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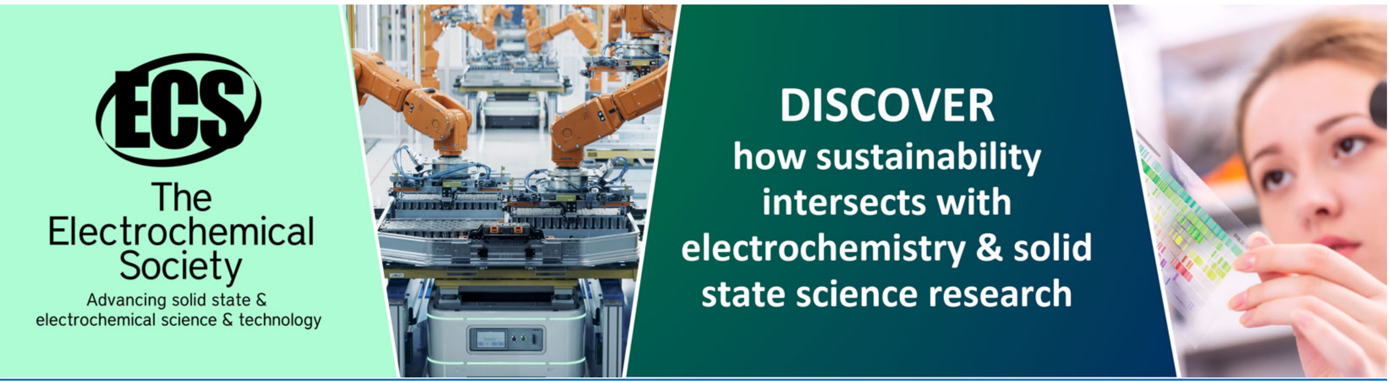

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Study on the Alloy Coatings Properties of the New Rare Earth Yttrium Zinc Aluminum Magnesium

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Abstract. Hot dip plating is a main methods of iron and steel protection, but the traditional hot dip galvanizing products can not meet the actual needs. The addition of aluminium (Al), magnesium (Mg), rare earth (Re) and other alloying elements in zinc solution has become a hot research topic. In order to obtain multicomponent alloy coating with high corrosion resistance, a new type of hot dip galvanizing coating was obtained by adding Re yttrium(Y) into Zn-Al-Mg plating bath. The influence of adding elements Re Y, Al and Mg on the corrosion resistance of hot dipped galvanized coatings was studied by conducting immersion tests, salt spray tests and electrochemical tests (Tafel, EIS), and the anticorrosion mechanism of the coatings was primarily explored. The results showed that rare earth yttrium can improve the corrosion resistance of hot dipped galvanizing, and Zn-2%Al-1%Mg-0.08%Re alloy coating has the best corrosion resistance. Hopefully, the present work uses the current hot dip galvanizing production equipment and technology, the established galvanizing technology can be applied in industry.

