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Durability against Steel Corrosion of HPFRCC with Bending Cracks

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Abstract

High Performance Fiber Reinforced Cementitious Composites (HPFRCC) develop micro-cracks under bending load. This study clarifies durability against steel corrosion in HPFRCC. Specimens made of HPFRCC or normal mortar with cracks were cured in a chloride or CO₂ environment and chloride ingress or carbonation progress was evaluated. The corrosion cell formation pattern and rate were also compared between HPFRCC and normal mortar, and their mechanism was discussed. The multiple cracks in HPFRCC were focused on in particular. It was found that chloride ingress and carbonation progress occur at many spots in HPFRCC, and that the advantage of HPFRCC against corrosion is due not only to the crack width but also the cracking pattern itself, which causes microcells instead of macrocells. From the above results, it was confirmed that the durability of HPFRCC against chloride or carbonation induced corrosion is higher than that of normal mortar.

1. Introduction

The destruction of concrete typically occurs as the result of fragility. High Performance Fiber Reinforced Cementitious Composites (HPFRCC) were developed and applied in order to overcome this weakness (Li and Kanda 1998; Li 2003; Naaman 2003; Kunieda and Rokugo 2006; Rokugo et al. 2009). Much research work to evaluate the structural behavior of this material has been conducted (JCI 2002; RILEM 2006; JSCE 2008). Two characteristics of HPFRCC are that 1) under the action of bending, a lot of minute cracks (multiple cracks) occur in HPFRCC, compared to normal mortar, and 2) the stress does not decrease after the crack occurrence, and apparent strain hardening occurs. In other words, stress increases with increases in strain. Based on the above, the performance of a structure has been confirmed to improve through the use of HPFRCC as the construction material, and this material is expected to be used widely in the future. However, there has been little research on the durability of HPFRCC particularly against attacks from chloride and carbonation (Sanjuan et al. 1997; Lawler et al. 2002; Maalej et al. 2003; Martinola et al. 2004; Mihashi et al. 2011).

Against this backdrop, the pattern of formation of cells such as macrocells and microcells (Miyazato and Otsuki 2010) and the rate of steel corrosion by chloride or carbonation were compared between beam specimens using HPFRCC and beam specimens using normal mortar, and the durability against steel corrosion of HPFRCC was clarified. The originality of this paper is that it evaluates the influences of multiple cracks in HPFRCC on steel corrosion. Therefore HPFRCC with multiple cracks and normal mortar with a single crack produced by subjecting each specimen to the same load level were used.

The flow of this paper is as follows. In Section 2, we explain the experiment procedure. In Section 3, penetration tests such as the chloride ingress and carbonation test are carried out. In Section 4, the corrosion cell formation pattern and rate are investigated through steel corrosion tests. Next, a hypothesis is considered based on results of Section 3. In Section 5, an experiment is added to verify the hypothesis. Finally, in Section 6, the primary results are summarized.

2. Experimental procedure

2.1 Materials

The types and characteristics of the materials used in the normal mortar and HPFRCC are listed in Table 1.

2.2 Specimens

The specimens used for the penetration test are shown in Figs. 1 and 2, and the specimens used for the steel corrosion test are shown in Figs. 3 and 4. The bending reinforcement steels in Figs. 3 and 4 were coated with epoxy resin. They were embedded to prevent breaking of the special divided steel bar when specimens were bent to generate cracks.

The mixture proportions of the normal mortar are listed in Table 2 and those of HPFRCC are listed in Table 3. The ratio of the fiber mixture content in HPFRCC is 1.5% by volume (Kunieda et al. 2002). Based on these two tables, internal stress in HPFRCC may develop to a much higher level than in normal mortar because HPFRCC contains a greater amount of cement and a lesser amount of sand. However, it is thought that this does not have a practical negative effect because the fibers are oriented.

