



# Article Effect of Mg-Ce Treatment on Inclusion Characteristics and Pitting Corrosion Behavior in EH420 Marine Steel

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Abstract: Reasonable regulation of nonmetallic inclusions in steel can significantly improve its strength, toughness, and corrosion resistance. In this paper, EH420 marine steel was treated with Mg, Ce, and Mg-Ce to modify the inclusions. The effects of different treatments on the morphology, composition, size distribution, induced intragranular ferrite (IGF) nucleation, and pitting resistance of inclusions were systematically analyzed using various methods. The results show that the Mg-Ce composite treatment can modify irregular MgAl<sub>2</sub>O<sub>4</sub> inclusions into spherical Mg-Ce-O composite inclusions and MgO-dominated inclusions. The density of inclusions is increased from 74.8/mm<sup>2</sup> to 186.0/mm<sup>2</sup>, and the average size of inclusions is decreased from 2.60  $\mu$ m to 1.07  $\mu$ m. The Mg-Ce-O composite inclusions are effective inclusions for inducing IGF. Furthermore, the pitting potential is increased from -503 mV to -487 mV, and the corrosion rate is decreased. The order of average electronic work function is  $\Phi$ MgO <  $\Phi$ Ce<sub>2</sub>O<sub>3</sub> <  $\Phi$ \alpha-Fe <  $\Phi$ Al<sub>2</sub>O<sub>3</sub>. Ce<sub>2</sub>O<sub>3</sub> is hard to induce pitting corrosion due to its similar electronic work function to the steel matrix. Thus, the Mg-Ce composite treatment is better than that for Mg and Ce treatment alone, and has better application prospects.

Keywords: inclusion; Mg-Ce composite treatment; pitting corrosion; electrochemistry; steel

# 1. Introduction

Marine steel with high strength, toughness [1], and corrosion resistance [2] is required to build large ships. As a significant indicator of steel quality, the characteristics of non-metallic inclusions in steel are intimately related to the various properties of steel [3]. Therefore, reasonable control of the morphology [4], composition [5–7], quantity [8,9], size [6,10], size distribution [11,12], and uniformity [13] of nonmetallic inclusions in steel can significantly improve the strength, toughness, and corrosion resistance.

Aluminum is a commonly used deoxidizing element in marine steel. Al<sub>2</sub>O<sub>3</sub> inclusions with a high melting point easily aggregate and grow during deoxygenation [14], which can lead clogging of the submerged entry nozzle during the continuous casting process, and influence the smooth operation of the continuous casting process. Adding Mg to steel can transform Al<sub>2</sub>O<sub>3</sub> inclusions into MgAl<sub>2</sub>O<sub>4</sub> and MgO [15–17]. Kimura S [18] pointed out that the force between Mg-containing composite inclusions formed after Mg treatment is approximately 1/10 of that between Al<sub>2</sub>O<sub>3</sub> inclusions. Therefore, Mg treatment can effectively reduce the large-sized inclusions in steel [19]. Due to special service conditions, marine steel also needs to show strong resistance to seawater corrosion.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Many scholars [15,20–23] have found that the addition of rare earth elements to steel results in the formation of rare earth inclusions, which can improve the corrosion resistance of steel.

Mg-Ce composite treatment is beneficial to the refinement of inclusions in steel. By adding earth-magnesium alloy to die steel, Xing Li [15] found that the average diameter and average area of inclusions in steel decrease from 2.18  $\mu$ m and 4.72/ $\mu$ m<sup>2</sup> to 1.88  $\mu$ m and  $3.57/\mu m^2$ , respectively. In addition, Mg-Ce composite treatment can modify the inclusions in steel. Yu Huang [24] studied the effects of Mg and rare earth elements on inclusions in H13 steel and found that for a Mg content of 6 ppm, as the cerium content in molten steel increases from 0 to 300 ppm, MgAl<sub>2</sub>O<sub>4</sub> is effectively modified into cerium oxide (Ce–O) and cerium oxy-sulfide (Ce–O–S), and the evolutionary process is as follows:  $MgAl_2O_4 \rightarrow CeAlO_3 \rightarrow Ce-O$  and Ce-O-S. Meanwhile, Mg-Ce composite treatment is also favorable for improving the properties of steel. Yang Li [25] studied the effect of Mg-Ce composite treatment on non-quenched and tempered steel and found that Al<sub>2</sub>O<sub>3</sub>-MnS and long-trip MnS inclusions can be transformed into Ce-Mn-Mg-O-S. The strength and impact toughness of steel were also improved. Wang C [26] found that Ti-Mg-Ce-O composite inclusions after Ce treatment in Ti-Mg killed steel can induce IGF nucleation, which significantly improves the low-temperature impact toughness of the heat-affected zone. Jeon S [27] pointed out that the addition of Ce to HDSS increases the resistance to pitting corrosion due to the formation of stable Ce oxide and the reduction of pitting initiation sites. As a result, Mg-Ce composite treatment can modify and refine inclusions, increase the strength and toughness of steel [28], and improve the corrosion resistance of steel [29]. However, systematic studies investigating the effect of Mg-Ce composite treatment on the inclusions of marine steel are not yet complete.

