Corrosion behavior of lithium silicate-based Zn-5.5Al-4.5Mg-0.3Ce coating

Shaoguang Han, Chengjin Shen and Shuzheng Zhou
School of Materials Science & Engineering, China University of Mining and Technology, Xuzhou, People’s Republic of China

E-mail: 1424148993@qq.com, cjshenxz@cumt.edu.cn and 2240278047@qq.com

Keywords: lithium silicate-based Zn-5.5Al-4.5Mg-Ce coating, layered double hydroxide (LDH), corrosion mechanism, Zn-5.5Al-4.5Mg alloy

Abstract
The effects of Ce on the microstructure of Zn-5.5Al-4.5Mg alloy and the corrosion mechanism of Zn-5.5Al-4.5Mg-0.3Ce alloy and its coatings were investigated in this research. The results show that the structure of Zn-5.5Al-4.5Mg-0.3Ce alloy is composed of hcp-Zn, fcc-Al and ternary eutectic structure (Zn/Al/MgZn2/Mg2Zn11), without dendritic tissue and MgZn2. The salt spray corrosion performance of Zn-5.5Al-4.5Mg-0.5CMC-2C coating was significantly better than that of Zn-5.5Al-4.5Mg-0.3Ce coating and Zn-5.5Al-4.5Mg alloy. Sodium carboxymethylcellulose and graphene improve the film formation and electrical conductivity of water-based lithium silicate resin. During corrosion of Zn-5.5Al-4.5Mg-0.3Ce series alloy and coatings, Zn and Mg2Zn11 dissolved preferentially to form corrosion products of Zn5(OH)6(CO3)2 and Zn5(OH)8Cl2·H2O. Mg6Al2(OH)16CO3·4H2O and Zn4Al2(OH)12CO3·3H2O bimetallic hydroxide colloidal membranes were formed, which attached and wrapped on the surface of early corrosion products. Mg6Al2(OH)16CO3·4H2O and Zn4Al2(OH)12CO3·3H2O, preventing the dissolution of soluble corrosion products, improved the corrosion resistance of Zn-5.5Al-4.5Mg-0.3Ce alloy.

1. Introduction
Zinc coatings have greatly contributed to improve the corrosion resistance of steels which exposed to corrosive environments [1]. Zn-Al-Mg coating is a new sacrificial anode material that does not impressed current to protect steel. At present, companies such as Roval coating company, Eckave-Werke in Germany, and Dacro in the United States have produced zinc-rich coatings. Inorganic lithium silicate resin is an environmentally friendly material but has some disadvantages, such as discontinuous film formation, slow curing speed, poor adhesion, easy cracking, peeling, and powder loss [2]. To improve its film-forming properties, sodium carboxymethyl cellulose, silane and graphene were added to the coating. The carboxymethyl cellulose aqueous solution has the advantages of thickening, film formation, and adhesion. Silane can enhance coating adhesion and improve its mechanical, water resistance and anti-aging properties. Graphene modified epoxy zinc powder primer has stable performance, good anti-corrosion performance [3, 4]. In the present study Zn-5.5Al-4.5Mg-0.3Ce coatings were made of carboxymethyl cellulose, silane, graphene and so on. The corrosion properties and mechanisms of the coatings were discussed.

2. Materials and methods

2.1. Materials
The metals of Zn, Al (99.99 wt%), Mg (with 99.85 wt%) and Ce were melted in medium frequency induction furnace at 600 °C. The molten alloy was homogenized by mechanical stirring. The cover agent with carbon
powder (6 wt%), mix chlorine salt (39 wt%) with MgCl₂, ZnCl₂ and KCl and CaF₂ (55 wt%), etc was covered the surface of melt liquid during smelting. Zn-5.5Al-4.5Mg-Ce alloy powder was prepared from molten superalloy liquid by atomization of 2MPa argon.

Alloy powder, water-based inorganic lithium silicate resin, sodium carboxymethylcellulose (CMC-Na) and graphene (mass ratio 70:30:0.5:2) were stirred for 30 min to make slurry. The slurry was coated on the surface of the sandblasted Q235 steel and solidified for 72 h at room temperature to form coating.