The production procedure of the specimen consisted in embedding steel bars of φ 9 mm to 20 mm in the cover.
In the specimens used for the steel corrosion test, a special divided steel bar was embedded to measure the macrocell corrosion current and the microcell corrosion current. A previously published procedure was employed for the production of this special divided steel bar (Miyazato and Otsuki 2010). First, lead wires were attached with solder to the ends of a steel element cut to a length of 15 mm. Two steel elements were connected and insulated with epoxy resin. The lead wires of the adjacent sides of contiguous steel elements were joined. As a result, the steel bar composed of 13 elements was considered to form a single unit electrically.

All the specimens were cured in water (20°C) for 28 days after casting. They were bent at a load of 20 kN to generate cracks. As a result, as shown in Table 4, the residual crack width of normal mortar was 0.3 to 0.4 mm. On the other hand, the residual crack width of HPFRCC...
was 0.1 mm or less, and a large number of cracks were generated. The crack widths were measured at 3 points on the surface with a vernier caliper after full unloading as shown in Fig. 5, and these values (w1, w2, w3) were averaged. As shown in Table 4, the residual crack depth of normal mortar was 80 mm. On the other hand, the residual crack depth of HPFRCC was 30 mm or less. The crack depths were measured at both sides using a vernier caliper after fully unloading as shown in Fig. 5, and the two values (d1, d2) were averaged.

The crack width was maintained during exposure. In the specimens of normal mortar, two pieces of stainless steel board of 0.1 mm thickness and 10 mm length were placed into the crack (Otsuki et al. 2000) for this purpose. On the other hand, the specimens of HPFRCC were bound as shown in Fig. 6 to maintain crack width because stainless steel boards could not be inserted in all the cracks in these specimens.

The cracked face was the exposed side. The other five faces of each specimen were coated with epoxy resin to prevent the penetration of corrosion factors from these faces.

The specimens were exposed to an environment promoting chloride attack for 28 days (=4 cycles). Here 3.0% salt water for 2 days and dry air with 60% relative humidity for 5 days were repeated in this one cycle. Also, the specimens were exposed under an environment promoting carbonation for 91 days (=6.5 cycles). Here dry air with 60% relative humidity and 5.0% carbon dioxide for 4 days, and wet air with 90% relative humidity for 10 days were repeated in this one cycle.

2.3 Experiment cases
The experiment cases are listed in Table 5. Two materials, normal mortar and HPFRCC, were tested, two deterioration factors, chloride and carbonation, were used, and two water cement ratios, 30% and 60%, were employed, for a total of eight experiment cases.

2.4 Measurement
(1) Chloride penetration depth
The specimens subjected to chloride attack were broken longitudinally and the steel was removed. Next, a silver nitrate water solution of 0.1 mol/l was sprayed over the cracked side, the part that turned silver-white as a result was measured with a vernier caliper, and the chloride ion penetration depth was measured (Otsuki et al. 1992). The locations used for measurement consisted of two locations, one “healthy part” and one “cracked part,” as shown in Fig. 7. When the chloride ion penetration depth of the “cracked part” in the HPFRCC specimen was measured, this was done by measuring a representative value at the crack with the maximum width.

(2) Carbonation depth
The specimens subjected to carbonation were broken longitudinally and the steel was removed. Next, a 1.0% phenolphthalein ethanol solution was sprayed over the cracked side, the part that turned purple-red as a result was measured with a vernier caliper, and the carbonation depth was measured in accordance with JIS A 1152.