The purpose of this work is to investigate the effect of Mg-Ce composite treatment on inclusion characteristics and pitting corrosion behavior in EH420 marine steel. Thermodynamic calculations were used to analyze the change in Mg and Ce content on the evolution of the inclusion composition in steel. Thermal simulation smelting experiments were used to compare the effects of Mg-free treatment, Mg treatment, Ce treatment, and Mg-Ce compound treatment on the composition, number, and size distribution of inclusions in steel. Electrochemical tests were utilized to evaluate the pitting resistance of various types of inclusions in experimental steels. Finally, the electronic work function of the inclusions mas calculated by first-principles calculations to clarify the mechanism of pitting corrosion in experimental steels.

### 2. Experimental Section

# 2.1. Materials and Procedure

The industrial steels were cut to appropriate squares samples by wire cutting. In a typical run, a MgO crucible (30 mm in diameter and 120 mm in height) which contained 500 g ingot of EH420 marine steel was placed in the even zone of a vertical MoSi<sub>2</sub> resistance furnace. The steel was heated to 1600 °C in an argon atmosphere. After melting, the top slag (CaO: 48 wt%, SiO<sub>2</sub>: 21 wt%, Al<sub>2</sub>O<sub>3</sub>: 16 wt%, MgO: 10 wt%, and CaF<sub>2</sub>: 5 wt%) was added to the molten steel to prevent oxidation. After the top slag melts, the Ni-Mg alloy (containing 30 mass% Mg) and Ce-Fe alloy (containing 30 mass% Ce) were deliberately added into the melts to achieve the desired content. After 5 min, the furnace was cooled to room temperature, and then the ingots were removed from the furnace. According to the different alloy additions, four groups of experiments were carried out: Mg-free treatment (standard steel), Mg treatment, Ce treatment, and Mg-Ce treatment, which were named LM, HM, HC, and MC, respectively.

The contents of the main alloying elements in the ingots were determined by an optical emission spectrometer (OES). The Mg and Ce contents were determined by using an inductively coupled plasma mass spectrometer (ICP–MS, PlasmaMS 300). The T.N. and T.O. contents were determined by using a nitrogen-oxygen analyzer. The analysis results are shown in Table 1. T.O. and T.N. denote the total oxygen and total nitrogen content of the test ingots, respectively.

Steel	С	Si	Mn	Ni	Cu	Р	S	Al	Ti	T.O.	T.N.	Mg	Ce
LM	0.08	0.34	1.68	0.31	0.23	0.0081	0.0040	0.010	0.015	0.004	0.0033	0.0006	_
HM	0.07	0.38	1.72	0.28	0.20	0.0072	0.0039	0.011	0.010	0.003	0.0032	0.0022	—
HC	0.06	0.42	1.72	0.29	0.20	0.0077	0.0035	0.011	0.011	0.003	0.0030	0.0008	0.034
MC	0.07	0.38	1.72	0.29	0.20	0.0070	0.0030	0.012	0.010	0.003	0.0028	0.0032	0.014

**Table 1.** Chemical compositions of the ingots in mass%.

### 2.2. Analysis Methods

Two test samples ( $15 \times 15 \times 3$  mm) were taken from the middle part of each ingot and used for inclusion analysis and electrochemical test, respectively.

The inclusion analysis samples were ground with a series of carborundum papers up to 2000 grit and polished with 0.15  $\mu$ m diamond polish. The morphology and composition of the inclusions were characterized by a scanning electron microscope equipped with an energy dispersive spectrometer (SEM–EDS, ZEISS ULTRA 55). Fifty continuous fields of view (total viewed area of 2.85 mm<sup>2</sup>) at 1000× magnification were selected to measure the number density and the size distribution of the inclusions. After inclusion analysis, these samples were etched with a 4% nitric acid solution for 10 s and the microstructure was observed with a Leica DMi8 microscope system.

