Microstructure, corrosion behavior and rust resistance of Ti and Ce added invar alloys

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Abstract
In this study, the effects of Ti and Ce on the microstructure, corrosion behavior and rust resistance of invar alloys were investigated in detail. The precipitation phase which can be used as the core of heterogeneous nucleation can be formed by adding an appropriate amount of Ti and Ce, which promotes microstructure refinement and homogenization of the invar alloy. Moreover, the electrochemical behavior of invar alloys with different Ti and Ce contents was studied. The results show that with the addition of alloying elements, the self-corrosion potential of the alloy becomes positive, and the self-corrosion current decreases, indicating that the addition of Ti and Ce is beneficial for improving the corrosion properties of the alloy. This is primarily because Ti and Ce combine easily with unfavorable elements to form precipitates, which reduces the factors affecting the corrosion resistance of the alloy. The invar alloy with superior corrosion resistance was selected for the dipping test. X-ray diffraction analysis showed that the addition of Ti and Ce increased the amount of $\alpha$-FeOOH and enhanced the protective effect of the antirust layer.

1. Introduction
Invar alloys have a significantly low coefficient of thermal expansion, which is below the Curie temperature [1–3]; therefore, they are often used in optical measuring instruments and electronic equipment that require high dimensional stability. Currently, invar alloys are also widely used in aerospace, liquefied natural gas (LNG) transportation and other fields [4–7]. For the LNG carrier, the inner tank (main secondary screen walls) of the storage tank is constructed using an invar alloy plate through a welding process. However, invar alloys have poor rust and corrosion resistances, especially under exposure to seawater, which leads to electrochemical corrosion and causes significant economic losses. Although Fe–Co–Cr invar alloy (stainless invar alloy) is being developed currently, it cannot satisfy the requirements of large-scale industrial production owing to the high cost of Co.

It is well known that the addition of different alloys significantly changes the microstructure of the alloy and affects its electrochemical properties. Wu et al [8] added 3% Ni to traditional weathering steel, and identified that the corrosion product of this new weathering steel can promote the transformation of $\gamma$-FeOOH to fine-grained $\alpha$-FeOOH, which hinders the penetration of $\text{Cl}^-$ ions and improves the corrosion resistance of the material. Although the invar alloy also contains a certain proportion of Ni, it cannot form a sufficiently dense protective layer in practical applications [9], therefore, further study is required. Ti and Ce alloy elements are among the most widely used elements to improve the corrosion resistance of alloys. Ti is an important trace element for improving the alloy properties. Zhao et al [10] observed that the addition of an appropriate amount of Ti can effectively hinder the penetration of $\text{Cl}^-$ ions at point defects and significantly improve the pitting corrosion.
resistance of the alloy when studying the corrosion behavior of Al$_2$-$x$CoCrFeNiTix series high-entropy alloys. When a rare earth element (Ce) was added to Zr–Ti deoxidized low-alloy steel [11], the TiN surrounded by the rare-earth-element-modified inclusions in the alloy would fall off after local corrosion occurs, thereby reducing the cathode of the electrochemical reaction on the alloy surface, forming stable corrosion-resistant pitting pits, and enhancing the corrosion resistance of the alloy. The addition of the rare earth element (Ce) weakens the accelerating effect of the second-phase micro-current on the electrochemical corrosion in the alloy [12]. Furthermore, Ti and Ce can also promote the formation of a stable rust layer in weather-resistant steel, seawater corrosion-resistant steel, and other alloys, which can improve the corrosion-resistance. Unfortunately, although there are several current studies on weathering steel, seawater corrosion-resistant steel, and stainless steel, little attention has been focused on the corrosion behavior of invar alloys. Therefore, a rare earth element (Ce) and Ti were added to the invar alloy and its corrosion behavior and rust resistance were studied for the purpose of further understanding the corrosion mechanism and developing a new invar alloy with excellent corrosion resistance.

2. Experimental procedure

2.1. Experimental material
In the experiment, a self-made small arc smelting furnace was used to prepare Fe–Ni–xM alloy (where x represents the content of the added elements, M represents the types of added elements, i.e., Ti, Ce, or Ce+Ti) under an argon protection environment. After smelting, the composition of the alloy was determined using ARTUS8 spectrometer. The chemical compositions are listed in Table 1. The heat source of the arc smelting furnace device was a Panasonic YC-300WX DC welder, and the electrode was a non-molten tungsten electrode. Argon was used as the shielding gas to prevent the oxidation of the alloy. The button ingot was cast in the melting furnace with an arc current of 150 A, and the melting time was 15s.

