Corrosion Resistance of Cr-bearing Rebar in Simulated Concrete Pore Solutions

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As a fundamental study on the Cr-bearing rebar with the necessary corrosion resistance for use in steel reinforced concrete structures under corrosive environments This study was investigated to corrosion resistance of Cr-bearing rebars in simulated concrete pore solutions with content of chloride ion. The rebars were made from steels containing Cr from 0 to 16 %. SUS304 stainless steel and SD345 carbon steel were also used. Simulated concrete pore solutions were saturated with $\text{Ca}(\text{OH})_2$, containing 0.27 %, 1.07 % and 21.4 % NaCl. The pH value of the solutions was adjusted to 12.5, 11, 10 and 9 by HCl. Pitting potential and impedance, corrosion morphology of the steels in the solutions were investigated.

The results of the study showed that the corrosion resistance increased as the Cr content increased regardless of the content of chloride ions, and that the Cr-bearing rebars with a Cr content of 5C% and 9 % showed good corrosion resistance in 1.07 % NaCl solutions at pH 12.5 and pH 10, respectively. Cr-bearing rebar with a Cr content of 16 % showed as good corrosion resistance as SUS304 steel even in 21.4 % NaCl solutions at pH 10.

KEY WORDS: Cr-bearing rebar; corrosion resistance; pitting potential; impedance; corrosion morphology.

1. Introduction

The corrosion of RC structures demonstrates very complicated forms of deterioration intermingled together but all pointing to a decrease in the durability of RC structures by the corrosion of the reinforcing bars.^{1,2)} For this reason, many studies have been performed to discover the best method of preventing corrosion in reinforcing bars. However, most of them have been disproportionately concentrated on the improvement of concrete quality such as the increase in concrete cover thickness, optimization of water-to-cement ratio or the addition of corrosion resistant materials. In Japan, epoxy-coating rebars are the only technology of rebars to prevent the corrosion. The epoxy coating rebars, however, requires special construction method to avoid scratch damages of the epoxy coating that affects reliability of corrosion protection.^{3,4)} In America and Europe, standardized high corrosion resistance stainless steel has already been employed in those areas damaged by salt as a method of enhancing the corrosion resistance of the reinforcing bar through its characteristic improvements.^{5–8)} Stainless steel rebars (e.g., type 316LN: 16%Cr–12%Ni–2%Mo–0.2%N) have shown very good performance in highly saline environments.^{9,10)} Type 304 (18%Cr–8%Ni) stainless steel rebars used for a concrete pier exposed to a tropical marine environment for 60 years showed little corrosion damage.¹¹⁾ Despite its excellent corrosion resistance, stainless steel has not been widely used, due to the high cost resulting from costly elements such as chromium (Cr)

and nickel (Ni), which also require additional manufacturing steps as compared with other general steel manufacturing processes.

However, considering the ever increasing maintenance cost for RC structures, it is desirable to conduct the study on the corrosion resistant reinforcing bars that does not require a life cycle cost. Accordingly, when a low stainless steel rebar containing fewer Cr and Ni elements (hereafter referred to as Cr-bearing rebar) is made available, the excessive concrete cover thickness can be reduced and the regulation on the water-to-cement ratio will become less strict, at which time the lifetime of RC structures can be extended by using the highly cost effective anticorrosion steel rebars that remain unaffected by corrosion under corrosive environments.

The objectives of the present study are to clarify the relationship between Cr content in rebars and the corrosion resistance in simulated concrete pore solutions, and to offer a guideline for the alloy design of corrosion resistant rebars.

2. Outline of Experiment

2.1. Materials

Eight types of steel with different Cr contents were immersed in solutions with chlorides simulating the environment within concrete pores (hereafter referred to as simulated concrete pore solutions) to measure their pitting potential and impedance and investigate their corrosion morphology. The simulated concrete pore solutions were pre-

