

Passive Layer Development and Corrosion of Steel in Concrete at the Nano-scale

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Editorial

It is necessary to use both electrochemical techniques and advanced nanotechnologies to conduct in depth nano-scale research on; the growth and breakdown mechanisms of passive film in aggressive environments, particularly chloride-laden environments; the correlation between chemical composition and micro/nano structures of the steel substrate and its corrosion resistance; and the adaptation of advanced nano techniques, such as scanning electronic microscopy, x-ray diffraction analysis, energy dispersive x-ray analysis, raman spectrometry, x-ray photo electron spectroscopy and atomic force micro-probing for applications in the surface analysis of corroding steel surfaces. Corrosion usually takes place and degrades material surfaces based on environmental chemistry. There are several popular ways of decreasing corrosion rates to improve the lifetime of materials and devices. As recently determined, some methods may incorporate nanostructured materials processing approaches. These include surface treatment methods, nanocomposite thin film coatings, top layer coatings and thermal barrier coatings. Test results show that the corrosion performance of materials is significantly improved as compared to materials processed using conventional methods. It's lucky for builders that steel and concrete have such an affinity for each other. Concrete contains large amounts of calcium and a small percentage of sodium and potassium ions that maintain a high alkalinity level. Steel exposed to concrete's high alkalinity forms a thin passive film on its surface that resists corrosion. It's the failure of that film that leads to corrosion and deterioration in bridges, buildings, platforms, tunnels and concrete pipes, yet little is understood about what actually happens when the film is disrupted. This editorial aims to find out what's happening when the film breaks down so that methods can be found to preserve and strengthen it. It's a nano-scale layer (a few nano-meters thickness) made up primarily of iron hydroxides.

The temperature dependence of the kinetics of electrode processes and processes of diffusion that take place in the concrete can be to a certain degree expressed by the Arrhenius equation [1]. Because of the complexity of the corrosion process in the concrete, there can be quite a significant deviation from this dependence [2]. It was suggested in the past research [3] that the corrosion current density measured at given field temperature can be adjusted to another temperature using some formulation given in the publication [3], Nishida [4] discussed the deterioration progress of reinforced concrete due to steel corrosion induced by chloride using the data of temperature of various cities in the world. It is well documented [5-8] that presence of chloride ions in reinforced concrete can cause steel to corrode if sufficient oxygen and moisture are present to sustain the reaction. Chloride induced corrosion is the most prevalent and damaging cause of corrosion of steel in concrete.

The mechanism of chloride induced corrosion of steel is not yet fully understood. It is generally believed [9-14] that the chloride ions become incorporated in the passive film, replacing some of the oxygen and increasing both its conductivity and its solubility. It has been suggested that chloride ions can complex with the ferrous ions produced by corrosion to form soluble complexes of iron (II) chloride. The resulting iron chloride complex ion then combines with hydroxyl ions to form $\text{Fe}(\text{OH})_2$ in solution and releases the chloride ions back to solution to complex more iron and thus essentially acts as a catalyst in corrosion reactions. The threshold concentration of chloride ions to initiate corrosion is controversial, because it is dependent on so many factors including quality of concrete (W/C ratio, mixture proportions, type of cement), relative humidity and temperature of the concrete, the pH of the pore solution and sulphate content [15-18]. The value of 0.4% of total chloride ions by weight of the cement is also considered by RILEM [8] as an appropriate threshold. For the typical concrete mixtures normally used in practice, the threshold chloride content is reported to be in the range of 0.60 to 0.83 kg of chloride ions per cubic meter of concrete.

Several nano-techniques are available for analysing materials at the nano-scale level in the present era. However nano-scale investigation of passive layer complete characterization as well as its breakdown and corrosion products formation for reinforced concrete under several environmental actions is yet to be fully explored. Ghosh and Singh [19] used electrochemical impedance spectroscopy (EIS), Raman spectroscopy, Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDXA), XRD studies etc. to study the kinetics and understand the mechanism of formation of hydrozincite (HZ) passive layer at the corroding interface. This study provided techniques for development of an eco-friendly protective passive layer on galvanized coatings prior to their embedding in concrete. Singh and Ghosh [20] also used XRD and SEM along with Electrochemical techniques to carry out the studies related to the role of surface condition (surface having black oxide, brown rust and bright & polished) of thermo mechanically treated (TMT) low carbon mild steel rebars embedded in chloride contaminated concrete mortars on their corrosion resistance.

