1. Introduction

Reinforced concrete structures ought to retain sufficient durability to achieve the required performance throughout their service lives. However, if the design and/or execution of a reinforced concrete structure are not suitable for its use conditions, it can undergo premature deterioration without retaining its functions intact throughout its required service life. Such deterioration of reinforced concrete over time and premature deterioration have been a serious social problem. The corrosion of reinforced concrete structures demonstrates very complicated forms of deterioration intermingled together but all pointing to a decrease in the durability of reinforced concrete structures by the corrosion of reinforcing bars. For this reason, a large number of studies have been conducted to prevent corrosion of reinforcing bars by the corrosion of reinforcing bars. For this reason, a large number of studies have been conducted to prevent corrosion of reinforcing bars having different Cr contents and supplying saltwater from the upper surfaces to allow chloride ions to penetrate into concrete, thereby forming macrocells, with the aim of developing Cr-bearing rebars having corrosion-preventing properties required under macrocell-corrosion conditions due to differences in the chloride concentrations. The time-related changes in the macrocell corrosion current density, soluble chloride ion content of concrete, and half-cell potential were then measured during corrosion-accelerating test up to eight months. Also, the corrosion area and corrosion loss of anodic and cathodic bars were measured at the end of the 8-month corrosion-accelerating test to investigate the corrosion-inhibiting property of Cr-bearing rebars in macrocell corrosion environments due to chloride ion concentration in concrete.

As a result, the Cr content required for corrosion inhibition was found to be more than 7% in macrocell corrosion environments with a difference in soluble chloride ion concentrations of not more than 2.4 kg/m³.

KEY WORDS: Cr-bearing rebar; corrosion resistance; macrocell corrosion; average corrosion rate.

Reinforced concrete specimens were prepared by embedding 10 types of Cr-bearing reinforcing bars having different Cr contents and supplying saltwater from the upper surfaces to allow chloride ions to penetrate into concrete, thereby forming macrocells, with the aim of developing Cr-bearing rebars having corrosion-preventing properties required under macrocell-corrosion conditions due to differences in the chloride concentrations. The time-related changes in the macrocell corrosion current density, soluble chloride ion content of concrete, and half-cell potential were then measured during corrosion-accelerating test up to eight months. Also, the corrosion area and corrosion loss of anodic and cathodic bars were measured at the end of the 8-month corrosion-accelerating test to investigate the corrosion-inhibiting property of Cr-bearing rebars in macrocell corrosion environments due to chloride ion concentration in concrete.

As a result, the Cr content required for corrosion inhibition was found to be more than 7% in macrocell corrosion environments with a difference in soluble chloride ion concentrations of not more than 2.4 kg/m³.

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Corrosion Resistance of Cr-bearing Rebar in Macrocell Corrosion Environments Due to Different Concentrations of Chloride Ions

Sung-Ho TAE,1) Takafumi NOGUCHI2) and Takumi UJIRO3)

1) Sustainable Building Research Center, Hanyang University, Ansan, 425-791, Korea. E-mail: jnb55@hanyang.ac.kr
2) Department of Architecture, Faculty of Engineering, University of Tokyo, Tokyo 113-8656 Japan.
3) Stainless Steel Research Department, Steel Research Laboratory, JFE Steel Corporation, Chiba 260-0835 Japan.

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In this study, specimens predisposed to macrocell corrosion were prepared by supplying saltwater from the top surfaces of specimens to allow chloride ions to penetrate into concrete as part of a number of studies for the development of Cr-bearing rebars withstanding corrosive environments. This approach was an application of the test method of ASTM G 109-92 (hereafter referred to as the ASTM corrosion test method). The macrocell corrosion current density, soluble chloride ion content of concrete, and half-cell potential were measured over a corrosion-accelerating test period of eight months. At the end of the corrosion-accelerating period, the corrosion area and corrosion loss of reinforcement were measured to investigate the corrosion-protecting properties of Cr-bearing rebars under the macrocell corrosion environment induced by the chloride ion concentration in concrete.

