

Review

The Role of Rare Earths on Steel and Rare Earth Steel Corrosion Mechanism of Research Progress

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Abstract: Corrosion has always been an important factor affecting the life of steel, which causes huge economic losses every year. How to improve the corrosion resistance of steel has always been a research focus. Adding rare earth elements into steel is an important method to improve the corrosion resistance of steel. In this paper, the effects of rare earth elements on steel are summarized, including the purification of molten steel, modification and modification of inclusions, improvement of grain boundaries by solid solution strengthening, the influence of phase transformation and the refinement of microstructure, and reduction in C and N desolubilization. On this basis, the progress of research on the corrosion resistance mechanisms of rare earth steel is summarized, focusing on rare earth-modified inclusions. This includes the changes in composition and sizes of inclusions by rare earth addition, promoting the transformation of MnS and Al₂O₃ in rare earth inclusions with regular shapes, smaller sizes and better performance, or composite rare earth inclusions. The corrosion pits that form in the early stages of corrosion are shallow in depth, fewer in number and light in corrosion degree. The effects of rare earth materials on the rust layer include: rare earth promotes the formation of a more stable corrosion product α -FeOOH, and rare earth promotes the formation of a dense rust layer, which covers the surface of the matrix and hinders the transmission of corrosion ions. The protective effect of the rare earth atomic layer on the substrate and the corrosion inhibition effect of rare earth ions are formed by the segregation of rare earth at the interface. In the end, the existing problems in the research into rare earth steel and future research directions are briefly put forward, including improving the addition process of rare earth steel, theoretical guidance on enhancing the corrosion resistance mechanism of rare earth steel, and extending the research from La, Ce, and Y steel to more rare earth steels.

Keywords: rare earth steel; corrosion mechanism; inclusions; rust layer; corrosion products; rare earth atomic layer



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1. Introduction

With the development of the economy as well as the needs of national construction, steel as a basic material has been applied in every aspect of life, from large aerospace materials and ships, to small screws and nuts, etc. The application of steel brings convenience to our lives. Due to the complex external environment, steel faces serious corrosion problems, which reduces the life and safety of steel products, and also causes huge economic losses. From the statistics of the United States and the United Kingdom since 1975, the annual loss due to corrosion in the United States accounted for about 4% of the gross national economic output value, and for the United Kingdom it was about 3.5% [1]. China's situation is similar; the annual economic losses due to corrosion are also huge, as China's annual corrosion losses account for 3% to 4% of the net national economic output value [2].

According to statistics, if effective protective measures are taken, corrosion losses can be reduced by 25% to 40%. A variety of corrosion mitigation methods have been studied in recent years, such as coatings, inhibitors, and polyalloying [3–6]. Coating corrosion protection involves forming a shielding coating on the surface of the metal as a way to isolate the metal from contact with the external environment, such as oxygen, water, and corrosive ions, but coating corrosion protection has certain limitations. Corrosion inhibitor-based corrosion prevention generally refers to applying a corrosion inhibitor at a certain concentration in the corrosion medium, mainly to change the nature of the corrosion medium, so that the corrosion of metal materials in the medium is reduced. Although both coating anti-corrosion and inhibitor anti-corrosion can inhibit the corrosion of metal in a certain environment, neither of them can fundamentally change the corrosion resistance of the metal itself. Alloying refers to the addition of other elements in the refining process to improve the performance of the metal. Some alloying elements can improve the corrosion resistance of steel; for example, the addition of Mo and V can improve resistance to hydrogen corrosion [7]. The addition of Nb and Ti can improve the resistance to intergranular corrosion [8]. But because of the high prices of these elements, and the diminishing mineral resources, they are not conducive to long term development [9].

Therefore, many researchers began to look for alternatives to traditional alloying elements, such as rare earth elements. As early as the 1950s, Carpenter Company in the United States tried to add rare earth elements into stainless steel, which improved the performance of steel. Since then, there have been many rare earth steel research projects, greatly promoting the development of rare earth in the iron and steel industry. The 1970s saw a period of rapid development of rare earth steel research. In the early 1970s, researchers in the United States mainly studied the role of rare earth steel in purifying liquid steel, and gradually began to study the addition method of rare earth materials and the physical and chemical actions and mechanisms in the late 1970s. In the 1980s, with the improvement of metallurgy, the cleanliness of steel increased, and the varieties of rare earth steel, such as cast steel, 10MnNb steel, 16MnRE steel, low-sulfur pipeline steel, and so on, also further increased. By the 1990s, the metamorphic effect of rare earth elements in steel was gradually studied, and this helped to promote the practical application of rare earth steels. In the 21st century, the number of rare earth steels was further increased to include die steels, high-manganese steels, electrical steels, etc. The research on rare earth steels was first conducted in China. China's research on rare earth steels first appeared in the late 1950s, the early years of the founding of the country, due to the country's emphasis on the development of heavy industry; it carried out microalloying research on nearly 100 kinds of steel. With the improvement of the metallurgical level and the deepening of the research on rare earth steels in the past seventy years, it has been found that in different steels, rare earth materials bring different effects. Adding rare earth to heavy rail steel mainly improves wear resistance. The application of rare earth in bearing steel, gear steel and high-performance die steel can improve the fatigue resistance. Rare earth used in stainless steel and low-alloy steel, such as weathering steel and ship plate steel, can improve the corrosion resistance of steel. The application of rare earths in steel is mainly divided into two kinds. One regards traditional metallurgical machinery, petrochemical, and other fields. One, which has been emerging in recent years, involves rare earth permanent magnetic materials, rare earth phosphors, rare earth hydrogen storage materials, rare earth catalytic materials and so on [10]. The application of rare earths in steel has been studied a lot, through weightlessness experiments, electrochemical experiments, and other methods that have also confirmed that rare earths can improve the corrosion resistance of steel, but there are fewer comprehensive discussions on the mechanisms of use of rare earth elements to improve the corrosion resistance of steel. This paper is mainly divided into two parts. The first part reviews the effects of rare earth elements on steel. The second part mainly reviews the progress of research into corrosion resistance mechanism of rare earth steel in recent years. We hope to provide a reference for improving the corrosion resistance of steel and the reasonable application of rare earth in steel in the future.

2. The Role of Rare Earths in Steel

Rare earth elements contain lanthanides as well as Sc and Y, for a total of 17 elements. After nearly 70 years of exploration by scholars at home and abroad, understanding of the effects of rare earths on steel has reached a consensus, mainly including the purification of steel, modification of inclusions, and rare earth microalloying [11,12].

2.1. Purification of Molten Steel

Oxygen affects the strength, plasticity, and fatigue resistance of steel, and the presence of sulfur reduces the plasticity, toughness, and weldability of steel, etc. Harmful elements such as P, As, and Sn affect the brittleness, weldability, and tensile strength of steel. Therefore, the process of steelmaking should seek to reduce the contents of S and O and the harmful elements of bias polymerization. Rare earths used in the purification of steel have two main properties; the first point is that rare earths can reduce the O and S content in the liquid steel to purify the liquid steel, and the second point is that rare earths can react with the harmful elements in the steel, such as P, As and Sn, to reduce the polarization at the grain boundaries, and thus purify the grain boundaries.

Rare earth elements are chemically active, with the outer electron arrangement of $[Xe]4f^n6s^2$ and $[Xe]4f^{n-1}5d^16s^2$, and they very easily lose their outer electrons and become positive ions. Rare earth elements have a strong binding ability with O, S, etc., and generate compounds with a low density, high melting point, and high stability. From Figure 1, it can be seen that the oxides of the rare earth elements La, Ce, Pr, and Nd have higher standard generation Gibbs free energies, which proves that the stability of the rare earth oxides is higher. In the field of metallurgy, rare earth elements are commonly used as deoxidizers and desulfurizers, which play a role in purifying and tempering to improve and enhance the properties of steel [13–16]. Mg, Al, Ti, and Ca are also commonly used as deoxidizers and desulfurizers in the steel industry, but Ca and Mg have low boiling points and high vapor pressures, which make them volatile when added to the steel. However, the boiling point of rare earth materials can reach more than 3000 °C. When adding rare earth materials to liquid steel, they can maintain a higher concentration, so the steel has a higher deoxidation and desulfurization capacity. The deoxygenation and desulfurization effects of rare earth elements are better than those of Mg, Al, and Ti, the deoxygenation effect is comparable to that of Ca, and the desulfurization effect is second only to that of Ca.