The electrochemical test samples were welded with copper wire and then embedded in epoxy resin. The experimental samples were ground with a series of carborundum papers up to 600 grit and then rinsed and dried. The exposed area for the experimental steel was 1 cm<sup>2</sup>. An electrochemical experiment based on "ASTM G61-86 (R2014)" was carried out using a three-electrode system, which comprised the experimental samples as the working electrode, a platinum plate as the auxiliary electrode, and a saturated calomel electrode (SCE, 232 Type) as the reference electrode. Potentiodynamic and potentiostatic polarization methods were performed to investigate the anti-pitting properties of inclusions in different treatment methods using an electrochemical workstation (PARSTAT 3000DX). The test time for the open-circuit potential is more than 10 min. The potential was scanned from a relative open potential of -0.6 V to 0.6 V with a scan rate of 0.3333 mV/s to obtain the dynamic potential polarization curve. The potentiostatic polarization was scanned at -0.5 V potential with 5 data per second to obtain the potentiostatic polarization curves.

### 2.3. Computational Details

All calculations for this work are performed in the framework of density functional theory (DFT) with the Cambridge Sequential Total Energy Package (CASTEP). The Broyden Fletcher Goldfarb Shannon (BFGS) criterion [30] is employed to optimize the geometry of the structures. The ultrasoft pseudopotential [31] is used to describe the interactions between ionic cores and valence electrons. The exchange correlation function used in the calculation is the Perdew-Burke-Ernzerhof (PBE) potential energy function of the generalized gradient approximation (GGA) [32]. The single point Kohn-Shan wave function is used to expand the plane wave base group, and the Brillouin zone is sampled with a Monkhorst-Pack k-point grid. After convergence tests of the total energy with respect to the cutoff energy and k-point, the cutoff energy was set as 570 eV for all structures, and the k-points of the surface materials were set as  $6 \times 6 \times 1$ . Furthermore, the self-consistent field, energy, force, atomic displacement, and stress components have convergence criteria of  $1.0 \times 10^{-6}$  eV/atom,  $1.0 \times 10^{-5}$  eV/atom, 0.03 eV/Å,  $1.0 \times 10^{-3}$  Å, and 0.05 GPa, respectively. A 15-Å vacuum layer along the z direction is adopted to eliminate the interactions between the slabs. The crystal structures obtained for all oxides are listed in Table 2.

Oxides	Pearson Symbol	Space Group (NO)	Atom Positions	Lattice Parameters (Å)
α-Fe [33]	cl2	Im-3m (229)	Fe 0, 0, 0	a = 2.866, b = 2.866, c = 2.866, $\alpha = 90^{\circ}$ , $\beta = 90^{\circ}$ , $\gamma = 120^{\circ}$
Al <sub>2</sub> O <sub>3</sub> [34]	hR30	R-3c (167)	Al 0, 0, 0.3520 O 0.3057, 0, 0.2500	a = 4.747, b = 4.747, c = 12.954, $\alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 120^{\circ}$
MgO [35]	cF8	Fm-3m (225)	Mg 0, 0, 0 O 0.5, 0.5, 0.5	a = 4.220, b = 4.220, c = 4.220, $\alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ}$
Ce <sub>2</sub> O <sub>3</sub> [36]	P-3m	P-3m1 (164)	Ce 0.3333, 0.6667, 0.2481 O 0.3333, 0.6667, 0.6447 O 0, 0, 0	a = 3.941, b = 3.941, c = 6.182, $\alpha = 90^{\circ}, \beta = 90^{\circ}, \gamma = 120^{\circ}$

Table 2. Crystal structures of all the oxides in this work.

### 3. Results and Discussion

3.1. Evolution of Inclusion in Marine Steel after Mg-Ce Addition

3.1.1. Effect of the Mg-Ce Addition on the Characteristics of Inclusions

The morphology and composition of the inclusions in the experimental steel were characterized using SEM–EDS, and the results are shown in Figure 1. The typical inclusions in LM steel are irregularly shaped MgAl<sub>2</sub>O<sub>4</sub>-dominated inclusions with trace SiO<sub>2</sub> and CaO. The average MgO and Al<sub>2</sub>O<sub>3</sub> contents in these inclusions are 30.33% and 62.77%, respectively. The typical inclusions in HM steel are spherical MgO-dominated inclusions with trace Al<sub>2</sub>O<sub>3</sub>. The average MgO and Al<sub>2</sub>O<sub>3</sub> contents are 87.86% and 7.87%, respectively. The typical inclusions in HC steel are spherical Ce<sub>2</sub>O<sub>3</sub>-dominated inclusions, with an average Ce<sub>2</sub>O<sub>3</sub> content of up to 98.48%. The typical inclusions for type I, as shown in Figure 1d, are Mg-Ce-Ti-O composite inclusions, in which the outer part consists of high Ce<sub>2</sub>O<sub>3</sub> inclusions observed as a bright white color and the inner part consists of MgO-dominated inclusions observed as a black color. As shown in Figure 1e, the typical inclusions observed as a black color. As shown in Figure 1e, the typical inclusions observed inclusions with trace Ti<sub>2</sub>O<sub>3</sub>, with an average MgO content of 78.47%. The dispersion of MgC-e-Ti-O composite inclusions with trace Ti<sub>2</sub>O<sub>3</sub>, with an average MgO content of 78.47%. The dispersion of MgC-e-Ti-O composite inclusions disperved in Figure 1 is due to the inhomogeneous composition.