The observation samples with dimensions of 10 mm $\times$ 10 mm $\times$ 2 mm were cut by a wire electrical discharge machining process at a position 2 mm above the bottom end of the button ingot. Diagrams of arc melting process and button-shaped casting ingot are shown in figure 1.

2.2. Experimental methods
After grinding and polishing, the samples were etched with a 30% FeCl$_3$ solution prepared with deionized water, and the microstructure of the invar alloy was observed using an inverted optical microscope (Axio Vert A1). An electron probe microanalyzer (EPMA, 8530F, JEOL Ltd.) was used for microzone detection and element distribution analysis.

CHI660E electrochemical workstation was selected for conducting the electrochemical experiments. A three-electrode system consisting of a calomel electrode as the reference electrode, which is linked with a salt bridge, a pure platinum sheet as the auxiliary electrode, and a working electrode was used. Electrochemical
impedance spectroscopy (EIS) test was performed under an open-circuit potential. The scanning frequency range of the test was $10^6$–$10^{-2}$ Hz, and the amplitude of the disturbance potential signal was 5 mV. After the test, ZSimpWin software was used for circuit fitting analysis. Relative to the open circuit potential, the test range of the Tafel curve was $-1 \sim 0.1$V, the scanning rate was 5 mV s$^{-1}$, and the test was performed at room temperature (25 °C). The controllable factors influencing the test should be maintained consistent during the test. After the test, the data of the self-corrosion potential, corrosion current density and passivation potential were collected using the software of the CHI660E electrochemical workstation. Then, the sample was immediately washed with deionized water, dehydrated with alcohol and dried in cold air.

Cyclical immersion tests were used to evaluate the rust resistance. After grinding, the samples were suspended and soaked in 3.5% wt.% NaCl solution. In the experiment, 12 h of immersion and 12 h of air oxidation acted as a single cycle, and 20 cycles of immersion and corrosion were conducted at room temperature (25 °C). The influence of alloying elements on the morphology and composition of the rust layer of the invar alloy was studied, and the protective effect of the composition and density of the rust layer on the alloy were further explored. The surface morphology and precipitated phase composition of the etched invar alloy were detected using a scanning electron microscope equipped with an energy-dispersive spectrometer (JEOL 7100F). The phase of the rust layer on the surface of the soaked sample was measured and analyzed using Rigaku Dmax-rA X-ray diffractometer (Cu target) from Japan. During the test, acceleration voltage was 40 kV, the scanning speed was 4° min$^{-1}$, step length was 0.02°, and scanning range was 20°–90°.

3. Results

3.1. Microstructure

The microstructure of the invar alloy with the different added elements is shown in figure 2; moreover, the average size of the austenite and substructure is shown in figure 3. From figures 2(a) and 3(a), it can be observed that the austenite grain boundary of the invar alloy without alloying elements is convoluted and has poor uniformity; moreover, the substructure uniformity is poor and the cell wall is thick. The average size of the austenite grain and substructure were approximately 177 and 23 μm, respectively. For the 0.2% Ti-added alloy (figures 2(a)–(d)), it can be observed that the austenite grain morphology and size of the invar alloy demonstrate little change. However, the substructure was significantly refined (approximately 14.02 μm, with a refinement rate of 39%). The cell wall of the substructure was thinned. When the Ti content was 0.5%, the austenite grain and substructure uniformity were evidently improved, and the substructure cell wall was further thinned. When 1.0% Ti was added, the minimum average size of the substructures reached 6.53 μm and the refinement rate was increased up to 71.8%. However, the distribution of substructures became disordered, homogeneity of the substructures became worse, and cell walls of the substructures began to thicken. Overall, within the scope of the amount of added Ti (0.2%–1.0%), with the increase in Ti content, the invar alloy austenitic grain size increased; then, the organization as a whole was homogenized and the grain boundary was straightened; moreover, the substructure size decreased gradually with the increase in the content; however, the maximum content added

![Figure 2. Microstructure of the invar alloy with no alloy element (a), and with the addition of Ti (b–d), Ce (e–i), and mixture of added Ti and Ce elements (j–l).](image-url)
was 1.0%, at which and the structure uniformity demonstrated a variation along with the thickening of the cell wall.

