Influence of defects at the steel-mortar interface on the corrosion behavior of steel

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HIGHLIGHTS

- The defects at the steel-mortar interface were investigated by X-ray CT non-destructively.
- EIS was used to study the electrochemical behavior of steels with different interfacial conditions.
- The interfacial defects play a dual negative role on steel corrosion behavior.

ARTICLE INFO

ABSTRACT

The different corrosion behaviors of top part and bottom part of horizontal steel (with respect to casting direction) in mortars after exposure to 3.5% NaCl solution were investigated. The results of electrochemical impedance spectroscopy (EIS), X-ray computed tomography (X-CT) confirm non-destructively that the formation of loose and porous defects at the bottom steel-mortar interface results in low corrosion resistance of adjacent steel, whereas few distinct defects can be found at the top steel-mortar interface. It is confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) analysis that the defects at the steel-mortar interface play a dual negative role on the corrosion resistance of steel: the passive films gradually lose their stability due to the depletion of the protective $Ca(OH)_2$ layer in the defects, and chlorides are prone to accumulate in the defects which further attack the passive films of steel.

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1. Introduction

Chloride-induced steel corrosion is one of the critical factors shortening the service life of reinforced concrete structure (RCS) in severe environments [1]. Chloride threshold level is the indication of the depassivation of steel and the onset of corrosion, and the corrosion rate of steel is the key parameter for the evaluation of corrosion propagation [2–5]. However, results of chloride threshold level and corrosion rate reported in the literature scatter over a large range, which significantly influences the service life prediction of RCS [4,5].

The cause of this scatter is very complicated, mainly including the different raw materials, different surface conditions of steel [6], the size effect of specimens [7], various measuring techniques and the complex corrosive environments [4]. Moreover, the presence of steel-concrete interface is also considered to affect the chloride threshold level and corrosion rate of steels significantly [1,4,8–11].

It is well known that there are two types of interfacial transition zone (ITZ) in RCS, namely, aggregate-paste interface and steel-concrete interface. It was confirmed that the presence of aggregate-paste interface has negative effects on the mechanical properties of concrete. Besides, the transport processes of water and chlorides were also influenced by the porous aggregate-paste interface [12–14]. It should be emphasized that the steel-concrete interface cannot be ignored in RCS, because it may reduce the steel-concrete bond strength and also affect the whole process of steel corrosion [15–19].

In most cases, steel-concrete interface widely exists in RCS. However, there are obvious differences for the defects at various steel-concrete interface conditions [2,8,20–24]. Water films are formed under the horizontal steels located mainly in the upper parts of RCS as a result of segregation, settlement and bleeding of fresh concrete, which was termed as "top bar effect" [8,16,17,21,22,25]. Thus, defects will be formed as the progressive hydration of cement at the steel-concrete interface and the

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evaporation of water outwards. Accordingly, the interfacial defects under the horizontally oriented steels are more pronounced than the up side.

The interfacial defects under the horizontally oriented steels have several effects on the durability of RCS: (i) The defects facilitate the accumulation of chlorides and lead to the early achievement of chloride threshold level for local region of steel surface [1,4,5,10,11]; (ii) The depletion of solid calcium hydroxide (portlandite) at the porous steel-concrete interface may lead to declining local pH-buffering capacity and thus to poor protection against corrosion due to the low local pH environment [10,24]; (iii) The ability of the defects at the steel-concrete interface to accommodate more corrosion products may have an benefit effect of prolonging the time to cracking of the concrete cover, though the porous structure of defects results in rapid generation of corrosion products owing to the enough oxygen and water close to steel surface [26,27]; (iv) Macrocell corrosion seems to develop between the defects under the horizontally oriented steels acting as an anode and the upper surface as the cathode [8,19,21].

Although it was confirmed the existence of defects at steel-concrete interface in RCS, most of the studies observed the defects on the basis of destructive specimens, and electrochemical methods were rarely employed to evaluate the effects of interfacial defects on the corrosion behaviors of steel in concrete [2,8,21,24]. X-ray computed tomography (X-CT) technique could detect the pores and cracks in damaged concrete without breaking specimens and it has been employed successfully to monitor the formation and the migration of corrosion products of steel in concrete [28–31]. Therefore, the aim of this work is to observe the defects at the steel-mortar interface non-destructively by X-CT and the microstructure and chemical composition of the interfacial defects were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) analysis. Electrochemical impedance spectroscopy (EIS) measurements were also utilized to investigate the effect of different defects at the steel-mortar interface for up and down sides of horizontally oriented steels on the corrosion resistance after different exposure days.