pared by adding sodium chloride (NaCl) to saturated calcium hydroxide ($\text{Ca}(\text{OH})_2$) solutions and adjusting the pH values using hydrochloric acid (HCl). Tests were conducted with four pH values (12.5, 11, 10, and 9) and three chloride (NaCl) concentrations (0.27, 1.07 and 21.4%). These NaCl concentrations correspond to the Cl^- concentrations in our research work¹²⁾ that investigated the corrosion resistance of Cr-bearing steel rebars in concrete with high chloride content. In the research work, the concrete contained chloride ion (0.3, 1.2, and 24 kg/m^3), water (185 kg/m^3), and other stuffs (cement, sand, coarse aggregate, and air entraining agent). 0.27%, 1.07%, and 21.4% NaCl correspond to the concentration of 0.3, 1.2, and 24 kg/m^3 of Cl^- in 185 kg/m^3 of water, respectively. Also, chemical compositions of steels are given in **Table 1**. The steels containing Cr from 0 to 16% were used to change the corrosion resistance in simulated concrete pore solutions. SD345 steel that is a typical carbon steel rebar and SUS304 steel that is a typical austenitic stainless steel were also used to compare the corrosion resistance to the Cr-bearing steels. All steels were produced from 100 kg vacuum-melted ingots. These ingots were hot forged and hot drawn at 1 100–1 150°C to 13 mm ϕ wires. These wires except SUS304 steel were annealed at 700°C for 2 h. SUS304 wires were annealed at 1 100°C for 5 min. All wires were pickled to remove surface oxides. The wires of the Cr-bearing steels and SD345 steel had ferritic microstructure. The wire of SUS304 steel had austenitic microstructure. These wires were sliced to 2 mm thick plates for corrosion test specimens.

3. Experiment Procedure

3.1. Pitting Potential

The pitting potentials were measured to evaluate the resistance to corrosion initiation. The plate specimens were polished to #800 finish, degreased with acetone, and coated with silicone sealant excepting the measuring area (10 mm in diameter). The pitting potentials in deaerated solutions at 30°C were measured using a potentiostat. Specimens were polarized in an anodic direction at a rate of 20 mV/min after 10-min immersion in the solutions. Pitting potentials were determined as the noblest potentials at which the anodic current exceeded 100 μA . A specimen with a less negative pitting potential is therefore less prone to corrosion.

3.2. Impedance

The impedance of various steel specimens while being

subjected to corrosion in the simulated concrete pore solutions was measured to evaluate their rate of corrosion. The impedance, the inverse of which is proportional to the rate of corrosion, allows relative comparison between the rates of steel corrosion in concrete. Specimens with the same shapes and dimensions as those for pitting potential were used for this measurement. The argon-deaerated solutions were adjusted to a pH value of 10, temperature of 30°C with two levels of NaCl concentrations (1.07% and 21.4%). The impedance was measured by keeping a potential nobler than the pitting potential to induce corrosion, while changing the measured frequency from 10 kHz to 10 mHz under potential vibration of ± 5 mV. The time required for measurement was approximately 6 min.

3.3. Corrosion Morphology

The corrosion morphology of steels with a Cr content of 0%, 5%, 9%, and 16% and SUS304 steel was observed in a pH 10 solution containing 1.07% NaCl after the impedance measurement. The corrosion morphology of 16Cr and SUS304 steels in a pH 10 solution containing 21.4% NaCl was also observed.

4. Results and Discussion

4.1. Pitting Potential

Pitting potentials of the specimens in simulated concrete pore solutions were measured at various NaCl concentrations and pH. **Fig. 1** shows the effect of Cr content on the pitting potentials. In the case of pH 12.5 solutions contain-

Fig. 1. Effect of Cr content on the pitting potentials of the steels in simulated concrete pore solutions containing 0.27%, 1.07%, and 21.4% NaCl.

Table 1. Basic compositions of reinforcing, mass %.

Steel	C	Si	Mn	P	S	Cr	Ni	Mo
SD345	0.2280	0.31	1.34	0.029	0.020	0.084	0.04	0.016
0Cr	0.0120	0.32	0.50	0.031	0.006	0.005	0.01	0.001
5Cr	0.0150	0.28	0.53	0.027	0.006	5.020	0.01	0.001
9Cr	0.0107	0.28	0.53	0.028	0.006	9.140	0.01	0.001
11Cr	0.0117	0.28	0.53	0.028	0.004	11.00	0.01	0.001
13Cr	0.0117	0.28	0.53	0.028	0.004	13.05	0.01	0.002
16Cr	0.0113	0.29	0.53	0.027	0.004	15.98	0.01	0.002
SUS304	0.0630	0.31	1.01	0.026	0.006	18.36	8.28	0.053

Fig. 2. Effect of pH on the pitting potentials of 0Cr, 5Cr, 9Cr, and 16Cr steels in simulated concrete pore solutions.

ing 0.27% and 1.07% NaCl, the pitting potential increased considerably with Cr content up to 11%. The increase of the pitting potentials was comparatively saturated in over 11% Cr range. In pH 12.5 solutions containing 21.4% NaCl, the increase of the pitting potentials with Cr content was not so large up to 11% Cr. However, the pitting potential jumped up to a noble direction in the range of more than 13% Cr. In the case of pH 10 solutions that corresponded to neutralization of concrete, pitting potentials of 0% Cr and 5% Cr steels were the same level. Pitting potentials increased with Cr content in over 9% Cr range. The corrosion resistance of SD345 steel was almost the same as that of 0% Cr steel. The corrosion resistance of SUS304 steel was slightly better than that of 16% Cr steel.