Yang's group [17] found that when Ce was added to IF steel, the O and S contents were 0.00056% and 0.00045%, respectively, before adding rare earths, and after adding rare earths, the O and S contents were reduced to 0.00020% and 0.00032%, respectively. In a study of the effects of rare earth Ce on the O and S contents of spring steel, the team of Liu [18] found that when the content of Ce was 0.10%~0.13%, the dissolved oxygen content in the steel was reduced by 15 ppm, and when the Ce content was 0.0455% to 0.065%, the total oxygen content in the steel was reduced from 28 ppm to 8 ppm, while with the addition of elemental Ce, the content of S was reduced by 30 ppm. Kang's group et al. [19] prepared rebar with a Ce content of 0.0032%, and found that the S content of the steel was reduced by about 77.78%. Elements such as Ti, Pb, As, Sb, Bi, Se, etc., are harmful to steel, and the excess rare earth elements remaining after completing deoxidation and desulfurization will form high-melting-point compounds with these elements, or form inclusions that precipitate out of the steel and into the slag before the steel solidifies, helping to achieve the purpose of purifying the steel [20–22]. Liu's group [18] et al. found that after the addition of the rare earth element Ce, the Ce-containing inclusions contained As, P, Pb, Sn, and other harmful elements, which proves that Ce can combine with harmful elements and reduce their segregation at grain boundaries. It shows that rare earth materials can be used for purifying steel.

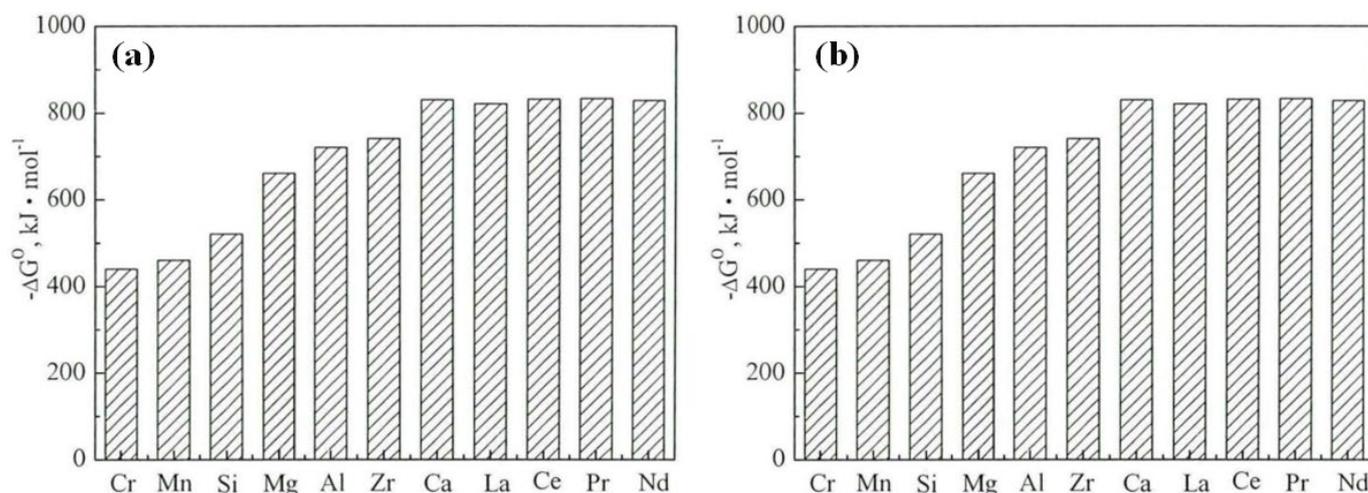


Figure 1. (a) The standard Gibbs free energy of generation for rare earth oxides as well as other metal oxides at 1650 °C; (b) The standard Gibbs free energy of generation for rare earth sulfides as well as other metal sulfides [23].

2.2. Spoilage Inclusions

Inclusions are impurities that are harmful to steel but cannot be completely eliminated. The physical and chemical properties of the inclusion itself and of the steel matrix, such as thermal expansion coefficient, plasticity, etc., are very different. So, in the process of rolling and cooling, micro-cracks easily generate, which have negative effects on the mechanical properties, corrosion resistance and fatigue resistance of steel. The composition, shape, size, and distribution of inclusions have a greater impact on the performance of steel. Therefore, inclusions should be distributed as evenly as possible, or we should improve the physical and chemical properties of inclusions or reduce the amounts and sizes of inclusions.

Adding an appropriate amount of rare earth elements to steel can effectively change the shape of inclusions and make the distribution of inclusions more uniform. Since the rare earth inclusions have a similar thermodynamic expansion coefficient to that of the steel itself, fewer cracks are produced during the rolling process compared to steel without rare earths, and therefore the overall performance of the steel is enhanced. Rare earths can either deform the inclusions into a regular spherical shape or denature the inclusions into rare earth inclusions. These two properties often co-exist and promote each other [24]. In the study of the effect of Ce on inclusions in EH36 ship plate steel, Li [25] found that after the addition of rare earth elements, MnS was denatured by the rare earth elements to become a spherical composite inclusion of Ce₂O₂S and MnS, with the size reduced to one-fifth of its original size. The irregularly shaped Al₂O₃ also yielded spherical composite inclusions, whose sizes changed from 5 μm to 1.5 μm, as shown in Figure 2. Liu [26] added Ce to 304 stainless steels, and the size of MnS was decreased by about 2 μm. A moderate amount of rare earth elements is beneficial to steel, but once too many rare earth elements are added, the size of the inclusions becomes larger, and the shape becomes irregular. Xi's group [27] prepared Ce contents of 0.006%, 0.012%, and 0.018%, respectively, and observed the inclusions' morphology. It was found that when the Ce content was 0.006%, some of the inclusions became spherical or oval rare earth inclusions; when the Ce content was 0.012%, all the inclusions were rare earth inclusions with regular shapes and decreasing sizes, but with the further increase in the rare earth content, the inclusions became larger and more irregular in shape. The corrosion resistance also increased and then decreased with an increase in rare earth content. Bao [28] performed a similar study; when the Ce content was 0.031%, the average size of inclusions was 2.32 μm, and the density was as low as 48.4/mm². However, when the Ce content was excessively increased to 0.041%, the small-sized inclusions were significantly reduced, and the average size of the rare earth

inclusions was increased to 2.86 μm . This also encourages us to pay attention to the number of rare earths added during the steel-making process.

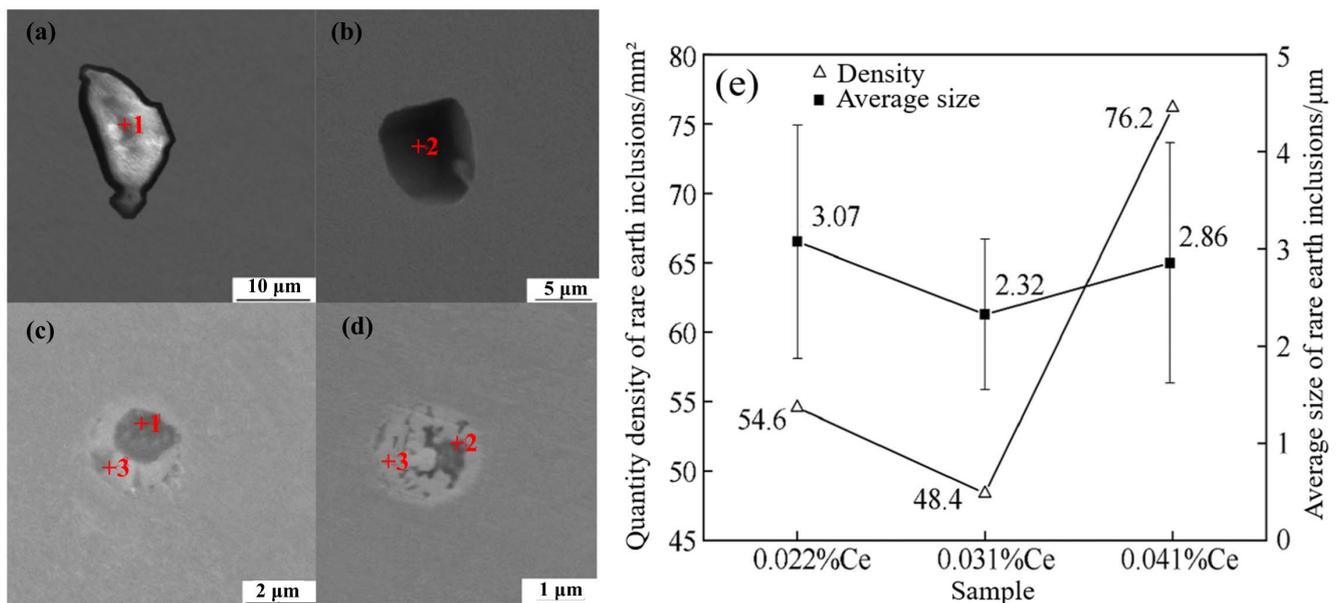


Figure 2. (a,b) The Al_2O_3 and MnS inclusions without the addition of rare earth elements, and (c,d) the composite inclusions modified and modified by Ce, respectively. 1, 2, 3 are Al_2O_3 , MnS and $\text{Ce}_2\text{O}_2\text{S}_2$ respectively [25]. (e) The variation in the number and density of rare earth inclusions with rare earth content [28].