2. Experimental

2.1. Materials and specimens

Portland cement (P·I 52.5) was used for preparation of mortar specimens and the chemical composition of cement is shown in Table 1. River sand with the fineness modulus of 2.5 and tap water were used as fine aggregate and mixing water, respectively. A schematic sketch of the mortar specimen (40 mm × 40 mm × 160 mm) is shown in Fig. 1a. The mixture proportion of mortar specimen is cement/water/sand = 1:0.53:1.5 (mass ratio).

Plain round steels with the diameter of 8 mm were used as the reinforcing steels in this study. The chemical composition (mass ratio) of steel is 0.20% C, 0.55% Si, 1.42% Mn, 0.026% P, 0.028% S and balance Fe. A copper wire was soldered to one end of the reinforcing steel, and both ends were covered with epoxy resin coating, leaving a free exposure length of 80 mm and exposure surface area of approximately 21.8 cm². Prior to casting, all steels were polished with sandpapers and cleaned with ethanol.

Two types of steel-reinforced mortar specimens were cast in this study. For scenario 1 (electrochemical measurements), the exposed surface of horizontally oriented steels was partially coated with epoxy resin (EpoFix resin) in order to investigate the different corrosion behaviors for top part and bottom part of steel (Fig. 1b and c). That is, coating top part of steel (labeled as top steel) was used to study the corrosion behavior of bottom part of steel (labeled as bottom steel), and vice versa. At first, for scenario 1, 6 specimens were prepared (3 for top steel and 3 for bottom steel) for electrochemical measurements. Unfortunately, one specimen for bottom steel was broken unexpectedly after 60 days of exposure. Therefore, only 5 specimens were intact for further tests. For simplicity, 4 specimens (2 for top steel and 2 for bottom steel) were utilized to exhibit electrochemical results.

For scenario 2 (X-CT and SEM-EDS measurements), the whole exposed surface of horizontally oriented steel was free of epoxy coating for comparing the different corrosion morphologies of top steel and bottom steel and the different microstructures of interfacial mortar in the same specimen after different exposure days. A total of 6 specimens were prepared in scenario 2 and after each exposure time (10 d, 60 d and 180 d) 2 specimens were broken for morphology observation of steel-mortar interface and steel surface. 24 h after casting, all mortar specimens were cured (temperature = 20 ± 2 °C, and RH > 95%) for 28 days. After curing, all mortar specimens were immersed in 3.5% NaCl solution.

2.2. Electrochemical measurements

The classical three-electrode arrangement was used for the electrochemical measurements with PARSTAT 2273 Potentiostat. Embedded steel was used as the working electrode. A saturated calomel electrode (SCE) and stainless steel sheet were used as reference and counter electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were conducted after 10, 60 and 180 days of immersion. EIS measurements were performed at a stable open circuit potential (OCP) using an ac amplitude of 10 mV rms in the frequency range from 1 MHz to 10 MHz at 4 points per decade. The EIS results were fitted with ZSimpWin software.

2.3. Microstructural characterization

In this study, after 10 days of immersion in 3.5% NaCl solution the mortar specimens were examined with Y.CT Precision System (YXLON, Germany) to observe the defects at the steel-mortar interface. The applied X-ray tube voltage and current were 195 kV and 0.6 mA, respectively. The detector type was flat panel Y.XRD1620, and the number of detector elements was 1024 × 1024. The number of projection was 1080, and the 2D pixel size was approximately 45 μm × 45 μm. The object rotation angles were 360 degrees.

The microstructure of interfacial mortar matrix and the corrosion morphology of steels were investigated after different exposure days by photographs. After 60 days of immersion, the microstructure of interfacial mortar was observed by field emission scanning electron microscopy (FESEM, Sirion). Energy dispersive X-ray spectrometry (EDS) analysis was employed to

Table 1
Chemical composition of portland cement (wt%).

CaO	SiO₂	Al₂O₃	Fe₂O₃	MgO	SO₃	Na₂O + K₂O	Loss on ignition
62.60	21.35	4.67	3.31	3.08	2.25	0.75	0.95