

Effect of montmorillonite modified with different intercalator on the protection property of sol-gel coating on AZ31B magnesium alloy

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Abstract. Composite coating was prepared on magnesium alloy AZ31B through different hyamine intercalated montmorillonite (MMT) doping in glycidoxypropyltrimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) hydrolyzed hybrid sol-gel system. Corrosion behaviors of different coated samples were investigated using potentiodynamic polarization. The results indicated an improvement of protective performance when modified MMT doped in, and the CC-MMT doped sol-gel coating showed better corrosion resistance than the CTA-MMT doped one. Combining the MMT characterization and structure of the coating, it could be concluded that this difference came from the tough bonding between CC-MMT and sol-gel system, while that did not exist in CTA-MMT/sol-gel coating. Due to this tough bonding, CC-MMT could guide the assembly of hydrolyzed silane molecules and silica sol particles, thus a denser structure and better protection performance.

Keywords: Hybrid sol-gel coating; montmorillonite; assembly; intercalation; tough bonding.

1. Introduction

As the lightest structural metals in practical applications, magnesium has aroused the attention of many researchers, as well as its high specific stiffness/strength high specific modulus, damping and shock absorption, compact molding performance, energy saving, electromagnetic shielding, superior cutting performance and easy recycling without pollution and many other advantages[1-4]. Despite the many advantages of magnesium alloys, they are highly prone to severe corrosion in the presence of aggressive ion such as Cl⁻ due to its high electrochemical active[5, 6]. Therefore, improving the corrosion resistance of magnesium is of crucial importance for its wider application. Many surface treatments, such as anodic oxidation, micro-arc oxidation (MAO), chemical conversion treatment, layered double hydroxides (LDHs), sol-gel coating have been adopted to enhance the corrosion resistance. Among these surface treatments, sol-gel method has significant advantages over other technologies, which reflected in mild reaction conditions, uniform particle distribution and controllable reaction process.

However, sol-gel coating is prone to cracking due to the evaporation of solvent, leading to the poor protection property or even failure of the coating. Many methods have been used to modify sol-gel coatings to reduce or eliminate these defects. Gobara et al.[7] produced a more smooth, intact nanocomposite hybrid coating with better anti-corrosion and durable protection by dispersing hydroxyapatite nano-platelets into silica sol-gel matrix, and this enhancement was due to the sensitive response of hydroxyapatite to pH and improved adhesion properties. Ashassi-Sorkhabi et al.[8] obtained the coating with corrosion inhibition ability by adding amino acids into silica sol. The introduction of amino acids made the surface of the coating uniform and more complete without cracks. In the meantime, the active adsorption sites of amino acids could adsorb on the surface of magnesium substrate, protecting it against corrosive media. Adsul et al.[9] obtained a silicon dioxide coating with good protection performance and corrosion inhibition performance by dispersing clay nanotubes/sheets loaded with corrosion inhibitor into silica sol matrix.

Montmorillonite is a kind of silicate material with low price and wide source, which is widely used in water treatment, corrosion inhibitor loading, composite material and so on, due to its high specific surface, swelling property, adsorption property and high cation exchange capacity (CEC). In this paper, two different hyamine, choline chloride (CC) and cetyltrimethylammonium bromide (CTA), were selected to prepare intercalated modified montmorillonite. Then, they were doped to the GPTMS/TEOS hydrolyzed hybrid sol-gel coating. The hyamine intercalated montmorillonite was characterized through XRD, FTIR, SEM and TEM. The surface and cross-sectional morphology of the obtained coatings were observed by SEM. Electrochemical test method was employed to study the effect of different MMT on the protection property of sol-gel coating.

2. Experimental

2.1 Materials

Extruded magnesium alloy AZ31B (purchased from Dongguan Jubao Magnesium Alloy Material Co., LTD) was used in this paper, and the nominal composition was listed in Table 1. Sodium montmorillonite (Na-MMT, 99.0%) was purchased from Hubei Sanding Technology Co., LTD (China). Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTMS) were obtained from Shanghai McLean Biochemical Technology Co., LTD (China), acetic acid (HAc), absolute ethanol from Shanghai Zhanyun Chemical Co., LTD (China). Hexadecyltrimethylammonium bromide (CTAB) and choline chloride (CC) were obtained from Sinopharm Group Chemical Reagent (Shanghai) Co., LTD. All the reagent was used without further purification.

