Effect of Rare Earth Element La on Corrosion Resistance of Powder Zinc Coating: Experiment and First Principle Calculation

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Abstract. Using a combination of first-principles calculations and experimental studies to study the effect of La on the corrosion resistance of Powder sherardizing layer in metal structures. Compared to other sherardizing rare earth elements (Re), La has better adsorption with the iron matrix and has the lowest binding energy on the adsorption surface (111) of the Fe matrix. Therefore, the rare earth element La is added to the powder sherardizing process for the rare earth chemical heat treatment to reduce the defects of the powder sherardizing faults formed, improve the surface uniformity and the quality of the permeation layer. On the basis of calculation, La element was added in the process of powder sherardizing, and the corrosion performance of the formed powder galvanizing layer was studied. After alternating salt spray experiments, the degree of corrosion of the layer is relatively small and the corrosion products are predominantly layered and spherical. Electrochemical tests of the layer show that the corrosion resistance of the layer after the rare earth chemical heat treatment has improved.

Keywords. Sherardizing, first principle, rare earth element.

1. Introduction

Most metal structures are exposed to the atmospheric or marine environment and corrosion is the main failure mode. By infiltrating the metal surface with a zinc layer that has a lower self-corrosion potential than the substrate, a protective layer is formed and the effect of protecting the substrate is realized. Powder sherardizing utilizes the permeation and diffusion of heated atoms to obtain an alloy layer by heat treatment under conditions where the temperature is lower than Ac1 and the base metal does not undergo a phase change. However, the alloy layer formed by powder sherardizing is defective and requires further research to improve the quality and corrosion resistance of the layer.

Yu Wangcheng et al. found that introducing rare earth element content into gas nitriding increased the thickness of nitriding, increased the content of the Fe₃N phase in the nitrided layer, and increased the corrosion resistance of the nitrided layer [1]. Ji Wenwen et al studied the effect of the addition of rare earths on the aluminization of 40Cr steel, and found that the addition of Re improves the aluminizing rate, improves the aluminized layer structure, and improves the hardness of the aluminized layer [2]. Su Zhenguo et al. found that introducing Nb into the powder boronizing process and adding 5% Nb element effectively increased the thickness and microhardness of the permeation layer and reduced the rate of corrosion of the permeation layer [3]. However, today there are few
studies on the effect of the introduction of rare earths on the corrosion resistance of the layer in the sherardizing of mechanical energy powder. Based on first-principles calculations, this paper studied the effect of the rare earth element La on the corrosion resistance of powder sherardizing layer. When studying the effects of Re, first-principles calculations provide a very attractive theoretical method, complementing experiments and understanding the mechanism of atomic action at the electronic and atomic levels. A study by Mohit Vishnoi found that there are four components that have a significant impact on the sherardizing results of powders during sherardizing: (CeO₂, La₂O₃, Nb, Zr) [4]. This paper studies the effects of atoms in the above four different components on the formation of powder sherardizing layer.

2. Calculation Details and Experimental Methods

2.1. Calculation Details

All first-principles calculations for this task are based on Density Functional Theory (DFT) using the Cambridge Serial Total Energy Package (CASTEP) of the Materials Studio software. The exchange correlation interaction is described by the Perdew-burke-Emznerhof exchange correlation density functional theory (PBESOL) modified within the Generalized Gradient Approximation (GGA). The calculation uses a cutoff energy of 400 eV plane wave energy. A 15 Å thick vacuum layer is used to avoid top and bottom interactions.

The following formula is used to calculate the adsorption energy [5]:

\[ E_{ads} = E_{RE/Fe} - E_{bulk\ Fe} - E_{isolated\ RE} \]  

Among them, \( E_{RE/Fe} \) represents the total energy of the system, \( E_{bulk\ Fe} \) represents the energy of bulk Fe, and \( E_{isolated\ RE} \) represents the energy of isolated RE atoms. Generally speaking, the more negative the adsorption energy, the greater the binding energy. In other words, the adsorption capacity is improved.

The purpose of this study is to clarify the influence and role of rare earth atoms in the formation of powdered sherardizing layers. First, the adsorption power of Re on the (100), (110), and (111) planes of the Fe matrix is investigated, and the plane on which the Fe matrix is most likely to adsorb rare earths is investigated during powder sherardizing. Next, we examine the binding energies of various Re and the Fe matrix to find out which element has the greatest impact on the powder sherardizing process. A compound of this element as a dopant is added to the powder sherardizing agent to act as an important influencing factor in the sherardizing process. Finally, observe the impact on quality and corrosion resistance of the layer before and after adding the Re to determine the importance and function of the element [6].

2.2. Experimental Methods

For sherardizing, select hexagon socket head screws with a mass of 100 kg and material of 40 Cr, heat them to 380 °C for carbonization and degreasing, and then put them in a shot blasting machine for shot blasting and delasting. After degreasing and rust prevention, the workpiece and sherardizer agent are put into the sherardizing furnace, and the mechanical energy-assisted permeation method is adopted for powder sheladering. The zinc powder temperature is 400°C and the holding time is 2 hours. Table 1 shows a comparison of the composition of the sheral dither in the experimental design with and without the rare earth element La.

