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The influence of Cr on the microstructure and electrochemical behavior of high strength low-alloy steel

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Abstract

The influence of Cr addition (0.13 wt%, 0.65 wt% and 1.07 wt%) on the microstructure, phase structure and electrochemical behavior of high strength low-alloy (HSLA) steel was investigated. The surface morphologies of HSLA steels were examined by Optical microscopy (OM) and Scanning electron microscopy (SEM). The phase structure was analyzed by x-ray diffraction (XRD). Electrochemical tests were used to study the corrosion behavior of high strength steel in 3.5 wt% NaCl solution. The results showed that the appropriate addition of Cr (1.07 wt%) alloying significantly refined grain, improved the electrochemical property and microstructure. The microstructure of all samples were the typical bcc (α) phase and the peaks including (110), (200), (211) and (220) got stronger with the increase of Cr content. Meanwhile, the T3 steel with 1.07 wt% Cr showed the best electrochemical reaction inhibition and corrosion resistance because of the highest Rt. And the corrosion morphology was from serious intergranular corrosion and pitting corrosion to slight localized corrosion with the increase of Cr contents.

1. Introduction

The steel will remain the backbone of metal materials for economic and social development in the future because of its advantages of microstructure, diversity phases, good combination of strength and toughness [1]. The advanced high strength steel (AHSS) has gone through three generations, and the high strength low-alloy steel (HSLA) belonging to the classical first generation is still used widely for the excellent strength, toughness and economy [2]. In recent years, HSLA steel is being widely used in the marine shipbuilding and oceanography engineering areas, but the resultant corrosion happens frequently [3]. Therefore, many researchers are concentrating on enhancing the corrosion resistance of the HSLA [4–6]. The microalloying elements such as Nb, V and Cr have an important influence on the corrosion process of HSLA. Zhang et al [7] researched the effects of Nb addition and the size of the NbC precipitates on the resistance of HSLA steel to hydrogen-induced cracking (HIC) and the results showed that the microalloying of Nb could significantly improve the HIC resistance and decrease the proportion of intergranular cracks through the hydrogen trapping effect and microstructure optimization of the HSLA steels. In order to study the effects of V addition of X80 pipeline steels on the precipitation characteristics of nanometre carbides, researches revealed that the microalloying of V could trap the hydrogen and decrease the diffusion coefficient of hydrogen and the possibility of hydrogen atoms diffusing into the sites of harmful defects [8, 9].

Researches had reported that the steels containing low Cr had high strength, good hardenability and corrosion resistance [10, 11]. Zhao et al [12] investigated the effects of Cr content on the passivation behavior of Cr alloy steel in a CO2 aqueous environment containing silty sand, and the results suggested that increasing Cr content was beneficial to improving the stability of passive film of steel. Xu et al [13] studied the corrosion performance of 1% Cr, 2% Cr, 3% Cr, 4% Cr, 5% Cr, and 6.5% Cr steels in a high-temperature and
high-pressure CO₂-containing environment to clarify the role of the Cr content in mitigating corrosion, and the results concluded that the steel with 3% Cr formed protective Cr(OH)₃ layer to possess prepassivation characteristics. Chen et al [14] studied the pitting corrosion and structure characteristics of carbon dioxide (CO₂) corrosion products on N80, 1Cr and 4Cr steel, and the results showed that Cr-containing steels could suppress pitting corrosion effectively because of the low electrical conductivity of corrosion products Cr(OH)₃.

Guo et al [15] analyzed the corrosion scale formed on API X65, 1Cr, 2Cr and 3Cr steels in CO₂ containing environment and reported that the Cr content could alter the crystalline state of corrosion scale via changing pH value. Amit et al [16] discussed the effects of temperature and chromium content in L80 OCTG steel on CO₂ corrosion and found that the 1Cr steel showed a lower corrosion rate compared to 3Cr steel at 135 °C. Jiang et al [17] investigated the corrosion behavior of carbon steel and Cr-containing steels (Fe-0.5Cr, Fe-2Cr, Fe-5Cr) during flow-accelerated corrosion and showed that the existence of the Cr could inhibit of the cathodic reaction and enhance the corrosion resistance of steel in 3.5 wt% NaCl solution under dynamic condition. Kermani and Morshed [18] reviewed the mechanistic understanding of carbon dioxide (CO₂) corrosion of carbon and low-alloy steels in hydrocarbon production and reported the CO₂ corrosion resistance could be improved about 2.5–4.0 times with 1–5Cr additive in steel and the cost penalty was less than 1.5 times that of carbon steel.