Table 1 Composition of commercial magnesium alloy AZ31B (in wt.%)

Al	Zn	Mn	Si	Cu	Ni	Mg
3.12	0.928	0.302	0.08	0.009	0.001	balance

2.2 Preparation of intercalating modified montmorillonite

1g Na-montmorillonite was mixed with 200ml deionized water to form uniform suspension. Then, 50ml aqueous solution of an intercalator (CC or CTAB) equivalent to twice the cation exchange capacity (CEC) was added to the mentioned suspension. The mixture was stirring in water bath under the condition of 80°C/8h to make the fully intercalation. After that, centrifugation was conducted to remove Na⁺ from Na-MMT and Cl⁻ or Br⁻ from intercalator. Subsequently, the final centrifugated precipitation was dispersed into small amount ethanol. Then, the dispersion was drying in an oven at 60°C. The obtained montmorillonite was labeled as CC-MMT and CTA-MMT, respectively.

2.3 Synthesis of hybrid sol-gel coating

The hybrid organic-inorganic sol was synthesized by the hydrolysis of TEOS and GPTMS. In brief, 2.6g TEOS, 8.86g GPTMS, 23g ethanol and 3.6g deionized water were added to a beaker under continually stirring to form homogeneous mixture, with 1 drop HAc used as catalyst. Then, the mixture was stirring continuously for 3 h in the condition of 50°C water bath to form the hybrid sol. 1.5wt.%hyamine intercalated montmorillonite(CC-MMT or CTA-MMT) was dispersed into the hybrid sol through ultrasonic for 1 h. Then, the mixture stays stirring for 24 h. Before painting, the AZ31B sample was cut into coupons with a size of 40 mm × 12mm × 5mm, and the surface was ground with 400#, 800#, 1200#, 1500# and 2000# sand paper, successively. Then, the sample was cleaned with deionized water and sonicated with ethanol for 15min. The coating was prepared through dipping magnesium alloy in sol for 1 h at 50°C. Afterwards, the coated samples were cured in an oven for 2 h at 120 °C.

2.4 Characterization

The morphology of the modified montmorillonite was observed by field-emission scanning electron microscopy (FESEM, JSM-7800F, Japan); the composition and structure of intercalated MMT were characterized by Fourier transform infrared spectrum (FTIR, PerkinElmer, America) and X-ray powder diffraction (XRD, Bruker D8, Germany). Effect of modified MMT on the structure of coating was characterized by the observation of surface morphology and cross section, also through FESEM. The existing form of different MMT in coating can be characterized by transmission electron microscopy (TEM, JEM-2100F, Japan).

2.5 Electrochemical test

The corrosion resistance of prepared coating was explored through series electrochemical tests. The electrochemical test were carried out in 0.05M NaCl solution at electrochemical workstation (Gamry Interface1000, America), and a traditional three-electrode system was used, in which the samples with 1cm² exposed area act as working electrode (WE), saturated calomel electrode (SCE) as reference electrode (RE) and platinum net as counter electrode (CE), respectively. Potentiodynamic polarization were tested at a potential window of -30mV to +100 mV (vs OCP) with a scanning rate of 0.5 mV/s. The obtained potentiodynamic polarization curve were analyzed with Cview software.

