Effect of rare earth lanthanum-cerium doping on corrosion behavior of zinc-aluminum-magnesium hot-dip galvanizing coatings used for transmission towers

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Abstract
Purpose – The purpose of this study is to improve the corrosion resistance of the transmission towers by Zinc-aluminum-magnesium (Zn-Al-Mg) coatings doped with rare earths lanthanum (La) and cerium (Ce) (denoted as Zn-Al-Mg-Re) in Q345 steel.

Design/methodology/approach – The phase structure of Zn-Al-Mg-Re composite coatings has been determined by X-ray diffraction, whereas their surface morphology and cross-sectional microstructure as well as cross-sectional elemental composition have been analyzed by scanning electron microscopy and energy-dispersive spectrometry. Moreover, the corrosion resistance of Zn-Al-Mg-Re composite coatings has been evaluated by acetic acid accelerated salt spray test of copper strip.

Findings – Experimental results show that doping with La and Ce favors to tune the composition (along with the generation of new phase, such as LaAl₃ or Al₁₁Ce₃) and refine the microstructure of Zn-Al-Mg galvanizing coatings, thereby significantly improving the corrosion resistance of the coatings. Particularly, Zn-Al-Mg-Re with 0.15% (mass fraction) La exhibits the best corrosion resistance among the tested galvanizing coatings.

Originality/Value – Zinc-aluminum-magnesium (Zn-Al-Mg) coatings doped with rare earths lanthanum (La) and cerium (Ce) (denoted as Zn-Al-Mg-Re) have been prepared on Q345 steel substrate by hot-dip galvanizing so as to improve the corrosion resistance of the transmission towers, and to understand the corrosion inhibition of the Zn-Al-Mg-Re coating.

Keywords Corrosion behaviour, Transmission towers, Hot-dip galvanizing, Rare earth (La and Ce) doping, Zn-al-mg coating

1. Introduction

Transmission towers, one of the most important equipment in power production, play a key role in power transmission (Han, 2012). Usually, the failure of transmission towers is because of the natural calamities, such as storm, flood, earthquake, landslide and cyclone, as well as faults associated with design, construction and aging (Albermania et al., 2009; Rao et al., 2012); metal corrosion is an important form of transmission towers failure. As to metal corrosion, industrial emissions and/or salty coastal climate are worth of special attention (Me and Cheng, 2004), because metals are usually susceptible to severe corrosion therein. To deal with this issue, researchers have developed various techniques and materials so as to mitigate and/or prevent metal corrosion (Jamali et al., 2015; Keppert et al., 2014; Fang et al., 2009; Mishra et al., 2007; Amadeh et al., 2008), and hot-dip galvanizing with pure Zn is a widely used anticorrosion technique for transmission towers (Liu et al., 2014). However, traditional hot-dip galvanizing does not satisfy the corrosion resistance need of metal towers, and hence it is gradually substituted by zinc-based alloy plating. For example, Lugschitz and coworkers found that the immediate introduction of an appropriate coating on newly hot-dip galvanized steel parts right after galvanizing helps to extend the service life of the transmission towers to 40-50 years (Lugschitz et al., 2004). Besides, it is well recognized that environmental-factor-induced corrosion of metals can even reduce the service life of the commonly used transmission towers with galvanizing protective coatings to three to four years, far below the designed lifespan (e.g. 20 years). Therefore, zinc-aluminum-magnesium (Zn-Al-Mg) alloy and Zn-Al-Mg-Re (lanthanum-cerium, etc.) coatings have been proposed to improve the corrosion resistance of the transmission towers.
La–Ce) rare earth coatings are increasingly receiving attention because of their improved corrosion resistance (Purcek et al., 2007; Katayama and Kuroda, 2013; Li et al., 2014; Liu et al., 2009). Of these coatings, Zn-Al-Mg-Re coatings are of special significance because, on the one hand, rare earths such as La and Ce are able to hinder scale growth and increase scale adhesion thereby protecting steels and other metallic alloys against oxidation and corrosion (Zheng et al., 2013; Zhang et al., 2011); on the other hand, rare earth elements including La, Ce, Y, Nd and Gd can effectively improve the corrosion resistance and mechanical properties of Mg alloy and Cu alloy (Yang et al., 2009; Mao et al., 2009; Zhang et al., 2013; Zhang et al., 2013; Zhang et al., 2008; Yi and Zhang, 2012; Chen et al., 2007; Wang et al., 2010). For example, yttrium, with a standard electrochemical potential (−2.372 V) equaling to that of Mg (−2.372 V), adds to the possibility for Mg alloys to be applied in biomedical field (Liu et al., 2010; Quach et al., 2008; Li et al., 2013) because the incorporation of yttrium in Mg alloy like as-cast AZ91 favors to promote the generation of thermally stable Al2Y species and inhibit the generation of less thermally stable Mg17Al12 species thereby increasing the corrosion resistance and creep resistance (Luo et al., 2009; Kashefi and Mahmudi, 2012).

