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Effect of W/C ratio and cover thickness on polarization characteristics of embedded steel in mortar

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Abstract: The effects of cover thickness and W/C (water-to-cement) ratio on polarization properties of embedded steel bar were investigated with electrochemical methods. Corrosion potentials shift to the noble direction with increasing the cover thickness. In addition, when the cover thickness increasingly becomes thinner and thinner, effect of the W/C ratio on variation of corrosion potential increases as well. Impedance value at 100 kHz indicating the resistance of cover thickness increases with the decrement of W/C ratio as well as the increment of cover thickness. However, in the case of W/C ratio at 0.6, impedance at 10 mHz shows the relatively larger value than that at W/C ratio of 0.4 or 0.5 in the range of cover thickness from 4 to 8 cm, which is probably expected that oxide film built up on the surface of steel bar due to strong alkali environment by hydration reaction with increasing W/C ratio is performed as the resistance polarization. It is also observed that liquid junction potential tends to increase with decreasing W/C ratio.

Key words: reinforced concrete; corrosion potential; impedance; cover thickness; water-to-cement ratio; liquid junction potential

1 Introduction

The use of reinforced concrete structures in marine environments has been increased with the rapid development of marine industry. These reinforced concretes are often exposed to severely corrosive environments such as offshore and contaminated sea water. Therefore, corrosion problems of the inner steel bars embedded in concrete are very important from a safety and economic point of view. As a result, there are some reports to examine the corrosion of reinforced concrete[1–8]. In particular, corrosion of the inner steel bars is easy to be more serious due to use of sand containing sea water as well as exposure in more contaminated marine environments. Furthermore, cover thickness and W/C (water-to-cement) ratio of concrete are significantly related to these corrosion problems mentioned above. Thus, there are some protection methods to control corrosion of inner steel bars and some papers are related to cover thickness, W/C ratio and other parameters etc.[9-12]. However, in the case where many concrete specimens are individually made to examine corrosion properties, their physical and electrochemical properties may be sometimes different from each other because these specimens were not produced in same condition. In this study, a complex body specimen consisting of 6 steel bars with variations of cover thickness was produced with parameters of W/C ratio to avoid some of the problems mentioned above. The effects of cover thickness and W/C ratio on electrochemical behavior of embedded steel bar were investigated with electrochemical methods such as measurement of corrosion potentials, impedance and liquid junction potential in natural sea water solution.

2 Experimental

The size of the molding box for the complex body test specimens was 37 cm(length) \times 20 cm(width) \times 17 cm(height), which is made of 1 cm-thick wood plate. Each hole with diameter of 1.5 cm was placed at a position of 2, 4, 6, 8, 10, and 12 cm from the upper side of molding box to direction of diagonal line. The clearance

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clearance of each hole was 5 cm. The length of steel bars with diameter of 1 cm was 26. Steel bars were polished with sand paper from No.200 to 2000, degreased with acetone, and inserted into each hole of the molding box. All other surfaces of the steel bars except 1 cm² of center were insulated with silicone epoxy. Sand-to-cement ratio was 2:1 and water-to-cement ratios were 0.4, 0.5 and 0.6. The cement used was Portland cement made in Korea and the chemical composition is shown in Table 1. After mortar was injected into the molding box for 24 h, a sea water tank having the size of 33 cm (length) × 12 cm(width) × 10 cm(height) was placed on the upper surface of the mortar specimen.

Measurements of corrosion potential and AC impedance were achieved at complex body specimen in each W/C ratio. Measurement of corrosion potential was carried out with two methods. In one case, the reference electrode (SCE) was immersed in the sea water tank; and in the other case, the reference electrode was placed on the dried outer surface of mortar specimen. All electrochemical measurements were performed with CMS–100 program (Wona Tech Company). The experimental apparatus is shown in Fig.1.

3 Results and discussion

Fig.2 shows the variation of corrosion potentials with immersion time for various cover thicknesses in the case of W/C ratio at 0.4. Cover thickness at 2 cm indicated the most negative corrosion potential compared with other cover thickness and it was observed that corrosion potential shifted to noble direction with increasing the cover thickness. Especially, 12 cm of cover thickness showed the most positive corrosion

Table 1 Chemical properties of ordinary Portland cement

potential. These patterns were also observed at W/C ratio of 0.5. Thus, it is considered that when W/C ratio is 0.4 or 0.5, their relationships between corrosion potential and cover thickness are well coincided. However, in the case of W/C ratio at 0.6, relations are not nearly coincided each other. Dissolved oxygen and chloride ion of seawater are difficult to approach the surface of embedded steel bar of mortar with increasing the cover thickness due to a closely tight space between a small cavity of cement gel and other chemical products of inner mortar with decreasing W/C ratio. Furthermore, fracture of oxide film formed on the surface of embedded steel bar is difficult as well.