The same target measurement areas and representative value measurement method as in the case of chloride ion penetration depth were used.
(3) Macrocell corrosion rate
In this paper, the current flowing between steel elements is defined as macrocell corrosion current. Figure 8 shows the measurement method. First a zero-resistance ammeter was connected between adjacent steel elements, and the electric current (macrocell corrosion current) was measured. Next, the electric currents flowing into the target steel element from both ends were added up. The value obtained by dividing the added up electric currents by the surface area of the steel element was the macrocell corrosion current density in each steel element. Thus, the macrocell corrosion current density can be expressed as in Equation (1).

\[
I_{\text{macro}} = \frac{I_{i-1,i} + I_{i+1,i}}{S_i}
\]  

where \(I_{\text{macro}}\) is the macrocell corrosion current density of steel element \(i\) (A/cm\(^2\)), \(I_{i-1,i}\) is the corrosion current flowing from steel element \(i-1\) to \(i\) (A), \(I_{i+1,i}\) is the corrosion current flowing from steel element \(i+1\) to \(i\) (A), and \(S_i\) is the surface area of steel element \(i\) (cm\(^2\)).

The corrosion current density was positive if the target steel element was an anode, while the corrosion current density was negative if the target steel element was a cathode. Finally a macrocell corrosion current density of 100 \(\mu\)A/cm\(^2\) was converted into a macrocell corrosion rate of 1.16 mm/year as shown in Equation (2).

\[
\text{corrosion current density} \times \frac{\text{weight of 1 mol of iron}}{\text{density of iron}} \times \frac{\text{period}}{2} = \frac{100 \times 10^{-6} \text{ (A/cm}^2\text{)}}{96500 (\text{C})} \times \frac{55.85 (\text{g/mol})}{7.86 (\text{g/cm}^3)} \times 60(\text{sec}) \times 60(\text{min}) \times 24(\text{hour}) \times 365(\text{day})
\]

\[= 1.16(\text{mm/year})\]

(4) Microcell corrosion rate
In this paper, the current flowing in a steel element only is defined as microcell corrosion current. Therefore, this microcell corrosion current is calculated by the polarization resistance (Stern and Geary 1957; Andrade and Gonzalez 1978; Tsuru et al. 1979). First a lead wire to connect between steel elements was cut once so as not to allow the passage of any electric currents between different steel elements. As shown in Fig. 9, the polarization resistance of the steel surface was measured by an alternating current impedance method using a frequency response analyzer (FRA). The range of the frequency was from 5 kHz to 5 mHz and voltage of amplitude 50 mV was recorded. The polarization resistance was calculated using a Bode diagram and a Cole-Cole plot. The microcell corrosion current density was calculated by Equation (3).

\[
I_{\text{micro}} = \frac{K}{R_{\text{p}}} 
\]  

where \(I_{\text{micro}}\) is the microcell corrosion current density of steel element \(i\) (A/cm\(^2\)), \(R_{\text{p}}\) is the polarization resistance of steel element \(i\) (\(\Omega\cdot\text{cm}^2\)), and \(K\) is a constant (0.0209 V) (Stern and Geary 1957; Andrade and Gonzalez 1978; Tsuru et al. 1979).

Finally, the microcell corrosion current density of 100 \(\mu\)A/cm\(^2\) was converted into the microcell corrosion rate of 1.16 mm/year.

(5) Total corrosion rate
The sum of macrocell corrosion rate and microcell corrosion rate was the total corrosion rate.

3. Penetration test
3.1 Observation examples
Examples of chloride ion penetration observation results are shown in Figs. 10 and 11. The water cement ratio of these specimens is 30%. Examples of the carbonation observation results are shown in Figs. 12 and 13. The water cement ratio of these specimens is 60%.
According to these figures, it can be confirmed that in the normal mortar specimen, the chloride ion penetrates or the carbonation progresses only in one place. The reason for this is thought to be that the chloride ion or the carbon dioxide penetrates the mortar inside from the outside along one crack, and then penetrates widely through the gap at the crack vicinity (Goto 1971; Kamiyama 1972) and around the steel.

On the other hand, it can be confirmed that in the HPFRCC specimen, the chloride ion penetrates or the carbonation progresses into some places. The reason for this is thought to be that the chloride ion or the carbon dioxide penetrates the mortar inside from the outside along some cracks, and then penetrates widely through the gaps at the crack vicinities (Goto 1971; Kamiyama 1972) and around the steel.