Currently, lanthanum is rarely used in galvanized coating to improve the protection of thermal corrosion protection of transmission tower. Therefore, in the present research, we have adopted hot-dip galvanizing technique to fabricate Zn-Al-Mg-Re (Re refers to La and Ce) coatings on transmission towers so as to acquire greatly improved corrosion resistance and prolong the service life of the towers. This paper reports the details about the preparation and corrosion resistance evaluation of as-fabricated Zn-Al-Mg-Re coatings, with the hope to promote the application of rare earth doping in corrosion-protection of transmission towers.

2. Experiment

Three kinds of Zn-Al-Mg-Re coatings with different contents of alloying elements were produced on Q345 steel (0.2 per cent C [mass fraction; the same hereafter], 1.0–1.6 per cent Mn, 0.55 per cent Si, 0.035 per cent P, 0.035 per cent S, 0.015 per cent Al, 0.02–0.15 per cent V, 0.015–0.060 per cent Nb, 0.02–0.20 per cent Ti and remainder Fe) via hot-dip galvanizing with which metallurgical bonding was acquired between zinc and steel in association with the generation of a series of iron-zinc alloys. The compositions of as-prepared alloy coatings are listed in Table I. Briefly, Q345 steel was pickled in 15 per cent (volume ratio) hydrochloric acid to remove the scale induced by milling, followed by rinsing in distilled water and drying in air, whereas a flux of zinc ammonium chloride was applied to inhibit oxidation of the cleaned steel surface upon exposure to air. The flux of zinc ammonium chloride was allowed to dry naturally on the steel thereby aiding the follow-up hot-dip galvanizing process. As-cleand-dried Q345 steel was then dipped into molten Zn-Al-Mg-Re bath to undergo hot-dip galvanizing for 80 s at 460°C. As-prepared hot-dip galvanizing coatings were directly used for structure characterization and corrosion resistance evaluation.

The thickness of hot-dip galvanizing coatings was measured with a TT220 instrument, with which the thickness was tested at different positions of the coatings, and at least ten measurements were conducted for each coating sample. The average of the repeat measurements is reported in this article.

The phase species of the coatings were analyzed by X-ray diffraction (XRD; Rigaku-D/max 2000 diffractometer), and the XRD data were collected over a 2θ range of 10°–90° at a step width of 0.1° (copper X-ray tube, 50 kV and 250 mA).

According to Chinese National Standard GB/T10125-1997 (“Acetic acid accelerated salt-spray test of copper strip”; the pH value of the acetic acid solution is 3.1 ~ 3.3), the salt spray test was carried out in 5 per cent NaCl aqueous solution. The salt spray environment [the salt settlement rate is 1–2 mL/(80 cm² · h)] in the salt spray test chamber was maintained at a constant temperature of 50°C. A group of to-be-tested specimens were exposed in the salt spray environment [the salt sedimentation rate is 1–2 mL/(80 cm² · h)]. The concentration of acetic acid and CuCl2 2H2O is 0.26 g/L and 0.02 g/L for different time of up to 240 h, and these were observed and weighed every 24 h. The morphologies of the corroded coating surfaces were observed with a Hitachi S-4800 scanning electron microscope (SEM; Hitachi Inc., Japan).