1. Introduction

For many years, people have been studying how to improve the properties of traditional hot-dip galvanizing coating by adding Single element or multicomponent alloying elements to Zn plating baths, such as aluminum, magnesium, rare earth, copper, nickel, titanium, tin[1,2]. Hot dip galvanizing is one of the methods for surface treatment of iron and steel. Its advantages lie in the simple processing process and the excellent corrosion resistance of the obtained products. Therefore, they are widely used in automobiles, household appliances and construction industries[3]. With the rapid development of modern industry, science and technology, the traditional galvanizing coating can not meet the need of corrosion prevention. Galvalume aluminum-zinc-silicon hot plating alloy which came out in 70s and Galfan zinc-aluminum rare earth hot plating alloy born in 80s occupy the market rapidly because of its excellent corrosion resistance[4]. However, the production of the above two kinds of hot-plated alloy coating need to make a great transformation of the traditional hot-plating production line, especially the steel wire coating. It is generally believed that adding a small amount of rare earth to zinc does not change the structure of the coating. The diffusion of rare earths in intermetallic compounds is inhomogeneous, and it is inferred that the segregation of rare earth elements at the interface between alloy zinc solution and solid iron inhibits the diffusion of aluminum, zinc and iron, and delays the growth of intermetallic compounds[5-9]. Rare earth elements are scandium, yttrium, and other lanthanides. Their contents in the earth's crust are rare, and their oxides are similar in nature to those of native elements such as calcium oxide, so they are named rare earth. Yttrium and cerium are the two elements with a large content in the earth's crust which are found first in rare earth elements and are cheaper than other rare earth oxides[10]. Zinc-based alloy coatings with higher corrosion resistance and special-performance coatings have also received increasing attention. Although the corrosion resistance of these coatings is greatly improved compared with the traditional hot-dip galvanizing, the production process is complicated and the production cost is expensive, and it is not widely used in domestic applications[11,12]. It is still one of the research trends in this field to study new coatings that have a production cost that is comparable to traditional hot-dip galvanizing and that have significantly improved corrosion resistance. In this work, using the current hot galvanizing production equipment and processes, a small amount of Al (2%), Mg (1%), and trace rare earth elements were added to the hot-dip Al-Mg-Zn alloy coating prepared by electrolysis activation plating method. A multi-alloy coating with high corrosion resistance was obtained. The effects of adding different elements on the corrosion resistance of the hot-dip galvanizing base alloy coating were comprehensively discussed.

2. Experiment

2.1. Experimental Materials
Zinc chloride, aluminum chloride hexahydrate, magnesium tape, rare earth Y. Pit furnace SGZ-5-10, Electronic balance FA2004N, Digital display regulator XMTA, Electric blast drying oven 101-2AB, Salt spray test box KD-200, Electrochemical workstation CS350, X-ray powder diffractometer M1 MISTRAL, Scanning electron microscope FEI-200.

2.2. Material Preparation
The pretreated and dried substrate was immersed in a molten alloy furnace at about 450°C for 2 minutes, extracted from a crucible resistance furnace at a suitable speed (0.1 to 0.3 m/s), and naturally cooled in air. 2% Al and 1% Mg were added to the zinc liquid (99.8%). The rare earth elements were added in the form of an intermediate alloy. The amount of each element was calculated according to the chemical composition of the preplated layer. In order to reduce the loss caused by the burning of alloying elements, the surface of the molten alloy was protected by flux. The main components of the alloy are $MgCl_2$, KCl and CaF_2, which were prepared at a mass ratio of 3:2:1.

2.3. Neutral Salt Spray Test and Electrochemical Test
The salt spray test is a method of rapidly corroding different kinds of deposits by creating an atmosphere similar to that of the marine atmosphere. This method can quickly assess the corrosion resistance of the coating and help people select the appropriate coating.
Electrochemical reactions occur during the metal corrosion process. Electrochemical experiments use artificially created electrochemical corrosion environments to study the changes in the electrochemical parameters during the metal corrosion process to analyze the corrosion resistance of the metal. The test conditions required for electrochemical tests are simple, the relevant parameters are easy to adjust, and they are more accurate and faster than the salt spray test. It is a relatively common method.

3. Results and Discussion

3.1. Analysis of Corrosion Resistance and Study of Mechanism
According to the results of the salt spray test, the following conclusions can be drawn: After adding alloying elements to the coating, the salt spray corrosion resistance of the coating can be improved to varying degrees. After Al and Mg are added, the corrosion rate of the coating is continuously reduced, and the coating is resistant to corrosion. Corrosion performance has also been continuously improved, among which the corrosion resistance of the Zn-2% Al-1% Mg alloy coating is optimal. The addition of rare earth elements to the Zn-Al-Mg alloy makes the corrosion resistance of the coating more significant than the pure zinc coating. In the range of less than 0.1% of rare earth content, the corrosion resistance of the coating continuously increases with the increasing of the amount of rare earth Y. When the content reaches 0.08%, the corrosion resistance is the best. When the content of rare earth continues to increase to 0.10%, the corrosion resistance decreases.