The corrosion resistance of the powdered sherardizing layer that formed with and without the addition of the rare earth element La to the shearedizer was tested by periodic alternating salt spray experiments to simulate the salt spray condition to the atmosphere in the environment. Then, the characteristics of the sample before and after corrosion were investigated. The OLS4100 laser scanning confocal microscope (LSCM) was used to observe the macromorphism of the sample surface before and after corrosion. In the low vacuum environment, a field emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector is used to
observe the surface micromorphology of the corroded layer after corrosion and characterized its composition. An X-ray diffractometer was used to analyze the phase composition of the corroded layer.

Table 1. Composition comparison of sherardizer (g).

|        | LaCl₃ | Zn Powder | NH₄Cl | Al₂O₃ |
|--------|-------|-----------|-------|-------|
| 0-a    | 0     | 2000      | 50    | 100   |
| 4.0-La | 90    | 2000      | 50    | 100   |

3. Results and Discussion

3.1. Atomistic Simulation

Since this article focuses on the study of Zn adsorption by the Fe matrix at 400 °C, subsequent studies will select α-Fe as the matrix material. Regarding the surface adsorption of the substrate, the adsorption surface has a great influence on the calculation result. Therefore, the three most characteristic crystal planes of α-Fe ((100), (110), (111)) are selected as the adsorption surfaces of atoms. And the situation of each adsorption surface is simulated to calculate in the process of surface adsorption. Figure 1 shows the structure of each adsorption surface of Fe element.

![Figure 1. Structure of each adsorption surface of Fe alone. a)(100);b)(110);c)(111).](image)

In this paper, the adsorption energies of different adsorption surfaces are calculated separately. Regarding the adsorption energy, the negative the binding energy, the larger the adsorption energy and the easier it is to adsorb to the interface. From table 2, it can be seen that the plane (111) has the most negative binding energy, that is the plane most likely to be adsorbed. The plane (100) has positive adsorption energy, and this plane is the most difficult to adsorb.

Table 2. Calculation result of adsorption energy to each crystal plane of Fe.

| Iron atom interface | La energy(eV) | Fe energy(eV) | La- Fe(eV) | Binding energy(eV) |
|---------------------|---------------|---------------|------------|-------------------|
| 110                 | -968.32       | -3443.13      | -4415.02   | -3.58             |
| 111                 | -968.32       | -1719.98      | -2691.96   | -3.67             |
| 100                 | -968.32       | -1723.37      | -5375.25   | 4.07              |

Table 3 shows the binding energies of the four compounds (CeO₂, La₂O₃, Nb, Zr) on the most adsorbed surface (111). For these elements, which can affect the adsorption of sherardizing, the binding energy of the La element to the Fe matrix is the most negative, indicating that it has strong adsorption energy, since it has the effect of adsorbing to the metal surface to form a zinc layer. In subsequent experimental studies, La was added to the powder sherardizing agent and the effect of La was investigated.
Table 3. Adsorption of various elements on the Fe matrix.

| element | Re energy(eV) | Fe energy(eV) | Re-Fe energy(eV) | Binding energy(eV) |
|---------|---------------|---------------|------------------|-------------------|
| Ce      | -1245.34      | -1719.98      | -2963.92         | 1.41              |
| La      | -968.32       | -1719.98      | -2691.96         | -3.67             |
| Nb      | -1655.67      | -1719.98      | -3370.64         | 5.00              |
| Zr      | -1292.09      | -1719.98      | -3009.44         | 2.63              |
| Zn      | -1786.98      | -1719.98      | -3506.27         | 0.69              |

It can also be found from table 3 that comparing with the adsorption of Zn on Fe matrix, the binding bond between La and Fe matrix is more negative and the adsorption force is greater. Therefore, La is adsorbed on Fe matrix earlier than Zn. Consequently, it can be considered that in the process of forming the powder zincification layer, the rare earth element La is the element firstly combined with the Fe matrix to form a more stable conjugate, and then the Zn element is adsorbed on the La element and diffused into the Fe matrix to form Zn-Fe compounds. So that the rare earth La may act as a channel. La atoms and Fe atoms act as a bridge to help Zn atoms adsorb on the surface of the substrate.

3.2. Corrosion Performance of Powdered Zinc Layer

Figure 2 shows the surface morphology of the 0-La permeable layer and the 4.0-La permeable layer before and after corrosion in the salt spray experiment. The surface of the 0-La permeation layer is uneven with continuous pits and cracks. After the rare earth chemical heat treatment, the surface integrity of the 4.0-La permeation layer is improved, the pits are reduced, and surface quality of the permeation layer is improved. From the first-principles calculations, we can conclude that the La element plays a certain role in activation and permeation during the permeation process. Powder sherardizing involves two main processes—the chemical reaction of thin film deposition and the vacancy diffusion of Zn and Fe atoms. Since Re have high surface adsorption activity that easily adsorbed on the surface, suppress the coalescence of crystal grains during the deposition process, prevent further deposition of metal ions, prolong the incubation time of crystal nuclei, and suppress grain growth. Grains are refined by rare earths to improve the uniformity of the powder sherardizing layer [5, 7].