3. Result and discussion

3.1 Montmorillonite characterization

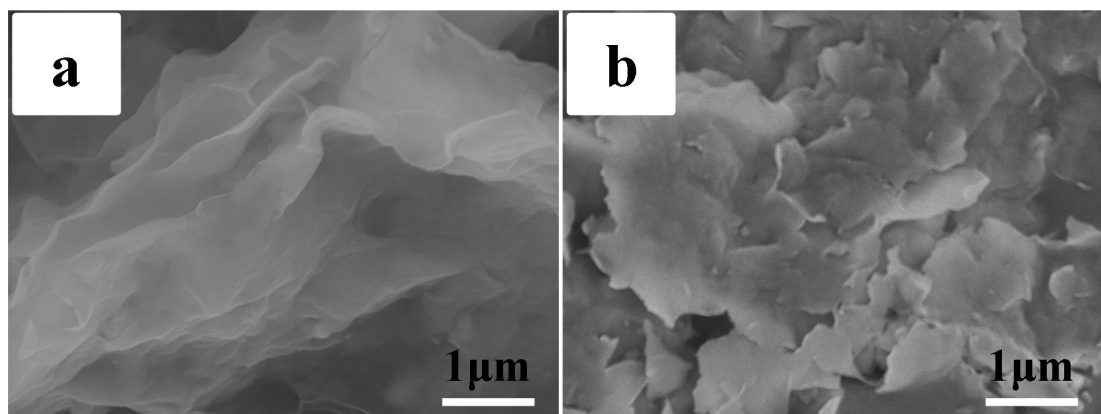


Fig. 1 SEM images of (a) CC-MMT and (b) CTA-MMT.

Fig. 1 shows the SEM morphology of two different hyamines intercalated montmorillonite. Two kinds of prepared montmorillonite remained good lamellar structure after intercalation modify. It can be seen that the CC-MMT has a better exfoliation compared to the CTAB intercalated one. The reason for this phenomenon could be attributed to the different dispersion in water of prepared MMT during the intercalation process. In brief, the molecular structure of CC has a hydroxy (-OH) in the opposite of quaternary ammonium group while that of CTAB was complete long-chain alkyl, leading to the poor dispersion in water.

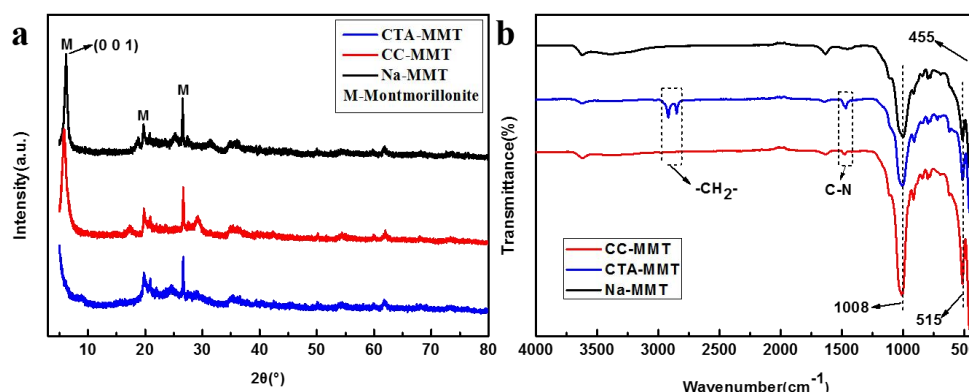


Fig. 2 (a) XRD pattern and (b) FTIR spectra of intercalation modified montmorillonite.

The XRD and FTIR of MMT before and after intercalation modified was shown in Fig. 2. As shown in Fig. 2(a), the peak at $2\theta = 6.15^\circ$ corresponds to the (0 0 1) lattice plane of the original montmorillonite. It can be seen that the diffraction peak position of the (001) latticeplane decreases below 5° when intercalated with CTAB. According to Bragg's law $2d\sin\theta = n\lambda$, the distance of (0 0 1) lattice plane was significantly enlarged after CTAB treated. Whereas, the 2θ of the same diffraction peak didn't have any obvious change after treated with CC. The layer spacing of prepared CTA-MMT is larger than that of CC-MMT due to the longer carbon chain of CTAB molecule.

The infrared absorption curves of origin and quaternary ammonium intercalated montmorillonite were shown in Fig. 2(b). Strong stretching vibrations of Si-O bonds at 1008 cm^{-1} and bending vibrations at 515 cm^{-1} and 455 cm^{-1} correspond to Al-O-Si and Si-O-Si bonds, respectively. The presence of these peaks indicates that the basic structure of the modified montmorillonite has not been destroyed. The absorption band at 1480 cm^{-1} corresponds to the C-N stretching vibration of hyamine, indicating successful insertion of hyamine between MMT layer. Absorption band at 2919 cm^{-1} and 2850 cm^{-1} corresponded to the asymmetric and symmetric stretching vibrations of C-H in $-\text{CH}_2-$. The absorption peak of MMT modified by CTAB was obvious here, while that modified by CC hasn't been found yet. This can also be ascribed to the different length of the carbon chain, which longer chains contain more C-H bonds. This is consistent with the XRD results.