Map scanning was used to further analyze the elemental compositions of typical Mg-Ce-O composite inclusion in MC steel, and the results are shown in Figure 2. The results of mapping analysis demonstrate that Ti and O elements are evenly distributed throughout the inclusion. Mg is the element concentrated in the core of the inclusion and overlaps with the black area in the inclusion. Ce and Al elements are primarily distributed in the outer part of the inclusion, resulting in a bright white color in the outer part of the inclusion. Mn, S, and C elements are not clearly enriched.

In general, the competitive relationship between Mg and Ce determines the evolution behavior of inclusions. After Mg treatment, [Mg] reacts with MgAl<sub>2</sub>O<sub>4</sub> inclusions in LM steel to form MgO-dominated inclusions due to the reducing properties of Mg. The rare earth Ce also acts as a strong deoxidizing element. [Ce] reacts with MgAl<sub>2</sub>O<sub>4</sub> inclusions in LM steel to form Ce<sub>2</sub>O<sub>3</sub> inclusions after Ce treatment. Upon Mg-Ce composite treatment, [Mg] with preferential addition reacts with MgAl<sub>2</sub>O<sub>4</sub> inclusions in LM steel to form MgOdominated inclusions with trace Ti<sub>2</sub>O<sub>3</sub>. Then [Ce] in the Ce-Fe alloy with subsequent addition shows a competitive relationship with [Mg]. Some MgO-dominated inclusions are reduced layer by layer by [Ce]. Finally, two types of inclusions are formed: one is the Mg-O composite inclusion, and the other is the Ce-Al-O composite inclusion.



**Figure 1.** The phase diagram of the MgO-Ce<sub>2</sub>O<sub>3</sub>-Ti<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> system and the morphology of typical inclusions. (**a**) Mg-Al-O inclusion; (**b**) Mg-O inclusion; (**c**) Ce-O inclusion; (**d**) Mg-Ce-Ti-O inclusion; (**e**) Mg-Ce-Ti-O composite inclusion.



Figure 2. Element distribution diagram of the Mg-Ce-O composite inclusion in MC steel.

3.1.2. Effect of Mg-Ce Addition on the Number and Size Distribution of the Inclusions

The inclusion number and size distribution are important indices to measure the properties of steel. Figure 3 shows the inclusion number density and average size in the test steels. The inclusion number densities in LM, HM, HC, and MC steels are 74.8, 141.1, 168.9, and 186.0/mm<sup>2</sup>, respectively. Mg treatment, Ce treatment, and Mg-Ce composite treatments significantly increase the inclusion number density. Compared to standard steel, the inclusion number density is increased by 88.64%, 125.80%, and 148.56%, respectively. The average size of the inclusions in LM, HM, HC, and MC steel is  $2.60 \pm 1.62$ ,  $1.08 \pm 0.99$ ,  $1.60 \pm 1.27$ , and  $1.07 \pm 1.01 \mu$ m, respectively. Obviously, HM and MC steels have the

smallest average size of inclusions, and the distribution is more concentrated. Due to the strong deoxidation of Mg and Ce, the Al content in inclusions will be reduced.  $Al_2O_3$  inclusion has strong force and action distance, and the decrease of Al content in inclusions will be conducive to the refinement and dispersion of inclusions. Therefore, the three treatment methods can improve the inclusion number density and reduce the size of inclusions, among which the Mg-Ce composite treatment has the most obvious effect.



Figure 3. Inclusion number density and average size in test steels.

The inclusion size distribution was further analyzed statistically, as shown in Figure 4. The majority of the inclusions in standard steel (LM) are around 1–5  $\mu$ m in diameter, accounting for 83% of the total. In addition, some large inclusions (5–10  $\mu$ m) are observed with a ratio of 6%. The proportion of small inclusions (<1  $\mu$ m) is significantly increased after Mg treatment, accounting for 70% of the total, which is 7.4 times that of standard steel. The proportion of 1–5  $\mu$ m inclusions is significantly decreased, and 5–10  $\mu$ m inclusions disappear. After Ce treatment, the proportion of small inclusions increases from 11% to 42%. The proportion of inclusions in the size range of 1–3  $\mu$ m shows no obvious change,. In terms of inclusion size distribution, MC steel and HM steel exhibit similar characteristics.



Figure 4. Inclusion size distribution in test steels.

As a result, incorporating Mg into steel can significantly increase the proportion of small inclusions. In addition, Mg-Ce composite treatment can significantly increase the inclusion density, and proportion of small-sized inclusions, and effectively reduce the average inclusion size.

