



# Temperature dependence of the formation of the passivation layer on carbon steel in high alkaline environment of concrete pore solution



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## ARTICLE INFO

### Article history:

Received 9 August 2016

Received in revised form 13 September 2016

Accepted 6 October 2016

Available online 8 October 2016

### Keywords:

Temperature

Carbon steel

Mott-Schottky

Concrete

Passive layer

Semi-conductivity

## ABSTRACT

In this study, the formation and the strength of the passive layer on carbon steel in concrete pore solution were investigated for temperatures ranging from room temperature to 850 °C. Two sets of carbon steel specimens were first exposed to different temperatures for an hour. One group cooled to room temperature in the air and the other one in the water. The steel specimens were then immersed in concrete pore solution and the passive layer formed on the steel was investigated. Results showed that in the extreme conditions, i.e. very high temperature, and water-cooled condition, the passive layer rarely formed on the steel. Increasing the exposure temperature led to a decrease in the thickness of the passive layer. This decrease was more apparent when steel was cooled in water compared to air cooled specimens. Results from this study contribute to the knowledge base that may be used to advance the state of the art in predictive models for steel reinforcement in concrete exposed to high temperatures (e.g., fire, power plants).

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## 1. Introduction

At potentials and pH levels normally measured in the concrete, a protective passive layer forms on the surface of carbon steel [1–3]. Partial or complete loss of the passive layer (mainly by chloride ions [4–6]) leads to active corrosion of the steel bars. Thus, the protectiveness of the passive layer has a direct impact on the subsequent corrosion of steel in concrete [7].

In general, the corrosion rate is negligible when the temperature is below the freezing point [8]. However, temperatures above room temperature have great effects on the corrosion rate of the metals [9,10]. In practice, reinforced concrete structures experience variable temperatures. However, a small number of studies were conducted on the impact of temperature on the corrosion of the reinforcing steel bars in concrete environment. Pour-Ghaz et al. found that the changes in kinetic parameters of corrosion due to the increase in temperature (10–50 °C) resulted in an increase in corrosion rate up to 20% [11]. A study at temperatures between 20 °C and 70 °C by Hussain et al. showed that the chloride concentration threshold value for the onset of reinforcement corrosion decreased strongly when the temperature increased [12]. Lopez et al. measured the corrosion rate of steel in mortar samples after one year of exposure to 0 °C, 30 °C and 50 °C at different relative humidities, i.e. saturated, 90% and 50%. Results of their work showed active corrosion in specimens stayed at 50 °C and passive state for specimens kept at 0 °C and 30 °C, regardless of humidity

condition [13]. Results from Ruan et al.'s study indicated that exposure of steel to high temperatures increased its corrosion activity in the alkaline environment of concrete pore solution [14]. Their results showed that cooling method had a minor impact on the amount of mass loss in specimens exposed to 200 °C and 500 °C. However, in severe exposure condition (850 °C), the water cooled specimens lost approximately 40% more mass compared to that in the air cooled specimens [14].

All the abovementioned studies clearly showed the adverse impact of the temperature on the corrosion of metals, including corrosion of steel bars in concrete. Nonetheless, to the best of the author's knowledge, there is no study on the impact of temperature on the formation of the passive layer on carbon steel in the high alkaline environment of concrete, which is the objective of this work. A wide temperature range from room temperature to 850 °C was used in this work. In addition, two different cooling methods, i.e. water-cooling and air-cooling, were used for all specimens. The impact of these temperatures and cooling methods on the semi-conductive behavior of the passive layer was investigated. The thickness of the passive layer was also estimated from the electrochemical impedance spectroscopy experiment and the microstructure of the steel specimens was studied.

## 2. Experimental procedures

### 2.1. Steel specimens

All steel specimens were prepared from a #4 ( $\phi = 0.5$  in. = ~12.7 mm) structural steel bar, meeting the requirements of ASTM A615 [15]. Specimens with a length of 101.6 mm (4 in.) were cut and

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exposed to different degrees of high temperatures and cooled at different rates. Then, the surface of each specimen was cleaned by wire brush. One end of the specimen was epoxy coated to the length of 25.4 mm (1 in.) and 25.4 mm left uncoated; then another 25.4 mm coated with epoxy. Epoxy coating provided a 25.4 mm (1 in.) exposure length and prevented extraneous effects. Concrete pore solution, with the composition given in [16] with a pH of 13.1 was used to simulate the concrete environment. For each temperature and cooling method, a container with three identical steel specimens was prepared. The specimens were immersed in pore solution and the container was sealed to minimize carbonation.

## 2.2. Elevated temperatures and cooling methods

To simulate exposure of steel to different temperatures, from mild to severe; naive heating and cooling steps were adapted in this study. The air circulated furnace was programmed to increase the temperature to the target value at the rate of 5 °C/min. After reaching the target temperature, the steel specimens were kept at that temperature for an hour and then removed and cooled to room temperature. Specimens were cooled using two methods: quenched rapidly in water and slowly cooled in the open air. Six different temperatures were used as followings: room temperature (ref), 50 °C, 80 °C, 200 °C, 500 °C, and 850 °C. These temperatures were selected to represent the high ambient temperatures (50 °C and 80 °C) as well as severe temperatures (200 °C, 500 °C and 850 °C) during an accident such as fire or explosion that a concrete structure may experience during its service life [17].