3.2 Results and discussion

According to Figs. 14 and 15, it can be confirmed that in the healthy parts, the chloride ion penetration depth and the carbonation depth of HPFRCC are deeper than those of normal mortar. The reason for this is thought to be that the penetration of the chloride ion or the carbon dioxide becomes easy because 10 vol% of the air content in HPFRCC is more than 2% of that in normal mortar (Shimizu et al. 2004) and because 395 or 281 kg/m³ of the unit weight of fine aggregate in HPFRCC is less than 1563 or 1312 kg/m³ that in normal mortar. However, it is thought that little chloride ion or carbon dioxide is supplied to the steel because the crack depth is shallower than the cover depth, as shown in Table 4.

On the other hand, according to Figs. 16 and 17, it can be confirmed that in cracked parts, the chloride ion penetration depth and the carbonation depth of HPFRCC are shallower than those of normal mortar. The reason for this is thought to be that the crack depth is shallow and the width is narrow in the HPFRCC specimen, while they are deep and wide in the normal mortar specimen, as shown in Figs. 1 and 2 and Table 4. That is, it is thought that the penetration of the chloride ion or the carbon dioxide is difficult in HPFRCC compared to normal mortar, because the depth of the crack is shallow and the width is narrow (Kato et al. 2005).

4. Steel corrosion test

4.1 Results

Figures 18 to 21 show examples of the experimental results. Figures 18 and 19 show the results for the case of chloride attack and water cement ratio of 30%.
20 and 21 show the results for the case of carbonation and water cement ratio of 60%.

Figure 18 shows that the corrosion rate is maximized at only one place in the normal mortar specimen. On the other hand, Fig. 19 shows that minute corrosion rates appear at various places in the HPFRCC specimen. Next, Fig. 18 shows that the macrocell corrosion rate is higher than the microcell corrosion rate at the place where the highest total corrosion rate appears in the normal mortar specimen. Therefore, it is judged that macrocell corrosion is high. On the other hand, Fig. 19 shows that the microcell corrosion rate is higher than the macrocell corrosion rate at the place where the highest total corrosion rate appears in the HPFRCC specimen. Therefore, it is judged that the microcell corrosion is high. Additionally, Fig. 18 shows that the highest total corrosion rate in the normal mortar specimen is 0.082 mm/year. On the other hand, Fig. 19 shows that the highest total corrosion rate in the HPFRCC specimen is 0.004 mm/year. Therefore, it is judged that the corrosion rate in the HPFRCC specimen is slower than that of normal mortar.

The judgments for all 8 cases are shown in Table 6. According to this table, it can be confirmed that 1) the corrosion cell formation pattern in the normal mortar specimen is macrocells, while that of HPFRCC is microcells, and 2) the corrosion rate of HPFRCC becomes slower than that of normal mortar.
4.2 Discussion

As shown in Fig. 22, the chloride ion penetrates at only one place in the normal mortar specimen. Similarly, carbonation progresses at only one place. Therefore, the macrocell is formed because the anode reaction \( (Fe \rightarrow Fe^{2+} + 2e^-) \) progresses locally in a single cracked part. Also the local corrosion rate is generally fast if the macrocell is formed (Bohni 2005; Miyazato and Otsuki 2010). On the other hand, as shown in Fig. 23, the chloride ion penetrates at various places in the HPFRCC specimen. Similarly, carbonation progresses at various places. Therefore, microcells are wholly formed because the anode reaction progresses at various cracked parts. Also the general corrosion rate is slow if a microcell is formed (Bohni 2005; Miyazato and Otsuki 2010).

5. Additional experiment for verification

5.1 Content

The crack width in the HPFRCC specimen is narrower than that of the normal mortar specimen as shown in Table 4. As a result, in HPFRCC, the supply of chloride ion, carbon dioxide and oxygen to the steel may decrease. Therefore, it can be thought that the corrosion rate becomes slow because the supply of corrosion factor is suppressed.