2.3. Microalloying

Nowadays, metallurgy is constantly improving; steel is becoming cleaner and the S and O contents are being reduced. The rich rare earths in liquid steel can be completely dissolved in the steel, thus reflecting the alloying effect of steel. The microalloying of rare earth elements is mainly determined by the interaction between rare earth atoms and other elements on the grain boundary. This causes changes in the structure of the grain boundaries, the chemical composition, and the energy, affecting the diffusion of other elements and the nucleation and growth of new phases, which ultimately leads to changes in the organization and properties of the steel [26,29–31]. At present, the main research conclusions about the effects of rare earth alloying are as follows:

1. Solid solution strengthening improves grain boundaries.

Hume–Rothery proposed a criterion for replacement solid solutions [32]; if the difference in radius between two atoms is between 8% and 15%, then a replacement solid solution can be formed. The radius of rare earth atoms is larger than that of Fe atoms by about 1.4 times. But due to polarization with other nonmetals, the radius will decrease, and rare earths and iron can form interstitial solid solutions. Although rare earths and Fe atoms can theoretically be totally dissolved, practical studies have shown that the amount of solid solution is very small, up to one part in 10,000 [30], and the amount of solid solution of rare earths is in the order of 10^{-6} – 10^{-4} [33,34]. However, the completely dissolved rare earths are mainly concentrated at the grain boundary, and interact with other hazardous elements with low melting points, such as As, P, S, and Sn, reducing enrichment at the grain boundary. This can strengthen the grain boundary, prevent the generation and diffusion of grain boundary cracks, and improve the plasticity of steel. Some researchers [35] observed the generation of RE–P, RE–As, and RE–Sn in steel, proving that rare earth elements can react with P, As, and Sn. The aggregation capacity of harmful elements is inversely proportional to the content of rare earth elements.

2. Interaction with elements such as C and N increases solubility and decreases desolvation.

If elements such as C and N are desolvated, the phenomenon of blue embrittlement will be seen [36]. The activity of C and N is reduced because of the addition of rare earths, and the solubility will be increased. So, the degree of dissolution is reduced, meaning that they cannot be desolvated into the internal stress zone or crystal defects, thus improving the toughness and plasticity of the steel.

3. Influence the phase transition and refine the microstructure.

It has been shown that the phase transition temperatures of steel such as Ac1, Ar1, Ac3, Ar3, Ms, and Mf change after the addition of rare earths [37]. The microstructure of steel has an important influence on the properties of steel. After the addition of rare earths, the microstructure will be refined; for example, for ferrite, we might see shape changes, size reductions, pearlite lamellae spacing reductions, lath martensite becoming refined, and so on. The strength, toughness, and corrosion resistance of the steel will also be improved. Li [25] found that after adding a small amount of Ce to the steel, the slaty and polygonal ferrite was gradually transformed into acicular ferrite, and the growth of bainite was also inhibited. Due to the fine structure of acicular ferrite, the strength and toughness of the steel were also increased. Zheng [38] and Jiao [39] added different amounts of rare earths to the steel, and found that the lamellar spacing of pearlite decreased after the addition of rare earths, as well as that the corrosion resistance of the steel was inversely proportional to the lamellar spacing of pearlite through weightlessness experiments; therefore, smaller lamellar spacing was more conducive to the enhancement of the steel's corrosion resistance, and the lamellar spacing is shown in Figure 3.

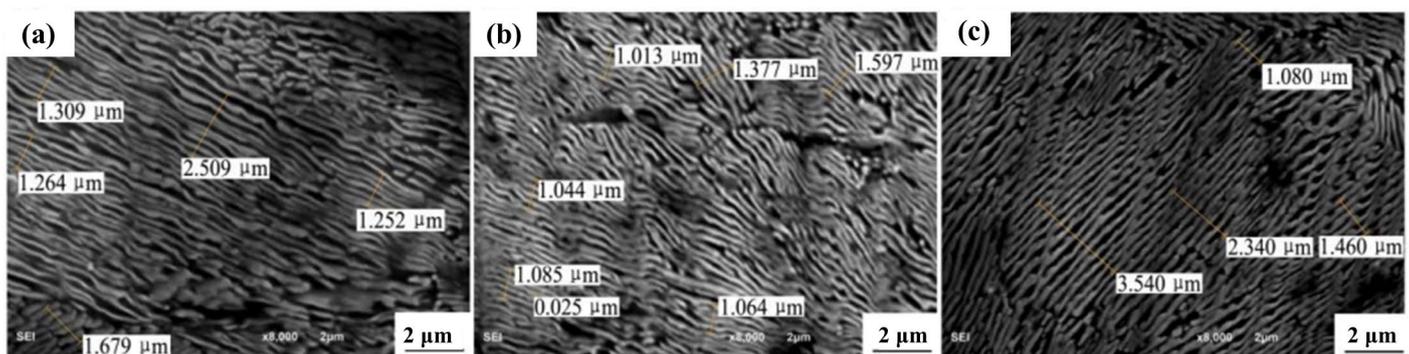


Figure 3. Pearlescent sheet layer spacing: (a) Ce is 0; (b) Ce is 40×10^{-6} ; (c) Ce is 80×10^{-6} [39].

3. Corrosion Resistance Mechanism of Rare Earth Steels

In recent years, there have been many studies on the corrosion resistance mechanism of rare earth steel. However, the effect of rare earth on steel corrosion is not a single factor, but several factors operating simultaneously. Inclusions often affect the initial stage of corrosion, and the corrosion products and density of the rust layer have important effects on the long-term corrosion of steel. The next section describes the reasons why inclusions affect corrosion.

3.1. Rare Earth Metamorphic Inclusions Improve Corrosion Resistance

3.1.1. Effect of Common Inclusions on Corrosion

In the steel smelting process, inclusions cannot be completely eliminated, which tends to increase the risk of corrosion and other hazards in steel. The corrosion of steel often starts with localized corrosion and then leads to uneven total corrosion. However, inclusions are active sites of corrosion, and are often considered important causes of localized corrosion [40–45]. The passivation film that develops at the inclusions is weak and susceptible to corrosive ions, and so pitting corrosion is easily formed [43,44]. Due to the different compositions of the inclusions and the steel matrix, galvanic coupling corrosion likely occurs between the inclusions and the steel matrix. Generally, galvanic coupling corrosion

occurs due to the direct contact of heterogeneous conductive materials with different corrosion potentials, which leads to localized corrosion at the contact site [46]. The mechanism of the galvanic couple pitting corrosion of stainless steel is often explained by the potential difference theory [42,47,48]. The composition and size of inclusions have an important influence on the formation and expansion of corrosion. MnS is a common inclusion in steel; initially, the addition of Mn elements to steel to a certain extent reduces the content of FeS, but it also reduces the occurrence of thermal embrittlement phenomena. However, with the continuous improvement of the metallurgical level, MnS is also gradually exposed to harm. Due to the strong ductility of MnS, the rolling process of steel often forms long inclusions with large sizes, thus reducing the service life of steel. There have been many studies on the corrosion mechanism of MnS. Due to the defects between the MnS inclusion and the matrix, corrosive ions can infiltrate between them. The larger the sizes of the MnS inclusions, the larger the effective corrosion area [43,49,50]. Since the standard electrode potential of MnS is -0.005 V, which is much higher than that of Fe (-0.41 V), the iron matrix around the inclusions acting as an anode is preferentially dissolved to form a corrosion pit, and the dissolved product, Fe^{2+} , enters the electrolyte to hydrolyze and thus generate H^+ , leading to a decrease in pH in the corrosion pit, and then the H^+ erodes the MnS inclusions themselves, generating HS^- , while H^+ and HS^- cause the surrounding matrix to erode, which in turn exacerbates the corrosion. Al_2O_3 is another common inclusion in steel, and Al_2O_3 is prone to clustering, forming large-sized inclusions. Because of the differences between Al_2O_3 and the surrounding elastic modulus, plastic strength, etc., the tip of the inclusions around the matrix is dissolved, resulting in micro-seams, as a result of which the matrix and the medium in the gap form a micro-cell, promoting the occurrence of corrosion. After the corrosion time is prolonged, the inclusions are partially dissolved, which mainly occurs when the tip part of the crevice is larger. The size of the tip part is related to the stress concentration that promotes corrosion, which is greater in the larger crevice parts due to Fe^{2+} hydrolysis to produce H^+ , as a result of which the acidity rises, resulting in the dissolution of Al_2O_3 .