2.2. Experimental method
The microstructure was observed by OLYMPUS metalloscope(OM) and Tecnai G2 F20 field emission transmission electron microscope(TEM). X-ray diffraction (XRD) measurement was performed on a Bruker D8 x-ray diffraction. Cu Kα radiation was used as x-ray source. A step-scan mode was used at the 2-theta range from 10° to 90° with a step length of 0.1°. The operating conditions were 40 kV and 30 mA.

The electrochemical properties of alloys and coatings were investigated using CHI604E electrochemical workstation (Shanghai CH Instruments Co, China). All tests were measured in 3.5% NaCl aqueous solutions at room temperature. The electrochemical polarization is conducted at a scanning rate of 1 mV/s using a saturated calomel electrode (SCE) as the reference electrode. A platinum flake is used as the counter electrode. The surface area of the sample exposed to the NaCl solution is 1 cm².

The full-immersion corrosion test of Zn-5.5Al-4.5Mg alloys and coatings were conducted in room temperature solution pH = 7, 3.5%(wt%)NaCl, and the solution was replaced every 7 days for 40 days.

Neutral salt spray test of Zn-5.5Al-4.5Mg-Ce coatings were investigated in 5% NaCl solution with a salt spray deposition of 1.5 ml/min and an ambient temperature of 35 ± 2 °C. The samples size were 150 × 60 × 8 mm.

3. Results and discussion

3.1. Composition and structure of alloy and powder
3.1.1. The effect of Ce on microstructure of Zn-5.5Al-4.5Mg alloy
With the addition of 0.3%Ce, Zn solid solution completely changed from heterogeneously distributed dendrites to spherical dispersion and uniform distribution in Zn-5.5Al-4.5Mg alloy (figure 1).

The microstructure of Zn-5.5Al-4.5Mg-0.3Ce alloy is homogeneous with spherical Zn solid solution, Al solid solution and ternary eutectic phase. The microstructure and composition uniformity of the alloy are completely superior to the dendrite structure of Zn-5.5Al-4.5Mg alloy (figure 2, table 1).

3.1.2. Effect of Ce on phase structure of Zn-5.5Al-4.5Mg alloy
The main phase structure of Zn-5.5Al-4.5Mg-0.3Ce alloy consists of Zn-rich solid solution, Al-rich solid solution and Zn/Al/Mg₂Zn₁₁ ternary eutectic structure, without MgZn₂. It can be known that Ce is beneficial for the formation of Mg₂Zn₁₁, or promote the transformation of MgZn₂ to Mg₂Zn₁₁. It shows that MgZn₂ phase is firstly generated at high temperature and then transformed into Mg₂Zn₁₁ phase in the solidification process of Zn-5.5Al-4.5Mg alloy [5, 6].

In order to further analyze the effect of Ce on the phase structure of Zn-5.5Al-4.5Mg alloy, TEM was used for STEM analysis of Zn-5.5Al-4.5Mg and Zn-5.5Al-4.5Mg-0.3Ce alloys, respectively. The diffraction spots in the 1, 2, 3 regions analyzed in figure 3.

Then the corresponding crystal face index respectively are (112), (202) and (110) and the angles between the diffraction spots are ΦAB = 30.49°, ΦBC = 59.93° and ΦAC = 90.42°. It shows that the 1st region is hcp-Zn solid solution. The crystal face index of solid solution are (002), (222) and (220) in the 2nd region, which is a solid solution of fcc-Al. The crystal face index of solid solution are (112), (110) and (022) in the 3rd region. It is Mg₂Zn₁₁ eutectic structure.

The MgZn₂ phase could be found by XRD, but the spot diffraction could not be found in a suitable position.

It was found that the elements were uniformly distributed in the solid solution phase and other tissues by STEM (figure 4). The crystal face index of solid solution are (112), (110) and (202) in the 1st region, which is a solid solution of hcp-Zn. The crystal face index of solid solution are (002), (222) and (220) in the 2nd region. It is a solid solution of fcc-Al. The crystal face index of solid solution are (211), (300) and (111) in the 3rd region. It is Mg₄Zn₁₁ eutectic structure. The characteristic phase of MgZn₂ was not found in the alloy, which was consistent with the XRD results.