The microstructure of the Ce-added invar alloy is shown in figures 2(e)–(i). It can be observed that when the content of added Ce was 0.05 or 0.1%, the microstructure refining effect, and uniformity are good. The austenitic grain sizes were approximately 144 and 140 μm, and the refinement rates were approximately 19 and 21% respectively. The structure sizes were approximately 14.7 and 14.1 μm, respectively, and the refinement rates were approximately 36.5 and 39.1%, respectively (as shown in figure 3(b)). However, when the addition amount reached 1%, the microstructure uniformity of the invar alloy became considerably poor (as shown in figure 2(i)), and its substructure became bulky and presented regular substructure boundaries (as shown in figure 2(i)). In addition, the addition of a large amount of Ce easily forms loose rare earth inclusions at the grain boundary, which can easily to fall off during the polishing and corrosion process, resulting in gullies that show black boundary characteristics.

It can be observed from figure 2 that Ti has the function of refining the substructure and homogenizing austenite grains, while Ce has a significant refining effect on austenite grains. Therefore, the austenite grain and substructure of the invar alloy with the simultaneous addition of Ce and Ti can be refined well when compared to that of the invar alloy where only Ti or Ce is added. It is worth mentioning that when either Ce is added alone...
or mixture Ti + Ce is added, the amount of Ce should be strictly controlled. If the addition amount is too high, black gullies will appear at the austenite grain boundaries and substructure cell walls, which is related to the limited solid solubility of rare earth elements.

3.2. Electrochemical properties

Figure 4 shows the Tafel curves of the invar alloys tested in 3.5 wt.% NaCl solution and their analysis results. As shown in figure 4(a), the Tafel curves of the invar alloy without the addition of Ti or Ce have a certain passivation range. This illustrates the formation of a passive film; in the process of corrosion, when the potential increased to around 0 V, the curve demonstrates an instantaneous rise as the corrosion current density increases rapidly, which indicates a damage to the passivation membrane by Cl-ions, resulting in accelerated corrosion. As shown in figure 4(b), the self-corrosion potential and self-corrosion current density of the invar alloy without added elements are −0.517V and 2.32 μA cm⁻², respectively. The self-corrosion potential is a thermodynamic parameter, which only represents the corrosion tendency. The more positive the potential is, the weaker the corrosion tendency will be. The self-corrosion current density is a kinetic parameter, which reflects the corrosion rate of the material. The higher the self-corrosion current density is, the faster the material will corrode once the corrosion starts. Figures 4(a) and (b) show the Tafel curves and analysis results of the Ti-added invar alloy. It can be observed that the self-corrosion potential first increases and then decreases with the increase in the amount of added Ti; conversely, the self-corrosion current density first decreases and then increases. According to the self-corrosion current density, the corrosion resistance of the alloy is ranked from high to low as follows: 0.2%Ti > 0.5% Ti > no Ti > 1.0% Ti. The improvement of
corrosion resistance is related to the grain size and uniformity. In general, under the same conditions, the fine and poor homogeneity microstructure has a relatively high corrosion tendency, because the grain boundary has more defects and high energy; consequently, the alloy is preferentially corroded in this area\cite{13}. For the invar alloy with 0.2 and 0.5% Ti, the austenitic grain size became thick but tended to be more uniform. The substructure became small, uniform and dense, which is conducive to a decrease in the corrosion tendency of the invar alloy. However, when the addition amount was 1.0%, although the coarse grain size was beneficial for reducing the corrosion tendency, the Ni element tended to concentrate in the cell wall, and the sharp increase in the cell-wall volume fraction led to a serious deterioration in the homogeneity of the microstructure composition. Therefore, the corrosion tendency increased with a negative shift in corrosion potential of the 1.0% Ti invar alloy.

Figures 4(c) and (d) show the Tafel curves and test results of the invar alloy with the addition of rare earth Ce. The corrosion current density decreased gradually with the addition of the rare earth element. The corrosion current density of the 0.2% Ce-added alloy was the lowest, decreasing by more than 90%. Further, the current densities of the alloys with 0.5% Ce, 0.1% Ce, 0.05% Ce, no Ce and 1.0% Ce are in increasing order. The solid solubility of rare earth elements in the matrix is significantly small; in the case where a lesser amount of rare earth element is added, the element achieves clean grain boundaries and the precipitation of the cathode-phase control function in the corrosion process is not sensitive to Cl\textsuperscript{−} rare earth oxides; moreover, the oxide of the corrosion product film helps to improve the stability of the corrosion product film to improve the protection\cite{14} of the matrix. However, when the rare earth content is higher (1.0%), it combines together easily; consequently, it does not protect the matrix as it has a greater negative potential when compared to the protected surface, and this results in increased micro-cell corrosion leading to accelerated corrosion. The Tafel curves of 1.0% Ce-added invar alloy has no obvious passivation range, which is an important reason. At the same time, it can be observed from the figure that a higher content of the rare earth element reduces the homogenization of the microstructure and also reduces the corrosion resistance of the invar alloy.