3.1.2. Effect of Rare Earth Inclusions on Corrosion

However, the addition of rare earth elements can modify inclusions in steel, and rare earths can modify MnS to produce rare earth sulfur oxides and rare earth sulfides. Studies have shown that if the value of RE/S is greater than 3, MnS can be completely modified to rare earth inclusions, and the hazards of MnS can be eliminated due to the similarity of the properties of rare earth inclusions and the Fe matrix. Rare earths can modify Al_2O_3 to REAlO_3 , and if the rare earth content increases, Al_2O_3 can be further modified to finely diffused $\text{RE}_2\text{O}_2\text{S}$ or RE_xS_y to eliminate the hazard of Al_2O_3 . Since the affinity of rare earth elements for O is greater than that for S, they are generally first generated as rare earth oxides. The literature shows [51–53] that if the sulfur–oxygen ratio is high, the inclusions are dominated by RE_2S_3 , and if the sulfur–oxygen ratio is low, REAlO_3 and $\text{RE}_2\text{O}_2\text{S}$ are mainly generated. In the vicinity of the inclusions, the initial corrosion mainly takes two forms. The first one is due to the existence of micro-gaps between the inclusions and the steel matrix; corrosion occurs in the steel matrix around the inclusions, and the corrosion crater is gradually formed. The second form is the dissolution of the inclusions themselves, gradually forming micro-pits. Which method of starting the corrosion depends on the properties of the inclusions themselves, such as the conductivity, stability, and coefficient of thermal expansion. If the inclusions are insulated, the inclusions do not corrode electrically with the matrix; if the stability of the inclusions is poor, the inclusions themselves easily dissolve in the corrosive solution, and if the coefficient of thermal expansion of the inclusions differs greatly from that of the steel matrix, microcracks can easily develop between the inclusions and the matrix. In addition, the size of inclusions is an important factor influencing the corrosion, because the smaller the size, the fewer the sites of corrosion reaction, and the smaller the areas of microcracks [46]. Studies have shown that corrosion pits are less likely to form when the size of inclusions is less than $1\ \mu\text{m}$ [54,55].

In recent years, there has been an increasing number of studies on the mechanism by which rare earth inclusions improve the corrosion resistance of steel, and there have been some examples of researchers combining calculations with experiments.

Zhang's group [56] combined theoretical calculations with previous experiments through first principle calculations, and found that the stability of microcracks and inclusions is an important factor causing pitting corrosion. The corrosion resistance mechanisms are not identical for different rare earth inclusions. Common inclusions in steel include Al_2O_3 and MnS, which provide the initiation point for pitting corrosion in carbon and stainless steels [45,57]. Al_2O_3 can also have a damaging effect on the corrosion resistance of steel [42–44]. After the addition of the rare earth element La, Al_2O_3 becomes LaAlO_3 , and MnS becomes Mn_3LaS_4 and La_2S_3 . Although the inclusions Al_2O_3 and LaAlO_3 are insulators and are not prone to galvanic corrosion, there are many micro-cracks between the inclusions Al_2O_3 and the steel matrix. These cracks provide channels for corrosive ions, which cause the dissolution of the matrix around the inclusion. Since the mechanical properties of LaAlO_3 are close to those of the steel matrix, uniform deformation occurs during steel rolling, so the microcracks between LaAlO_3 and the steel matrix are reduced, and the channels for corrosive ions are reduced, thus reducing the sites where corrosion occurs. Through first principle calculations, it was found that the figure of merit of MnS is lower than that of Mn_3LaS_4 , and the lower the figure of merit, the easier it is for the compound to dissolve in the corrosion solution. Therefore, MnS is more easily dissolved than Mn_3LaS_4 , meaning corrosion is more likely to occur, MnS is prone to clustering, and the clustered MnS forms larger corrosion pits when dissolved, which negatively affects the steel matrix. From a combination of computational and experimental results, it was demonstrated that rare earths can improve the corrosion resistance of steel. This is because the inclusions are denatured and have better physicochemical properties when rare earths are added. Other inclusions, such as SiO_2 , CaS, and TiN, have also been reported to negatively affect the corrosion resistance of steel [41,43,58].

Zhang's group [59] used Nb steel and rare earth steel without rare earth elements as research objects to study the effects of rare earth elements on the corrosion resistance of steel, analyzed the corrosion resistance mechanism of rare earth steels from the point of view of inclusions, and calculated the work function of the inclusions by using the first nature principle. They found that the corrosion range of rare earth steel was smaller after immersing both steels in 0.5% NaCl for the same time, as shown in Figure 4. The results of electrochemical tests show that the corrosion current density of rare earth steel is half that of Nb steel. And the smaller the corrosion current density is, the better the corrosion resistance of the steel is. The SEM and EDS results show that the inclusions in Nb steel are mainly polygonal Al_2O_3 with dimensions of 3–6 μm (e.g., Figure 5a), and the main inclusions in rare earth steels overlap around $(\text{RE})_2\text{O}_2\text{S}$ and REAlO_3 with dimensions of 2–4 μm (e.g., Figure 5b). It can be seen that the addition of rare earths changes the Al_2O_3 inclusions into composite inclusions of reduced size.

The corrosion process of the two steels is demonstrated in Figure 3, produced after analyzing the metallographic, SEM observations and EDS results of the two steels after 1 h immersion. The magnitude of the work function of several inclusions is calculated as $(\text{RE})_2\text{O}_2\text{S} < \text{REAlO}_3 < \text{Fe} < \text{Al}_2\text{O}_3$ by use of the first nature principle. The dissolution capacity is inversely proportional to the magnitude of the work function. Although the Al_2O_3 itself is not dissolved, due to the gap between Al_2O_3 and the matrix, and its own large size, the corrosion initially begins between the inclusions and the matrix, and the matrix around the inclusions is gradually eroded until the Al_2O_3 falls off, forming a larger corrosion pit. However, in rare earth steels, $(\text{RE})_2\text{O}_2\text{S}$ is the first to dissolve because of its small work function, and the enhancement in acidity after the release of H^+ promotes the dissolution of REAlO_3 . In contrast, the dissolution process of the inclusions has at this point not yet damaged the matrix itself, and ultimately a more stable pit is formed. Due to the small size of the rare earth inclusions, even after the inclusions are dissolved, the surface area of the exposed matrix is smaller, and the pitting pits formed are shallower compared

with the steel without rare earths. Corrosion is less likely to spread. Zhang’s group [60] counted the density and depth of pitting pits, and found that after adding rare earths, the density and depth of pitting were reduced, although the mechanism of pitting nucleation was not altered. A similar finding has been made previously [24]. This was attributed to the change in inclusions’ compositions with the addition of rare earth inclusions, and a more uniform distribution of inclusions with reduced numbers as well as sizes.

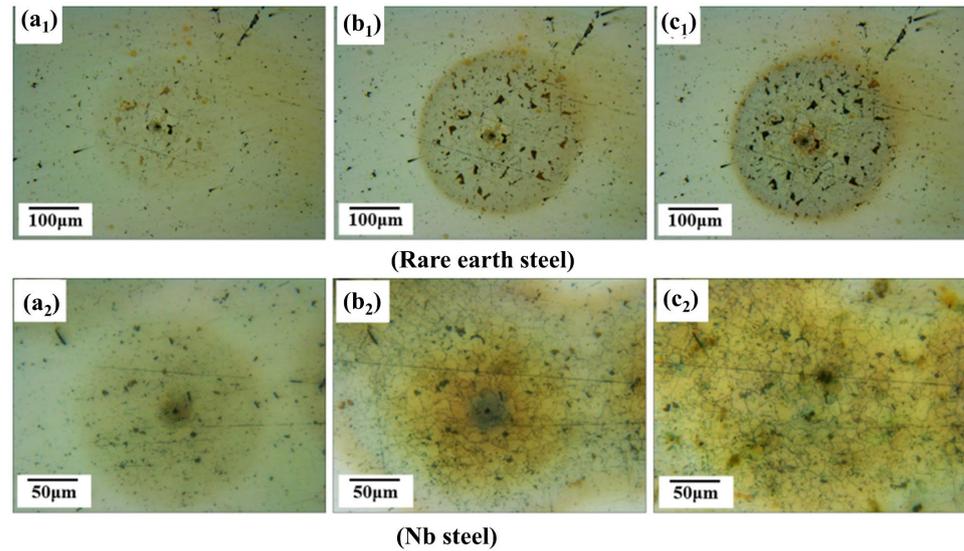


Figure 4. Metallographic images of Nb steel and rare earth steel in 0.5% NaCl solution. (a₁,a₂) 10 min; (b₁,b₂) 30 min; (c₁,c₂) 60 min [59].

