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Influence of chloride concentration and pre-passivation on the pitting corrosion resistance of low-alloy reinforcing steel in simulated concrete pore solution

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HIGHLIGHTS

- New low-alloy steel has been developed for application in concrete.
- The passive film could improve the pitting corrosion resistance.
- The compact Cr-enriched rust layer delays the propagation of corrosion pits for low-alloy steel.

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ABSTRACT

The effect of chloride concentration and pre-passivation on the pitting corrosion resistance of low-alloy steel and conventional low-carbon steel in simulated concrete pore solution was investigated using electrochemical techniques and surface analysis measurements. The results show that the passive film could enhance the pitting corrosion resistance for both investigated steels. Low-alloy steel exhibits slightly lower pitting corrosion resistance at low chloride concentration compared to low-carbon steel, regardless of the passivation condition. However, at high chloride concentration, low-alloy steel shows higher pitting corrosion resistance due to the formation of Cr-enriched protective rust layer.

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1. Introduction

In severe environments, the main process that may cause premature degradation of the service life of reinforced concrete structures is steel corrosion. When steel is exposed to alkaline pore solution of concrete, protective passive film is formed on steel surface. However, carbonation and chloride attack can breakdown this passive film and finally lead to active corrosion of steel [1,2]. So far, many techniques have been employed to mitigate steel corrosion [3–8] in reinforced concrete. Due to the high performance/cost ratio, low-alloy reinforcing steels with a small amount of corrosion-resistant alloying elements have attracted more and more attention [6–15].

It was found that low-alloy steel with 0.13 wt.% Cu and 0.10 wt.% Cr exhibited 2–3 times lower corrosion rate than plain carbon steel when exposed to simulated concrete pore solutions with 3.5 wt.% NaCl, due to the formation of very stable, adherent and protective rust layer on the surface of low-alloy steel [7]. It was confirmed that the alloying elements (Ti and V) induced grain refinement was the main reason for the improved corrosion resistance of low-alloyed mild steels in saturated calcium hydroxide [9]. Moreover, it was reported that iron/steel with different contents of phosphorus exhibited good corrosion resistance, which was related to the formation of inhibitive phosphate [13,14].

It must be emphasized, however, in some cases unexpected lower corrosion resistance for low-alloy steel was identified compared with low-carbon steel in the literature [8,16]. It was reported that during the initial period of exposure to simulated concrete pore solutions with 3.5 wt.% NaCl, low-alloy steel (0.26 wt.% Cu + 0.07 wt.% Cr + 0.10 wt.% Ni) exhibited inferior resistance to corrosion compared with thermo-mechanically treated steel. However, after long-term exposure, this trend was reversed [8]. This was primarily explained by its especial microstructure of low-alloy steel, which was more susceptible to chloride-induced corrosion [6,16,17]. Therefore, on the basis of the results obtained, it is rea-

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sonable to deduce that the corrosion resistance of low-alloy steel is not only dependent upon the alloying elements, but also on the altered microstructure of steel [6–9,11,12,16,17].

Cyclic potentiodynamic polarization (CPP) technique has been widely used to achieve the pitting corrosion resistance of reinforcing steels by many researchers [18–26]. It is well known that passive layer will be naturally formed on steel surface when exposed to alkaline solution. In the pore solution of concrete, it appears that in most cases sufficient time was provided for the formation of passive film before the steel was attacked by chlorides and carbonation [27]. However, there are no universal standards for considering if steel should be naturally passivated in alkaline solution prior to CPP measurements. Therefore, most of the researchers conducted CPP measurements for reinforcing steel before the formation of stable passive film [10,20,23,25], while only a few studies employed CPP measurements after steel was fully passivated [21,26]. Additionally, few previous works so far have focused on the influence of naturally formed passive film on chloride-induced pitting corrosion resistance of steel [18,19], although it is generally recognized that well-formed passive film plays a vital role on the pitting corrosion resistance of steel in concrete [27–31].

In this study, the chloride-induced pitting corrosion resistance and corrosion morphology of low-alloy steel in simulated concrete pore solution with various chloride concentrations were investigated. Furthermore, the effects of naturally formed passive film on the pitting corrosion resistance were also evaluated.

2. Experimental

2.1. Materials

The low-alloy hot-rolled deformed steel (labeled as LA steel) was specially designed through the optimization of alloy composition and technological process. The conventional low-carbon hot-rolled deformed steel (labeled as LC steel) was also tested for comparison purpose. Compared with LC steel, LA steel contains 0.859 wt.% alloying element Cr and a very small amount of alloying elements Cu and Ni (Table 1). In order to meet the requirements of carbon equivalent, the content of Mn in LA steel is obviously lower than that in LC steel.

The cylinder steel specimens with the thickness of 10 mm were cut from deformed rebar. The cross-section of steel specimens were wet ground with SiC grinding paper successively to 1200 grits, and then polished with diamond polishing agent. After that, the polished steel specimens were cleaned with ethanol, and then dried for metallographic analysis and electrochemical measurements.