When Ce and Ti were added simultaneously, the corrosion resistance of the invar alloy also improved to a certain degree, as shown in figures 4(e) and (f). With the increasing content of Ce+Ti, the self-corrosion potential and current density of the invar alloy show the same change rule as that of the Ce-added alloy. The corrosion resistance of the 0.5% Ce+Ti invar alloy was the best, and its self-corrosion current density decreased by nearly 50%. When the addition amount of Ce+Ti was more than 0.5%, the increase in the self-corrosion current density is related to a significant amount of deterioration in the microstructure uniformity. Overall, the effect of Ce+Ti on the improvement of corrosion resistance of the invar alloy is lower than that when Ce was added alone. According to the self-corrosion current density, the order of corrosion resistance from strong to weak is as follows: 0.5% Ce+Ti, 1.0% Ce+Ti, 0.2% Ce+Ti, and no addition.

The test results of the different systems of the invar alloy in 3.5 wt.% NaCl solution using EIS are shown in figure 5. It can be observed that the Nyquist figures of the system of invar alloys in the high-frequency region shows a large capacitive reactance arc, which is related to the reaction of the corrosion product film deposition; thus, the greater the radius of the capacitive reactance arc on behalf of the charge-transfer resistance, the greater is the alloy corrosion resistance.

Figure 5(a1) shows the Nyquist plot of the invar alloy with the added Ti. The strength of the corrosion resistance law obtained by analyzing and comparing the radius of the capacitive reactance arc in the Nyquist plot measured for each invar alloy system is consistent with the test results of the Tafel curves. The measured Bode graphs of each system of the invar alloy show two peaks, indicating that the system contains two time constants, indicating the existence of two reaction interfaces. The peak in the high-frequency region primarily reflects the solution resistance (R_s), while the peak in the low-frequency region is primarily related to the capacitance of the double electric layer and the charge-transfer resistance. Therefore, the (R(\sigmaQR)) circuit diagram shown in figure 6 can be used for circuit fitting of EIS. Considering that the surface of the material is rough and has a strong dispersion effect, the constant phase angle element Q is often used to replace the pure capacitance element C. In the equivalent circuit, R_s is the solution resistance, R_f is the corrosion product film resistance, R_i is the charge-transfer resistance, Q_f is composed of the corrosion product film capacitor C_f and dispersion index n_1, and Q_d is composed of the double-layer capacitance C_d and dispersion index n_2. The invar alloy system and the superior corrosion resistance of the EIS fitting results of the circuit are presented in table 2. It can be observed that the addition of Ti and Ce increases the film resistance or charge-transfer resistance of the corrosion product to varying degrees, which indicates that corrosion products have good protection, which is conducive to the improvement of corrosion resistance of the invar alloy.

3.3. Rust layer morphology
In summary, from the above experimental results, it is concluded that an appropriate content of Ti and Ce is beneficial for the improvement of the corrosion resistance of the invar alloy. Three types of invar alloys (with
0.2% Ti, 0.2% Ce, and 0.5% Ce+Ti demonstrated superior corrosion resistance, and were adopted to study the influence of alloying elements on the morphology and composition of the rust layer and the protection of the rust layer against the corrosion of the substrate.

After soaking in a 3.5 wt.% NaCl solution for different amounts of time, the macroscopic morphology of the rust layer of the invar alloys with different alloying elements was obtained, as shown in figure 7. It can be observed that, at the early stage of corrosion, the invar alloy without alloying elements does not exhibit obvious
corrosion, while the other invar alloys exhibit obvious corrosion. After 15 cycles, the invar alloy began to corrode on a large scale. The alloys with 0.2% Ti, 0.2% Ce, and 0.5% Ti+Ce corroded more uniformly and formed a rust layer covering the entire matrix. With the increase in corrosion time, accelerated and uneven corrosions began to occur in the invar alloy without alloy elements. Figure 7(a4) clearly shows that the rust layer is loose and can easily fall off. In the corrosion process, the loose, non-dense, and discontinuous rust layer is conducive to the formation of microcell corrosion, which accelerates the process of local corrosion.