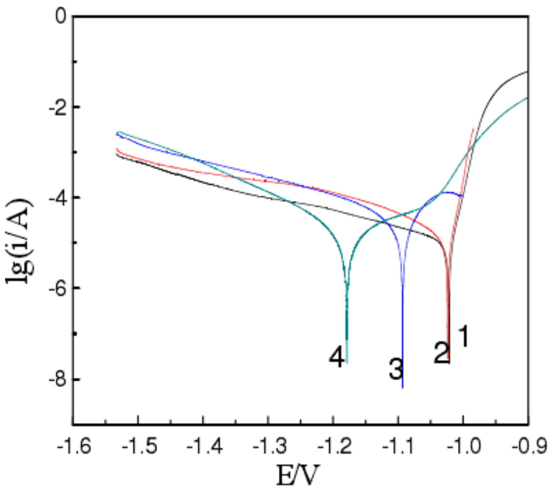

Figure 1. Polarization curves of coatings with different additions of rare earth Y in 3% NaCl solution (1.0.03Y 2.0.05Y 3.0.08Y 4.0.10Y).

3.2. Surface Morphologies and Elemental Analysis of Hot dip Zn-Al-Mg-Y

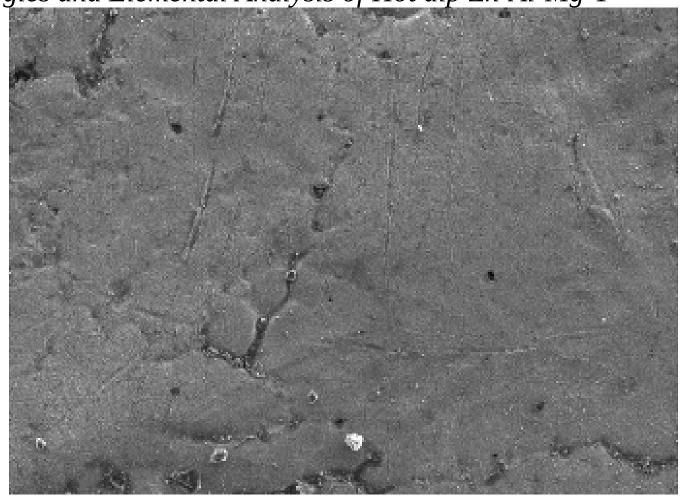

Figure 2. Surface Morphologies of Hot dip Zn-Al-Mg-Y.

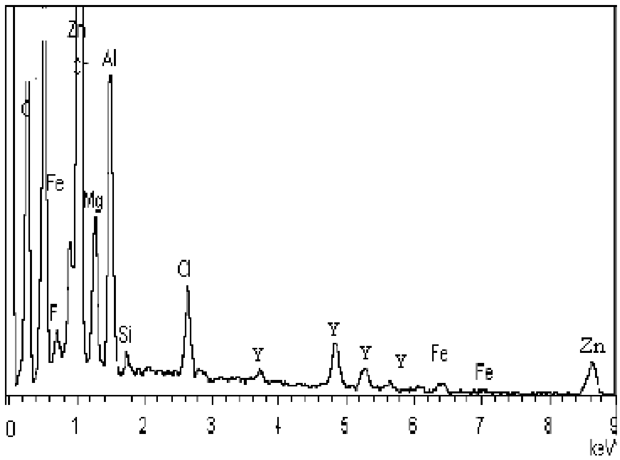

Figure 3. Elemental Analysis of Hot dip Zn-Al-Mg-Y.

For the hot dip coating with rare earth, the hot dip coating with Y content of 0.08% is now taken as an example to analyze the surface characteristics of the coating. Figure 2 shows the surface topography of

