Journal of Electroanalytical Chemistry 736 (2015) 38–46

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Electrochemical characterization of mild steel in alkaline solutions simulating concrete environment

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ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 13 October 2014
Accepted 19 October 2014
Available online 28 October 2014

Keywords:
Mild steel passivation
Cyclic voltammetry
Electrochemical characterization
Simulated concrete pore solutions

ABSTRACT

The majority of the studies on corrosion mechanism and protection of reinforcing steel bars are performed in alkaline solutions simulating the concrete environment, thus avoiding the complications related to the preparation of representative reinforced concrete samples. In this work the electrochemical behavior of B450C mild steel was studied in saturated $Ca(OH)_2$ solution by cyclicvoltammetry. Comparison with the electrochemical response in 1 M NaOH was also carried out, being such electrolyte the most commonly used for iron passivation studies. Results confirm the coexistence of two main processes, one leading to $Fe(OH)_2$ and the following (reversible) to Fe(III) oxo-hydroxides. The latter appears more relevant to the growth of a protective layer and in turn strictly connected to the operative condition of the cyclic voltammetry. The influence that time has on the passive film growth was then investigated by means of anodic polarization and electrochemical impedance spectroscopy. All the results indicated that at least three days of immersion in $Ca(OH)_2$ are required to guarantee the stabilization of the electrochemical response, thus leading to a protection similar to that observed with reinforced concrete.

1. Introduction

It has been widely recognized that deterioration of reinforced concrete structures is a serious issue, strongly affecting the durability and the service life of civil structures. Structural damages result in enormous economic loss due to extremely high maintenance and repair costs [1,2]. In the United States, the costs of repairing buildings and bridges are estimated to be around $150 million per year. Among the different causes leading to concrete structure deterioration, reinforcing bar corrosion is by far the most frequent and significant, counting roughly for the 80% of the cases [3]. In sound concrete, due to the high alkalinity of the interstitial solution ($pH \approx 13$), reinforcing bars result to be covered by a protective oxide layer that, as clearly indicated by the iron Pourbaix diagram, is able to maintain the metallic surface in the passive state for the whole domain of water stability [4]. The most common causes for the transition to an active behavior are an overall pH decrease due to carbonation, which leads to generalized corrosion, or the ingress of aggressive species such as chlorides, which leads to localized attack [4,5].

The long time necessary for chloride penetration, or for complete carbonation of the concrete cover, together with complications related to the production of representative reinforced mortar samples, can be avoided by using alkaline solutions simulating the concrete environment. Sound concrete is generally simulated with alkaline solutions such as aqueous NaOH, KOH or $Ca(OH)_2$ [5,6]. Among the various possibilities, saturated $Ca(OH)_2$ seems to be the most used solution for such a purpose [4–10]. Different quantities of chlorides can be added to such solutions to study the onset of a localized attack, while a carbonated environment is usually simulated using a sodium carbonate/bicarbonate buffer of pH around 10 [4,5].

The most studied passive Fe/electrolyte systems are Fe in borate buffer (pH 8.4) [11–13], and in 1 M NaOH or KOH [14–19]. In the open literature referring to concrete simulation, there appears to be lack of in-depth electrochemical characterization of steel in saturated $Ca(OH)_2$ solution, which prompted us to systematically investigate the electrochemical behavior of mild steel in such solution.

With respect to the passive behavior of iron in alkaline solutions, results are sometimes controversial, and the nature of the passivating layer is not unambiguously established. However, it is well accepted that anodic oxidation of iron in alkaline solution implies at least two steps. First, iron is converted to $Fe(OH)_2$ and then, different oxy-hydroxy Fe(III) species are formed. More recent works have investigated the structure of the oxide film, pointing out the presence of a denser inner layer formed by mixed iron

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http://dx.doi.org/10.1016/j.jelechem.2014.10.023
1572-6657/

oxides like magnetite (Fe_3O_4), overlapped by an outer hydrous (FeOOH) gelatinous layer, which confers passivity to the metallic substrate [20,21].

According to [22], electrochemical steady state measurements on iron in alkaline media are relatively difficult and scarcely reproducible. In the present work, a non-steady-state technique such as cyclic voltammetry was used to characterize the behavior of B450C mild steel immersed into a saturated $Ca(OH)_2$ solution.

As steel bars are embedded in concrete to produce reinforced samples, a curing time (generally 28 days) is needed for complete hydration of the cement. This implies that the steel surface remains in contact with an alkaline environment for a long time, which allows the growth of a protective layer. Accordingly, in the present work we decided to investigate the influence of the passivation time on the electrochemical response of metallic samples immersed in the alkaline solution. In the open literature there is no consensus on the time necessary to obtain the growth of a representative oxide layer, so much that different authors use times ranging from half an hour to several days [4,5,7,23]. The stabilization of the electrochemical response, being related to the growth of a stable and protective oxide layer, was investigated by means of open circuit potential monitoring, linear polarization resistance, potentiodynamic anodic polarization and electrochemical impedance spectroscopy.