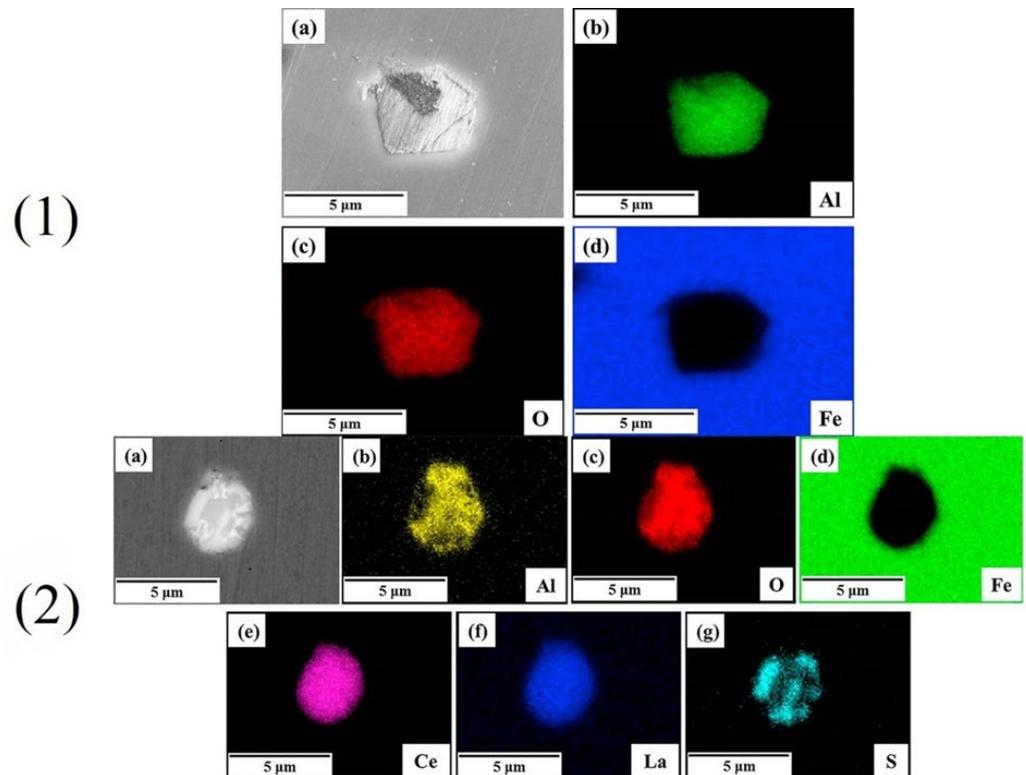


Figure 5. SEM maps and EDS results of inclusions and corrosion apparent morphology of Nb steel (1) and rare earth steel (2) [59].

Liu’s group [61] also conducted a similar study. They investigated the effect of rare earth elements on the localized corrosion mechanism of Zr-Ti deoxidized steel. Here, 1# steel was Zr-Ti deoxidized steel and 2# was deoxidized steel of Zr-Ti doped with La and Ce, with a 0.036% rare earth content. Characterization methods such as SEM and EDS revealed that 1# steel contains $ZrO_2-Ti_2O_3-Al_2O_3$ inclusions, and 2# steel forms overlapping $(RE)_2O_2S-(RE)_{xS_y}-(RE, Zr, Ti)O_x-(RE)AlO_3$ rare earth composite inclusions. The oxide regions in the rare earth steels 1# and 2# are less susceptible to dissolution because they are more stable than the steel matrix. However, there are differences in the thermal change value and thermal expansion coefficient between the inclusions and the matrix in 1# steel. There is a large crack between the inclusions and the matrix, so corrosive ions are more likely to erode the crack between the inclusions and steel matrix, and the matrix around the inclusions is more likely to dissolve. Corrosion is more likely to occur in 1# steel. After a longer time, the corrosion of 2# rare earth steel occurs at the sulfur-containing region of the micro crater domains, which are preferentially dissolved to generate H^+ and HS^- ; this leads to the enhancement of acidity within the micro-pit and promotes the dissolution of $(RE, Zr, Ti)O_x-(RE)AlO_3$ in the sulfur-free region.

In addition, Liu’s group [62] prepared Q460NH steel containing rare earth elements, and found by analysis that the inclusions in the rare earth steel were composite inclusions of $(RE)AlO_3$ wrapped with $(RE)_2O_2S-(RE)_3S_2$; they also concluded that the dissolution of sulfur-containing inclusions produced an acidic environment after the dissolution of the sulfur-free inclusions, and then dissolved them again. The dissolution process is shown in Figure 6. After the study, it is believed that the rare earth inclusions may undergo the following reactions:

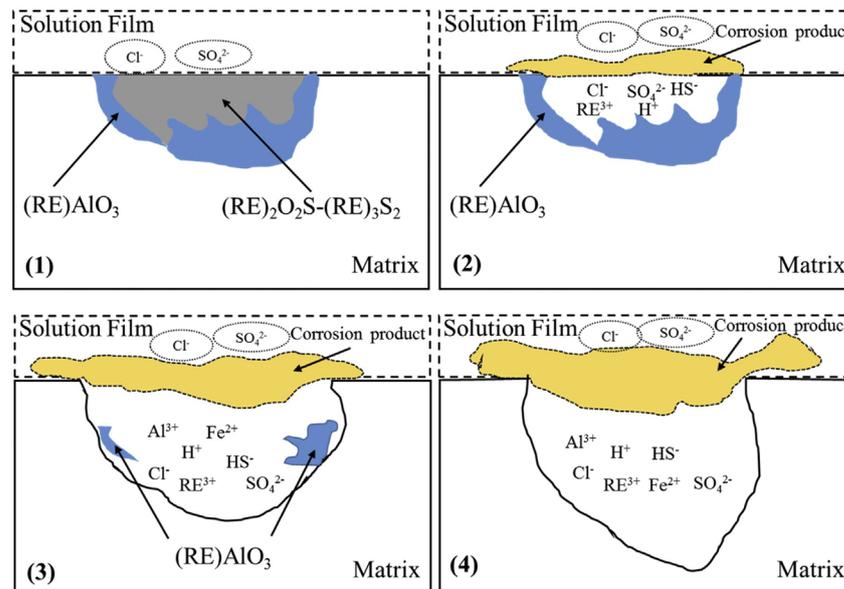
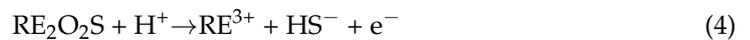
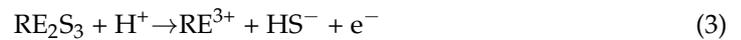
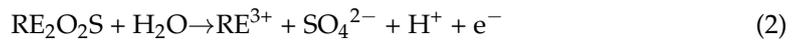
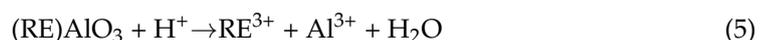


Figure 6. (1–4) Dissolution of the inclusions [62].

The generation of H^+ and HS^- leads to an increase in acidity and promotes the complete dissolution of inclusions in the sulfur-free zone.



The addition of rare earths to steel often results in the formation of different types of rare earth inclusions, such as rare earth sulfides, rare earth oxides, and rare earth sulfur oxides [62,63]. Rare earth oxides and rare earth sulfur oxides are formed preferentially over rare earth sulfides [64]. The different corrosion mechanisms of common inclusions and rare earth inclusions are mentioned above. However, the order of dissolution of different rare earth inclusions is also different. Tang's group [65] also investigated the corrosion mechanism of different rare earth inclusions by combining theory and calculation. They prepared RE-Zr/Ti deoxidized rare earth steel and Al deoxidized rare earth steel containing equal amounts of the same rare earth elements, respectively. These were compared with ordinary steel without rare earths. Through a weight loss experiment and electrochemical test, it was found that the weight loss rate and corrosion current density of deoxidized rare earth steel containing Zr/Ti were the smallest, followed by Al deoxidized rare earth steel. Both of them were smaller than that of ordinary steel. This confirms that the addition of rare earth elements can improve the corrosion resistance of steel, and the corrosion resistance of Zr/Ti deoxidized rare earth steel is better. Next, the types and sizes of inclusions were counted by SEM and EDS in an area of 30 mm². It was found that both rare earth steels have the same types of inclusions, i.e., MO_x, MS_x, and MO_xS_y (M is a rare earth element), but the size of inclusions in the Zr/Ti deoxidized steel is smaller, which also proves that the size of inclusions has an important effect on the corrosion resistance of the steel. The corrosion behavior after immersion in 0.5 wt. % NaCl was observed and analyzed by SEM and EDS. As can be seen in Figure 7, MO_x is still present but MS_x and MO_xS_y have dissolved. First-principles calculations yielded a work function size of (La₂O₃ ≈ Fe ≈ La₂O₂S) > La₂S₃ for several inclusions, i.e., sulfides are preferentially dissolved. This is consistent with the experimental results.