Compared with Zn-5.5Al-4.5Mg alloy, Zn-5.5Al-4.5Mg-0.3Ce alloy has of hcp-Zn, fcc-Al and ternary eutectic structure without MgZn₂ phase. The microstructure and composition distribution of the alloy are more uniform.
Figure 1. Metallographic structure images of Zn-5.5Al-4.5Mg alloys with different Ce contents: (a) Zn-5.5Al-4.5Mg, (b) Zn-5.5Al-4.5Mg-0.3Ce, (c) Zn-5.5Al-4.5Mg, (d) Zn-5.5Al-4.5Mg-0.3Ce.

Figure 2. XRD patterns of prepared specimens.

Table 1. Elemental composition of different locations in figure 1.

| Positions | Zn (wt%) | Al (wt%) | Mg (wt%) |
|-----------|----------|----------|----------|
| c1        | 97.6     | 2.4      | 0        |
| c2        | 79.97    | 20.03    | 0        |
| c3        | 89.95    | 5.5      | 4.56     |
| d1        | 98.02    | 1.98     | 0        |
| d2        | 68.19    | 31.5     | 0.31     |
| d3        | 91.85    | 4.76     | 3.37     |
3.1.3. Morphology of Zn-5.5Al-4.5Mg-0.3Ce powder
The morphology distribution of Zn-5.5Al-4.5Mg-Ce alloy powder was observed (figure 5). Alloy powder is spherically dispersed, with particle sizes ranging from 2 to 6 μm. Scanning energy spectrum analysis results show that the main components of Zn-5.5Al-4.5Mg-0.3Ce coating are Zn, Al, Mg, Si, O (table 2). Si and O in the coating come from inorganic lithium silicate resin. The elements of coating and powder are slightly different.

3.2. Corrosion law of Zn-5.5Al-4.5Mg-0.3Ce coatings
The Electrochemical behavior of the Zn-5.5Al-4.5Mg alloys and coatings were investigated by the three-electrode method. Representative polarization curves in 3.5% NaCl solution for Zn-5.5Al-4.5Mg alloys and
coatings with different conditions are presented in figure 7. While the addition of Ce makes the structure and composition of Zn-5.5Al-4.5Mg alloy more uniform and has not obvious effect on its corrosion potential. The electrode potential of the Zn–5.5–4.5Mg-0.3Ce coatings are higher than that of alloys. In the alloy system, Ce can make the corrosion potential of the alloy positively shifted. Ce plays the role of refining grain, increasing the repair speed of surface film and reducing the corrosion tendency [7].

The anodic polarization curve of Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC alloy coating is at the top. The Zn-5.5Al-4.5Mg-0.3Ce coating with graphene showed lower corrosion current under the same condition. The addition of graphene and CMC reduced the corrosion current of Zn-5.5Al-4.5Mg-0.3Ce coatings.

| Area                  | Zn (wt%) | Al (wt%) | Mg (wt%) | Si (wt%) | O (wt%) |
|-----------------------|----------|----------|----------|----------|---------|
| Zn-5.5Al-4.5Mg-0.3Ce powder | 90.04    | 5.85     | 4.11     | —        | —       |
| Zn-5.5Al-4.5Mg-0.3Ce coating | 85.10    | 5.25     | 2.31     | 1.42     | 5.92    |
The self-corrosion potential of the Zn-5.5Al-4.5Mg-0.3Ce, Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC and Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C coatings have been improved to some extent, but they were still at the protective potential of steel in sea water (−0.85∼−1.0 V vs. SCE) (table 3). On the other hand, the corrosion current density of Zn-5.5Al-4.5Mg alloy decreased significantly from 5.879 μA/cm² to 3.960 μA/cm² with the addition of Ce. However, compared with the alloy, the corrosion potential and corrosion current density of Zn-5.5Al-4.5Mg-0.3Ce coating increased slightly. CMC and graphene reduced the corrosion current density of Zn-5.5Al-4.5Mg-Ce coatings to different degrees. Zn-5.5Al-4.5Mg-0.5CMC-2C coating has the lowest corrosion current density of 3.217 μA/cm².

3.3. Salt spray corrosion characteristics of Zn-5.5Al-4.5Mg-0.3Ce coatings

Corrosion test of surface topography of coatings as shown in figures 8, 9 and 10. There was no sign of rust at the scratch of the Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C coating after 700 h. Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C coating had better cathodic protection and corrosion resistance than Zn-5.5Al-4.5Mg-0.3Ce, Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC coatings. It was found that CMC-Na and graphene could significantly improve the film formation performance of the coating that made the film formation more continuous and the coatings conductivity more excellent.