Figure 2 shows the effect of pH values on the pitting potentials in simulated concrete pore solutions containing 1.07% and 21.4% NaCl. The bold lines in the graphs represent 0 V Ag/AgCl (-0.1 V CSE), *i.e.*, the least negative half-cell potential of Cr-bearing rebars in concrete. As is well known, pitting corrosion begins when the half-cell potential becomes nobler than the pitting potential. The specimens were therefore judged in this study as not being corroded while the pitting potential is nobler than 0 V Ag/AgCl. As shown in Fig. 2, the pitting potential becomes more negative as the pH value decreases. This tendency is more significant in the 1.07% NaCl solution, in which a reduction in the pH value from 12.5 to 11 causes the pitting potentials to become substantially baser. Nevertheless, pH values lower than 11 led to no marked changes in the pitting potential.

Fig. 3. Guideline map of Cr-bearing corrosion resistant rebars in simulated concrete pore solutions at pH 12.5.

In the 1.07% NaCl solutions, the pitting potential of specimens containing no Cr (0Cr steel) is more negative than 0 V Ag/AgCl even with a pH value of 12.5. As for specimens containing 5% Cr (5Cr steel), the pitting potential is nobler than 0 V Ag/AgCl with a pH value of 12.5 but becomes more negative as the pH value decreases to 11. On the other hand, steels containing 9% or more Cr show pitting potentials nobler than 0 V Ag/AgCl. In the 21.4% NaCl solutions, only 16Cr shows pitting potentials nobler than the threshold value.

Accordingly, in a solution with a pH value of 12.5 and NaCl concentration of 1.07%, steels containing 5% or more Cr are considered to resist corrosion. In a solution with a pH value of 12.5 and NaCl concentration of 21.4%, corrosion resistance is assured by steel with a Cr content of at least 16%.

Figure 3 shows the Cr content related to the NaCl concentration in simulated concrete pore solutions with a pH value of 12.5. Since this is a guideline for the risk of corrosion onset, another guideline for service life should also be investigated in terms of the rate of corrosion. However, this figure allows a conservative judgment on the Cr content of steel reinforcement related to NaCl concentration, as steel is retained safe unless corrosion occurs. Assuming that uncarbonated concrete is alkaline with a pH value of 12.5, Cr-bearing rebar with a Cr content of 3% or more (5Cr steel in this paper) is expected to be corrosion-resistant in concrete with a chloride content corresponding to 1.07% NaCl.

4.2. Impedance

In addition to the investigation from the aspect of corrosion onset discussed above, the rate of corrosion should also be investigated to ensure sufficient service life of reinforced concrete structures. As the failure of concrete structures is primarily caused by the volumetric expansion of steel reinforcement due to corrosion products, such structures can attain their required service lives even if corrosion occurs, provided the corrosion rate is sufficiently low.

The corrosion reaction resistance was determined by measuring the impedance of specimens in simulated concrete pore solutions with a pH value of 10 to compare the rates of corrosion. The measurement of the impedance under the same conditions allows relative comparison between corrosion rates, as the inverse of reaction resistance is proportional to the corrosion rate. Figure 4 shows the in-

(1) 0Cr, 5Cr, 9Cr

(2) 16Cr, SUS304

Fig. 4. Inverse of impedance of each steel in simulated concrete pore solutions with a pH value of 10.

verse of the corrosion reaction resistance, R_p , of each steel. When the NaCl concentration, pH value, and applied potential are 1.07%, 10, and -0.4 V Ag/AgCl, respectively, the corrosion rate of 5Cr steel is approximately 1/44 of that of 0Cr steel. When these parameters are 1.07%, 10, and 0.1 V Ag/AgCl, the corrosion rate of 9Cr steel is approximately 1/17 of that of 5Cr steel. In contrast to the similar pitting potentials of 0Cr and 5Cr steels with a pH value of as low as 10, their corrosion rates significantly differ, with 5Cr steel showing corrosion resistance superior to 0Cr steel. When comparing 16Cr steel and SUS304, the corrosion rate of the former is 1.7 times higher than that of the latter with 1.07% NaCl, pH 10, and 0.3 V Ag/AgCl. With 21.4% NaCl, pH 10, and 0.05 V Ag/AgCl, however, the corrosion rate of SUS304 is 6.7 times higher than that of 16Cr steel. 16Cr steel can therefore be more resistant to corrosion where the chloride concentration of concrete is extremely high. **Figure 5** shows an example of impedance measurement of 9Cr steel in pH 10 solutions containing 1.07% NaCl held at 0.1 V Ag/AgCl, which is about 0.1 V nobler than its pitting potential. This is typical impedance spectra. R_p was determined as the difference between the maximum impedance measured nearly between 1 and 10 Hz and the value at 10 kHz.