# 3.2. Analysis of the Thermodynamic Mechanism of Inclusion Evolution

3.2.1. Analysis of Equilibrium Inclusion Evolution Based on Phase Diagram

FactSage 8.0 was used to calculate the dominant regions of deoxidation products with different Mg and Ce contents. FTmisc and FToxid were selected for the database. The calculated chemical compositions are shown in Table 1.

Figure 5 shows the dominant regions of deoxidation products with different Mg and Ce contents. Spinel and monoxide phases are mainly composed of MgAl<sub>2</sub>O<sub>4</sub> and MgO. When the Mg content is 6 ppm, the inclusion changes according to the route of Al<sub>2</sub>O<sub>3</sub>  $\rightarrow$  Al<sub>2</sub>O<sub>3</sub> + AlCeO<sub>3</sub>  $\rightarrow$  Spinel + AlCeO<sub>3</sub> + Al<sub>11</sub>O<sub>18</sub>Ce $\rightarrow$ Spinel + AlCeO<sub>3</sub>  $\rightarrow$  AlCeO<sub>3</sub>  $\rightarrow$  Ce<sub>2</sub>O<sub>3</sub> + AlCeO<sub>3</sub>  $\rightarrow$  Ce<sub>2</sub>O<sub>3</sub> as the Ce content increases. When the content of Mg is 6–8 ppm, with increasing Ce content, the inclusion is changed according to the route of spinel + AlCeO<sub>3</sub>  $\rightarrow$  AlCeO<sub>3</sub>  $\rightarrow$  Ce<sub>2</sub>O<sub>3</sub> + AlCeO<sub>3</sub>  $\rightarrow$  Ce<sub>2</sub>O<sub>3</sub>. When the content of Mg is 16–42 ppm, with increasing Ce content, the inclusion is changed according to the route of spinel  $\rightarrow$ spinel + AlCeO<sub>3</sub>  $\rightarrow$  spinel + monoxide + AlCeO<sub>3</sub>  $\rightarrow$  monoxide + AlCeO<sub>3</sub>  $\rightarrow$  monoxide + Ce<sub>2</sub>O<sub>3</sub> + AlCeO<sub>3</sub>  $\rightarrow$  Monoxide + Ce<sub>2</sub>O<sub>3</sub>. When the Mg content is >42 ppm, the inclusion does not change with increasing Ce content.



Figure 5. Dominant regions of deoxidation products with different Mg and Ce contents.

According to the Mg and Ce contents given in Table 1, it can be concluded that the equilibrium inclusion in LM steel is  $MgAl_2O_4$ . The equilibrium inclusions in HM and HC steel are  $MgO + MgAl_2O_4$  and  $Ce_2O_3$ . When the Mg and Ce content are 32 and 340 ppm, respectively, MgO and  $Ce_2O_3$  coexist as equilibrium inclusions in MC steel.

### 3.2.2. Analysis of Inclusion Modification Based on Reducing Ability

As shown in Figures 1 and 5, the MgAl<sub>2</sub>O<sub>4</sub> inclusions in standard steel are primarily modified to MgO and Ce<sub>2</sub>O<sub>3</sub> after various treatments. As a result, dissolved [Al], [Mg], [Ce], and [O] equilibrations in standard steel at 1600 °C are calculated to better explain the evolutionary behavior of inclusions. Table 3 shows the deoxidation equilibrium of Al, Mg,

and Ce. The interaction coefficients involved are shown in Table 4. Based on Henry's Law and Wagener's model, the calculation results are shown in Figure 6. It can be concluded that [Al] has poor deoxidation ability compared to [Mg] and [Ce]. When the [Mg] content is <10.5 ppm, the deoxidation ability increases with the increase of [Mg] content. On the contrary, the deoxidation ability decreases. Unlike [Mg], the deoxidation ability of [Ce] will be enhanced as its content increases.

Table 3. Equilibrium constants used in this study [37–39].

Reaction	$ riangle \mathbf{G}^{m{ heta}}$ /(J·mol $^{-1}$ )
$Al_2O_3(s) = 2[Al] + 3[O]$	1202000-386.3T
MgO(s) = [Mg] + [O]	728600-238.4T
$Ce_2O_3 = 2[Ce] + 3[O]$	1827424-643.8T