2. Outline of Experiment

Specimens predisposed to macrocell corrosion were fabricated applying the ASTM corrosion test method as shown in Fig. 1. Four bars of two types were embedded in each specimen. The bars of the same type were arranged with one above the other on the same side. After being seal-cured for 7 d, specimens were demolded and air-cured for 7 d in a thermo-hygrostatic room at 20°C and 50% RH. During the air-curing period, a cord was soldered to the end of each bar to measure the potential difference between the anodic and cathodic bars, while coating both ends of the bars with epoxy resin to prevent initiation of corrosion from the ends. After the above-mentioned initial curing, corrosion-accelerating test was carried out. Each specimen was subjected to chloride ion penetration from saltwater placed in a diked section on its top surface in a thermo-hygrostatic room at 40°C and 60% RH. The macrocell corrosion current density, soluble chloride ion content in concrete, and half-cell potential were measured during the eight-month corrosion-accelerating period. The corrosion area and corrosion loss of anodic and cathodic bars were also measured at the end of the test period. Note that the upper (anodic) and lower (cathodic) bars were partially wrapped with anti-corrosion tapes so that their area ratio would be 1 : 2 to accelerate corrosion as specified in the ASTM corrosion test method. Tables 1 and 2 give the materials and concrete mixture proportions, respectively.

Also, a total of 8 types of rebar specimens were used in this experiment, including SD345 conforming to JIS G 3112 (Steel bars for concrete reinforcement), 6 types of Cr-bearing rebars with different Cr contents and SUS 304 stainless steel rebars. The specimens for corrosion testing were 13 mm-diameter bars stripped of their oxidized coating. The chemical compositions of steels are given in Table 3.

3. Experiment Procedure

3.1. Corrosion-accelerating Test

After initial curing, corrosion-accelerating test was carried out to form a corrosion macrocell resulting from chloride ion concentration gradients between the upper and lower bar areas. Each specimen was subjected to chloride ion penetration from saltwater placed in a diked section on its top surface in a thermo-hygrostatic room at 40°C and 60% RH, with each cycle consisting of two weeks with saltwater and two weeks without saltwater. Though temperature and relative humidity conditions of 20°C and 50% are specified in the ASTM corrosion test method, 40°C and 60% RH were adopted in this study in consideration of the corrosion rate of Cr-bearing rebars being lower than that of normal steel reinforcement. Figure 2 shows corrosion-accelerating cycles.
3.2. Soluble Chloride Ion Content

The soluble chloride ion content was analyzed in accordance with JIS A 1154 (Methods of test for chloride ion content in hardened concrete) based on measurements by potentiometric titration at two-month intervals during corrosion-accelerating test. 10-gram samples were taken by drilling at depths of 2.65, 7, and 10 cm from the top surface of concrete to represent the upper bar, intermediate, and lower bar levels, respectively, as shown in Fig. 3. At the end of the eight-month corrosion-accelerating test, specimens were longitudinally cleft in the direction of chloride seepage, and the cleft surfaces were sprayed with a 0.1 N aqueous solution of AgNO₃. The parts that turned white were designated as areas permeated with chloride ions. Figure 3 and Fig. 4 show the points of chloride ion content measurement and potentiometric titration setup, respectively.

3.3. Half-cell Potential

As shown in Fig. 2, the half-cell potential was measured immediately after removing saltwater from the diked section on top of each specimen, i.e., immediately after the end of the saltwater supply phase of each cycle. A saturated copper–copper sulfate electrode (CSE) used as the reference electrode was placed on the section from which saltwater was removed to measure the half-cell potential of the upper bar.

3.4. Macrocell Corrosion Current Density

The macrocell corrosion current density between the upper bar (anode) and the lower bar (cathode) was determined as follows: Measure the voltage between the bars at 1-h intervals, with a known resistance of 10 Ω in between, using an automatic measuring system consisting of a switch box, data logger, and personal computer, calculate the corrosion current based on Ohm’s law, and divide the current by the surface area of the anodic bar. The surface area of the anodic bar was 61.23 cm² (1.3 cm × π × 15 cm). The cumulative amount of corrosion for up to 8 months of corrosion-accelerating test was also calculated from the macrocell corrosion current density using Faraday’s law, which is as given in Eq. (1).

\[ G = \int V_{corr} \, dt = \frac{M}{nF} \int I_{corr} \, dt \] ........................(1)

where \( V_{corr} \) is rate of corrosion (g/cm²/s); \( G \) is corrosion loss (g/cm²); \( M \) is atomic weight of Fe (= 55.8); \( F \) is Faraday number (= 96 500, C/mol); and \( I_{corr} \) is corrosion current density (A/cm²).