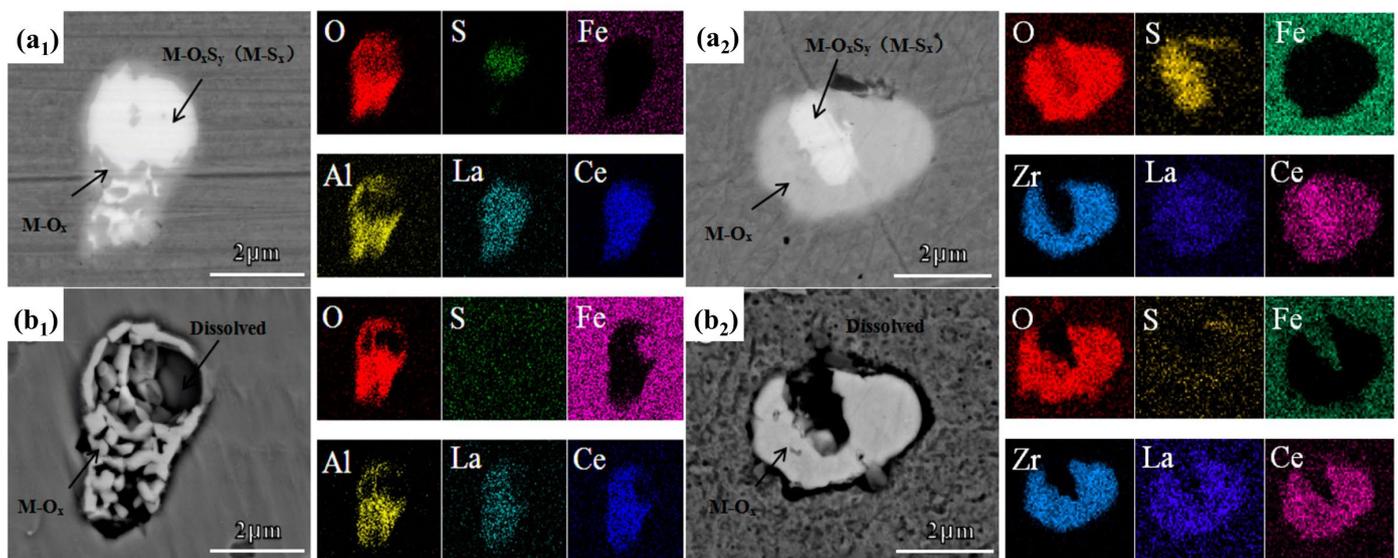


Figure 7. In situ dissolution behavior of inclusions in Al deoxidized rare earth steel, Ti/Zr deoxidized rare earth steel after 10 min immersion in 0.5 wt. % NaCl (a₁,a₂) before corrosion and (b₁,b₂) after corrosion [65].

Wei's group [66] analyzed the corrosion mechanism of rare earth inclusions and two overlapping composite inclusions, RE_xZr_yO_z-RE₂O₂ and RE_xZr_yO_z-RE₂O₂S-TiN, using SEM, EDS, and in situ microelectrochemical measurements (SVET) on Zr-Ti deoxidized steel with a rare earth content of 0.04%. Similar to the above, the rare earth sulfides dissolved preferentially, followed by the rare earth oxides from the periphery inwards, and finally stable craters were formed. SVET measurements can illustrate the microelectrochemical mechanism of inclusion generation. After immersion in NaCl solution for 0.5 h and 2 h, respectively, it was found that the anodic current density peaked at the inclusions at 0.5 h,

which proved that corrosion occurred at the inclusions. After 2 h, the current density at the inclusions was approximately equal to that of the matrix. This shows that stable micro-pits were formed after the inclusions were completely dissolved, and the corrosion was inhibited. It is also easy to see that inclusions have an important effect on corrosion.

From the above discussion, it is easy to see that inclusions are unavoidable and microcracking is an important cause of corrosion, but the addition of rare earths can make the cracks smaller and change the type as well as the size of inclusions. Rare earths do not change the mechanism of pitting nucleation. Because rare earths can make inclusions more uniform in distribution, and reduce size, the depth and density of the pits will be reduced, and the degree of corrosion is also reduced. Different rare earth inclusions' dissolution orders are also different, but most of them adhere to the law whereby rare earth oxides are more stable, and rare earth sulfides preferentially dissolve and produce H^+ and HS^- , promoting the dissolution of rare earth oxides, and then the formation of pitting pits. Therefore, future steelmaking approaches should minimize the generation of rare earth sulfides, and as far as possible encourage the generation of inclusions that are smaller in size and have more uniform distribution. Although some researchers have begun to combine focus on theory, most researchers study the mechanism through experimental phenomena, and still lack complete theoretical support. This is also a major hot spot, and difficulty, for future research.

3.2. Effect of Rare Earths on the Rust Layer

As the corrosion time increases, the influence of the rust layer on the corrosion becomes greater. Another reason for the strong corrosion resistance of rare earth steels is that rare earth elements enable the generation of a denser rust layer and promote the transformation of corrosion products in a more stable direction. α -FeOOH, β -FeOOH, γ -FeOOH, Fe_3O_4 , etc., are common corrosion products. The electrical conductivity, porosity, ionic selectivity, and reducibility of the corrosion products all have important effects on corrosion [67]. If the electrical conductivity of the rust layer is low, the impedance of the rust layer will be elevated, which hinders the charge transmission to a certain extent. The porous property of the rust layer can affect the migration of corrosion ions in the rust layer. The selective penetration of the rust layer products to cations and ions can accelerate or delay the corrosion. If the reducibility of corrosion products is strong, the products will further reduce and this will promote the occurrence of corrosion. Generally speaking, if the rust layer has good anion selectivity, it will promote the intrusion of corrosive ions such as Cl^- , which has a certain promotion effect on corrosion, and vice versa. Miyuki's group [68] investigated the ion-selective permeability of rust layers, and they concluded that the order of magnitude of the anion selectivity of several common corrosion products is: $Fe_3O_4 < \alpha$ -FeOOH $< \gamma$ -FeOOH $< \beta$ -FeOOH. The properties of several common corrosion products are shown in Table 1. It can be seen that α -FeOOH steel corrosion resistance has a favorable impact.

Table 1. Main properties of several common corrosion products.

Rust Layer Composition	Main Properties
Fe_3O_4	It is an electrical conductor, has certain reducing properties, has good densification and stability, and does not have anionic selectivity.
α -FeOOH	It is an insulator, essentially electrochemically inactive, with low reducibility, good densification, and low anion selectivity.
γ -FeOOH	It is a semiconductor and electrochemically active, can undergo reduction reactions, and has some anionic selectivity.
β -FeOOH	Crystal structure with tunnel-like cavities, electrochemically active, reducible, high anion selectivity.

3.2.1. Promotion of α -FeOOH Generation by Rare Earths

Many previous studies have demonstrated that after the addition of rare earths, the rust layer becomes denser and less prone to fall off, covering the surface of the steel matrix, hindering the contact of the matrix with corrosive ions, and providing a certain degree of protection to the steel itself. It has been shown that γ -FeOOH is generated first [69–71]. Then, γ -FeOOH is transformed into α -FeOOH and Fe_3O_4 [72]. γ -FeOOH is less stable and is not conducive to the protection of the matrix, and it tends to be transformed to the more stable α -FeOOH after the addition of rare earths [73,74]. α -FeOOH is insulating, more stable, and has a regular shape that has a protective effect on the matrix and is conducive to the enhancement of the corrosion resistance of steel [75,76]. Some researchers proposed the rust layer protective parameter (α/γ) as the mass ratio of α -FeOOH to γ -FeOOH [77]. The larger the value of α/γ , the more protective the rust layer is. Lian's group [78] investigated the effect of rare earth elements on steel and the corrosion mechanism under alternating wet and dry conditions by using Q235B, Q355B, Q235BM, and Q355BM steels, with the addition of the mixed rare earths La and Ce as materials. It was found that the weight loss rates of both Q235BM and Q355BM were lower than those of their counterparts, Q235B and Q355B. Macroscopic corrosion morphology showed that the rust layers of Q235BM and Q355BM were dense and not easily removed, while the rust layers of Q235B and Q355B were thicker and had more pores. The microscopic morphology of the corrosion products is shown in Figure 8, and it is obvious that the corrosion products become more homogeneous and less porous with the addition of La and Ce. It is here proven that the rust layer of rare earth steel is denser and hinders the entry of corrosion ions. Through XRD, the corrosion products were analyzed qualitatively and quantitatively, and it was found that γ -FeOOH decreased while the proportion of α -FeOOH increased in Q235BM and Q355BM. After the addition of rare earths, the corrosion products became more stable and enhanced the protection of steel.

