Effect of Cr on Corrosion Performance of Steel Bar in Chloride Environment

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Abstract. In this article, microscopy observations, thermodynamic calculation and dry–wet cyclic corrosion test were carried out, and microstructure, properties and corrosion resistance of high strength rebar with different amounts of Cr were studied. The results show that Cr addition restrains the pearlite transformation and increases the phase change temperature range of bainite, and the Cr-contain rebars show higher pitting corrosion resistance. When the Cr content is in the range of 1–3.5%, the Cr-contain rebars show better corrosion resistance than Cr-free steel in the beginning of corrosion and the corrosion resistance is correlated positively with Cr content. As the corrosion time going, Cr-contain rebars have high corrosion rate than Cr-free steel and corrosion rate is also correlated positively with Cr content.

1. Introduction
The most important reason for failure of reinforced concrete structures in advance is corrosion of reinforcing rebar [1], and the existence of aggressive ions in corrosive medium such as chlorides would accelerate the corrosion of steel [2]. Chloride is widely found in all the service environment of concrete projects, and it role in various ways and various internal penetration into the concrete structure, eventually led to damage of the passivation film on the rebar [3-4]. Cr is an effective element that can improve the steel’s corrosion resistance in chloride environment by inhibiting the cathodic reaction, promoting dense anti rusting layer formation, repairing cracks and voids of the corrosion layers and so on [5-7]. Therefore, Cr is particularly preferred as a further means of imparting corrosion resistance to the steel, such as stainless steel and low-alloy corrosion resistant steel MMFX and Cr10Mo1[8-10]. While on the other hand, Cr can induce pit corrosion and accelerate corrosion in a certain condition for that hydrolysis of Cr\textsuperscript{3+} will reduce the pH value of the corrosion environment [11]. In the literature related, it can lead to a negative effect to the corrosion resistance of the steel by Cr addition at relatively high content due to the hydrolysis of metal chlorides [12]. In particular, Sun et al find that low content Cr in the steel play different role in different stages of corrosion [13].

Thus, in this work, the steel rebar with four different Cr contents were studied to identify the relationship between the Cr content and the corrosion resistance of the steel in chloride environment. Microscopy observations, thermodynamic calculation and dry–wet cyclic corrosion test were used to study the effect of Cr in steel with Cr content of between 0 to 3.49 percent.
2. Materials and Methods

2.1 Composition and methods
The main additive elements of three kinds of low Cr steels (marked as C1, C2 and C3) are listed in table 1, and the carbon steel C0 is used for comparison. The manufacturing procedures of C1, C2 and C3 Cr-bearing steels are as follows: the φ160mm ingots were prepared by induction melting in laboratory, and then the ingots were hot forged into φ70 mm and φ50mm rods successively, finally the φ50mm rods were hot rolled φ25mm steel rebar at 900~950℃ and cooled naturally in air. C0 is produced in steel mill.

Table 1 Main additive elements of the steels(weight percent)

| Steel | Ni  | Mo  | Cr  |
|-------|-----|-----|-----|
| C0    | residual | residual | residual |
| C1    | 0.45 | 0.25 | 1.01 |
| C2    | 0.52 | residual | 2.02 |
| C3    | 0.51 | residual | 3.49 |

2.2 Experimental program
The tensile strength, yield strength and break elongation are tested on SHT4605 microcomputer control electron universal testing machines using about a 500mm long sample. According to GB/T13298-2015,φ25mm×15mm specimens of cross section of the steel bar were mechanically polished and etched with a 4% nital solution for microstructure examination, and the metallography examination was carried on Axio Lab.A1 optical microscopy. Meanwhile, CCT diagrams of four kinds of steels listed in table 1 are calculated Jmatpro software. The practical change of rebar’s temperature after rolling is measured by Raynger 3i Plus infrared thermometer.

50mm-long cylinders with surface roughness Ra of 0.8 μm is processed for corrosion test, and a φ2.5mm hole is 5mm away from one end of each cylinder. Samples for corrosion layer's SEM observation have the same requirements as the corrosion samples except that they are 20mm long. According to YB/T 4367-2014, the corrosion test was carried out in indoor accelerated test method on LF-65A apparatus for cyclic dry/wet accelerated laboratory test for 24, 72 and 120 hours in 2 wt% NaCl solution. After corrosion test, the morphology of the corroded and derust specimens were observed, and the corrosion rates were obtained based on the weight loss (equation 1) and weight gain (equation 2) of the specimen. QUANTA-650 scanning electron microscope is used to observe the interface of substrate and rust layer.

Corrosion loss rate(g/m²·h): \[ \frac{W_0 - W_i}{(0.5d + l) \times \pi \times d \times t} \times 10^6 \] (1)

Corrosion gain rate(g/m²·h): \[ \frac{W_c - W_0}{(0.5d + l) \times \pi \times d \times t} \times 10^6 \] (2)

Where \( W_0 \) is the initial weight of the sample(g), \( W_i \) is the weight of the sample after derust(g), \( W_c \) is the weight of the sample after corrosion test(g), \( d \) is diameter of the sample(mm), \( l \) is length of the sample(mm), \( t \) is the time of corrosion (hours).