3.2 Surface and cross-sectional morphology

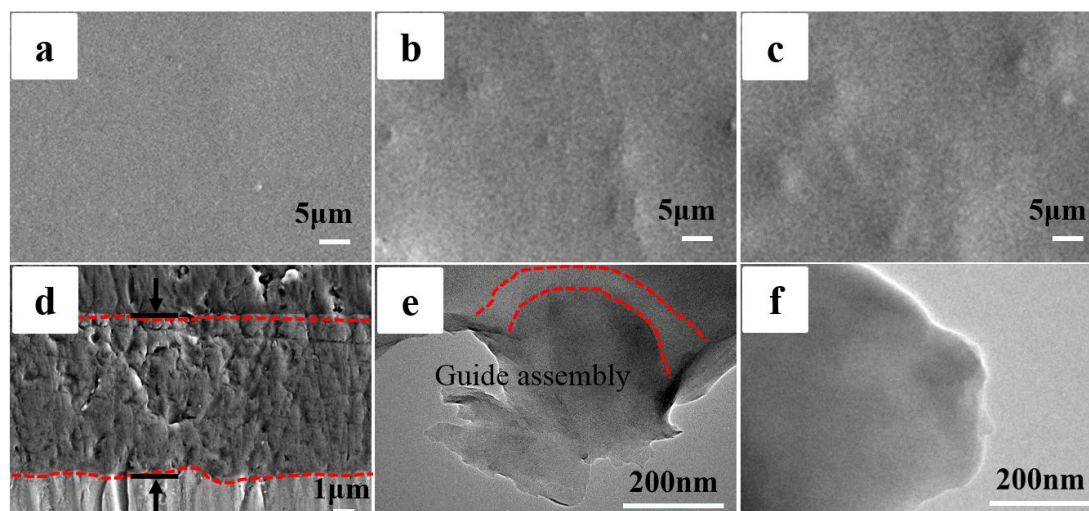


Fig. 3 Surface morphology of (a) pure sol-gel coating, (b) CC-MMT/sol-gel coating and (c) CTA-MMT/sol-gel coating; (d) cross-sectional morphology of prepared coating; TEM imagines of (e) CC-MMT and (f) CTA-MMT in sol-gel coating.

Fig. 3(a-d) shows the surface and cross-sectional morphology of different coating. It's clear that the pure sol-gel coating was flat and smooth, while the CC-MMT and CTA-MMT doped coating exhibited a typical uplift morphology. Uplift appeared in the CC-MMT/sol-gel coating and CTA-MMT/sol-gel coating was due to the aggregation of doped MMT to some extent. The MMT aggregated on the coating surface could provide more complex and variable electrolyte diffusion channels. From the cross-sectional morphology, it can be seen that the thickness of prepared coating was about $7.5\mu\text{m}$. The existing stage of different MMT in sol-gel coating was characterized by TEM, as shown in Fig. 3(e, f). It's obvious that the MMT in CTA-MMT/sol-gel coating was thicker than that of in CC-MMT/sol-gel coating. Combining the previous XRD analysis, the CTA-MMT with larger layer spacing should be more easily dispersed in the sol-gel system. However, there seems to be a greater degree of aggregation of MMT in CTA/sol-gel coating. This can be ascribed to the different molecular structure of CC and CTAB. The CC-MMT with alcohol hydroxyl group in the interlayer is more likely to interact with GPTMS/TEOS sol-gel system, leading to a better dispersion stability in sol-gel system. The profile formed by CC-MMT guiding the assembly of hydrolyzed silane molecules was marked in Fig. 3(e).