3. Results and discussion

3.1 Microstructure of as-prepared Zn-Al-Mg-Re (La–Ce) coatings

The XRD patterns of Zn-Al-Mg-Re (La–Ce) coatings with different contents of alloying elements are shown in Figure 1. It is seen that Zn-Al-Mg-Re-1 coating consists of Zn matrix and LaAl3 alloy, Zn-Al-Mg-Re-2 coating consists of Zn matrix as well as AlMg2Zn3 and AlMg2Zn alloys, and Zn-Al-Mg-Re-3 coating consists of Zn matrix as well as Mg2Zn11, AlMg2Zn and Mg2Zn11 alloys. No Mg secondary phase is detected in Zn-Al-Mg-Re-1 coating by XRD. Besides, no new phases of rare earth elements (La and Ce) are detected in Zn-Al-Mg-Re-2 coating, which is because the doped rare earths (La and Ce) tend to chemically combine with O or S to form inclusion floating in the pool, leaving only a small amount of rare earths to incorporate into the solid solution. Moreover, combining XRD patterns of Zn-Al-Mg-Re-1 coating and Zn-Al-Mg-Re-3 coating provides evidences to the observation that the doped rare earth elements promote the formation of solid solution in Zn-Al-Mg-Re coatings, because of the accelerated reaction with Al giving rise to new phases, such as LaAl3 and Al11Ce3.

3.2 Anticorrosion behavior of as-prepared Zn-Al-Mg-Re coatings

Figure 2 shows the weight losses of Zn-Al-Mg-Re galvanizing coatings subjected to different durations of salt-spray corrosion test. In addition, some data coming from the other paper (Fang et al., 2011) was involved as shown in Figure 2. It is seen that all the three kinds of Zn-Al-Mg-Re composite coating exhibit
much smaller weight loss than pure Zn coating, and Zn-Al-Mg-Re-1 composite coating exhibits the smallest weight loss among the tested galvanizing coatings. In the meantime, the weight loss of the composite coatings is less than 50 per cent of that of pure Zn coating tested under the same conditions. Therefore, it can be concluded that doping rare earths such as La and Ce favors to significantly improve the corrosion resistance of Zn-Al-Mg galvanizing coatings. Particularly, the Zn-Al-Mg composite coating doped with 0.15 per cent (mass fraction; the same hereafter) La-Ce exhibits the best corrosion resistance among the tested galvanizing coatings.

Table II lists the thickness and corrosion rate of the tested galvanizing coatings and the time at which the coatings undergo initial rust. The thickness of the pure Zn coating is about 90 \( \mu \text{m} \), and that of the three kinds of composite coatings doped with rare earths is about 80 \( \mu \text{m} \). Besides, the three kinds of doped coatings have quite similar corrosion rate, and all these experience the initial rust after 240 h of salt-spray tests. However, pure Zn coating exhibits a much higher corrosion rate than the doped composite coatings, and its initial rust emerges after only 96 h of salt-spray corrosion test. This also proves that rare earth doping is beneficial to improving the corrosion resistance of Zn-Al-Mg galvanizing coatings.

Figure 3 shows the polarization curves of the three kinds of rare earth-doped composite coatings in 3.5 per cent NaCl solution, where the average electrochemical corrosion rate is obtained on the basis of Tafel extrapolation. It is seen that all the three kinds of rare earth-doped Zn-Al-Mg composite coatings have much lower corrosion current than pure Zn coating, which well corresponds to the above-mentioned observation that rare earth (La-Ce) doping helps to greatly improve the corrosion resistance of Zn-Al-Mg galvanizing coatings. Particularly, LaAl\(_3\) possesses better corrosion resistance than binary or ternary phases of Zn/Al/Mg, which is why Zn-Al-Mg-Re-1 coating exhibits better corrosion resistance than Zn-Al-Mg-Re-2 coating and Zn-Al-Mg-Re-3 coating. In the meantime, ternary phase of Zn/Al/Mg exhibits better corrosion resistance than binary phase of Zn/Al/Mg. As a result, Zn-Al-Mg-Re-2 coating exhibits better corrosion resistance than Zn-Al-Mg-Re-3 coating (the former has a lower content of Mg/Zn binary phase than the latter). Moreover, Zn-Al-Mg-Re-1 coating containing intermetallic compound LaAl\(_3\)
exhibits better corrosion resistance than Zn-Al-Mg-Re-3 coating containing intermetallic compound Al$_{11}$Ce$_3$.