Figure 8 shows the micromorphology of the outer rust layer of the invar alloys with different alloying elements. From figure 8(a), it can be observed that the outer rust layer of the invar alloy with no modifiers is not dense and can easily fall off owing to the poor adhesion with the inner rust layer, resulting in a poor protective effect. In certain parts, owing to the falling off of the outer rust layer, the surface morphology of the inner rust layer can be clearly observed (figure 8(b)). The exposed inner rust presents a unique ‘wellhead’ morphology, which is closely related to the composition and microstructure of the material. It is generally believed that the corrosion potential difference between the cell wall and the inner cell is the key factor that causes the formation of such a morphology. As it can be observed in figure 8(c)–(d), after adding Ti and Ce elements, the microstructure of the invar alloy changes to a fine, uniform, and compact structure, and an increase in flocculation and the spherical structure can be observed.

Furthermore, the X-ray diffraction (XRD) results of the outer rust layer of the invar alloys with the addition of different alloying elements (as shown in figure 9) show that the primary components of the rust layer of the four systems are $\alpha$-FeOOH, $\gamma$-FeOOH, Fe$_2$O$_3$, Ni/FeNi$_3$, and Fe(OH)$_3$. Moreover, it can be inferred that the
increased flocculent or spherical structure is due to the $\alpha$-FeOOH phase, which is conducive to the formation of a more stable protective layer.

3.4. Electrochemical analysis of alloys after immersion

To determine the protection of the rust layer generated after 20 cycles of immersion, polarization and electrochemical impedance tests were performed. Figure 10 shows the Tafel curves and analysis results of each component invar alloy after soaking in 3.5 wt.% NaCl solution for 20 cycles. The test results show that the invar alloys with 0.2% Ti and 0.5% Ce$^+$Ti have a smaller self-etching current density than the invar alloy without the addition of alloy elements. The passivation interval of the invar alloy with 0.2% Ti was not significantly different from that of the invar alloy without Ce and Ti; however, the corrosion current density decreased to approximately 26.8 $\mu$A cm$^{-2}$, demonstrating a reduction of 17.2%. The passivation zone was obvious in the invar alloy with 0.5% Ce$^+$Ti, and the self-corrosion current density was approximately 23.13 $\mu$A cm$^{-2}$, which decreased by nearly 28%. In addition, the corrosion potential of the alloy demonstrated an obvious positive shift, which indicates that the rust layer has a good protective effect.
Figure 11 shows the measured AC impedance spectra. The Nyquist curves of each invar alloy (as shown in Figure 11(a)) consist of a small capacitance arc in the high-frequency region and a large capacitance arc in the middle- and low-frequency regions, indicating that the corrosion rate is primarily controlled by the migration rate of corrosion charge particles in the rust layer. While considering the capacitive reactance arc in the high-frequency area and the capacitance and resistance of the outer layer of rust, which are related to the reaction of the corrosion product film deposition, it can be noted that as the radius of the capacitive reactance arc increases on behalf of the charge-transfer resistance, the alloy corrosion resistance correspondingly increases [15]. Owing to the addition of 0.5% Ti+Ce to the invar alloy, the high-frequency area showed the biggest capacitive reactance arc radius, which can explain the reason for the outer rust layer having excellent protection. From Figure 11(c), it can also be clearly observed that the addition of 0.5% Ti+Ce to the invar alloy resulted in a significant increase in the resistance, which showed that the corrosion resistance increased [16]. In the Bode diagram (Figure 11(b)), the three peaks (superimposed peaks in the high-frequency region and the middle- and low-frequency regions, respectively) represent three time constants. The peak in the high-frequency region is primarily related to the formation and stability of the outer rust layer, while the peak in the middle- and low-frequency regions is primarily related to the obstruction of the inner rust layer to the migration of charged...
particles such as Cl\textsuperscript{−} ions and the presence of the double capacitor layer. Therefore, the equivalent circuit can be fitted using the R(CR)(C/(R(QR))) circuit diagram shown in figure 12. In the figure, Rs represents the solution resistance, C0 represents the capacitance of the outer rust layer, R0 represents the resistance of the outer rust layer, Cε represents the capacitance of the inner rust layer, and Re represents the resistance of the inner rust layer. Qp is composed of the capacitance Cp and dispersion index n at the interface between the rust layer and the matrix, and Rp represents the charge-transfer resistance. The fitting results of the ZSimpWin software for electrochemical impedance data are listed in table 3.