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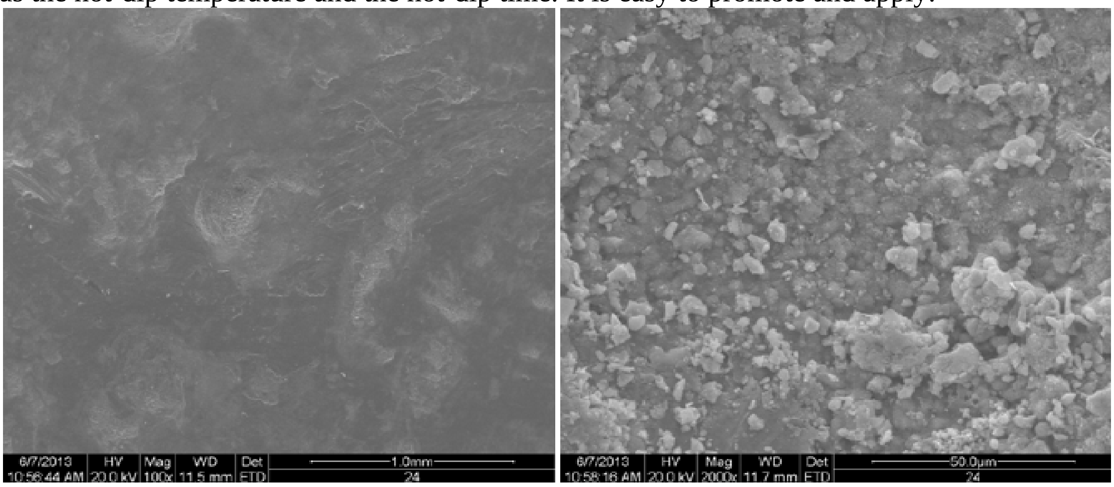
the sample. It can be seen from the SEM that the surface of the coating is complete without significant defects. Occasionally, a small amount of particulate matter adheres to the surface.
In addition, the surface also contains a small amount of Fe, O, C1 and other elements, mainly from the surface oxidation and plating agent. The continuous phase in the coating is Zn, dark inlays are Zn-Al alloys, and the white attachments are mainly Mg and Y.

3.3. Plating Microtopography of Sample
Adding Al, Mg and Re to the zinc solution， the corrosion resistance of the hot-dip zinc layer will be enhanced. Al can form a dense oxide film on the surface of the coating, Mg can refine the grains to form a eutectic structure and Re has a high chemical activity and can play a role in purifying the alloy solution and coating of the surface. The work can be produced without changing the conditions of the hot-dip galvanizing line, because in several alloy coatings, Al, Mg and Re are added in a small amount and the process parameters are not much changed compared to the conventional hot-dip galvanizing, such as the hot-dip temperature and the hot-dip time. It is easy to promote and apply.



(d1)x500 3000h Zn-2%Al-1%Mg-0.08%Yd2)x2000 3000h Zn-2Al-1Mg-0.08Y

Figure 4. Surface morphology of the coating after 3000h salt spray test.

In addition, the addition of rare earth elements in the alloy liquid will reduce the surface tension of the alloy liquid, so that the plating liquid and the substrate are fully wetted. The addition of trace rare earth can refine the grain, which is related to the change of surface tension. Because the surface tension of the alloy liquid decreases, the specific surface energy of the solid-liquid interface also decreases, then the surface energy of the nucleation system decreases. Studies show that rare earth， the element can reduce the wetting angle of the zinc solution. As the temperature of the zinc bath increases, the wetting angle becomes gradually smaller. Surface tension of zinc liquid. It decreases with the increase of the amount of rare earth elements. But when added to a certain amount, it does not change. When rare earth is added in excess, rare earths and metals or form intermetallic compounds, these intermetallic compounds are more active, they have Greater corrosion tendency, so the corrosion resistance of the plating layer becomes worse. Eventually, the critical nucleus radius decreases, the nucleation rate increases, and the crystal grain is fine.

4. Conclusion
In this paper, based on the study of Zn-Al-Mg coatings, different amounts of rare earth Y elements are added to Zn-Al-Mg baths. The hot-dip plating process of zinc-based multi-element alloy coating was studied, and the optimal content and addition method of rare earth were determined. Based on above studies, a Zn-Al-Mg-Y alloy coating was prepared, its corrosion resistance and corrosion mechanism were studied. With the addition of rare earth elements, the resulting corrosion products continuously cover the surface of the coating, and the morphology of the corrosion products is also relatively dense. And the dense corrosion products prevent the intrusion of corrosive media and protect the substrate.

Acknowledgments
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