Table 4.	Interaction	coefficients of	elements <i>i</i> and	<i>i</i> in molten steel	at 1600 °C	40].
	III COLOROIDIE	coorrection of		, mi moren secon		

e <sup>j</sup> <sub>i</sub>	С	Si	Mn	Ni	Р	S	Al	Ti	0	Ν	Mg
Al	0.091	0.056	-0.004	-0.0173	0.0046	0.030	0.045		-6.6	-0.004	-0.13
Mg	-0.24	-0.088		-0.012			-0.12	-0.64	-404		
Ce	-0.077		0.13		1.746	-39.8	-2.25		-5.03	-6.599	
0	-0.45	-0.131	-0.021	0.006	-0.3	-0.133	-3.9	-0.34	-0.20		-266

$$10^{-2}$$

$$10^{-3}$$

$$10^{-3}$$

$$10^{-4}$$

$$10^{-4}$$

$$10^{-5}$$

$$10^{-5}$$

$$10^{-4}$$

$$10^{-5}$$

$$10^{-4}$$

$$10^{-5}$$

$$10^{-4}$$

$$10^{-3}$$

$$10^{-2}$$

$$10^{-1}$$

$$[\%M]$$

 $(r_{Mg}^{O} = 527,000; r_{Mg}^{Mg,O} = -122,000; r_{O}^{Mg} = 40,000; r_{O}^{O,Mg} = 596,000).$ 

Figure 6. Relationship between solubility [%M] (M = Mg/Ce/Al) and [%O] in liquid iron at 1600 °C.

When Mg or Ce is added to liquid steel,  $Al_2O_3$  inclusions in MgAl<sub>2</sub>O<sub>4</sub> will be transformed into MgO or Ce<sub>2</sub>O<sub>3</sub> inclusions by [Mg] or [Ce], respectively, due to the strong deoxidization ability. Simultaneously, [Mg] or [Ce] will react directly with [O] in liquid steel to generate MgO or Ce<sub>2</sub>O<sub>3</sub> inclusions, respectively. When Mg-Ce composite treatment, the addition of Mg preferentially makes the inclusions in the steel evolve into MgO. The increased Ce concentration will then be able to undergo a displacement reaction with MgO. However, it is insufficient to entirely replace all of the [Mg] in MgO due to insufficient [Ce] content. As a result, the inclusion types in MC steel are finally generated. In conclusion, the evolution mechanism of inclusions can be shown in Figure 7.



Figure 7. Schematic diagram of evolution mechanism of inclusions by Mg-Ce treatment.

# 3.3. Analysis of Mg-Ce-O Composite Inclusion-Induced Acicular Ferrite Nucleation Ability

The Mg-Ce-O composite inclusions are effective inclusions for inducing IGF. Figure 8 shows the SEM micrograph and elemental distribution of a typical effective inclusion in MC steel. The inclusion is a composite, containing Mg–Ce–O elements. According to the elemental distribution, it is found that the inclusion can be divided into three parts: MgO in the inner part and Ce<sub>2</sub>O<sub>3</sub> in the outer layer. The inclusion in Figure 8 induces the nucleation of IGF, and a higher Ce concentration is found to exist at the position of IGF nucleation.



**Figure 8.** SEM micrograph and elemental distribution in a typical effective inclusion in MC steel. (a) mapping and (b) scanning images of the Mg-Ce-O composite inclusion.

The capacity of inclusion heterogeneous nucleation is controlled by the interface's free energy change, which is mainly impacted by the disregistry effect. Bramfitt's planar lattice disregistry model [41] was used to calculate the disregistry between Ce<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe. This model is defined as follows:

$$\delta_{(hkl)n}^{(hkl)s} = \sum_{i=1}^{3} \frac{|d[uvw]_{s}^{i}\cos\theta - d[uvw]_{n}^{i}|}{3d[uvw]_{n}^{i}} \times 100\%$$
(1)

where (hkl)s and (hkl)n are the low-index plane of substrate and nucleated solid, respectively; [uvw]s and [uvw]n are the low-index direction in (hkl)s and (hkl)n, respectively; d[uvw]s and d[uvw]n are the interatomic spacing along [uvw]s and [uvw]n, respectively;  $\theta$  is the angle between the [uvw]s and [uvw]n directions.

The crystal structures obtained for Ce<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe in this work are listed in Table 2, and the mismatch model is shown in Figure 9. The calculation result shows that the disregistry between (001) Ce<sub>2</sub>O<sub>3</sub> and (111)  $\alpha$ -Fe is 2.77% (<6%). Therefore, Ce<sub>2</sub>O<sub>3</sub> inclusions have a good ability to promote heterogeneous nucleation of  $\alpha$ -Fe, which can effectively induce IGF nucleation. Mg-Ce-Ti-O composite inclusions can effectively induce IGF nucleation due to the Ce<sub>2</sub>O<sub>3</sub> in the outer part.



