently attached pendant phosphonate groups were processed by a sol–gel method. A hydrolysis and condensation route was used involving a phosphonato-silane and resultant films were evaluated as prospective coatings for magnesium AZ31B alloy substrates. The inclusion of phosphonate functionalities into the coating matrix was achieved by a co-condensation of the phosphonato-silane with other organo-functional silanes followed by blending the resultant phosphonate-functionalized silicate oligomers with another sol–gel matrix material to form an interpenetrating network structure. The effect of synthesis composition on the hydrophobic/hydrophilic balance and film barrier properties was examined by several methods, including constant immersion and electrochemical tests. The observed enhancement in corrosion protection properties was attributed to a combination of the barrier properties of the organo-silicate matrix along with strengthening of the coating/substrate interface due to chemical bonding of the phosphonate groups to the metal surface.

1. Introduction

Sol–gel-derived organo-silicate hybrids, also known as organically modified silicates (ORMOSILs) have attracted significant interest as versatile, easily processed coating materials with potential to replace chromate-based corrosion protection surface treatments for low density metals and their alloys [1–4]. The performance of such surface treatments is dependant upon a combination of barrier properties, adhesive bond strength to the substrate, and compatibility with any subsequent organic protective paints/coatings to be applied. Optimal adhesion and barrier properties can be achieved through introduction of various organo-functional groups into the ORMOSIL material, thus tailoring its chemical composition.

In a recent publication on surface treatments for magnesium alloy substrates, we investigated phosphonate-modified sol–gel based surface coatings processed by a co-reaction of the phosphonato-silane with triethoxysilane [5]. The approach represented a promising way to incorporate phosphonate groups into ORMOSIL coating materials through sol–gel processing with commercially available phosphonato-silanes. The presence of pendant phosphonate groups covalently linked to the ORMOSIL network can substantially increase the ability to chemically react with certain metal substrates, leading to improved metal/coating adhesion. In particular, the phosphonate functionalities are capable of strong chemical bonding with the surface metal oxide layer on magnesium, aluminum and titanium substrates [6–8], making phosphonate-modified ORMOSILs very attractive materials for developing surface treatments and protective coatings for these low density metals and their alloys.

The development of protective surface treatments for magnesium alloys is especially important due to the growing industrial demand for structural applications in the automotive, aerospace, and electronics industries. Because of the high chemical reactivity of magnesium, industrial applications of such materials almost always require the use of surface treatments to provide the necessary corrosion protection and paint adhesion [9,10].

In this paper, we report further developments on these phosphonate-containing ORMOSILs. In the first part, the effect of various silane co-reagents that impart different degrees of hydrophobicity on resultant films was studied. In the second part, various phosphonate-modified sol–gel oligomers were blended with another crosslinkable ORMOSIL matrix to form films with an interpenetrating network (IPN) structure. The corrosion protection properties of the films obtained by both these approaches and a comparison of the coatings with interpenetrating network formation versus coatings made via layer-by-layer deposition are discussed.

2. Experimental

Tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane (DMDES), diethylphosphonatoethyl-triethoxysilane (PHS), and 3-glycidoxypropyl-trimethoxysilane (GPTMS)

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were purchased from Gelest (Tullytown, PA, USA). Diethylenetriamine (DETA) was purchased from Aldrich. All chemicals were used as-received without additional purification. Reagent grade Type I water and HPLC grade ethanol (Aldrich) were used for preparation of sols.

The organo-silicate sols were prepared via acid-catalyzed hydrolysis and condensation of a mixture of PHS and a chosen silane (typically at 1:4 molar ratios) in ethanol/water solution. For example, the sol of PHS:TEOS with 1:4 molar ratio was prepared by mixing of 0.02 mol of PHS and 0.08 mol of TEOS with 6.8 ml of 0.05 M acetic acid, followed by the addition of ethanol to make a total volume of 70 ml. The solution was vigorously stirred and aged for 3 days in a closed vial. The prepared sols were applied on cleaned AZ31B magnesium alloy coupons by a dip-coating procedure using a Model 201 dip-coater (Chemat Technology, Inc.) with a withdrawal speed of 10 cm/min.

In the IPN formulations, the abovementioned phosphonate-modified sols were mixed with sol–gel-processed nano-sized particles with peripheral epoxy-groups [4]. The residual mixture was crosslinked through the epoxy-amine chemistry using DETA as a low molecular weight amine crosslinker. For example, 10 ml of a 3-day-old sol made with PHS and TEOS (1:4 molar ratio) was mixed with 20 ml of the epoxy-functionalized GPTM-TMOS sol prepared as previously described [4]. After addition of non-ionogenic surfactants [4], 0.5 ml of DETA, and the final dilution with water up to 35 ml of total volume, the solution was vigorously stirred for about 0.5 min, and applied by a dip-coating procedure to a pre-cleaned magnesium substrate.

Coupons of sheet magnesium alloy AZ31B (2″ × 3″) were initially degreased in hexane and then cleaned in an acetic-nitrate pickle solution according to ASTM D 1732-03 standard procedure [11], and subsequently rinsed with distilled water and wiped with dry lintless cloth immediately after the bath.