3.3 Electrochemical behavior

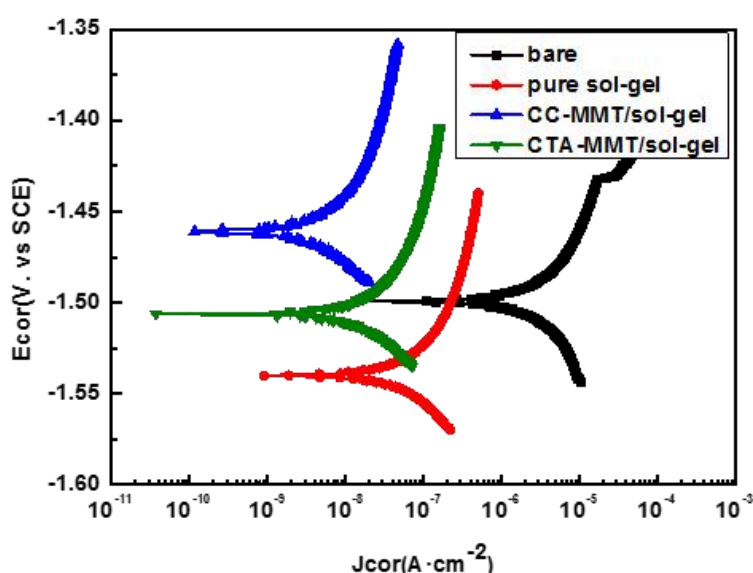


Fig. 4 Polarization curve of bare, pure sol-gel, CC-MMT/sol-gel and CTA-MMT/sol-gel coated AZ31B sample.

Table 2 Electrochemical parameters of polarization curve.

Sample	bare	pure sol-gel	CC-MMT/sol-gel	CTA-MMT/sol-gel
$E_{cor}(\text{V. vs SCE})$	-1.4993	-1.5398	-1.4609	-1.5062
$J_{cor} (\text{A} \cdot \text{cm}^{-2})$	1.4421×10^{-5}	3.3484×10^{-7}	4.3982×10^{-8}	9.0643×10^{-8}

The potentiodynamic polarization curve of several coated sample in 0.05M NaCl solution and corresponding fitting parameters were shown in Fig. 5 and Table 2, respectively. From the fitting parameters, the corrosion current density of coated sample decreased 2-3 orders of magnitude compared uncoated bare AZ31B alloy. Thus, all coated AZ31B sample exhibit better corrosion resistance. For the coated sample, the corrosion resistance can be arranged in increasing order as follows: the pure sol-gel coating (-1.5398V , $3.3484 \times 10^{-7} \text{A} \cdot \text{cm}^{-2}$) < the CTA-MMT/sol-gel coating (-1.5062V , $9.0643 \times 10^{-8} \text{A} \cdot \text{cm}^{-2}$) < the CC-MMT/sol-gel doped coating (-1.4609V , $4.3982 \times 10^{-8} \text{A} \cdot \text{cm}^{-2}$). This indicates an enhancement in corrosion resistance when modified MMT doped in,

and the CC-MMT doped coating shows better corrosion resistance than the CTA-MMT doped one. As mentioned before, the CC-MMT could interact with hydrolyzed silane and guide the assembly of hydrolyzed silane molecule. Compared to the simple mechanical mixture in CTA-MMT/sol-gel coating, the force between CC-MMT and sol-gel system in CC-MMT/sol-gel coating results in a denser coating structure, thus a better protection performance of CC-MMT/sol-gel coating.

4. Summary

(1) Two different hyamines (CC and CTAB) intercalated montmorillonite were prepared successfully. Both CC-MMT and CTA-MMT remained layered structure after intercalation modification.

(2) Pure sol-gel, CC-MMT/sol-gel and CTA-MMT/sol-gel coating was employed on AZ31B magnesium alloy and exhibited good corrosion resistance. When MMT (whatever CC-MMT or CTA-MMT) doped in, the sol-gel coating showed more durable corrosion protection compared to the pure one. Meanwhile, the CC-MMT doped sol-gel coating exhibited better corrosion resistance than CTA-MMT doped one.

(3) Better protection performance of CC-MMT/sol-gel coating originated from the tough bonding between CC-MMT and sol-gel system.

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