Abreu et al. [21] used AFM and XPS nano-techniques to study the behavior and evolution of passive films generated on AISI 304L for a long immersion time in chloride containing media. A combination of electrochemical (cyclic voltammetry and electrochemical impedance spectroscopy) and surface analysis techniques including AFM and XPS are used in the work in order to analyze the changes that chlorides induce in those films as immersion time increases. Veleva et al. also used AFM and XPS to study the passive layers grown on AISI 316 stainless steel in solutions that simulate concrete pore environments contaminated with Cl ions. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) techniques have been used by Sanchez-Moreno et al. [22] to study passive layers anodically grown on steel rebars in an aqueous alkaline solution simulating the electrolyte

of the concrete pores. A theoretical impedance function was deduced by Alonso et al. [23] for a proposed mechanism of passive film formation of steel in contact with alkaline aqueous media involving two reaction intermediates: mixed oxide with similar stoichiometry to magnetite and Fe(III)-oxides.

Zhang et al. [24] used the multi-sweep cyclic voltammetry to study the corrosion resistance of C⁺Mo dual-implanted H13 steel. The phase formation conditions for corrosion resistance and its effects were researched. The super-saturation solid solution of Me⁺ and C⁺ atoms was formed in Mo⁺C dual implanted steel. Precipitate phase with nanometer size Fe₂Mo, FeMo, MoC, Fe₃C₃ and Fe₇C₃ were formed in dual implanted layer. Abreu et al. [25] studied the growth and evolution of the passive layers formed on the tested electrodes by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy, Scanning Electron Microscopy and X-ray powder Diffraction. These techniques were used for the morphological and chemical characterization of the generated passive films. Olga et al. [26] used AFM and EIS to study the protective properties of three crystalline and one amorphous phosphate films on the surface of a reinforcing steel bar in two different media: alkaline chloride solution and reinforcing concrete, used in the construction of bridges. Accelerated corrosion tests in a neutral salt spray chamber and immersion in a 5% NaCl solution were applied. Poursaei and Hansson [27] used Raman Spectroscopy and LPR techniques to study the corrosion behavior of steel in concrete, mortar and simulated pore solution. They claimed that it is essential to allow enough time for the steel to create a passive layer which was the subject of the study. Evolution of the passive films formed on AISI 304L and duplex stainless steel SAF 2205 in NaOH 0.1M was investigated by Aberu et al. [28] using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS). Special attention was paid to the effect of Mo in the generation of the films. Results point out to the stabilizing effect of the molybdates on the surface of the film, enhancing the formation of a thin layer on the SAF 2205 with a higher Cr/Fe ratio.

Valcarce and Vazquez [29] used SEM imaging to study the effect of chloride and nitrite ions on the passivity of steel in alkaline solutions. Four nitrite dosages were tested, resulting in various nitrite/chloride ratios. The behavior of steel was evaluated on electrodes aged during 1 and 90 days, measuring electrochemical parameters such as the corrosion, pitting and repassivation potentials, the corrosion current density, the weight loss and performing electrochemical impedance spectra. The effect of concrete pore solution composition on the protective properties of the oxide films that form on black reinforcing steel has been experimentally investigated by Ghods et al. [30,31] using anodic polarization and electrochemical impedance spectroscopy (EIS). The tests were conducted on oxide films grown in saturated calcium hydroxide solutions that included different representative amounts of NaOH, KOH, and Ca(SO₄), which are compounds that are commonly observed in most ordinary portland cement concrete types. The influence of stress on passive behaviour of steel bars in concrete pore solution was studied with electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy by Feng et al. [32]. The passive ability of steel decreased as the applied load increased and higher load had much greater influence on passivation than repeated loading of small magnitude. Ghods et al. [30,31] used X-ray photoelectron spectroscopy (XPS) to study the properties of passive oxide film that form on carbon steel in saturated calcium hydroxide solution and the effect of chloride on the film properties. The thickness of the oxide films was determined to be approximately 4 nm

and was not affected by the exposure time. Near the film/substrate interface the concentration of the Fe²⁺ oxides was higher than the concentration of the Fe³⁺ oxides; the layers near the free surface of the film mostly contained Fe³⁺ oxides. Chloride exposure decreased the thickness of the oxide films and changed their stoichiometry such that near the film/substrate interface Fe³⁺/Fe²⁺ ratio increased. Oxide film thickening on reinforcement steel at early stage of formation is followed in naturally aerated Ca(OH)₂ solutions, recalling the natural behaviour in concrete, by measuring the open-circuit potential with time up to 4 hours. The final potentials are reached from negative values indicating oxide film growth. The rate of oxide film thickening decreases by increasing the concentration and pH of the solution and by raising the temperature [33]. However, nano-scale investigation of the above for the various stages of the development of passive layer remained as scope for future research. Also, the above studies need to be carried out also in simulated concrete pore solution in addition to the saturated calcium hydroxide solution. It is known that solid calcium hydroxide may act to inhibit chloride induced corrosion of steel in concrete. This hypothesis was extended by Glass et al. [34]. But, the nano-scale verification of this phenomenon is also yet to be accomplished.