Based on the previous researches, composition of the Cr which is less than 1% on the microstructure, microhardness and electrochemical behavior of HSLA steel is unclear. In order to meet the requirements of marine industry for Cr microalloyed steel, effects of the Cr addition which was less than 1% on the morphology, microstructure and electrochemical behavior of HSLA steel were systematically analyzed.

2. Material and methods

2.1. Materials preparation

The as-cast was prepared by vacuum arc melting and casted into small ingot with diameter of 25 mm. Table 1 and figure 1 show the chemical compositions (mass percentage) and heat treatment processes of the experimental HSLA steel. T1, T2 and T3 represented for the samples with Cr content of 0.132, 0.65, 1.07 wt% respectively.
2.2. Characterization

2.2.1. Morphologies observation

The surface morphologies of samples were characterized by optical microscope (Olympus BC51M) and scanning electron microscope (SEM, Phenom XL) equipped with energy dispersive x-ray analysis (EDAX). The surface of specimens for tests (with a 10 mm × 10 mm × 1.5 mm size) were ground with SiC abrasive papers from No.400 to 2000 and polished with 2.5 μm diamond paste, and then the polished planes of the samples were etched with the 10% nitrate alcohol solution to observe the microstructure and prior austenite grains size. The phase composition of samples was identified by the x-ray diffraction (XRD, D8 advance BRUKER, Germany). The microhardness of samples was measured by Micro Vickers Hardness Tester (HVS-1000Z) with a load of 0.98N for 10 s. The Micro Vickers Hardness was calculated as the equation

\[ Hv = \frac{1854.4P}{d^2} \]

Where Hv is Micro Vickers Hardness (gf/mm²), P is load (gf) and d is the diagonal length of the indentation (μm).

2.2.2. Electrochemical tests

The electrochemical impedance tests and Tafel polarization tests were carried out in a neutral aqueous solution of 3.5 wt% NaCl to evaluate the corrosion properties of samples. The electrochemical tests were tested in a three-electrode system, consisting of a saturated calomel electrode (SCE) as the reference electrode, a platinum plate as the counter electrode and the experimental steels as the working electrode. The electrochemical tests were measured by using a Chenhua electrochemical work station.

The electrochemical impedance spectroscopy (EIS) measurements were carried out with a scanning frequency ranging from 0.01 to 10 000 Hz and an applied AC amplitude of 10 mV, the working electrodes had been immersed in 3.5 wt% NaCl solution for 30 min before the EIS and Tafel polarization tests. The Tafel polarization tests were measured with potentials ranging from −1.2 VSCE to 0 VSCE at a potential dynamic scanning rate of 1 mV/s. Each sample (1 cm²) was coupled to a copper wire by conducting resin and mounted using epoxy resin. One side of mounted sample was ground by SiC abrasive papers from No.400 to 2000 and then rinsed in ethanol and in acetone prior to the electrochemical measurements. All solutions used in the tests were prepared with deionized water and analytical reagents. And all measurements were carried out in naturally aerated aqueous solutions at room temperature of about 25 °C.

3. Results and discussion

3.1. Microscopic morphologies

Figure 2 illustrates representative optical micrographs and SEM images depicting the microscopic morphologies of samples with Cr different content. The samples taken from the centerline regions of the experimental steels basically revealed equiaxed grains of austenite. When the Cr content increased from 0.13 wt% to 1.07 wt%, the size of PAGs decreased from 60 μm to 20 μm due to the more hindrances were formed to hinder the growth of basically revealed equiaxed grains of austenite. When the Cr content increased from 0.13 wt% to 1.07 wt%, the size of samples with Cr different content. The samples taken from the centerline regions of the experimental steels were ground with SiC abrasive papers from No.400 to 2000 and polished with 2.5 μm diamond paste, and then the polished planes of the samples were etched with the 10% nitrate alcohol solution to observe the microstructure and prior austenite grains size. The phase composition of samples was identified by the x-ray diffraction (XRD, D8 advance BRUKER, Germany). The microhardness of samples was measured by Micro Vickers Hardness Tester (HVS-1000Z) with a load of 0.98N for 10 s. The Micro Vickers Hardness was calculated as the equation