The coated samples were dried under ambient conditions for at least 24 h prior to testing. The thickness of the coatings was estimated from the scanning electron microscopy (SEM) micrographs of the cross-section view of the samples. The SEM was performed with a Leica Cambridge 360 FE electron microscope using a secondary electron image detector at 15 kV and 100 pA probe current.

The water contact angle data were obtained using a FTA200 contact angle analyzer (First Ten Angstroms Inc.).

Constant immersion tests and potentiodynamic scan (PDS) measurements were performed in dilute Harrison's solution (0.35 wt% $(NH_4)_2SO_4$ and 0.05 wt% NaCl). Electrochemical measurements were performed using a Gamry PC4/300 potentiostat coupled with Gamry Corrosion Measurement System CMS100. A one-chamber, three-electrode cell set-up was used, with the working electrode consisting of an exposed area of 6 cm^2 on the surface of the sample. The reference and auxiliary electrodes were a saturated calomel electrode (SCE) and a platinum mesh electrode, respectively. The PDS scans were acquired in the range from −0.1 V up to 0.3 V versus open circuit potential at the rate of 1 mV/s. Prior to testing the samples were immersed in electrolyte solution either for 2 min (thinner films, Fig. 4) or for 10 min (IPN samples, Fig. 5).

3. Results and discussion

Chemically, magnesium is the most reactive among structural metals and highly susceptible to corrosion. When magnesium is protected by a barrier coating, localized corrosion in aqueous solution can be initiated from any pin–hole defects and/or water uptake through the full coating system. The onset of corrosion is accompanied by an increase in pH due to the formation of magnesium hydroxide as the corrosion by-product [9]. Therefore, the ability of the coating system to withstand exposure to an alkaline environment will most likely result in improved corrosion protection properties.

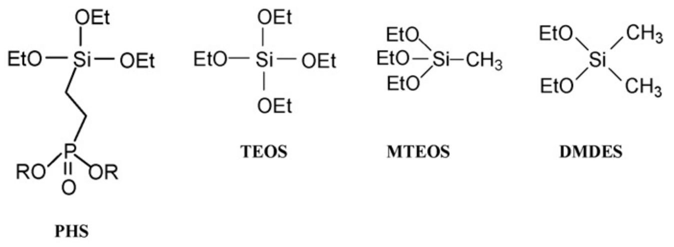

Fig. 1. Chemical structures of the organo-functional silanes used for the sol–gel processing of hybrid coatings with phosphonate functionalities.

In the case of ORMOSIL hybrid coating materials, it is expected that the stability against alkaline hydrolysis can be enhanced by increasing the amount of non-hydrolizable silicon–carbon bonds, suggesting a higher ratio of organic content for better performance. Since silica itself is slightly soluble at a basic pH, it is reasonable to assume that the presence of hydrolytically stable silicon–carbon bonds will improve the stability of hybrid organo-silicates against alkaline hydrolysis as compared to pure silicate sol–gel materials. Under this assumption, we have tried to choose matching silanes with a systematically increasing number of silicon–carbon bonds (as shown in Fig. 1) for co-reaction with PHS. Since PHS itself has only one silicon–carbon bond, the PHS–TEOS co-condensation products have the least amount of such bonds and have the highest inorganic (silica) content, whereas the PHS–DMDES oligomers have the highest number of silica–carbon bonds and the lowest inorganic-to-organic ratio. Accordingly, as the number of such non-hydrolizable methyl groups is increasing in the following order, PHS–TEOS < PHS–MTEOS < PHS–DMDES, the sol–gel material becomes increasingly more hydrophobic, as indicated by the water contact angle data shown in Table 1.

However, contrary to our expectations, as we examined the performance of resultant coatings subjected to the constant immersion test, we found the corrosion protection decreasing in the order of the increased hydrophobicity of the materials: PHS–TEOS > PHS–MTEOS > PHS–DMDES (Fig. 3). The PHS–TEOS coating demonstrates the highest corrosion protection, whereas PHS–DMDES coating shows very limited corrosion protection despite initial thoughts that such a material with a high amount of non-hydrolizable methyl groups will be the most stable against alkaline hydrolysis. This behavior might be explained by the possibly lower crosslinking density of the PHS–DMDES films (due to lower amount of the silanol groups) and the possible nanoscale phase separation due to increasing differences between the hydrophilic silica and hydrophobic methyl-siloxane clusters, leading to increased porosity (i.e., lower film barrier properties).

The electrochemical (PDS) measurements data for resultant coatings are shown in Fig. 4 and are in generally good agreement with constant immersion test results. In the PDS experiments however, both PHS–TEOS and PHS–MTEOS demonstrate similar cor-

Table 1
Coatings characteristics.

Composition	Molar ratio	Thickness, μm	Contact angle (water), °
PHS–TEOS	1:4	0.65–0.70	62
PHS–MTEOS	1:4	0.65–0.70	75
PHS–DMDES	1:4	0.65–0.70	81
IPN (matrix only)	–	1.5–2	55
PHS–TEOS–IPN	–	1.5–2	57
PHS–MTEOS–IPN	–	1.5–2	55
PHS–DMDES–IPN	–	N/A[a]	78

[a] Visible phase separation resulting in a non-uniform coating.