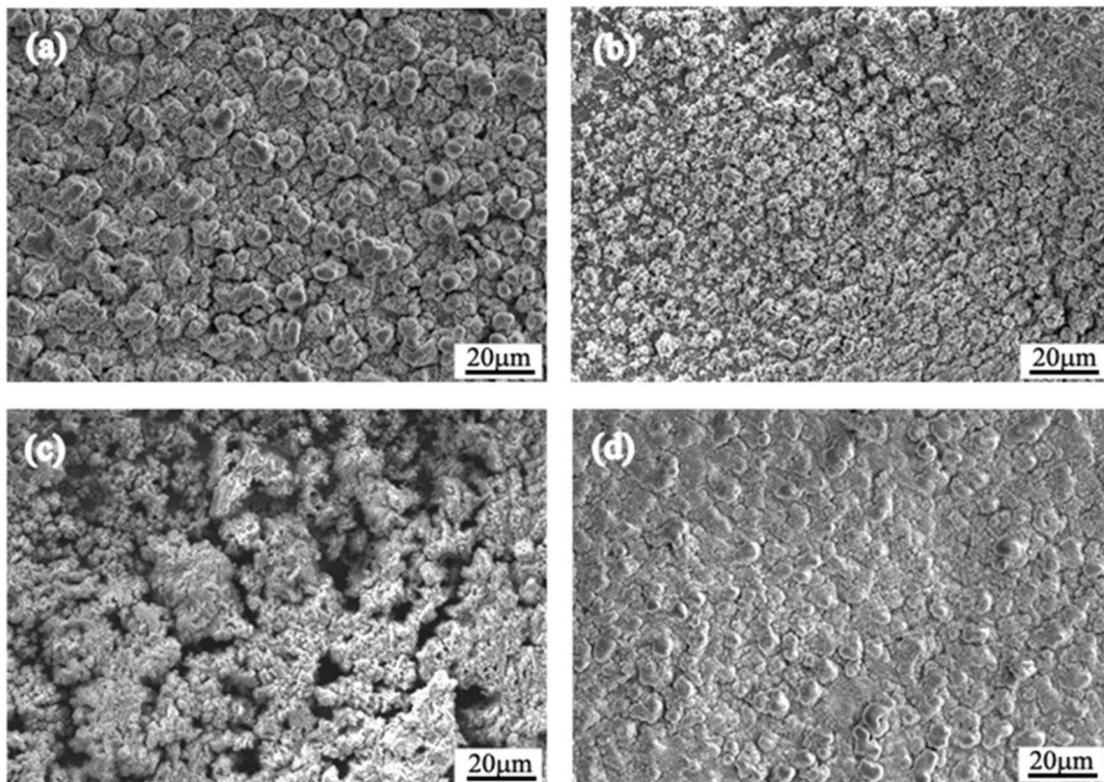


Figure 8. Oxide products on the surfaces of rusted samples after a 144 h immersion test: (a) Q235B; (b) Q235BM; (c) Q355B; (d) Q355BM [78].

There are many similar studies. Dai's group [79] added La and Ce mixed rare earths to A572 Gr.65 steel. This was analyzed by XRD; the amount of γ -FeOOH in the corrosion products of A572 Gr.65 steel containing rare earths was about half of that of A572 Gr.65, while the amount of α -FeOOH was greatly increased, and the rust layer became more stable. The corrosion micromorphology was observed by SEM, and the rust layer became denser and more inhomogeneous after the addition of rare earths, which impeded the contact of corrosive ions with the matrix. Dong's group [80], in verifying the effect of Ce on the steel of offshore platforms, similarly found that the Ce-containing steel had better corrosion resistance, and the rust layer was more compact with a higher amount of α -FeOOH.

3.2.2. Generation of Rare Earth Protective Film

Another reason is the effect of rare earth polarization at the interface on corrosion. Rare earth atoms are active and have a much larger radius than Fe atoms. They can easily polarize at the interface, which affects the diffusion of other elements and inhibits the synthesis of new phases [81]. This also accounts for the microalloying effect of rare earths. Rare earth atoms aggregated at the interface alter the corrosion resistance of the steel. Again, Lian's group [78] analyzed the elemental distribution of the cross-sectional morphology (shown in Figure 9), and it can be seen that the elements Ce and La are mainly present in the matrix; furthermore, close to the rust layer, the content increases significantly. This verifies the enrichment of rare earth elements at the interface. A rare earth atomic layer is formed between the matrix and the rust layer, which inhibits corrosion ions from approaching the steel matrix. The corrosion resistance mechanism is shown in Figure 10. Steel without rare earth elements has pores on the corrosion products, due to which corrosion ions can pass through and come into contact with the steel itself; however, in rare earth steels, the rare earth atoms fill in the pores and prevent corrosion ions from approaching the steel. Thus, the addition of rare earths slows down the corrosion of steel.

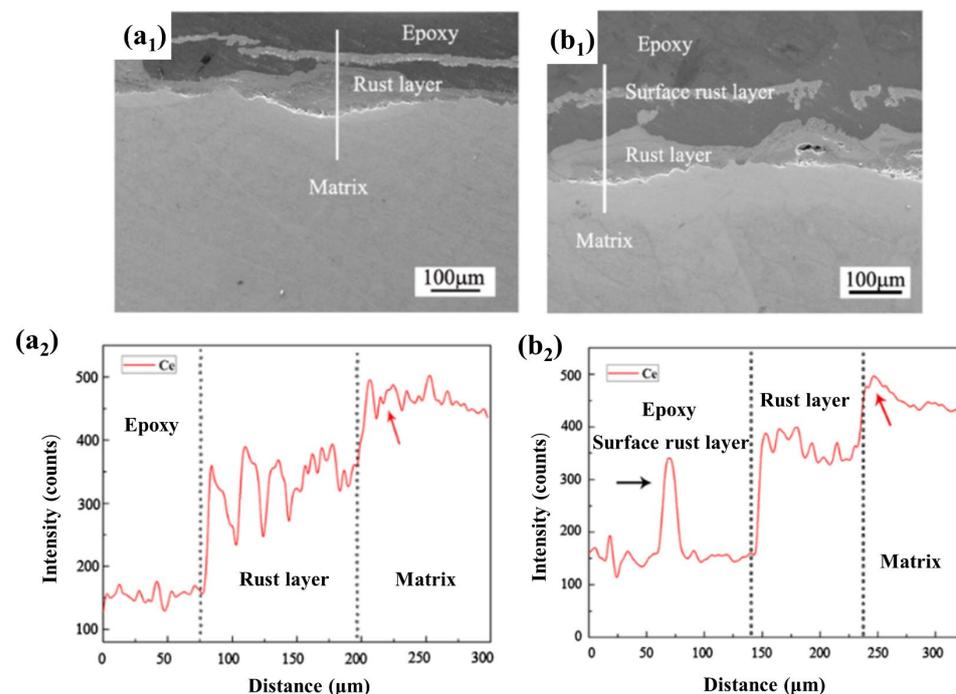


Figure 9. (a₁,b₁) The cross-sectional morphology of the rust layers of Q235BM and Q355BM after 144 h of immersion, respectively; (a₂,b₂) the elemental distribution of Q235BM and Q355BM after 144 h of immersion, respectively [78].

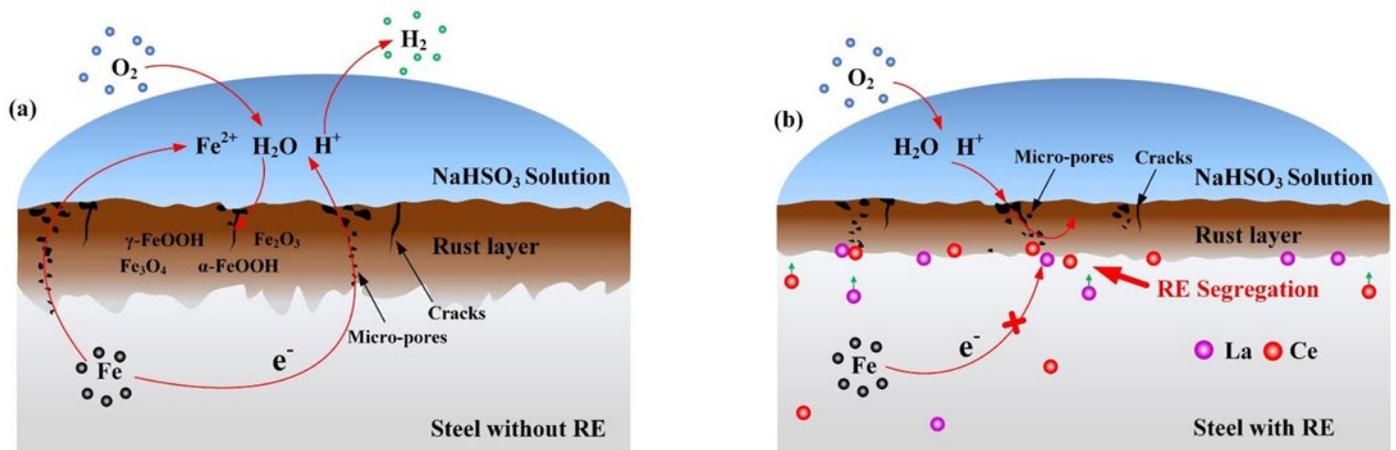


Figure 10. Demonstration of the corrosion resistance mechanism of rare earth atomic layers (a) for steel without rare earths; (b) for steel with rare earths La and Ce added [78].