3.4. Zn-5.5Al-4.5Mg-0.3Ce alloy and Coating corrosion mechanism

The corrosion rate of Zn-5.5Al-4.5Mg-0.3Ce coating was lower than that of Zn-5.5Al-4.5Mg alloy. The SEM morphologies of corrosion products on the surfaces of Zn-5.5Al-4.5Mg alloy, Zn-5.5Al-4.5Mg-0.3Ce alloy and Zn-5.5Al-4.5Mg-0.3Ce coating were observed. The corrosion morphologies of Zn-5.5Al-4.5Mg alloy are shown in figures 11(a) and (b). The corrosion products were loose straw pellets or blade-like aggregates, which gradually form into a flocculent soluble product. The corrosion products were mainly composed of Zn₅(OH)₆(CO₃)₂ and Zn₅(OH)₆Cl₂·H₂O, which were consistent with the results in relevant literatures [8]. The corrosion morphologies of Zn-5.5Al-4.5Mg-0.3Ce alloy and coating are shown in figures 11(c) and (d). The corrosion products were spherical in relatively dense structure, and the spheres were stacked on top of each other. The surface of the sphere is enveloped by a denser membrane. The surface of the sphere is a gastric wall structure with a larger specific surface area. Further XRD analysis was carried out on the corrosion products (figure 12). In addition to Zn₅(OH)₆(CO₃)₂ and Zn₅(OH)₆Cl₂·H₂O, the corrosion products also contained...
Zn$_4$Al$_2$(OH)$_{12}$CO$_3$·3H$_2$O and Mg$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O. Zn$_4$Al$_2$(OH)$_{12}$CO$_3$·3H$_2$O and Mg$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O are Zn-Al and Mg-Al bimetallic hydroxide with colloidal membrane properties [9].

Zn-5.5Al-4.5Mg-0.3Ce alloy had lower corrosion rate than Zn-5.5Al-4.5Mg. Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C coating had lower corrosion current density than Zn-5.5Al-4.5Mg-0.3Ce coating. It was found that Ce could make the structure and composition of Zn-5.5Al-4.5Mg alloy more uniform and electrochemical corrosion process more stable. CMC-Na could improve the film forming performance of Zn-5.5Al-4.5Mg-0.3Ce coating, and the corrosion performance of the coating was better than that of Zn-5.5Al-4.5Mg-0.3Ce coating. The combined action of CMC-Na and graphene not only improved the film forming performance of Zn-5.5Al-4.5Mg-0.3Ce coating, but also greatly improved the electrical conductivity of the coating. When Zn-5.5Al-4.5Mg-0.3Ce alloy coating was corroded, hcp-Zn and Mg$_2$Zn$_{11}$ phases are preferentially corroded and

Figure 8. Morphologies of the Zn-5.5Al-4.5Mg-0.3Ce coating with different paints mist corrosion.

Figure 9. Morphologies of the Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC coating with different paints mist corrosion.

Figure 10. Morphologies of the Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C coating with different paints mist corrosion.
dissolved to form $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$. With the increase of $\text{Mg}^{2+}$ and $\text{Al}^{3+}$ concentration in the corrosive environment, the layered double hydroxide (LDH) of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot4\text{H}_2\text{O}$ and $\text{Zn}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3\cdot3\text{H}_2\text{O}$ are formed [9]. The LDH film wraps around the surface of spherical $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$, forming a relatively dense corrosion product film. The corrosion process of Zn-5.5Al-4.5Mg-0.3Ce alloy was slowed down, and the transformation of corrosion products $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ from spherical to soluble flocs was slowed down [10]. Graphene also forms a physical barrier layer in the coating, improving the corrosion resistance of the coating [11]. So that the corrosion rate of Zn-5.5Al-4.5Mg-0.3Ce-0.5CMC-2C alloy coating is the lowest.

![Figure 11](image1.png)  
**Figure 11.** The corrosion morphology of coatings with different Ce contents for 40 days. (a) Zn-5.5Al-4.5Mg alloy; (b) magnified picture of the local area in (a); (c) Zn-5.5Al-4.5Mg-0.3Ce alloy and coating; (d) magnified picture of the local area in (c).