**Figure 9.**  $Ce_2O_3(001) \| \alpha$ -Fe(111) mismatch model.

### 3.4. Effect of Inclusion Type on the Resistance to Pitting Corrosion

The corrosion resistance of test steels was measured by electrochemical potentiodynamic polarization curves and potentiostatic polarization curves. Pitting corrosion often initiates and grows up in the early stage of steel corrosion. In general, the pitting potential (Ep) refers to the breakdown potential for damaging the passive film, which reflects the order of pitting caused by inclusions in steel. A high pitting potential indicates strong pitting resistance of the test steels [42,43]. Figure 10 shows the results of electrochemical tests. As shown in Figure 10a, the Ep is determined by the slope beginning to change from positive to negative. Based on the increased rate of current density, the potentiostatic polarization curve is divided into stages I and II, with a time of 200 s as the boundary, as shown in Figure 10b. In stage I, the corrosion current density increases rapidly, mainly including corrosion initiation and expansion. In stage II, the corrosion current density is stable at a high level, which means a uniform corrosion of the matrix mainly occurs. The slope of 0–200 s in the potentiostatic polarization curve reflects the corrosion rate of the initial pitting corrosion of inclusions.



**Figure 10.** Polarization curves for the test steels. (**a**) Potentiodynamic polarization curve; (**b**) potentiostatic polarization curve.

The analysis results are shown in Table 5. The pitting potential and slope of stage I (K<sub>I</sub>) for LM and HM steel are -503 mV and 0.173 mA/(cm<sup>-2</sup>·s<sup>-1</sup>), -509 mV and 0.193 mA/(cm<sup>-2</sup>·s<sup>-1</sup>), respectively, which means the two steels are less resistant to pitting corrosion due to the low pitting potential and large KI. It is noteworthy that the pitting potential and KI for HC steel are -456 mV and 0.052 mA/(cm<sup>-2</sup>·s<sup>-1</sup>), respectively. This means that HC steel has the best pitting resistance, followed by MC steel.

Table 5. Pitting position and slope of stage I for the test steels.

Steel	LM	HM	НС	МС
Ep/mV	-503	-509	-456	-487
$K_I/mA \cdot cm^{-2} \cdot s^{-1}$	0.173	0.193	0.052	0.136

The pitting morphologies of typical inclusions after potentiodynamic polarization are shown in Figure 11. Compared to LM steel, HM steel exhibits severe pitting corrosion around high MgO inclusions, meaning that Mg treatment deteriorates the corrosion resistance of the steel matrix. Only minor pitting corrosion occurs around the Ce-containing inclusions in the HC and MC steels, which could improve pitting resistance.



**Figure 11.** Pitting morphologies of typical inclusions. (**a**) MgAl<sub>2</sub>O<sub>4</sub> in LM steel; (**b**) High-MgO in HM steel; (**c**) High-Ce<sub>2</sub>O<sub>3</sub> in HC steel; (**d**) Mg-Ce-Al-Ti-S-O in MC steel.

In summary, high MgO inclusions are prone to matrix pitting compared to MgAl<sub>2</sub>O<sub>4</sub> inclusions, whereas Ce-containing inclusions can significantly improve the pitting resistance of steel. The Mg treatment reduces the size of the inclusions, but simultaneously increases their number density. As a result, more corrosion sites result in lower pitting resistance for HM than LM steel. MC steel has the better corrosion resistance due to Ce<sub>2</sub>O<sub>3</sub> inclusions formed after Ce treatment. The formation of rare-earth composite inclusions after the treatment of Mg-Ce composites can improve the pitting resistance of steel. Therefore, the order of pitting resistance for the four experimental steels is HC > MC > LM > HM.

# 3.5. Analysis of Inclusions for Pitting Corrosion Resistance Based on Electronic Work Function

The electron work function is defined as the minimum energy required for an electron to escape from the interior to the surface of a solid. Previous studies have indicated that the electron work function is closely related to corrosion potential and can serve as a sensitive parameter to study corrosion mechanisms [44]. This parameter reflects the material's corrosion tendency and can be calculated using Equation (2).

$$\Phi = E_{\rm vac} - E_{\rm F} \tag{2}$$

where  $\Phi$  represents the electronic work function;  $E_{vac}$  represents the electrostatic potential energy;  $E_F$  represents the fermi energy.

In order to compare the electronic work function between inclusions and Fe, the potential difference is calculated by Equation (3).

$$\Delta U = \Phi_{\text{oxide}} - \Phi_{\text{Fe}} \tag{3}$$

where  $\Delta U$  represents the potential difference between the steel matrix and the inclusion;  $\Phi_{\text{oxide}}$  represents the electronic work function of the inclusion, and  $\Phi_{\text{Fe}}$  represents the electronic work function of the  $\alpha$ -Fe(110) plane.

