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Spatial distribution of crystalline corrosion products formed during corrosion of stainless steel in concrete

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ABSTRACT

The mineralogy and spatial distribution of nano-crystalline corrosion products that form in the steel/concrete interface were characterized using synchrotron X-ray micro-diffraction (μ-XRD). Two types of low-nickel high-chromium reinforcing steels embedded into mortar and exposed to NaCl solution were investigated. Corrosion in the samples was confirmed by electrochemical impedance spectroscopy (EIS). μ-XRD revealed that goethite (α-FeOOH) and akaganeite (β-FeOOH) are the main iron oxide–hydroxides formed during the chloride-induced corrosion of stainless steel in concrete. Goethite is formed closer to the surface of the steel due to the presence of chromium in the steel, while akaganeite is formed further away from the surface due to the presence of chloride ions. Detailed microstructural analysis is shown and discussed on one sample of each type of steel.

1. Introduction

In non-carbonated and chloride-free concrete, embedded steel reinforcement is protected from corrosion by a protective oxide film that forms on the steel surface. However, in less-than-ideal conditions this is not the case. A decrease in concrete alkalinity may cause failure of the stable chemical environment around the steel reinforcement. Also, a rise of the concentration of chloride ions above a threshold value in the vicinity of steel reinforcement may lead to a localised breakage of the passive layer [1]. Once the passive layer is dissolved or broken corrosion is initiated, and a second stage of corrosion starts, i.e., the corrosion propagation period, during which corrosion products are formed on the surface of the steel [2]. These corrosion products are mainly iron oxides and iron oxide–hydroxides, which have a larger specific volume than pure iron. The resulting volume expansion during the build-up of corrosion products creates radial pressure at the steel/concrete interface, leading to concrete cracking and delaminating, and eventually structural instability and failure [3]. Models that consider the radial pressure at the interface between the cement matrix and reinforcing steel – which leads to tensile stresses greater than the concrete tensile strength and thus cracking – take into account properties of concrete (e.g., residual compressive and tensile strength, stiffness, modulus of elasticity) and properties of corrosion products (e.g., rate of formation, depth of penetration into the matrix, volume, and morphology of corrosion products) [4–11]. Due to the critical role that corrosion products play in understanding the propagation of corrosion, cracking and the eventual failure of concrete, several comprehensive studies were performed to characterize the different iron oxides and iron oxide–hydroxides that form during corrosion of carbon steel reinforcement [13–17] and weathering steels [12,18,19]. However, previous studies investigating corrosion products formed on carbon steel reinforcement in concrete [13–16] have not reported the spatial distribution of the crystalline phases in the corrosion products near the steel-cement matrix interface. This information is critical to better understand the corrosion process, the formation of corrosion products, and the generation of stress on the interface leading to concrete cracking.

Nowadays, stainless steels are widely utilized as reinforcement instead of carbon steel, especially when durability due to aggressive environment exposure is a concern. Because of rising nickel prices, however, new types of corrosion resistant steels with lower percentages of alloying elements have been developed, e.g., low-nickel, high-chromium corrosion-resistant steels, which can be a cost-effective corrosion resistant alternative to highly alloyed stainless steels. So far, published research on these types of steel as concrete reinforcement has focused on the corrosion initiation phase, mainly on the characterization of the passive film, and on the critical conditions for the onset of corrosion [20–24]. Long-term research of

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corrosion behaviour of these steels in concrete is very scarce, especially those aiming at evaluating the real-time propagation of corrosion and the formation of corrosion products. Until now, research on laboratory samples and long-term exposure of real concrete reinforced structures to marine environments have shown that, besides longer initiation periods, these steels have a prolonged propagation period (i.e., more time is needed to achieve a certain level of corrosion activity) [25,26]. The available literature on corrosion products formed under the influence of alloying elements concentrates mainly on synthesized iron oxide–hydroxides, created and tested under laboratory-controlled conditions [12,27–31]. These studies have demonstrated that adding specific alloys influences the type of iron–hydroxide phases created during the corrosion process.

The present study aims at determining the type, morphology, and in-situ spatial distribution of the crystalline phases of corrosion products that form during natural (non-accelerated) corrosion of two types of low-Ni, high-chromium Cr corrosion resistant steel embedded in mortar. Reinforced mortar samples were exposed to an aggressive chloride solution for two years, during which their corrosion activity was confirmed by (1) monitoring the corrosion potential and (2) by analysing electrochemical impedance spectra (EIS) at the open circuit potential (E_{OC}). Next, corrosion products formed in the steel–cement matrix interface were analysed with synchrotron radiation to determine their type and distribution relative to the surface of the reinforcement. Using synchrotron-based X-ray micro-diffraction (μ-XRD), two-dimensional maps showing the distribution of crystalline phases with a high spatial resolution were obtained. Besides the μ-XRD used for identification of crystalline phases, X-ray micro-fluorescence (μ-XRF) was also used for elemental mapping to differentiate between corrosion products and the cement paste matrix, thus locating areas of interest (e.g., iron-rich or chromium-rich areas). Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectrometry (EDS) was used for imaging and to determine the chemical composition of recognized corrosion products.