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Figure 3 shows the XRD patterns of samples with different content of Cr addition. It indicated the presence of the typical bcc (α) phase. As calibrated in the pattern, all samples indicated four strong peaks including (110), (200), (211) and (220) planes. According to the standard α-ion and Cr pattern, it can deduce that the experimental steels can be characterized as the Fe–Cr solid solution with a bcc (α) crystal structure. It can’t distinguish bainite from ferrite by XRD pattern because both ferrite and bainite are bcc (α) crystal structure. Besides, the peaks which were characterized as FeC and Cr₇C₃ were found in XRD patterns, which inferred the patterns of carbide precipitation in samples. Compared the three patterns of T1, T2 and T3, the peaks including (110), (200), (211) and (220) planes got stronger and stronger with the increase of Cr content, it suggested that the content of the Cr had influence on the crystallization process, and the grain formation became better. According to Sheerer equation, the precipitates size can be expressed a.s.
Where \( D \) is the dimension in the exponential direction of the diffraction plane, \( K \) is constant (0.89), \( \lambda \) is x-ray wavelength (0.154 08), \( \beta \) is half height and half width, and \( \theta \) is the diffraction angle. The result showed that the precipitates size of samples decreased from 40 nm to 33 nm when the Cr content increased from 0.13 wt% to 1.07 wt%, moreover, the quantity of precipitates revealed rising tendency with increasing of Cr in figure 2, so the plentiful and fine precipitates resulted in the high microhardness of T3.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(2)

Table 2. Microhardness of the experimental steels.

| Samples | Microhardness of ferrite phase/HV\textsubscript{0.1} | Microhardness of bainite phase/HV\textsubscript{0.1} |
|---------|---------------------------------|-----------------------------------------------|
| T1      | 185                             | 266                                           |
| T2      | 135                             | 232                                           |
| T3      | 299                             | 365                                           |

Figure 2. OM and SEM micrographs depicting the microstructures: T1 ((a) and (b)), T2 ((c) and (d)), T3 ((e) and (f)).
3.2. Electrochemical corrosion
Tafel polarization and EIS tests were implemented to research the electrochemical corrosion characteristics of the three samples with the different content of Cr during short-term exposure to the 3.5 wt% NaCl solution. Tafel polarization curves of the three specimens measured in 3.5 wt% NaCl solution are shown in Figure 4. It indicated that the anodic current density and corrosion potential were different with the change of Cr content. Table 3 lists the key electrochemical parameters obtained from the polarization curves, and the datum are the average values based on more than three parallel samples. Obviously, it could be found that the \( E_{\text{corr}} \) increased with the increase of the Cr, and the most positive \( E_{\text{corr}} \) of T3 indicated that T3 steel had better thermodynamic stability, which was consistent with other researchers [23]. Usually, the \( i_{\text{corr}} \) which presents the corrosion kinetics of a material suggests corrosion rate of the steel [24], and the \( i_{\text{corr}} \) value of each sample can be obtained from the Tafel extrapolation of both the cathodic and anodic branches of the polarization curves. As calculated by the Tafel extrapolation, the \( i_{\text{corr}} \) value of T3 was median of three samples, which illustrated that the corrosion rate of T3 steel was greater than that of T1 and less than that of T2.

Figure 5 shows the typical EIS Phase angle-frequency plots (a) and Nyquist plots (b) of the steels obtained after immersion in 3.5 wt% NaCl solution for 30 min. It could be seen from the Nyquist plots that all experimental steels revealed a single arc. The plots of T3 and T2 showed a capacitive arc at middle frequency and an inductive arc at low frequency, and the plot of T1 showed only a capacitive arc at low frequency. According to the researches [25–27], the

![Figure 3. XRD pattern of samples.](image)

### Table 3. Electrochemical parameters of obtained from the polarization curves.

| Samples | \( E_{\text{corr}} \) (V) | \( i_{\text{corr}} \) (\( \mu \text{Acm}^{-2} \)) |
|---------|----------------|------------------|
| T1      | −0.485         | 2.605 ± 0.008    |
| T2      | −0.449         | 5.080 ± 0.006    |
| T3      | −0.433         | 4.547 ± 0.005    |
Figure 4. Polarization curves of the samples tested after immersion in 3.5 wt% NaCl for 30 min.