Figure 2. Surface morphology of 0-La and 4.0-La sherardized layers before and after corrosion. (a) (b)Surface morphology of 0-La and 4.0-La layer before corrosion; (c) (d)Surface morphology of 0-La and 4.0-La layer after corrosion.
After alternating salt spray experiment, corrosion products accumulated on the surface of the layer, and a large amount of white rust and red rust were observed, and corrosion pits appeared. Compared with the 4.0-La layer, the surface of the 0-La layer is more severely damaged, the corrosion product layer is thicker, pitting and local corrosion are more serious, there are large areas of corrosion pits, and even the corrosion products are peeled off. The degree of corrosion of the 4.0-La infiltration layer is relatively light, which may be related to the formation of a dense passivation film on the surface of the layer [8]. Therefore, the quality of the powder sherardizing layer after rare earth chemical heat treatment has been improved, and the corrosion resistance of the layer has been enhanced.

The figure 3 shows the corrosion morphology of the powder sherardizing layer at various magnifications after alternating salt spray experiment. The corrosive surface of the layer is partially complete after rare earth chemical heat treatment. Corrosion products are primarily present in defects such as cracks and pits in the layer, and the solution easily penetrates these defects in the permeation layer and begins to corrode the layer or even the substrate. Corrosion products come in two main forms, one layered in random directions and the other thick, agglomerated spheres. There is a certain space between the particles of the corrosion product. Compared to flaky multi-layer corrosion products, the corrosion products that are densely packed in small spheres serve to resist the penetration of corrosive ions, solutions, and moisture into the surface of the layer [9]. The properties of the corrosion products formed on the surface of the layer were determined by XRD (figure 4). From the figure 4, it can be seen that the corrosion products of the layer are mainly composed of Zn(OH)$_2$ and ZnO. During the immersion process, Zn can chemically react with the solution and the corrosion equation is (2) and (3). After Zn dissolves, Zn$^{2+}$ reacts with OH$^-$ and O$_2$ to form ZnO and Zn(OH)$_2$ corrosion products that are aggregates generating on the surface of the layer. This can reduce the rate of corrosion of the permeation layer [10].

$$2\text{Zn} + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Zn(OH)}_2 \quad (2)$$

$$\text{Zn}_2 + \text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (3)$$

**Figure 3.** (a) Morphology of corrosion products of 0-La layers under different magnifications; (b) Morphology of corrosion products of 4.0-La layers under different magnifications.
Figure 4. XRD Phase Analysis of Corrosion Products of powder sherardizing layer.

Figure 5 shows the changes in the microstructural properties of the powder sherardizing layer before and after the rare earth chemical heat treatment and the subsequent effects on the corrosion behavior of the layer. From figure 5(a), it can be seen that powder sherardizing layer is a monolayer alloy layer is locally non-uniform, has non-uniform edges, and exists pits and internal through-through cracks. After chemical heat treatment of rare earths, the quality of the layer can be effectively improved and the defects generated in the powder can be eliminated. The surface of the permeation layer becomes smoother, internal cracks are reduced and become thinner. The rare earth La also helps to form uniform particles in the permeation layer (figure 5(b)). In the process of infiltration layer corrosion, cracks and holes are the active parts that may be corroded. Comparing to the 0-La layer, the 4.0-La permeable layer has better corrosion resistance, which may be related to the dense microstructure of the layer and the more uniform permeable layer. Due to the finer grains and higher grain boundary density of the rare earth chemical heat treatment, the infiltrated layer is more prone to chemical reactions to form an oxide film composed of ZnO, Fe$_2$O$_3$, etc., which is beneficial to provide better protection for the iron matrix. And the rare earth element La can inhibit the corrosion process and reduce the stress related to crack propagation, providing better corrosion protection for the matrix [7].

Figure 5. Changes in the microstructural characteristics and corrosion mechanism of the layer: (a) before chemical heat treatment of rare earths; (b) after rare earth chemical heat treatment.

4. Conclusions
La element plays a very important role in the formation of sherardizing layer. According to the above calculation and experimental research, we can get the following conclusions.

1) In the powder sherardizing process, Fe matrix crystal planes (111) is the most easily adsorbed surface; comparing with other atoms (CeO$_2$, La$_2$O$_3$, Nb, Zr), the adsorption energy of La on the most easily adsorbed surface (111) of Fe matrix is lower, and it is easier to adsorb on the surface of
Fe matrix. In the sherardizing process, La is easier to bond with Fe matrix than Zn, so that rare earth La may act as a channel. La atoms and Fe atoms act as a bridge to help Zn atoms adsorb on the surface of the substrate.

2) After adding the rare earth element La to the sherardizing agent and undergoing rare earth chemical heat treatment, the grains of the sherardizing layer are refined and uniform, defects such as pits and cracks are reduced, and the quality of the infiltrating layer is improved. The corrosion resistance of the layer is also improved. The corrosion products are mainly lamellar and spherical, which can form a certain passivation film to provide a certain protection for the substrate during the corrosion process.

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