Table 3. Fitting results of EIS for invar alloys with the addition of different alloying elements.

| Elements       | Rs/(Ω·cm\textsuperscript{−2}) | C0/(μF·cm\textsuperscript{−2}) | Cε/(μF·cm\textsuperscript{−2}) | Rp/(Ω·cm\textsuperscript{−2}) | n     |
|----------------|-------------------------------|---------------------------------|---------------------------------|-------------------------------|-------|
| With no modifiers | 3.56                          | 0.25                            | 3.96                            | 53.67                         | 1.57  |
| 0.2%Ti         | 3.25                          | 0.36                            | 3.45                            | 40.00                         | 0.26  |
| 0.2%Ce         | 2.73                          | 0.03                            | 30.62                           | 1.08                          | 677.10|
| 0.5%Ce+Ti      | 2.75                          | 0.26                            | 5.08                            | 405.00                        | 3.21  |

Figure 11. EIS diagrams of invar alloys with different alloying elements after immersion in 3.5 wt.% NaCl solution for 20 cycles: (a) Nyquist curve; (b)–(c) Bode diagram.

Figure 12. Equivalent circuit of Nyquist curve.
4. Discussion

4.1. Corrosion behavior

After 20 cycles of immersion corrosion, the ‘wellhead’ morphology of the invar alloy showed similar morphological characteristics to pitting and crevice corrosions. Such a corrosion behavior is helpful for continuously eroding into the depth of the matrix with the accumulation of Cl\(^-\) ions [17, 18]. Therefore, it is important to analyze the formation process of the ‘wellhead’ morphology for the protection of the rust layer of the invar alloy. It can be observed from the analysis of the EPMA test results of the cross section of the invar alloy (Figure 13) that the Ni content at the austenite grain boundary is lower. However, the Ni segregated along the substructure cell wall and Fe mostly existed in the cell, which led to an increase in Ni in the cell wall, resulting in an enhancement of the corrosion resistance of the cell wall and weakening of the corrosion resistance in the cell. Thus, the cell wall and cell could easily form a corrosion micro-battery. Therefore, the substructure cell will be preferentially corroded to form corrosion pits, and the corrosion in the cell wall will occur relatively slowly during the corrosion process. Moreover, it is easy to form occluded cells in the initial corrosion pits to accelerate corrosion. Hence, the ‘wellhead’ corrosion morphology is formed as the corrosion progresses. The corrosion products of these ‘wellhead walls’ and ‘inside the well’ together form an inner rust layer. Therefore, the composition, density, and adhesion of the outer rust layer are particularly important for the protection of the entire rust layer. In addition, it can be observed that certain precipitates appeared after the addition of Ti and Ce. The composition of these phases and their influence on the corrosion resistance of the invar alloy are explained in section 4.2.

4.2. Corrosion mechanism

It is generally believed that α-FeOOH with a compact flocculent or spherical morphology is the most stable hydroxyl iron oxide in the rust layer, which can effectively isolate Cl\(^-\) ions from contact with the alloy matrix, slow down the electron transfer between the anode and cathode, and achieve the best protective effect on the matrix. However, γ-FeOOH with a needle-like shape is more reactive and easily reduced, resulting in a relatively poor protection effect.
The XRD results show that the rust layer of the invar alloy without alloying elements is predominantly composed of $\alpha$-FeOOH, $\gamma$-FeOOH, Fe$_2$O$_3$, Ni$/$FeNi$_3$, and Fe(OH)$_3$. When the invar alloy was eroded in 3.5 wt.% NaCl solution and in the air-oxidation-based corrosion system, the primary reaction in the anode was the oxidation of Fe:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$$  \hspace{1cm} (1)\]

The cathodic reaction was complex, including the reduction of dissolved oxygen and the reaction of $\text{Fe}^{2+}$ with OH$^-$. The primary reactions are as follows.

$$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- = 2\text{OH}^-$$  \hspace{1cm} (2)

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2$$  \hspace{1cm} (3)

Among them, the reaction of the dissolved oxygen in the solution with Fe atoms on the surface is as shown below.

$$2\text{Fe} + \text{O}_2 + 2\text{H}_2\text{O} = 2\text{Fe(OH)}^+ + 2\text{OH}^-$$  \hspace{1cm} (4)

As the corrosion progresses, a part of Fe(OH)$_2$ oxidizes with OH$^-$ to form Fe$_2$O$_3$, and a part of Fe(OH)$_3$ is oxidized. Conversely, during the formation of the rust layer, Fe(OH)$^+$ continues to react to form protective FeOOH.