On the other hand, in the case of higher W/C ratio at 0.6, it is expected that the effect of cover thickness on corrosion potential seems to be smaller compared with W/C ratio at 0.4 or 0.5 because dissolved oxygen and chloride ion of sea water are easy to approach the surface of embedded steel bar due to a big space induced by evaporation of remaining water of inner mortar with increasing W/C ratio. As a result, oxide film of the surface is also easy to corrode regardless of cover thickness. Therefore, the effect of W/C ratio on corrosion potential becomes larger when cover thickness is 6 cm and below. However, when the cover thickness is 8 cm and above, the effect of W/C ratio is rather small. It is expected that when cover thickness becomes 6 cm and below, dissolved oxygen and chloride ion etc are somewhat easy to approach the surface of embedded steel bar due to short distance. However, when cover thickness is 8 cm and above, it is difficult for them to approach the surface of embedded steel bar due to long distance irrespective of W/C ratio. Therefore, cover thickness may be more important than W/C ratio to

$\frac{\text{SiO}_2 \text{Al}_2\text{O}_3 \text{Fe}_2\text{O}_3 \text{CaO} \text{MgO} \text{SO}_3}{210-225} = 4.5-6.0 = 2.5-3.5 = 36.5-66.0 = 0.9-3.3 = 1.0-2.0 = 0.5-1.3 = 0.2-0.9$			Lomition loss/0/	Incoluble regidue/0/				
210-225 45-60 25-35 365-660 09-33 10-20 05-13 02-09	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	Ignition Ioss/ 76	Insoluble Tesidue/ 76
21.0 22.5 4.5 0.0 2.5 5.5 50.5 00.0 0.7 5.5 1.0 2.0 0.5 1.5 0.2 0.7	21.0-22.5	4.5-6.0	2.5-3.5	36.5-66.0	0.9-3.3	1.0-2.0	0.5-1.3	0.2-0.9



Fig.1 Experimental apparatus for measuring corrosion potential and impedance



Fig.2 Variation of corrosion potential as function of thickness with immersion time in natural sea water solution (W/C ratio: 0.4)

control of corrosion of embedded steel bar under severely corrosive environment.

Fig.3 shows the variation of corrosion potential with immersion time at W/C ratio of 0.4. It was measured by two methods. One is that reference electrode is immerged in sea water solution of sea water tank. The other is that reference electrode is directly placed on the outer dried surface of the mortar specimen. When corrosion potentials were measured with reference electrode immerged in sea water tank, their values showed nobler potentials than those measured with reference electrode placed directly on the outer surface of test specimen. These results show that liquid junction potential caused by difference of mobility of ion as well as difference of concentration of solution is more added in the case of measuring dry outer side of test specimen.

Fig.4 shows the variation of impedance at 100 kHz as a function of W/C ratio. The results of measured impedance can be commonly drawn with many different



Fig.3 Variation of corrosion potential measured with reference electrode immerged in sea water solution or placed on outer dried surface (Cover thickness: 2 cm; W/C ratio: 0.4)

types of equivalent circuits. Fig.5 shows two types of equivalent circuit diagrams. Type I would be a simple circuit to evaluate the electrochemical behavior of surface of bare steel in electrolytic solution. On the other hand, it is well known that type II is generally used to examine a polarization behavior of deposited film of coated steel etc. Impedance value measured at 100 kHz in Fig.4 is a resistance of cover thickness and its value is thought to be nearly the same as the total resistance(R_1) of type I because cover thickness of mortar specimen is significantly larger compared with deposited film of generally coated steels and its conductivity is also lower than that of coated steel. Therefore, impedance value tends to increase with increasing the cover thickness. However, although cover thickness may be the same, its impedance value at W/C ratio of 0.4 clearly showed the larger value than that at W/C ratio of 0.5 or 0.6. In addition, in the case of W/C ratio at 0.6, the relationship between impedance value and cover thickness was not well coincided as well. As a result, it is thought that some amount of water remained in inner side of mortar



Fig.4 Variation of impedance at 100 kHz as function of thickness and W/C ratio



Fig.5 Equivalent circuit diagrams for analysis of measured impedance with variation of surface condition (R_1 : Total resistance of solution and mortar; R_p : Polarization resistance; C_1 : Double-layer capacitance; R_2 : Solution resistance; C_f : Film capacitance; B_f : Film resistance)

as well as sea water invaded by numerous hair crack due to the fact that the increment of W/C ratio may induce the decrease of the resistance of cover thickness. Fig.6 shows the variation of impedance at 10 mHz with cover thickness and W/C ratio. Impedance at 10 mHz would indicate total resistance including resistance of cover thickness(R_1) and polarization resistance(R_p) such as concentration polarization, activation polarization and resistance polarization of the surface of embedded steel bar.

However, as shown in Fig.6 in all range of cover thickness only except cover thickness at 12 cm, their impedance values showed a comparatively hunting phenomenon. For example, even though impedance value at 100 kHz at W/C ratio of 0.4 appears a relatively large value compared with other W/C ratio at 0.5 or 0.6 in the range of cover thickness from 6 to 12 cm, their impedances at 10 mHz at W/C ratio of 0.6 in the range of cover thickness from 4 to 8 cm showed the relatively large values than those of other W/C ratios of 0.4 and 0.5. This shows that oxide film formed on the surface of embedded steel in mortar due to strong alkali environment by hydration reaction with increasing W/C ratio seems to be operated as the resistance polarization.



Fig.6 Variation of impedance at 10 mHz as function of thickness and W/C

4 Conclusions

Corrosion potential tended to shift to noble direction with increasing the cover thickness. In addition, when cover thickness increasingly becomes thinner and thinner, effect of W/C ratio on corrosion potential increases as well. Impedance at 100 kHz indicating resistance of cover thickness increases with the decrease of W/C ratio as well as the increment of cover thickness. In the case of W/C ratio at 0.6, their impedance values at 10 mHz show the relatively larger values than those of W/C ratios of 0.4 and 0.5 in the range of cover thickness from 4 to 8 cm, which is probably expected that oxide film formed on the surface of embedded steel bar due to strong alkali environment by hydration reaction with increasing W/C ratio is performed as the resistance polarization. It is also observed that liquid junction potential tends to increase with decreasing W/C ratio and is more added to corrosion potential in case of measurement of dry side of the specimen.

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