2. Experimental program

2.1. Materials

Two types of low-Ni, high-Cr steel were studied. One of the steels had 10 wt.% Cr (UNS S41008, EN 1.4003) and the other 16 wt.% Cr (UNS S20430, EN 1.4597). Both steels had significantly lower Ni content compared to classical stainless steel (less than 2 wt.%, compared to typical alloyed stainless steel with 8 to 13 wt.%). Table 1 lists their chemical composition. Both tested steels are commercially available on the market as corrugated reinforcing steel, and both were embedded into the mortar as received from the manufacturer. The surface of the reinforcing steels was not additionally pre-treated, with an intention to simulate what would happen during real construction in the case of application of these steels as reinforcement. Production processes of both of the tested steels are protected by the producers. Based on the appearance of the surface of the steel, it could be assumed that 10% wt Cr steel was not pickled, while 16% steel was pickled in the production phase.

The mortar used to embed the steels was prepared using cement CEM I 42.5 (cement without mineral admixture, similar to ASTM cement Type I), with a 0.7 water-to-cement ratio. Crushed limestone with a maximum particle size of 4 mm was chosen as the aggregate. The mortar mix proportion was chosen so that the ratio between constituent materials (water, cement and aggregate) was identical to the concrete labelled C(0.7) according to European standard EN 1766: 2000. In this standard, the preparation of reference concrete is described, which is used to perform comparative tests for evaluating the influence of products and systems for repair and protection of reinforced concrete structures. Therefore, to evaluate the influence of corrosion resistant steel composition on the corrosion behaviour of reinforced concrete and to keep the concrete quality constant for both steel types, a similar mortar to that C(0.7) of known properties was prepared. Corrosion was not accelerated electrochemically; rather, it was allowed to initiate and propagate naturally. To obtain a significant amount of corrosion products in a reasonable time, a mortar with high water-to-cement ratio was used. It is assumed that a better quality concrete would not change the morphology or chemical composition of the corrosion products; however, it would prolong the time to onset of active corrosion, change the properties of the interfacial zone between steel and matrix, and influence the mobility of ions inside the cement matrix. However, since the aim of the paper is to compare two different types of steel in the same mortar mixture, it can be expected that this influence would be similar for both steel types.

The mortar was cured for 28 days in a humidity chamber, with controlled humidity (95% RH) and temperature (20 ± 2 °C). After 28 days, the compressive strength of the mortar was measured as 32.7 MPa. The mortar also showed a low resistance to chloride penetration (non-steady state chloride migration coefficient tested according to NT BUILD 492; measured as 2×10^{-11} m^2 s^{-1}).

2.2. Preparation of the samples

The 14 mm-diameter steel rebar from the selected two different steels were cut into 100 mm-long pieces, providing an approximate steel testing area of 45.5 cm^2 for each segment. A copper wire was welded to the top end of each segment for the electrical connection. The weld was protected with a polyester-based sealing material. This connection was necessary to monitor the corrosion potential and obtain impedance spectra of the steel during the two-year-long exposure of the samples to aggressive conditions that simulated a marine environment. The steel segments were placed into 40 mm-diameter and 140 mm-long plastic moulds and fresh mortar was then placed into the moulds embedding the steel. A special holder for moulds was prepared, consisting of 10 samples. The wire which was connected to the reinforcing steel for electrochemical testing was fixed on the bottom of the holder, to ensure that the steel will stay in the centre of the mould. Once the mortar was placed inside the mould, the mould holder with all samples was placed on a vibrating table to ensure full compaction of the samples. Samples were checked after demoulding, to ensure that there were no visible defects of the samples. Three replica samples were prepared as described and were cured in a humidity chamber for 28 days with controlled humidity (95% RH) and temperature (20 ± 2 °C) and were subsequently partially submerged into a 3.5 wt.% NaCl solution (0.6 mol dm^{-3}). A schematic sketch of the sample assembly is shown in Fig. 1(a). Oxygen penetration was expected to proceed from the upper part of the samples and chloride penetration from the submerged part of the specimen. Based on the corrosion potential

Table 1
Elemental composition of the investigated steels.

Steel type	Elemental composition, wt.%									
	C	Si	Mn	S	N	Cr	Cu	Mo	Ni	Fe
10% Cr steel	≤0.03	≤1.00	≤1.50	≤0.015	≤0.03	10.50	–	–	0.30	*Bal.*
16% Cr steel	≤0.10	≤2.00	7.50	≤0.003	0.15	16.00	2.00	≤1.00	<2.00	*Bal.*