Fig. 1 shows the optical micrographs of the microstructure, observed under an Olympus optical microscope, of LC and LA steels after etching in 4% nital solution (4 ml HNO_3 mixed with 96 ml ethanol). Both LC and LA steels show similar metallographic structure with two dominant phases, ferrite (lighter area) and pearlite (darker area), which are the typical phases in reinforcing steel widely used in civil engineering [32]. In addition, it can be seen that the grain size of LA steel (Fig. 1b) is larger than that of LC steel (Fig. 1a) due to the different heat treatment processes. The addition of ferritizer element Cr results in higher transformation temperature for LA steel, which thus promotes the growth of ferrite grain at high-temperature zone [33].

The simulated concrete pore solution (SCPS) used in this study was 0.1 mol/L NaOH + 0.2 mol/L KOH + 0.1 mol/L $Ca(OH)_2$ + 0.003 mol/L $CaSO_4$ [28]. The pH of SCPS was 13.3 under normal room temperature. Excessive amounts of undissolved $Ca(OH)_2$ in SCPS was used to compensate the pH reduction by carbonation during the period of electrochemical testing [18,21,28]. All reagents used were of analytical grade, and the deionized water was used as the solvent.

2.2. Electrochemical measurements

The classical three-electrode set-up was used for electrochemical measurements. Saturated calomel electrode (SCE) and platinum electrode were used as the reference electrode and the counter electrode, respectively. The exposed area of steels was fixed to 1 cm^2 in the corrosion cell. PARSTAT 2273 potentiostat was employed to perform the electrochemical measurements. All potentials mentioned herein are referred to the saturated calomel electrode (SCE). Electrochemical impedance spectroscopy (EIS) measurements were conducted at the open circuit potentials with the AC perturbation amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz. Cyclic potentiodynamic polarization (CPP) curves were measured from 200 mV_{SCE} negative to E_{corr}, then up to +800 mV_{SCE}, and finally reversed to E_{corr} [21]. The scan rate of CPP measurements was 2 mV/s [21–23].

In this study, steels without passivation and with pre-passivation for 10 days in chloride-free SCPS were prepared before CPP measurements. For the case without passivation, steels were all immersed in chloride-free SCPS for 1 h to reach stabilization of the open circuit potentials. It should be noted that stable passive film cannot be formed during such short exposure time [19,27,28]. Afterwards, steels were exposed to SCPS with three different NaCl concentrations of 0.1 M (lower than the threshold chloride content), 0.3 M (close to the threshold chloride content) and 1.0 M (high chloride content in severe marine environment) for characterization of pitting corrosion resistance [20]. For pre-passivation case, steels were immersed in chloride-free SCPS for 10 days to form a stable passive film prior to the addition of chlorides [19,21,27,28]. Afterwards, the experimental procedure for the characterization of pitting corrosion resistance was the same as the non-passivation case. Triple steel specimens were prepared for each case in order to ensure the reproducibility of results.

2.3. Surface morphology of corrosion products

After the electrochemical measurements, steel specimens were rinsed with deionized water in order to remove the loose precipitates and retain the corrosion products on steel surface. Then, specimens were dried and stored in a desiccator for microstructure observation.

Table 1
Chemical composition of LC and LA steels.

Steel type	Chemical composition (wt.%)									
	Fe	C	Si	Mn	P	S	V	Cr	Cu	Ni
LC	Bal.	0.22	0.53	1.44	0.025	0.022	0.038	–	–	–
LA	Bal.	0.199	0.654	0.571	0.0267	0.0076	0.0323	0.859	0.056	0.033

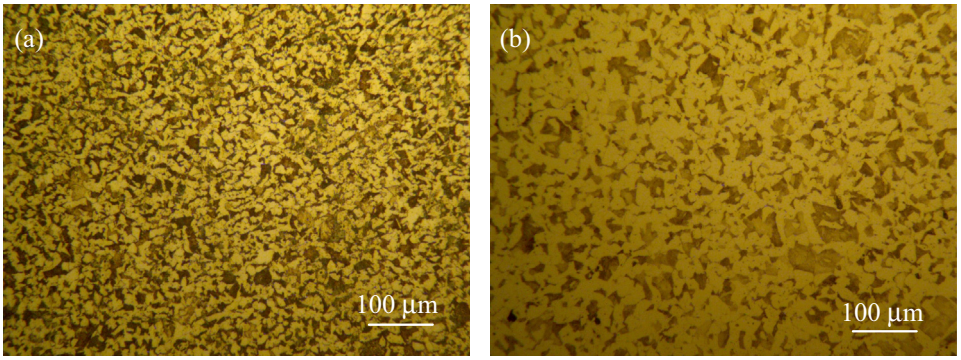

Fig. 1. Optical micrographs of etched (a) LC steel and (b) LA steel.

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