3.5. Corrosion Area and Corrosion Loss

After corrosion-accelerating test for eight months, reinforcing bars were chipped out of specimens to measure the corrosion area and corrosion loss. The corrosion area and corrosion loss of the upper and lower bars were calculated in regard to the parts in contact with concrete, i.e., the parts not wrapped with anticorrosion tapes.

The corrosion area was calculated using an automatic area measuring software after copying the corroded areas of rebars using a transparent sheet and blacking the areas. The weight losses by corrosion were measured in accordance with the method of evaluating corrosion of reinforcing steel in concrete in the “Test methods and standards related to corrosion of concrete structures (draft)” established by the Japan Concrete Institute. SD345, 0Cr and 5Cr rebars were immersed in a 10% aqueous solution of diammonium citrate, while rebars with a Cr content exceeding 5% were immersed in a 30% aqueous solution of nitric acid, to remove rust. The mass of the bars were then measured to a precision of 0.01 g using an electronic balance. The weight losses were calculated using Eq. (2).

\[ \Delta W = \frac{(W_0 - W) - W_s}{W_0} \times 100 \] ........................(2)

where \( \Delta W \) is weight loss (%), \( W_0 \) is initial rebar mass (g), \( W \) is rebar mass after rust removal (g), \( W_s \) is amount of uncorroded part dissolved (g) (separately measured).
4. Results and Discussion

4.1. Soluble Chloride Ion Content

Figure 5 shows the changes in the soluble chloride ion content over time at three depths, i.e., 26.5, 70, and 100 mm from the top surface of concrete. This figure reveals that the soluble chloride ion content tends to decrease as the depth from the top surface increases and increases at all levels as the corrosion-accelerating period proceeds. Also, a soluble chloride ion content grading is noticed between the areas near the upper and lower bars from an early stage of corrosion-accelerating test and found to widen as the test proceeds. It should be noted that the soluble chloride ion content at the upper bar level exceeds 1.2 kg/m³, which is the lower limit of the established threshold for corrosion onset on carbon steel, at as early as four months from the beginning of the corrosion-accelerating test. It is therefore inferred that microcell corrosion occurs along with macrocell corrosion when the soluble chloride content in concrete near the anodic bar exceeds the threshold for corrosion onset of the steel type. In the present test, the soluble chloride ion contents near the upper and lower bars at the end of corrosion-accelerating test for eight months were 2.4 and 0 kg/m³, respectively. The state of chloride ion penetration after the test is shown in Fig. 6. Chloride ions are found to have penetrated halfway between the upper and lower bars but have not reached the lower bar, being consistent with the measurement.

4.2. Half-cell Potential

Figure 7 shows the changes in the half-cell potential of the upper (anodic) bars over time. The bold lines in the graph indicate a potential value of −0.35 V (vs. CSE), which can be regarded as corroded with 90% certainty according to the corrosion criteria of ASTM C 876-80. Figure 7 reveals that the half-cell potential of SD345 containing no Cr is less noble than −0.35 V beginning from the first cycle throughout the eight cycles of corrosion-accelerating test with saltwater. That of 3Cr steel containing 3% Cr is noble than −0.35 V in the first cycle but becomes less noble than −0.35 V from the second cycle onward. The potential of 5Cr also shows a similar downturn between the second and third cycles. These phenomena agree well with the results of macrocell corrosion current density measurement, in which macrocell corrosion current began to be detected during the first, second, and third cycles on SD345, 3Cr, and 5Cr, respectively, as described in the next section. On the other hand, the half-cell potential of Cr-bearing rebars with a Cr content of 7% or more remained noble than −0.35 V throughout the eight cycles.

