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Electrochemical and microscopic investigation on passive behavior of ductile iron in simulated cement-mortar pore solution

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HIGHLIGHTS

- Passivation on the surface of ductile iron surface needs a high alkaline solution.
- Increase of solution alkalinity leads to short passive time and compact passive film.
- Mechanism of passivation on the surface of ductile iron is revealed by EIS/SEM/XPS.

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ABSTRACT

The passive behavior of ductile iron in simulated cement-mortar pore (SCMP) solution with different alkalinity was investigated by electrochemical measurements, such as open circuit potential (OCP), Tafel polarization curve (TP), electrochemical impedance spectroscopy (EIS), and microscopic tests, including scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Results show that, with increase in immersion time, the SCMP solution with the high pH value can cause the increase of OCP and capacitive loop of ductile iron surface, a morphology of growing surface film, and the high Fe^{2+}/Fe^{3+} ratios in its surface Iron-oxide compounds, presenting the formation of passive film on the surface of ductile iron. But in the SCMP solution with low pH value, its OCP, TP curve and EIS show no obvious change, and also produce the corrosion morphology of rust with low Fe^{2+}/Fe^{3+} ratios, indicating loss of surface protection on the ductile iron.

1. Introduction

The cement-mortar-lined ductile iron pipe has been developed as water pipeline with large diameter, high bearing capacity, good durability and safe operation when buried deeply in the underground [1–3], widely used in all aspects of water transport engineering, such as urban water supply and drainage [4–6]. Similar to the passive behavior of reinforcing steel in concrete [7,8], in high alkaline pore solution provided by lined cement mortar, a stable and tenacious iron oxide layer, namely passive film, can be formed on the surface of ductile iron, and it can protect the ductile iron pipe against corrosion [9]. However, some service conditions, such as calcium leaching under flowing water [10] and atmospheric carbonation in the absence of water [11,12], result in the reduction of the alkalinity of pore solution at the interface of ductile iron/cement mortar. The alkaline reduction can affect the formation and stability of the passive film on the surface of ductile iron, and the surface film becomes unstable or even breakdown [13–15].

At present, many researches have investigated the passive behavior of carbon steel, such as reinforcing steel and stainless steel, in concrete or pore solution by electrochemical and surface techniques [16–19], but the passivation of metals, including carbon steel and ductile iron, in alkaline solution is influenced by their chemical compositions and solution environment [20–22]. Because the composition and structure of the passive film formed on the surface of different metal is still completely unknown, their passivation in alkaline solution is not yet fully understood [8,23]. Furthermore, due to some differences in chemical composition (carbon content) between ductile iron and carbon steel [13,24,25], recent researches on the passive behavior of carbon steel cannot be directly used to reveal the corrosion-resistance mechanism of ductile iron pipe lined with cement mortar, and some knowledge about the growth mechanism, structure and composition of passive film at the ductile iron-cement mortar interface is still uncertain. So, the passive behavior of ductile iron in the simulated cement-mortar pore (SCMP) solution, including the growth

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of passive film and its passive time, electronic and chemical properties, need further study by electrochemical and microscopic analyses [26–28].

Electrochemical measurement, such as electrochemical impedance spectroscopy (EIS), is a powerful technique to evaluate the passive behavior of metals in different alkaline solutions, including their electrochemical and electronic properties [29–31]. By analyzing equivalent circuits corresponding to EIS diagrams, the electrochemical parameters, such as open circuit potential, polarization resistance or charge transfer resistance, capacitance, current density, which varies with the immersion time, can be obtained to characterize the passive behavior of some metals like reinforcing steel, ductile iron and strainless steel in simulated concrete/cement-mortar pore solution [30,32,33]. Apart from the electrochemical property, the physicochemical property of passive film can also be used to describe the passive behavior of these metals in the alkaline solution. Microscopic analysis, such as X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) [34,35], can provide a direct method to study the physicochemical property, such as its chemical composition and microstructure morphology, of passive film formed on the surface of ductile iron [19]. Thus, the simultaneous studies on the electro- and physico-chemical property at the ductile iron-cement mortar interface is helpful to reveal the corrosion-resistance mechanism of ductile iron pipes lined with cement mortar.

This paper discusses the passive behavior of ductile iron in the SCMP solution with different alkalinity, and the characterization of its electrochemical behavior by using the open circuit potential (OCP), Tafel polarization (TP) and electrochemical impedance spectroscopy (EIS). Also, the change of its physicochemical property with immersion time in the alkaline environment was investigated by means of scanning electron microscopy (SEM) together with Energy Dispersive X-ray Spectroscopy (EDS) and X-ray photoelectron spectrometer (XPS). The goal of this study is to summarize electrochemical and electronic properties, chemical composition and microstructure morphology of the surface of ductile iron in alkaline environment for better understanding of the corrosion-resistant mechanism of cement-mortar-lined ductile iron pipe.