3. Results and discussion

3.1. Mechanical properties and microstructure
The results list in table 2 show the ultimate yield strength (YS), tension strength (TS) and break elongation (EI) of the test steel rebar. With the addition of Cr in the steel rebar, its strength increases and ductility decreases. The microstructure of four kinds of steel rebars are showing in figure1. Showning from chart the grain sizes of Cr-containing rebars are significantly smaller than Cr-free rebar. The microstructure of C0 steel is mainly ferrite, pearlite and small amount of bainite, while there is more bainite and fewer ferrite and pearlite in C1, C2 and C3 steel than C0 steel.
Table 2 The mechanical properties of the test steel rebar

| Steel | YS/MPa | TS/MPa | El/% |
|-------|--------|--------|------|
| C0    | 435    | 615    | 25   |
| C1    | 595    | 665    | 20   |
| C2    | 510    | 655    | 22   |
| C3    | 705    | 825    | 13   |

Figure 1 Metallography of C0(a), C1(b), C2(c) and C3(d) steel

3.2 Analysis of phase transformation during cooling

By comparing the calculated CCT diagrams of four kinds of steels (figure 2), it is found that addition of 1~3.5% Cr could restrain the pearlite transformation and increase the bainite start temperature. At same cooling speed after deformation, it is obviously easier to form more bainite in Cr-containing steel than in C0 steel, which leads to high strength and drop of elongation.
3.3 Experimental results of cyclic dry/wet test

Figure 3 shows the appearance of these steels after corrosion test in NaCl solution for different time. The results reflect that the initial 24 hours cycle test has the characteristics of localized corrosion. Then corrosion became far more uniform after 72 hours. However, after 120 hours duration, pitting corrosion became the typical characteristic of the C0 steel, and other steels still show typical uniform corrosion. The fact that the appearance of the Cr-addition steels is better than Cr-free steel after 120h test prove that Cr can reduce sensitivity of steel to local corrosion in chloride environment, according with the equation for PREN(pitting resistance equivalent number, a predictive measurement of a steel's resistance to localized pitting corrosion in chloride environment) value:

\[
\text{PREN}_{\text{wt}} = \text{wt}[\text{Cr}] + 3.3\text{wt}[\text{Mo}] + 1.65\text{wt}[\text{W}] + 30\text{wt}[\text{N}] \quad [14].
\]

Figure 4 depicts the corrosion rate trend of the four kinds of steels in the course of test. Both corrosion loss rate and corrosion gain rate present the same rules in the accelerated laboratory corrosion test. Results showed that Cr could improve corrosion resistance in the beginning of corrosion and the corrosion resistance is positive interrelated with the Cr content, but the opposite effect of Cr is shown in the late stage of corrosion, in other words, the higher the content of Cr is, the worse of corrosion performance of steel is.
This abnormal phenomenon result from the reduction of pH value with the hydrolysis of Cr\(^{3+}\) in etching pits of Cr contain steel (equation 3 and equation 4)[11]. With the decrease of pH value, enrichment of chlorion in the etching pits will be happen and then accelerated the rust in the etching pits. These etching pits will be cross propagation further, due to which some no corrosion small particles will dropping from the matrix owing to the corrosion of surrounding metal. From the SEM appearance at the interface of substrate and rust layer (figure 5) it is clear that etching pits had expanded in the Cr contain steel especially in C2 and C3 steels.

\[
\begin{align*}
[\text{Cr(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} &\rightarrow [\text{Cr(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}_3\text{O}^+ \quad (3) \\
\text{Cr}^{3+} + \text{H}_2\text{O} &\rightarrow \text{Cr(OH)}_3 + 3\text{H}^+ \quad (4)
\end{align*}
\]

3.4 Pattern of initial dynamic corrosion

The quantitative relationship between corrosion quantity and time accords with power function [15]:

\[
W_{\text{corr}} = \frac{\Delta m}{A} = C_1 t^{C_2}
\]
the corrosion rate can be acquired through taking a derivative with respect to time:

\[ V_{corr} = \frac{dW_{corr}}{dt} = C_1C_2t^{C_2-1} = Dt^n \]

where \( \Delta m \) is the changes of samples weight during corrosion, \( A \) is the surface area of the sample, \( C_1, C_2, D \) and \( n \) are constant, \( t \) is the corrosion time.