In this section, the hypothesis mentioned in Section 4 is verified. That is, the influence that the distribution of the penetration spot of corrosion factor has on the corrosion formation pattern and the rate is investigated. Therefore, under the condition where the crack widths are the same in the normal mortar and HPFRCC specimens, the influence of the number of cracks on the corrosion formation pattern and the rate is evaluated. Experiments using HPFRCC specimens with some cracks that are not minute cracks are added for this purpose.

5.2 Experimental procedure

The used specimens, used materials, the experiment cases and the exposure conditions were the same as those of the experimental procedure described in Section 2. That is, the specimens were as shown in Fig. 4, the used materials were as shown in Table 1, the mixture proportions were as shown in Table 3, and the experiment cases were as shown in Table 5. However, the HPFRCC specimen was bent at the load of 40 kN so that the maximum residual crack width became 0.3 to 0.4 mm. Therefore, the maximum residual crack width in the HPFRCC specimen became equal to that of the normal mortar specimen as shown in Table 7. Also, the crack pattern of HPFRCC after being further loaded to 40 kN was similar to that of HPFRCC after being loaded to 20 kN. However, the residual crack depth in the HPFRCC specimen was shallower than in of the normal mortar specimen, as shown in Table 7. The reason for this is thought to be the bridge effect of the fibers.

5.3 Results and verification

Figures 24 and 25 show examples of the experimental results. Figure 24 shows the result in the case of chloride attack and water cement ratio of 30%. Figure 25 shows the result in the case of carbonation and water cement ratio of 60%.

It can be confirmed that the results shown in these figures are the same as those in Figs. 19 and 21. That is, the corrosion rates appear in various places. Also the microcell corrosion rate is higher than the macrocell corrosion rate at the place where the highest total corrosion rate appears. Therefore, it can be verified that the microcell corrosion is excellent in the HPFRCC specimen even if the crack width increases.
of 0.3-0.4 mm is 0.082 mm/year. On the other hand, Fig. 24 shows that the highest total corrosion rate in the HPFRCC specimen with the crack widths of 0.3-0.4 mm width is 0.019 mm/year. Therefore it can be verified that even if the crack widths are the same in the normal mortar specimen and HPFRCC, the corrosion rate of HPFRCC is slower than that of normal mortar. The first reason for this is that even if the crack width is wide in the HPFRCC specimen, the corrosion formation pattern is that of a microcell. As a result, the general corrosion rate is slow (Bohni 2005; Miyazato and Otsuki 2010). The second reason is that even if the crack width in the HPFRCC specimen is equal to that of the normal mortar specimen, the latter crack depth is shallow as shown in Tables 4 and 7. In other words, the inside crack width of HPFRCC is narrow because of the bridge effect of the fibers (Yang et al. 2008). As a result, less oxygen is supplied to the steel. Therefore, it is thought that the corrosion rate is low because the cathode reaction \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \) is suppressed.

The results of the corrosion cell formation pattern and the highest total corrosion rate in all verification experiments are shown in Table 8. This table shows that microcells are formed in HPFRCC with some cracks. It also shows that the corrosion rate in HPFRCC is slower than in normal mortar even if the crack width is equal.

### 6. Conclusion

The conclusions are as follows:

1) Because the crack in normal mortar occurred only in one place, corrosion factor materials penetrated only in one spot. On the other hand, in HPFRCC, corrosion factor materials penetrated in many spots because many cracks occurred at various places.

2) The chloride penetration depth and the carbonation depth at the cracked part in HPFRCC were shallower by a quarter compared to normal mortar.

3) The advantage in terms of durability against corrosion of HPFRCC is not only due to the crack width but also due to the cracking pattern itself, which causes microcells and not macrocells. For example, the corrosion rate of HPFRCC was one-tenth that of normal mortar.

4) From these conclusions, it can be judged that durability against steel corrosion by chloride or carbonation at bending cracks of HPFRCC is higher than that of normal mortar.

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