2. Experiment

2.1. Sample preparation

Two types of samples, electrode and microscopically observed samples, were prepared to study the passive behavior of ductile iron by using electrochemical measurement and microstructure observation. The chemical composition of ductile iron in this study is listed in Table 1. For the electrochemical measurement, the ductile iron was firstly processed to a cylinder with the size of Φ11.3 mm × 25 mm, the cross sectional area of which is 1.0 cm^2. Secondly, an end surface of the cylinder is treated as the working surface, while the other is connected with a 250 mm-long copper wire. The cylinder with the wire is finally put into a 20 mm-diameter PVC tube, filled and solidified with the epoxy resin to leave a working surface. For the microstructure observation, the ductile iron was cut into some disk-shape samples with the size of Φ11.3 mm × 2.0 mm, the bottom surface of which is used as working surface of passivation. Before the electrochemical measurement and microstructure observation, the working surfaces of the two samples were sequentially ground with the SiC papers of $320^{\#}$, $500^{\#}$, $1000^{\#}$, $1200^{\#}$, $1500^{\#}$, $2000^{\#}$, $2500^{\#}$ and $3000^{\#}$ grits. The prepared samples were ultrasonically cleansed with acetone and alcohol for 5 min each, and then dried in cooling air. The experimental ductile iron samples are shown in Fig. 1.

2.2. Simulated pore solutions

According to the ionic composition in pore solution of cement mortar [36], the mixed solution was prepared by 0.6 M KOH, 0.2 M NaOH and 0.001 M $Ca(OH)_2$, and it was used to simulate the pore solution of cement mortar (SCMP) [37,38], in which the passive behavior of ductile iron was studied. $NaHCO_3$ was used to adjust the alkalinity of SCMP [39], the pH values of which were respectively adjusted to 13.6, 12.5 and 11.5, as listed in Table 2. The alkalinity of SCMP was controlled by the pH meter with the range of 0.01–14, resolution of 0.01 and an accuracy of ±0.02 pH. KOH, NaOH, $Ca(OH)_2$ and $NaHCO_3$ are the analytical reagents while purified water was used as the solvent.

2.3. Immersion

For the electrochemical measurement and microscopic observation on the passivation of ductile iron, two types of ductile iron samples in Fig. 1 were simultaneously immersed into the respective SCMP solutions with different pH values [30], as listed in Table 3. In order to conveniently describe the passivation of ductile iron in the SCMP solution, ZM1 and ZMM1 are respectively defined as the electrochemical and microscopic samples immersed in the SCMP solution with a pH value of 13.6, similarly, ZM2 and ZMM2, ZM3 and ZMM3 represent the electrochemical and microscopic samples in the SCMP solutions with pH of 12.5, 11.5 respectively. After the immersion, the containers filled with sample and solution were sealed to reduce the volatilization of the SCMP solution. Table 3 lists two types of ductile iron samples and their SCMP solutions.

2.4. Electrochemical measurement

Electrochemical measurement was performed at room temperature (25 °C ± 2) in a three-electrode system [40]. The ductile iron electrode sample, the commercially saturated calomel electrode (SCE) and platinum electrode were used as the working electrode, reference electrode and counter electrode, respectively. Fig. 2 is a schematic of the measurement setup. The OCP, Tafel and EIS were used to analyze the passive behavior of ductile iron in the SCMP solution [41]. The OCP, Tafel and EIS of the electrode samples were measured every 24 h by the electrochemical measurement system, and the charge transfer resistance R_{ct} of samples can be obtained by fitting of ZSimpWin software on the EIS data [42]. The EIS measurement was conducted in the frequency range of 100 kHz and 0.1 Hz. Sinusoidal voltage of ±10 mV was supplied, and direct current (DC) potential was set to the OCP, and all potentials reported in this study are shown versus SCE. The electrochemical measurement instrument used in the experiment was CHI660E electrochemical workstation with current range: 250 mA, current measurement resolution: <0.01 pA, input impedance >1 × 10^{12} Ω.

Table 1
Chemical composition of ductile iron (% by wt).

Elements	Fe	C	Si	Mn	Mg	P	S	Ti	Cr	Cu	V	Ni
Content	92.77	4.02	2.33	0.40	0.2	0.08	0.07	0.03	0.025	0.03	0.035	0.01