![Figure 12](image2.png)  
**Figure 12.** XRD patterns of corrosion products of alloy and coating samples for 40 days.
4. Conclusions

The structure of Zn-5.5Al-4.5Mg-0.3Ce alloy and the corrosion performance optimization of Zn-5.5Al-4.5Mg-0.3Ce coating of lithium silicate were analyzed experimentally and theoretically, the main conclusions are as follows:

1. Zn-5.5Al-4.5Mg alloy is composed of hcp-Zn, fcc-Al and ternary eutectic Zn/Al/MgZn2/Mg2Zn11 phases. The addition of Ce to the Zn-5.5Al-4.5Mg alloy significantly improves homogeneity of the Zn-rich dendrite solid solution, rod Al-rich solid solution and non-uniform eutectic structure (Zn/Al/MgZn2) distribution, and inhibits the precipitation of MgZn2.

2. The trace element of Ce has little effect on the corrosion potential of Zn-5.5Al-4.5Mg alloy. The corrosion current density of the alloy decreased from 5.879 μA/cm² to 3.96 μA/cm². The self-corrosion potential of Zn-5.5Al-4.5Mg-0.3Ce coating is obviously higher than that of alloy. The corrosion current density of Zn-5.5Al-4.5Mg coating is lower by a small amount of graphene and CMC-Na. Zn-5.5Al-4.5Mg-0.5CMC-2C alloy coating has the lowest corrosion current density of 3.217 μA/cm².

3. The corrosion products of Zn-5.5Al-4.5Mg alloys and coating contain Zn5(OH)6(CO3)2, Zn5(OH)8Cl2·H2O, Mg6Al2(OH)16CO3·4H2O and Zn4Al2(OH)12CO3·3H2O. Zn and Mg2Zn11 phase preferentially corroded and dissolved to form corrosion products of Zn5(OH)6(CO3)2 and Zn5(OH)8Cl2·H2O. As the corrosion process continued, the layered double hydroxides (Mg6Al2(OH)16CO3·4H2O and Zn4Al2(OH)12CO3·3H2O)-LDH wrap on the surface of spherical Zn5(OH)6(CO3)2 and Zn5(OH)8Cl2·H2O, decreasing the gap between the corrosion products balls, slowing down the transformation of Zn5(OH)6(CO3)2 and Zn5(OH)8Cl2·H2O to floccular soluble corrosion products, and delaying the corrosion process of Zn-5.5Al-4.5Mg-0.3Ce alloy.

Acknowledgments

This work was partially supported from Jiangsu Provincial Key Research and Development Program (NO. BE2018061).

Funding

This research was funded by Jiangsu Provincial Key Research and Development Program, grant number BE2018061.

Conflicts of interest

The authors declare no conflict of interest.

ORCID iDs

Shaoguang Han  https://orcid.org/0000-0002-5334-4929
Chengjin Shen  https://orcid.org/0000-0002-9714-7580
Shuzheng Zhou  https://orcid.org/0000-0002-5641-8460

References

[1] Naderi R and Attar M M 2010 Corros Sci 52 0 1286
[2] Canosa G, Alfiari P V and Giudice C A 2012 Progress in Organic Coatings 73 178–85
[3] Cheng L et al 2019 Journal of Alloys and Compounds 774 255–64
[4] Nair R R, Wu H A, Jayaram P N, Grigorieva I V and Geim A K 2012 Science 335 442–4
[5] Honda K, Yamada W and Ushioda K 2008 MATERIALS TRANSACTIONS 49 1395–400
[6] Prosek T, Nazarov A, Bexell U, Thierry D and Serak J 2008 Corros Sci 50 2216–31
[7] Huang G R, Sun Y M, Li Z and Liu Y L 2018 Journal of Materials Engineering 46 105–11
[8] Prosek T et al 2016 Corros Sci 110 71–81
[9] Zhou S, Shen C, Han S, Tao Q and Chen Z 2019 Materials Research Express. 6 086508
[10] Diler E, Rouvellou B, Bioual S, Lescop B, Vien G N and Thierry D 2014 Corros Sci 87 111–7
[11] Praael D, Tubercquia J C, Harl R R, Jennings G K and Bolotin K I 2012 Ac Nano 6 1102–8