Figure 5. EIS Phase-frequency (a) and Nyquist (b) plots of experiment steels tested after immersion in 3.5 wt% NaCl solution for 30 min.
capacitive arc related to the metal dissolution during the corrosion process, and the arc diameter was associated with charge transfer resistance ($R_t$) (i.e., corrosion resistance). Moreover, a larger arc diameter usually meant better corrosion resistance, and the highest phase angle usually meant less corrosion damage. Obviously, the capacitive arc diameter of T3 steel showed to be the biggest compared to that of T1 and T2, which indicated a better corrosion resistance of T3.

Figure 6. SEM morphology of the corrosion initiation of samples.

| Samples | $R_d$ (Ωm$^2$) | $R_t$ (Ωm$^2$) | $Q$ (µF cm$^{-2}$) | $R_L$ (Ω cm$^2$) | $L$ (H cm$^2$) |
|---------|----------------|----------------|-------------------|-----------------|---------------|
| T1      | 10.80 ± 0.5    | 1.261 ± 0.05 × 10$^3$ | 0.8301 ± 0.04     | /               | /             |
| T2      | 8.329 ± 0.6    | 1.181 ± 0.13 × 10$^3$ | 0.8423 ± 0.03     | 2.814 ± 0.15 × 10$^3$ | 5.613 ± 0.17 × 10$^4$ |
| T3      | 11.39 ± 0.4    | 1.635 ± 0.06 × 10$^3$ | 0.8227 ± 0.04     | 5.528 ± 0.09 × 10$^3$ | 6.860 ± 0.12 × 10$^3$ |
Besides, the highest phase angle of T3 was the median of three steels with the value of 66.6°. It illustrated that the corrosion damage to T3 was not serious. The result was in concordance with the Tafel polarization tests.

In order to analyze the corrosion behavior of the samples, ZSimpWin software was used to fit the EIS Nyquist plots, and the fitted electrochemical parameters were listed in Table 4. Figure 5(b) shows that the experimental data of T2 and T3 which could be simulated by an equivalent circuit of \( R_s(Q_1R_1|LR_1) \). While the experimental impedance data of T1 could be simulated by \( (R_s|Q_1R_1) \). Where \( R_s \) is the solution resistance, \( R_1 \) is the charge transfer resistance, \( Q_1 \) is often replaced by the constant phase angle element and represents capacitance behavior of the steels’ passive films. It could be seen from Table 4, the \( R_s \) of T3 was maximum, so the electrochemical reaction inhibition and the corrosion resistance of T3 were the greatest.

Combining the Tafel polarization and EIS tests, it can be inferred that the T3 steel shows satisfactory corrosion resistance during the short-term exposure to the 3.5 wt% NaCl solution.

3.3. Corrosion mechanism
Figure 6 reveals the corrosion morphology of T1, T2 and T3 after the electrochemical accelerated corrosion. It could be found that the corrosion morphology of T1 showed serious general corrosion, intergranular corrosion and pitting corrosion. And the corrosion morphology of T2 revealed general corrosion. The corrosion morphology of T3 displayed only slight localized corrosion. By contrast, the corrosion extent of T3 showed minimal. Besides, the corrosion pits of T1 showed to be located on the boundary of crystalline grains. The reason is that the Cr depleted zone is formed at the grain boundary as shown in Figure 2(a), which is susceptible to corrosion.

4. Conclusion
The morphology, microstructure, microhardness, corrosion resistance and corrosion mechanism of HSLA steels with different Cr content were investigated. The following conclusions could be drawn.

1. The size of prior austenite grains (PAGs) decreased with increasing the Cr content from 0.13 wt% to 1.07 wt%, and the PAGs of T3 were the finest because the proportion of undissolved carbides increased with the increase of Cr additive. The microstructures of all samples were equiaxed ferrite-bainite, and the average microhardness of dual-phase steel samples were \( T_3 > T_1 > T_2 \).

2. The XRD patterns showed that all samples were the typical bcc (\( \alpha \)) phase. And the peaks including \( (110), (200), (211) \) and \( (220) \) were got stronger with the increase of the Cr content. The patterns of carbide precipitation were FeC and Cr7C3.

3. The results of EIS and Tafel polarization tests showed that the T3 steel revealed the best thermodynamic stability and moderate corrosion rate. Moreover, the T3 showed the best electrochemical reaction inhibition and corrosion resistance because of the highest \( R_s \).

4. The corrosion morphology of T1 revealed serious general corrosion, intergranular corrosion and pitting corrosion. The corrosion morphology of T2 appeared the characterization of general corrosion. The corrosion morphology of T3 showed only slight localized corrosion.

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