2. Experimental

2.1. Materials and testing environment

Tests were carried out with 8 mm diameter B450C mild steel reinforcing bars with chemical composition: C 0.22%, Cr 0.13%, Ni 0.15%, Mn 0.78%, Mo 0.03%, N 0.007%, Si 0.24%, Cu 0.56%, S 0.039%, P 0.013%. Bars were purchased from Feralpi Group (Lonato, Brescia, Italy).

Small specimens were produced by cutting samples of 15 mm length that were subsequently embedded into a thermoplastic resin leaving a 0.6 cm^2 cross-section as exposed area. Before embedding, specimens were softly brushed to remove the abundant rust deposits. Electrical connection was realized with a 3 mm diameter AISI 304 threaded rod by drilling a hole at the opposite end of the specimen. Before electrochemical testing, the metallic surface was polished with emery paper from 320 to 1200 grit and ultrasonically degreased in hexane for 10 min.

Test solutions were prepared using NaOH pellets and $Ca(OH)_2$, purchased from Sigma–Aldrich as ACS reagent grade. Saturated $Ca(OH)_2$ solution (pH 12.6) was filtered prior to use.

2.2. Electrochemical experiment setup

All electrochemical measurements were performed using a conventional three electrode cell (electrolyte volume: 300 ml), in which the active steel surface acted as working electrode, a Pt wire as counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. Specimens were mounted into the cell with the working surface facing downwards, thus keeping the electrical connection above the electrolyte level.

Each experiment was repeated at least three times, using a new polished surface each time, to check the reproducibility and reliability of the results. Measurements were carried out at 23 ± 2 °C.

2.2.1. Cyclic voltammetry (CV)

The electrochemical characterization of the growing oxide layer was carried out by cyclic voltammetry at 100 mV/s. Prior to each testing, the electrolyte was deaerated for 30 min by nitrogen bubbling, and a potentiostatic cathodic pretreatment at -1.5 V vs SCE was carried out for 10 min to guarantee uniform surface conditions with reduction of the surface oxides in the hydrogen evolution region [14–17]. The CV was started in the anodic direction from the potential of the cathodic pretreatment .

The electrochemical response to multiple triangular potential waves (CV) was checked over diverse potential windows, the larger being the one including oxygen and hydrogen evolution at the anodic and cathodic limits, respectively.

Correlations between different current peaks were investigated with a systematic variation of the anodic limit ($E_{\lambda a}$). Three cycles were completed before regenerating the surface with 10 min cathodic polarization at -1.5 V vs SCE, switching then to a more anodic limit. The anodic limits ranged from -1.2 to 0.8 V vs SCE [15].

The effect of the oxide film ageing was studied through a set of 1 to 20 min anodic potentiostatic polarization inserted every three voltammetric cycles. Conversely, cathodic potentiostatic polarizations were introduced every three cycles aiming to investigate the response of the passive film to a reductive process.

2.2.2. Potentiodynamic polarization (PD), linear polarization resistance (LPR) and impedance spectroscopy (EIS)

How the passivation time affects the electrochemical response of mild steel was studied by immersing several specimens in saturated $Ca(OH)_2$ for different times. The resulting electrochemical behavior was investigated by OCP and LPR monitoring (measurements performed every 20 min for the first day, and every hour in the following days), and by means of anodic potentiodynamic polarization and electrochemical impedance spectroscopy (measurements performed 0, 4, 24, 48, 72 and 96 h of immersion). Cyclic anodic potential sweeps were performed at the scan rate of 0.1667 mV/s. The same value was used for linear polarizations while corrosion currents were calculated using the Stern-Geary equation: $i_{corr} = B/LPR$, being parameter B a function of the Tafel slopes. In the present work, the B values used for calculations were those suggested by Andrade and Alonso [24], i.e. 26 mV (active behavior) was used for the Tafel parameter in the first 6 h, switched to 52 mV (passive behavior) for all successive measurements. The above described experiments were performed with a PAR 273A potentiostat.

The EIS measurements were obtained with a Gamry potentiostat at the open circuit potential resulting from a five minutes equilibration time in the testing media. The frequency range was 10^5 to 4×10^{-3} Hz, with a logarithmic sweeping frequency of 10 points per decade. The modulation amplitude of potential was 10 mV (rms).

3. Results and discussion

3.1. Cyclovoltammetric characterization

3.1.1. Cyclic voltammetry in 1 M NaOH and saturated $Ca(OH)_2$

The cyclovoltammetric response to a ten cycles perturbation performed in 1 M NaOH at a scan rate of 100 mV/s is reported in Fig. 1(a).

In agreement with literature, the E/I plot exhibits a complex contour which changes with cycling. Starting from the positive forward scan, two small, stable anodic peaks (1 and 2) were detected at -1.1 V and -0.95 V, respectively. Peak 3 (-0.7 V) was characterized by higher currents and a continuous increase in height with cycling. A further interesting feature of peak 3 is its asymmetric shape, being characterized by the presence of a shoulder on the more positive potential side that is commonly referred to as peak 3′. Such shoulder was followed by a wide capacitive region, which extended for about 0.9 V, and ended with a sudden current