\( D \) and \( n \) are determined by disposing corrosion test data using the regression method, and their values are shown in table 3. The value of \( D \) and \( n \) of a steel can be used for parameters to evaluate magnitude of initial corrosion rate and the effectiveness of the rust layer in protecting the steel respectively [16]. For instance, the smaller \( D \) value is, the better the corrosion resistance in the initial period is, and the order of better initial corrosion resistance in chloride environment is \( C_3 > C_2 > C_1 > C_0 \). The smaller of \( n \), the more effective corrosion inhibitive characteristic of corrosion film produced on surface has.

| Table 3 The Regression value of D and n |
|--------------------------------------|
| Steel grade | D    | n    |
|-------------|------|------|
| C0          | 20.2954 | 0.7303 |
| C1          | 4.7488  | 1.0215 |
| C2          | 1.7355  | 1.2440 |
| C3          | 0.4208  | 1.5088 |

4. Conclusion
The effect of Cr in rebar is studied when the content is in the range of 1-3.5%, and the following conclusions can be made:

1. When the Cr content is in the range of 1–3.5%, the Cr-contain rebars show better pitting corrosion resistance than Cr-free steel during whole chloride corrosion stage. However, the effect of Cr on corrosion rate of steel were different in Cl− circumstance environment in different periods, Cr could improve the initial corrosion resistance of the rebar, but is not benefit to corrosion resistance at the later period of corrosion test. The order of better initial corrosion resistance is \( C_3 > C_2 > C_1 > C_0 \), but in the latter stage, \( C_0 > C_1 > C_2 > C_3 \).

2. The unexpected results that corrosion resistance decreases with corrosion time extending for chromium steel is because the reduction of pH value with hydrolysis of \( Cr^{3+} \) in etching pits, by which corrosion of this zone will be promoted and then small fresh metal particles dropped from the matrix owing to etching pits expanding.

3. Combining with the experimental results, exponential regression model for corrosion rate based on time are given. All indexes in power function Cr contain steel of corrosion models is bigger than 1, and it is considered that rust layer formed on the surface of Cr contain steel cannot effectively prevent substrates from further corrosion.

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References
[1] Mehta, P.K. (1991) Durability of concrete-fifty years of progress. In: Proceedings of 2nd international conference. Montreal. pp. 1–31.
[2] Adam, N. (1995) Chloride attack of reinforced concrete: an overview. Mater. Struct, 28: 63-70.
[3] Da, B., Yu, H., Ma, H., et al. (2018) Reinforcement corrosion research based on the linear polarization resistance method for coral aggregate seawater concrete in a marine environment. Anti-Corros. Methods Mater., 65: 458-470.
[4] Angst, U., Elsener, B., Larsen, C. K., et al. (2009) Critical chloride content in reinforced concrete — A review. Cem. Concr. Res., 39: 1122-1138.

[5] Bomi, K., Soojin, K., & Heesan, K. (2018). Effects of alloying elements (Cr, Mn) on corrosion properties of the high-strength steel in 3.5% NaCl solution. Adv. Mater. Sci. Eng., 2018, 1-13.

[6] Song D., Jiang J., Sun W., et al. (2017) Effect of chromium micro-alloying on the corrosion behavior of a low-carbon steel rebar in simulated concrete pore solutions. J. Wuhan univ. technol. -Mater. Sci. Ed., 32:1453-1463.

[7] Liu, M., Cheng, X., Li, X., et al. (2017). Corrosion behavior of low-Cr steel rebars in alkaline solutions with different pH in the presence of chlorides. J. Electroanal. Chem., 803:40-50.

[8] Baddoo, N. R., (2008). Stainless steel in construction: a review of research, applications, challenges and opportunities. J. Constr. Steel Res., 64: 1199-1206.

[9] Abed, F., Abdul-Latif, A., Voyiadjis, G. Z. (2020). Performance of MMFX steel rebar at elevated temperatures. J. Eng. Mech., 146: 4020126-4020121.

[10] Ai, Z. Y., Sun, W., Jiang, J. Y., et al. (2016). Passive behavior of alloy corrosion-resistant steel Cr10mol in simulating concrete pore solutions with different pH. Appl. Surf. Sci., 389: 1126-1136.

[11] Guo, S., Xu, L., Zhang, L., et al. (2012). Corrosion of alloy steels containing 2% chromium in CO2 environments. Corrosion Science, 63: 246-258.

[12] Park, S. A., Le, D. P., Kim, J. G. (2013). Alloying effect of chromium on the corrosion behavior of low-alloy steels. Mater. Trans., 54: 1770-1778.

[13] Sun, B., Zuo, X., Cheng, X., et al. (2020). The role of chromium content in the long-term atmospheric corrosion process. https://www.nature.com/articles/s41529-020-00142-5.

[14] Jeon, S. H., Kim, S. T., Lee, I. S., et al. (2011). Effects of copper addition on the formation of inclusions and the resistance to pitting corrosion of high performance duplex stainless steels. Corros. Sci., 53: 1408-1416.

[15] Cai, Y., Xu, Y., Zhao, Y. et al. (2020) Atmospheric corrosion prediction: a review. Corros. Rev., 38: 299-321

[16] Li, X. G. (2018) Corrosion resistant low alloy structural steels. Metallurgical industry press, Beijing.