$$2\text{Fe(OH)}_2 + 2\text{OH}^- \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 2e^-$$  \hspace{1cm} (5)

$$4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3$$  \hspace{1cm} (6)

$$4\text{Fe(OH)}^+ + 4\text{OH}^- + \text{O}_2 \rightarrow 4\text{FeOOH} + 2\text{H}_2\text{O}$$  \hspace{1cm} (7)

The Cl$^-$ ions in the solution also participate in the redox reaction of electrochemical corrosion, which destroys the densification of corrosion products.

$$\text{Fe(OH)}_2 + \text{Cl}^- \rightarrow \text{Fe(OH)}^+ + \text{Cl}^- + \text{OH}^-$$  \hspace{1cm} (8)

$$\text{Ni} \rightarrow \text{Ni}^{2+} + 2e^-$$  \hspace{1cm} (9)

$$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2$$  \hspace{1cm} (10)

$$\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NOOOH} + \text{H}_2\text{O} + e^-$$  \hspace{1cm} (11)

The corrosion development process in the invar alloy is shown in figure 14.

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$$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2$$  \hspace{1cm} (10)

$$\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NOOOH} + \text{H}_2\text{O} + e^-$$  \hspace{1cm} (11)

Therefore, the formation of the rust layer is significantly complicated. Asami et al [19] suggested that the protective effect of the rust layer can be quantitatively analyzed by the ratio of $\alpha$-FeOOH/$\gamma$-FeOOH, and as the ratio increases, the protective effect correspondingly improves. There were peaks with low intensity of $\alpha$-FeOOH in the XRD patterns of the invar alloy without alloy elements. It can be observed from figure 9 that the rust layer was primarily composed of the coarse needle-like $\gamma$-FeOOH phase [20], which has poor density, limited blocking effect on corrosive media such as Cl$^-$ and O$_2$, and a poor protective effect. However, with the addition of 0.5% Ti, the $\gamma$-FeOOH in the outer rust layer of the invar alloy was refined and compacted, while the $\alpha$-FeOOH [21] content of the flocculent and spherical structure increased to a certain extent.

Ti is an element with a fast diffusion rate and strong oxidation tendency. The addition of Ti to the invar alloy can effectively inhibit the transportation of S and O elements to the alloy matrix at the initial stage of corrosion, promote the uniform dissolution of the alloy surface, and reduce the occurrence of pitting corrosion. In the invar alloy, C primarily exists in the matrix in the form of a solid solution. The electrode potential of C is significantly higher than that of Fe. Fe–C corrosion micro-batteries can be easily formed in the corrosion environment of NaCl solution to accelerate the corrosion of the alloy. However, as a strong carbide-forming element, Ti easily combines with C to form precipitated TiC [22] (the analysis result of the precipitated phase is
shown in figure 15(a)), which not only reduces the number of corrosion micro-batteries, but also acts as the core of crystal nucleation of iron oxide and promotes the formation of $\alpha$-FeOOH with a protective effect. In addition, the 0.006% C in the invar alloy is insufficient to consume all Ti. The excess Ti reacts with Al and Ni in the matrix to form the strengthening phase $\gamma'$-(Al, Ti)Ni$_3$ [23, 24]. During the solidification process of the invar alloy, TiC and the strengthening phase $\gamma'$-(Al, Ti)Ni$_3$ precipitated at the cell wall with a decrease in temperature, which
hindered the growth of the substructure, and thereby uniformly refined the substructure and reduced the number of defects, which can decrease the number of preferred locations for the formation of corrosion galvanic cells.

In addition, there is some oxygen in the precipitate phase, which may be the Ti$_2$O$_3$ that is formed during the solidification process of the alloy. J. H. Shim [25] indicated that Ti$_2$O$_3$ can combine with MnS in the alloy to form a heterogeneous nucleation core, thus reducing the amount of MnS. Generally, the MnS [26] in the alloy is poorly fused with the matrix, and Cl$^-$ ions aggregate here, which increases the corrosion in the form of pitting corrosion when compared to other areas. Therefore, reducing the amount of MnS can effectively improve the corrosion resistance of the alloy.