4.3. Corrosion Morphology

Figure 6 shows the corrosion morphology of each steel after impedance measurement. Only 16Cr and SUS304 were investigated in solutions with pH 10 and 21.4% NaCl, since a Cr content of at least 16% was deemed necessary

Fig. 5. Example of impedance measurement of 9Cr steel [1.07% NaCl, pH 10, 0.1 V Ag/AgCl].

(1) pH 10, NaCl 1.07%

(2) pH 10, NaCl 21.4%

Fig. 6. Corrosion morphology of each steel in simulated concrete pore solutions with a pH value of 10.

for resisting such a fierce environment. The figure reveals uniform corrosion of 0Cr and 5Cr in the solution with pH 10 and NaCl 1.07%. Though similar pitting potentials were observed for these steels in a solution with pH 10 and NaCl 1.07%, the corrosion rate of 5Cr was found lower than that of 0Cr. The low corrosion rate of 5Cr is observed as the small area of erosion in Fig. 6. For steels with a Cr content of 9% or more, corrosion is localized (pitting) in a solution with a pH value of 10 and NaCl concentration of 1.07%, with the corroded area of 9Cr steel being slightly greater than those of 16Cr steel and SUS304. In a highly corrosive environment with pH 10 and 21.4% NaCl, 16Cr shows localized corrosion, whereas SUS304 shows uniform corrosion. The lower corrosion rate of 16Cr steel than SUS304 shown in Fig. 4 is presumably derived from their different modes of corrosion. **Table 2** presents the results for pitting potential, impedance, corrosion morphology that were derived from the electrochemical tests.

Table 2. Corrosion data from the electrochemical tests.

Steel	Cr	Pitting Potential (mV vs Ag/AgCl)												Inverse of Impedance (Ω^{-1})		Corrosion Morphology	
		PH 9			PH 10			PH 11			PH 12.5			PH 10		PH 10	
		0.27	1.07	21.4	0.27	1.07	21.4	0.27	1.07	21.4	0.27	1.07	21.4	1.07	21.4	1.07	21.4
SD345		-450	-482	-568	-469	-487	-493	-391	-384	-464	176	-86	-284	-	-	-	-
0Cr		-467	-487	-533	-474	-465	-495	-408	-413	-438	155	-141	-292	0.026 (0.1V)	-	UC	-
5Cr		-431	-500	-499	-432	-448	-489	-309	-309	-421	308	255	-223	0.001 (0.1V) 0.746 (0.4V)	-	UC	-
9Cr		59	-3	-424	84	-4	-386	129	70	-291	614	504	-138	0.044 (0.4V)	-	PC	-
11Cr		137	88	-227	131	64	-246	170	126	-155	709	426	-115	-	-	-	-
13Cr		144	98	-158	189	83	-127	227	188	-197	706	614	130	-	-	-	-
16Cr		264	226	-61	277	225	-41	307	292	41	697	636	140	0.032	0.040	PC	PC
SUS304		276	229	-58	234	234	13	351	268	53	677	690	225	0.021	0.308	PC	UC

UC : Uniform Corrosion, PC : Pitting Corrosion

5. Conclusions

For the purpose of developing Cr-bearing rebars that can be used under corrosive environments, experiments were conducted on the corrosion resistance of Cr-bearing rebars in simulated concrete pore solutions.

The following was obtained from these experiments:

(1) The corrosion resistance of steels in simulated concrete pore solutions increased as the Cr content increased.

(2) The pitting potential of steels became more negative as the chloride concentration in the simulated concrete pore solution increased and as the pH value of the solution decreased.

(3) In simulated concrete pore solutions with an NaCl concentration of 1.07%, steel specimens with a Cr content of 5% or more and 9% or more showed resistance to corrosion under pH values of 12.5 and 10, respectively.

(4) In a simulated concrete pore solution with a pH value of 10 and NaCl concentration of 21.4%, steel specimens with a Cr content of 16% showed resistance to corrosion.

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