The possibility and location of dissociation reactions were determined based on the electronic work function of the inclusions and the steel matrix. When  $\Delta U$  is less than 0, the inclusion acts as the anode that dissolves first. Conversely, when  $\Delta U$  is greater than 0, the anode changes to the steel matrix and would dissolve first. When  $\Delta U$  is close to 0, no dissociation reaction would occur [45]. To determine the dominant crystalline surfaces of the steel and inclusions, the minimum surface energy principle was utilized, with  $\alpha$ -Fe(110) [46], Al<sub>2</sub>O<sub>3</sub>(0001) [47], MgO(100) [48], and Ce<sub>2</sub>O<sub>3</sub>(0001) [49] identified as the respective surfaces. Surface convergence tests on slab models were performed to ensure sufficient atomic layer thickness and representative bulk material properties, with a 15 Å thick vacuum layer employed to neutralize the interaction of the terminal atoms. Finally, first-principles calculations were used to calculate the electronic work function after structural optimization, and the results are presented in Table 6.

The electron work function of the  $\alpha$ -Fe(110) plane is 4.706 eV. The electronic work function of MgO is lower than that of the steel matrix, ranging from 4.174 eV to 4.291 eV, while the electronic work function of Al<sub>2</sub>O<sub>3</sub> is generally greater than that of the steel matrix, ranging from 4.108 eV to 6.398 eV. Ce<sub>2</sub>O<sub>3</sub> has an electronic work function that is similar to that of the steel matrix, ranging from 3.036 eV to 5.360 eV. Figure 12 illustrates that the average electronic work function order is  $\Phi$ MgO <  $\Phi$ Ce<sub>2</sub>O<sub>3</sub> <  $\Phi\alpha$ -Fe <  $\Phi$ Al<sub>2</sub>O<sub>3</sub>. This indicates that when MgO acts as a pitting source in steel, it can induce pitting corrosion, which begins with MgO and progresses to the steel matrix. On the other hand, Al<sub>2</sub>O<sub>3</sub> does not decompose, but pitting corrosion can still occur in the steel matrix near the inclusions due to large potential differences. The electronic work function of Ce<sub>2</sub>O<sub>3</sub> is similar to that of steel matrix, indicating that pit corrosion, with the outer part consisting of high Ce<sub>2</sub>O<sub>3</sub> inclusions and the inner part consisting of MgO-dominated inclusions, can significantly reduce the possibility of pitting corrosion.

Surfaces	<b>Terminated Plane</b>	Electronic Work Function/eV
α-Fe(110)	1	4.706
	1	5.636
	2	6.404
	3	4.108
	4	5.632
	5	6.215
	6	4.108
	7	5.594
	8	6.399
A1 Q (0001)	9	4.108
AI <sub>2</sub> O <sub>3</sub> (0001)	10	6.043
	11	6.216
	12	4.108
	13	5.573
	14	6.401
	15	4.108
	16	5.638
	17	6.398
	18	4.108
M-Q(100)	1	4.174
MgO(100)	2	4.291
	1	3.036
	2	4.655
Ce <sub>2</sub> O <sub>3</sub> (0001)	3	5.360
	4	5.152
	5	4.664

**Table 6.** The electronic work function of different terminated planes of  $\alpha$ -Fe and oxide surfaces.



Figure 12. The potential difference of different terminated planes of simple oxide.

# 4. Conclusions

1. The typical inclusions in EH420 marine steel are MgAl<sub>2</sub>O<sub>4</sub>. After Mg treatment, the inclusions can be transformed into MgO-dominated inclusions. After Ce treatment, the inclusions can be transformed into Ce<sub>2</sub>O<sub>3</sub> inclusions. After Mg-Ce composite treatment, the inclusions can be transformed into Mg-Ce-O composite inclusions and MgO-dominated inclusions with trace Ti<sub>2</sub>O<sub>3</sub>. The experimental results are consistent with the thermodynamic calculation results;

- 2. Mg treatment, Ce treatment, and Mg-Ce composite treatment can increase the number of inclusions and refine the size of the inclusions. Among them, the effect of Mg-Ce composite treatment is the most significant. After Mg-Ce composite treatment, the inclusion number density in MC steel is increased by 2.5 times, and the average size is reduced to 2/5 of standard steel;
- 3. High MgO inclusions formed after Mg treatment are prone to pitting corrosion. The inclusions containing rare earth elements after Ce treatment can significantly improve the pitting resistance of steel and reduce the corrosion rate. Compared with Mg treatment, Mg-Ce composite treatment can be used to improve the corrosion resistance of steel;
- 4. Based on first-principles calculations, it was determined that the average order of the electron work function is  $\Phi$ MgO <  $\Phi$ Ce<sub>2</sub>O<sub>3</sub> <  $\Phi\alpha$ -Fe <  $\Phi$ Al<sub>2</sub>O<sub>3</sub>. As a result of its low electron work function value, MgO can dissolve and cause pitting corrosion. In contrast, Ce<sub>2</sub>O<sub>3</sub> has a similar electron work function value to that of the steel matrix, making it hard for it to induce pitting corrosion.

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