It is usually accepted that the corrosion resistance of alloy coatings is closely related to the composition and thickness as well as grain size and microstructure. Because the thickness of Zn-Al-Mg galvanizing coating is quite similar to that of the three kinds of rare earth-doped Zn-Al-Mg composite coatings, we can suppose that the noticeable difference in the corrosion resistance of the two categories of galvanizing coatings should be attributed to the difference in their composition and/or grain size and microstructure. In other words, doping La and Ce leads to changes in the composition as well as the grain size and microstructure of Zn-Al-Mg galvanizing coating, thereby providing effectively improved corrosion resistance. This supposition is supported by the surface and cross-sectional SEM images of the tested galvanizing coatings as shown in Figures 4, 5, 6 and 7, where the cross-sectional images of the elemental composition of all the tested galvanizing coatings are also given for comparisons. Pure Zn coating consists of coarse grains and contains obvious pores and interfacial cracks (Figure 6); and in particular, a high amount of O is detected beneath the interface toward the steel substrate, whereas a high amount of Fe is detected above the interface toward the coating surface. This implies that structure defects such as pores and cracks act as the channels for the corrosion medium to penetrate through the pure Zn coating, thereby leading to severe corrosion. Differing from pure Zn coating, all the three kinds of rare earth-doped Zn-Al-Mg composite coatings are compact and nearly free of defects including cracks and pores, and these consist of fine grains as well (Figures 5, 6 and 7), which well correspond to their much better corrosion resistance than that of pure Zn coating. Corresponding SEM images of the elemental composition of the three kinds of rare earth-doped Zn-Al-Mg composite coatings show that these contain less O and Fe around the coating-substrate interface, which also gives evidences to the conclusion that rare earth

**Figure 4** SEM images of (a) surface and (b) cross-section as well as (c) cross-sectional linear SEM-EDS of pure Zn coating

**Notes:** Red: O; green: Zn; blue: Fe

**Figure 5** SEM images of (a) surface and (b) cross-section as well as (c) cross-sectional linear SEM-EDS of coating ZAMR-1

**Notes:** Red: O; green: Zn; blue: Fe
(La-Ce) doping favors to tune the composition and refine the microstructure of Zn-Al-Mg coating, thereby leading to significantly improved corrosion resistance. In other words, surface active rare earths tend to concentrate on the surface of Zn-Al-Mg galvanizing coatings to form a dense and uniform protective layer along with a transition layer upon the diffusion of Fe and Zn between the substrate and the coating, thereby inhibiting the corrosion caused by S, O and other impurities with higher electronegativity such as S and O that can accelerate corrosion of metals.

Usually, zinc is liable to white rust, a rapid and localized corrosion attack characterized by the occurrence of a voluminous white deposit. Such a rapid corrosion process can completely remove zinc from a localized area, thereby reducing the service life of the steel equipment protected with Zn coating. Figure 8 shows the optical micrographs of a part of the real transmission towers protected by conventional galvanizing coating and Zn-Al-Mg-Re-1 composite coating (the optical pictures were taken after the transmission towers were tested in the field for one year). It can be seen that the Zn-Al-Mg-Re-1 composite coating can effectively prevent the transmission towers from corrosion in the field, whereas conventional galvanizing coating is less competitive in this respect.

**4. Conclusions**

Zn-Al-Mg-Re coatings have been successfully prepared on Q345 steel substrate by hot-dip galvanizing. Doping La or Ce gives rise to new phase such as LaAl$_3$ or Al$_{11}$Ce$_3$ in Zn-Al-Mg galvanizing coatings thereby tuning the composition and refining the microstructure of the coatings. As a result, Zn-Al-Mg-Re galvanizing coatings exhibit much better corrosion resistance than the conventional hot-dip galvanizing coating.
resistance than Zn-Al-Mg galvanizing coating. Particularly, Zn-Al-Mg-Re galvanizing coating with 0.15 per cent La possesses the best corrosion resistance among various tested coatings and is able to prevent the steel substrate from white rust even after 168 h of acetic acid accelerated salt-spray test of copper strip, showing promising application in corrosion prevention of the transmission towers.

References


properties and corrosion behavior of die-cast mg 4Al-based alloys containing la and/or ce”, Materials Science and Engineering: A, Vol. 489 No. 1, pp. 113-119.


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