4.3. Macrocell Corrosion Current Density

Figure 8 shows the time-related changes in the macrocell corrosion current density of steels. Macrocell corrosion current density, which was appreciable only on SD345, 3Cr, and 5Cr bars, tends to rapidly increase immediately after the beginning of saltwater supply to shift from a dry phase to wet phase. The macrocell corrosion current density progressively decreases thereafter during the wet phase and rapidly decreases at the beginning of the dry phase. This rising and falling pattern is repeated toward the end of eight cycles in all the three cases. As shown in the figure, the peaks and troughs correspond to the wet and dry phases, respectively. In regard to SD345, the first peak in the first cycle is very high but progressively lowered in the following cycles, converging to a stationary level, while the troughs also converge to its stationary level. The initial cor-
Corrosion rate of steel is normally attenuated over time, converging to a stationary corrosion rate. Such attenuation of early corrosion rates can be attributed to the accumulation of corrosion products due to the following: (1) suppression of ferric ion and dissolved oxygen diffusion; (2) increase in the electrical resistance; and (3) reduction in the cathode-to-anode area ratio. Items (1) and (2) above are the states of corrosion in which the corrosion products inhibit ionization of steel and diffusion of dissolved oxygen while acting as a resistance in the corrosion circuit, thereby reducing the rate of corrosion reaction. Item (3) is the case where the cathodic area decreases in relation to the anodic area, obstructing the oxygen supply to be consumed by cathodic reaction. In other words, cathodic reaction controls the rate of corrosion reaction. Such a phenomenon applies to the case of low oxygen supply, such as underwater structures and thick cover concrete, and the case where the anodic reaction rate is so high that the rate of steel corrosion is limited by the rate of diffusion/penetration of oxygen, such as steel exposed to a chloride-containing environment. These causes are considered to have a comprehensive effect on the attenuation of the corrosion rate over time. In regard to steels with a high Cr content, however, the amount of oxygen necessary for cathodic reaction to match the rate of anodic reaction is marginal, as the higher the Cr content, the lower the corrosion rate. It is therefore likely that cathodic reaction should not control the corrosion rate of steels with a high Cr content, even if the oxygen diffusion rate is low, in general corrosion environments as well as environments with limited oxygen supply. In other words, the effects of items (1) and (2) are relatively stronger than that of item (3) on Cr-bearing steel.

The macrocell corrosion current of 3Cr and 5Cr bars, which was detected beginning during the second and third cycles, respectively, also formed peaks and troughs corresponding to the saltwater supply phases and dry phases, respectively. Declining tendencies of the current density over time were observed similarly to SD345. Figure 9 shows the cumulative corrosion amounts of anodic bars determined by applying the measured corrosion current density to Faraday’s law. This figure reveals that the cumulative corrosion amount tends to increase as the corrosion-accelerating test proceeds. Also, the cumulative corrosion amount of SD345 is the greatest, whereas those of 3Cr and 5Cr are nearly the same.

4.4. Corrosion Area and Corrosion Loss

Figures 10 and 11 show the changes in the corrosion area and corrosion loss, respectively, of steels over time. As shown in Fig. 10, the corrosion area tends to decrease as the Cr content increases. Those of Cr-bearing steel with a Cr content of more than 7% show little corrosion. This agrees with the measurement of macrocell corrosion current, in which no macrocell corrosion current was measured on Cr-bearing steel with a Cr content of more than 7%. Figure 11 reveals that, similarly to corrosion area, the corrosion loss tends to decrease as the Cr content increases, with those of steels with a Cr content of more than 7% being nearly 0%.

According to these measurement results of half-cell potential, macrocell corrosion current density, corrosion area, and corrosion loss, Cr-bearing rebar with a Cr content of more than 7% is expected to be immune to corrosion against a soluble chloride of up to 2.4 kg/m³, the examination in this paper.

5. Summary

Concrete specimens predisposed to macrocell corrosion were fabricated by applying an ASTM test method with the aim of investigating the corrosion-inhibiting properties of Cr-bearing rebars under macrocell corrosion environments induced by chloride ion in concrete. The time-related changes in the half-cell potential and macrocell corrosion current density during 8-month corrosion-accelerating test, as well as the corrosion area and corrosion loss at the end of the test period, were then measured. The results revealed the following:

(1) The soluble chloride ion content tended to decrease as the depth from the concrete surface increased and increased as corrosion-accelerating test progressed at all measuring points.

(2) The macrocell corrosion current density decreased as the Cr content increased. No macrocell corrosion current density was detected on steel with a Cr content of more than 7%.

(3) A Cr content of more than 7% was necessary for a
macrocell corrosion environment with a soluble chloride ion concentration not more than 2.4 kg/m³.

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