Shortcomings in the Previous Research

As can be seen from the above literature review, several advanced nano-techniques have been employed in the past for the study of different complex aspects of corrosion in steel. However, little information is available on the actual original passive film developed on steel rebars and its deterioration mechanism at the nano-scale level. In view of the above literature review, the following shortcoming can be depicted:

- Passive film formed of steel rebars in concrete is believed to be a few nanometres thick and primarily composed of iron oxides and hydroxides. However, little is known about the accurate chemical composition and the structure of the passive film itself.
- Although the role chlorides play in inducing corrosion is well understood (through competing with hydroxide ions, which stabilize the passive film), the adverse interactions between chlorides and the passive film are unclear. It is believed that the chlorides disrupt the passive film, reduce the pH level of the pore solution or serve as a catalyst for oxidation. Empirical observations have found when chlorides reach a certain critical concentration, the passive film is damaged and corrosion is accelerated.
- The limited understanding of passive film and the associated depassivation and corrosion mechanism is primarily due to the fact that corrosion is a complex electrochemical reaction between steel and concrete which is complicated further by environmental exposure conditions. This makes it difficult to characterize corrosion, evidenced by the fact the chloride threshold value of steel measured by conventional electrochemical techniques can vary greatly.
- While electrochemical techniques measure corrosion on a macro scale, the growth and deterioration of passive film actually takes place on the nano-to-micro scales and is governed by the elemental compositions and nano-microstructure of the steel as well as the chemistry of the concrete pore solutions. To address this, nanotechnology can be used as an advanced tool to obtain a more precise characterization of passive film in terms of nano-microstructural material properties.

- It is critical to apply both electrochemistry and nanotechnology to establish a quantitative relationship between the governing factors and the durability of passive film. This in turn will lead to better corrosion assessment, more precise characterization of corrosion resistance of steel and, eventually, better predict the service life and lifecycle performance of concrete structures.
 - It is necessary to use both electrochemical techniques and advanced nanotechnologies to conduct research on: the growth and breakdown mechanisms of passive film in aggressive environments, particularly chloride-laden environments; the correlation between chemical composition and micro/nano structures of the steel substrate and its corrosion resistance; and the adaptation of advanced nano techniques, such as scanning electronic microscopy, atomic force micro-probing, for applications in the surface analysis of corroding steel surfaces.
 - Corrosion usually takes place and degrades material surfaces based on environmental chemistry. There are several popular ways of decreasing corrosion rates to improve the lifetime of materials and devices. As recently determined, some methods may incorporate nanostructured materials processing approaches. These include surface treatment methods, nano-composite thin film coatings, top layer coatings and thermal barrier coatings. Test results show that the corrosion performance of materials is significantly improved by the use of above techniques in comparison to materials processed using conventional methods. However, more research is needed in this area at the nano-scale.
 - While the mechanisms of steel corrosion are well understood, the deterioration of the protective film is not. If reinforcing steel is removed from the concrete, it no longer displays the same characteristics it displayed when bonded to concrete. When the sample is removed, one changes its environment and alters its properties.
 - The influence of ambient condition of high temperature and temperature variation on the passive layer has not been explored.
 - There is a difference of opinion and conflict in the results obtained by researchers in the past using different nano-techniques which needs to be either clarified or verified.
- Effect of high temperature/temperature variation on the passive layer and the corrosion reaction.
 - Determination of corrosion potential for various steel sources available around the world under the effect of local harsh environment involving chloride ions and hot weather conditions.
 - Development of empirical relations between macro scale (half-cell corrosion potential), micro scale (steel chemistry, chloride and temperature) and nano scale (chemical composition and thickness of passive layer) variables.
 - Clarify and/or verify the difference of opinion and conflict in the results obtained by researchers in the past using different nano-techniques for the same sample.

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Scope for Future Research

The above editorial summarized the shortcomings in the present knowledge regarding the actual original passive film developed on steel rebars and its deterioration mechanism at the nano-scale level. Most of these points should be considered in the future research as outlined below:

- Determination of accurate chemical composition and microstructure of passive layer especially for locally available steel in different areas of the world and its comparison.
- Role of steel chemistry and microstructure on the development and breakdown of passive film.
- Investigation of various stages during the formation and development of passive layer.
- Comparison of passive layers developed in different pore solution environments.
- Reaction of Cl⁻ ions with the passive layer in different concentrations and determination of the dividing line concentration.
- Accurate quantitative characterization of the effect of ions in the pore solution on the passive layer and the corrosion reaction.

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