Guo's group [82], Liu's group [83] and others also demonstrated that rare earths were enriched at the interface, enabling them to form a rare earth atomic layer. Liu's group [83] studied and compared 09CuPcrNi steel and RE-09CuPcrNi steel with the addition of Ce and La. It was also demonstrated that the corrosion resistance of RE-09CuPcrNi steel was stronger than that of 09CuPcrNi steel in the salt spray test. Via elemental analysis and Auger AES analysis, it was confirmed that rare earth atoms were enriched at the interface. This enhanced the adhesion of the rust layer, and made the corrosion of the steel slow down. Also, after elemental analysis via Roche electron spectroscopy AES analysis, it was determined that the rare earth atoms were enriched at the interface, which the adhesion of the rust layer was enhanced and the corrosion of the steel slowed down. Similarly, Wu's group [84] and others invented rare earth steel with a 2–5-times higher corrosion resistance, and by elemental analysis, it was determined that the rare earth atoms were polarized at the junction of the rust layer and the matrix. Even though there have been claims about the rare earth atomic layer in recent years, to determine how the rare earth atomic layer changes in the following, and whether it dissolves or not, further research is needed.

Some studies also suggest that rare earth elements exist in the form of rare earth oxides or rare earth hydroxides in the corrosion products, which is conducive to the formation of protective films [24,85]. Zhang's group [60] comprehensively analyzed the effects of including rare earth elements in microalloyed steel in the early stage of corrosion to full-scale corrosion. Rare earth steel with a Ce content of 0.018% and La content of 0.008%, as well as ordinary microalloyed steel, were used as experimental materials. Both steels were immersed deep in an environment of simulated seawater, as well as in a surface environment, and the rare earth steel showed better corrosion resistance than the ordinary steel. The precipitation of the products is closely related to the degree of supersaturation, which means the higher the degree of supersaturation, the easier it is for precipitation to generate. Through the observation of the rust layer and the calculation of the degree of supersaturation, it was found that the degree of supersaturation of Ce (OH)₃ was significantly higher than that of Fe (OH)₂ and La (OH)₃, and including Ce in rare earth steel preferentially generates Ce (OH)₃ precipitation to promote the generation of the protective film, which impedes the transfer of corrosive ions. The supersaturation magnitude is shown in Figure 11.

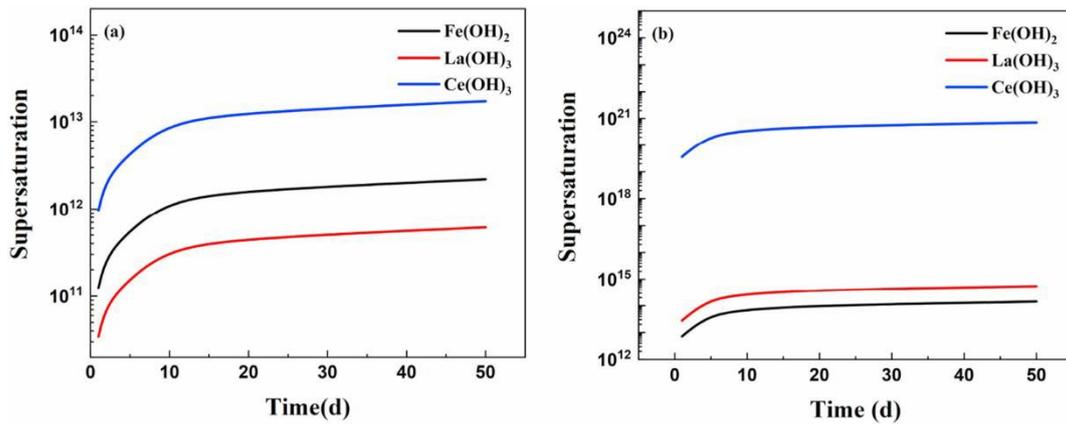


Figure 11. Supersaturation of different corrosion products in the surface environment (a) and deep environment (b) [60].

3.3. Other Corrosion Mechanisms

In addition to rare earth inclusions and dense stable rust layers playing a positive role in the corrosion resistance of steel, there are other corrosion mechanisms.

Considering the adsorption theory, the less Cl^- that is adsorbed on the steel surface, the less likely it is for the oxide film on the steel surface to be destroyed, and the more corrosion-resistant the steel is. The surface charge state φ ($\varphi = E_{\text{corr}} - E_q = 0$) measures the tendency of the metal's surface to adsorb ions. If φ is positive, the metal surface tends to adsorb anions, and vice versa for cations. Zhang's group [60] calculated the φ value of steel after immersion in NaCl solution for 20 days (see Table 2), and found that the φ values of both steels were positive in both deep and surface environments, but the φ values of rare earth steels were lower, such that the rare earth steels were weaker in terms of the adsorption of Cl^- compared to ordinary steels. This proves that rare earths can reduce the surface electrochemical activity of steel, and the reduced adsorption of Cl^- is a reason for the improved corrosion resistance of rare earth steels. Earlier studies also suggested that rare earth ions have a certain corrosion-inhibition effect [86]. In an acidic environment, Ce generates Ce^{3+} and La generates La^{3+} . However, the existence of these two trivalent rare earth cations in the solution has a certain slowing effect on the corrosion of steel.

Table 2. Values of surface charge parameters after 20 d of immersion in 3.5 wt. % NaCl solution [60].

Samples		E_{corr} (V vs. SCE)	$E_q = 0$ (V vs. SCE)	$\varphi = E_{\text{corr}} - E_q = 0$ (V)
Surface environment	Reference steel	−0.122	−0.94	0.818
	RE steel	−0.137	−0.89	0.753
Deep environment	Reference steel	−0.108	−1.01	0.902
	RE steel	−0.254	−1.01	0.756

Regarding the influence of rare earth materials in the corrosion process of steel, many researchers have only inferred the mechanism of rare earth corrosion resistance based on experimental phenomena. Although the research has made a lot of progress, it still lacks theoretical support.

In recent years, the research on rare earth steel has been a hotspot, and the smelting methods have been shown to be slightly different for different kinds of steel. Many metallurgists are improving the metallurgical method, increasing the addition rate of rare earths, and preparing purer steel with better performance. Diao's group [87] invented the manufacturing method of composite corrosion resistant steel, which mainly produced composite corrosion-resistant steel by use of the technology of crystallizer wire feeding. They solved the prewise problems of adding a large amount of alloy, the high temperature of output steel, and the high production temperature. The corrosion test also proved

that the corrosion resistance of steel was improved. Huang's group [88] developed a preparation method for rare earth microalloyed high-strength 690 MPa steel, whereby the corrosion resistance of the steel increased by 3.9 times. Wu's group [84] invented a rare earth corrosion-resistant steel plate preparation method, which had high strength, thin thickness, good corrosion resistance, and a long service life. The corrosion resistance was improved by 2–5 times compared with the steel without rare earths. Lu's group [89] developed a smelting method for rare earth microalloyed steel, whereby the fine rare earth inclusions were uniformly distributed, and the corrosion resistance, fatigue resistance, and low-temperature impact resistance of this kind of steel were improved.

4. Conclusions

After nearly seventy years of research, it has been concluded that rare earths have three main effects on steel: purification of the liquid steel, metamorphic inclusion, and microalloying.

Inclusions lead to the development of a weak protective film on steel's surface, and corrosion occurs preferentially near inclusions. Therefore, it is particularly important to change the properties and size of inclusions. After the addition of rare earth elements, inclusions develop into rare earth sulfides or rare earth sulfur oxides. The properties of inclusions are better, the micro-gaps between inclusions and the matrix are reduced, and the channels for corrosive ions to approach the steel matrix are reduced. The size of the rare earth inclusions is made smaller and the number of corrosion sites is also reduced. In the later stages of corrosion, corrosion products have a greater influence on corrosion. Rare earths favor the generation of a denser and more stable rust layer; in addition to this, rare earth atoms can form a layer of rare earth atoms between the matrix and the rust layer, which hinders contact between the matrix and the corrosion medium.

However, the research on rare earth steel mainly focuses on Ce, La, and Y, and there are few specific studies on the effects of the corrosion mechanism and properties of other rare earth elements in steel. Moreover, there is a lack of theoretical guidance on the influence of rare earths on the whole process of corrosion, which mostly concerns the analysis of experimental phenomena. This will also remain a hotspot and difficulty in the future. After reading the literature, it has been found that there are only a dozen kinds of rare earth steels widely used. This is mainly because the rare earth addition process is still not mature enough, the research on the mechanisms by which rare earths improve the corrosion resistance of steel is not deep enough, and there is a lack of theoretical guidance.

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