When compared to other metal elements in the invar alloy, the Gibbs free energy of the reaction products of Ce with S and O is lower; consequently, it will react preferentially to form rare earth sulfides and rare earth oxides. The reaction equation and the corresponding Gibbs free energy functions are as follows.

\[
[\text{Ce}] + \frac{3}{2}[\text{O}] = \frac{1}{2} + \text{Ce}_2\text{O}_3
\]

\[\Delta G^\theta = -715100 + 179.5T\]  

(12)

\[
[\text{Ce}] + \frac{4}{3}[\text{S}] = \frac{1}{2}\text{Ce}_3\text{S}_4
\]

\[\Delta G^\theta = -497670 + 146.3T\]  

(13)

\[
[\text{Mn}] + [\text{S}] = \text{MnS}
\]

\[\Delta G^\theta = -131624 + 79.07T\]  

(14)

It can be observed from the latter two formulas that S tends to combine with Ce during the entire smelting process, thereby reducing the elongated MnS. Subsequently, all rare earth sulfides and certain rare earth oxides collide and recombine to form dispersed rare earth oxysulfides (Ce$_2$O$_2$S) [12, 27]. This type of rare earth oxysulfide has poor conductivity and cannot cause micro-area corrosion, thus reducing the probability of pitting corrosion. The light rare earth element Ce is highly active and can be easily segregated at the grain and phase boundaries. This not only effectively prevents cations from diffusing outward but also significantly reduces the precipitation of C at grain boundaries, which effectively alleviates grain boundary corrosion. In addition, when compared to the invar alloy with 0.2% Ti, the invar alloy with 0.2% Ce is primarily composed of \(\alpha\)-FeOOH in the outer rust layer, and the density is significantly high (as shown in figure 9), which indicates that the rare earth element Ce can obviously increase the content of \(\alpha\)-FeOOH in the rust layer. Meanwhile, the precipitation of Ce

Figure 16. Reactants of the elements Ti and Ce.
can purify the grain boundary [28], which is conducive to the improvement of corrosion resistance. However, when Ti and Ce are added in the invar alloy, Ti can reduce the element segregation element. Ce has a modification effect on the inclusion, which can optimize the protective effect of the corrosion product film. The formation of rare earth oxysulfide is favorable for TiC adsorption nucleation, and the inclusion size is small and dispersive, which destroys the conditions of Cl\(^{−}\) aggregation on the surface. Therefore, adding Ti and Ce together significantly improves the corrosion resistance of the alloy. The Ti and Ce elemental reactions are shown in figure 16.

When combined with the fitting results of the two EIS fitting circuits of the invar alloy, it can be observed that the corrosion resistance of the invar alloy was improved to a certain extent after adding Ti and Ce. The corrosion resistance of the corrosion products of the invar alloy mixed with Ti and Ce is significantly improved; however, the microstructure homogenization of the invar alloy with 0.5% Ti+Ce, as shown in figure 2(k), is significantly poor, which may be the reason why the corrosion resistance of the invar alloy is lower than that of the invar alloy with 0.2% Ce.

5. Conclusions

The corrosion behavior of the invar alloy after adding Ti and Ce elements was studied. Through the detection and analysis of the microstructural changes of each system of the invar alloy, the following conclusions were drawn.

(1) The corrosion resistance of the invar alloy with only Ti and Ce elements or with the mixture of Ti+Ce elements first increased and then decreased with the increase in the addition amount. In each system, the superior corrosion resistance of the invar alloy was observed in the case of the following additions: 0.2% Ti, 0.2% Ce, and 0.5% Ti+Ce.

(2) After soaking for 20 cycles, the unadded elements showed a unique ‘wellhead’ morphology owing to tile alloy corrosion layer, which is primarily caused by Ni segregation. The XRD results showed that the outer rust layer was mainly composed of α-FeOOH, γ-FeOOH, Ni or FeNi\(_3\), and Fe\((OOH)\)_3. However, there was a small amount of α-FeOOH in the rust layer of the invar alloy without alloying elements, and it was primarily composed of coarse and nondense γ-FeOOH.

(3) After adding 0.2% Ti, Ti combined with C in the invar alloy to form TiC, reducing the number of Fe–C corrosion micro-batteries. The precipitated TiC and γ\(^{′}\) phase can inhibit the growth of the substructure, homogenize the structure, and reduce defects. In addition, the oxide of Ti can attract MnS, which can reduce pitting corrosion and improve corrosion resistance.

(4) The addition of Ce can effectively prevent the cation from spreading outward and significantly reduce the precipitation of C at the grain boundary. Moreover, the combination of Ce with O and S forms rare earth oxysulfide, which reduces the amount of pitting source MnS, which is conducive to the improvement of corrosion resistance. However, the corrosion resistance of the 0.5% Ti+Ce invar alloy was lower than that of the invar alloy with only Ce, which may be owing to the decrease in the degree of microstructure homogenization.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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