## 2.3. Electrochemical measurements

Due to the nature of the passive films on metals, they usually show electrochemical properties of a semi-conductor [18–25]. The charge distribution at the interface between a semi-conductor and an electrolyte is often determined by measuring the surface capacitance,  $C_{sc}$ , as a function of the electrode potential (E). Mott-Schottky equation shows the relationship between the capacitance and the potential, when the space charge double layer serves as a depletion layer [19,26]:

$$\frac{1}{C_{sc}^2 q N} = \frac{2}{\epsilon \epsilon_0} \left( E - E_{fb} - \frac{kT}{q} \right) \quad (1)$$

where N represents the donor ( $N_D$ ) or acceptor density ( $N_A$ ),  $\epsilon$  is the dielectric constant of the passive film,  $\epsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12}$  F/m), q is electron charge of an electron (+e for electron, -e for vacancy,  $e = 1.602 \times 10^{-19}$  C),  $E_{fb}$  is the flat band potential, k is

the Boltzmann constant ( $k = 1.38 \times 10^{-23}$  J/K) and T is the absolute temperature.  $N_D$  and  $N_A$  can be determined from the slope of the experimental  $1/C_{sc}^2$  vs. E plots and the extrapolation for  $1/C_{sc}^2 = 0$  is used to find  $E_{fb}$ . In this study, the Mott-Schottky plots were acquired at 1000 Hz, in the polarized potential range of -1.0 V to +0.4 V versus the reference electrode, with a perturbing AC signal of 10 mV.

EIS was also used to study the passivation process and the capacitive properties of the passive layer were extracted from the results of this test and used to estimate the thickness of the passive layer formed on the surface of steel treated at different temperatures and cooling conditions. EIS measurements were carried out using a 5 mV alternating potential perturbation over the frequency range from  $10^3$  Hz to  $10^{-4}$  Hz.

## 2.4. Microscopic analysis

One specimen in each group (not exposed to pore solution) was prepared for microscopic analysis. A 10 mm piece of each specimen was cut by a high precision saw and mounted into a low shrinkage epoxy resin. Then each specimen was grounded and polished to 1  $\mu$ m. To reveal the microstructure of the specimens, after polishing, they were cleaned and etched in 1% Nital solution.

## 3. Results and discussions

Fig. 1 shows the Mott-Schottky plots, after 168 h exposure to the pore solution. As can be seen, the slopes of the plots were positive, indicating the properties of n-type semi-conductors. The slopes for the specimens exposed to elevated temperatures were lower than those for the reference specimens for both air- and water-cooled conditions. While no clear trend was observed among different temperatures for air-cooled specimens (except for 850 °C), the decrease in the slope was proportional to the increase in temperature in the water-cooled specimens. In both cases (air- and water-cooled) the smallest slope belonged to the 850 °C specimens, indicating a thinner space-charge layer and consequently a weaker passive layer compared to the other specimens.

The donor densities versus time obtained from the Mott-Schottky plots (measured every 24 h) are shown in Fig. 2. The density of current-carrying components in the passive layer was increased up to 24 h and then started to decrease. This observation can be attributed to the formation of the passive layer within the first 24 h after exposure to the pore solution. When the passive layer formed, the conductivity of the surface decreased which led to the decrease of the donor density after 24 h. This corresponded well to the previously determined time of passivation [16]. In all specimens, the slopes of the graphs were slightly negative, suggesting strengthening and growth of the passive

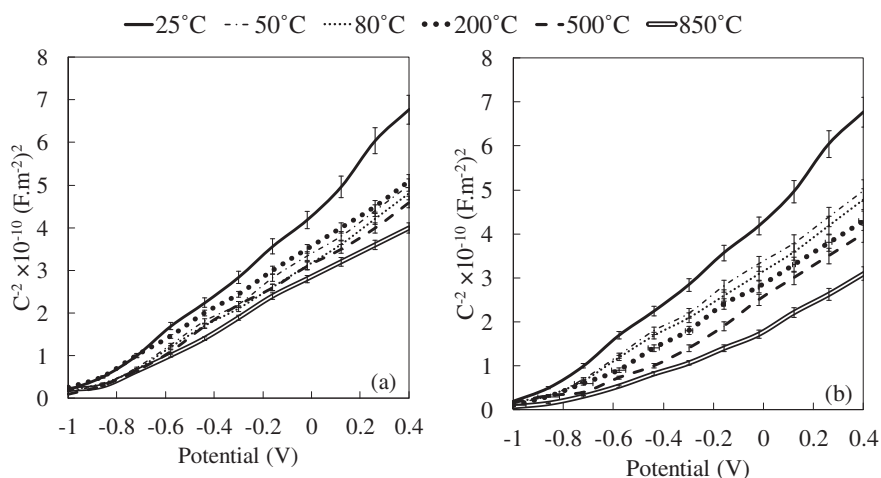


Fig. 1. Mott-Schottky plots, 168 h after immersion in the pore solution for (a) air-cooled specimens and (b) water-cooled specimens. The error bars indicate the standard deviation for the three specimens.

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