

Multi-Scale Investigation of the Formation and Breakdown of Passive Films on Carbon Steel Rebar in Concrete

The multi-scale investigation presented in this thesis was carried out to understand better the mechanisms of passivation and chloride-induced depassivation of carbon steel reinforcement in concrete. The study consisted of electrochemical experiments (electrochemical impedance spectroscopy, linear polarization resistance, free corrosion potential, anodic polarization), microscopic examinations (scanning electron microscopy, transmission electron microscopy, selected area diffraction, convergent beam electron diffraction), numerical modeling (finite element method), and spectroscopic studies (x-ray photoelectron, energy dispersed x-ray, electron energy loss).

Electrochemical and microscopic studies showed that the composition of the pore solution and the surface conditions of the rebar affect the passivity and depassivation of carbon steel in concrete. It was demonstrated that crevices between mill scale and steel may become potential sites for depassivation and pit nucleation. The numerical investigation that was carried out to test this hypothesis confirmed that the ratio of chloride to hydroxide concentrations, Cl^-/OH^- , in crevices increased to levels higher than that of the bulk pore solution, making crevices more vulnerable to depassivation. Therefore, it was concluded that the variability associated with reported chloride thresholds might be attributed, at least in part, to the variability in mill scale properties resulting from the variability in manufacturing.

The nano-scale microscopic and spectroscopic studies indicated the formation of 4-10 nm-thick passive oxide films on carbon steel in simulated concrete pore solutions, and these films consisted of two layers separated with an indistinct border. The inner layer was mainly composed of protective Fe^{2+} -rich oxides that are in epitaxial relationship with the underlying steel surface; while the outer layer mostly consisted of (possibly porous) Fe^{3+} -rich oxides, through which chlorides can penetrate. It was proposed that, in the presence of chlorides, Fe^{2+} -rich oxides in the inner layer transform into Fe^{3+} -rich oxides and potentially become un-protective. Although how this transformation occurs is still subject of future research, there are evidences showing that the process most likely leads to the formation of local anodic and cathodic sites on the steel surface.

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