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Chloride-induced corrosion mechanism and rate of enamel- and epoxy-coated deformed steel bars embedded in mortar

Fujian Tang [a], Genda Chen [a,*], Richard K. Brow [b]

[a] Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO 65409-0030, United States
[b] Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65401, United States

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ABSTRACT

The chloride-induced corrosion mechanisms of uncoated, pure enamel (PE)-coated, mixed enamel (ME)-coated, double enamel (DE)-coated, and fusion bonded epoxy (FBE)-coated deformed steel bars embedded in mortar cylinders are investigated in 3.5 wt.% NaCl solution and compared through electrochemical tests and visual inspection. Corrosion initiated after 29 or 61 days of tests in all uncoated and enamel-coated steel bars, and after 244 days of tests in some FBE-coated steel bars. In active stage, DE- and FBE-coated steel bars are subjected to the highest and lowest corrosion rates, respectively. The uncoated and ME-coated steel bars revealed relatively uniform corrosion while the PE-, DE-, and FBE-coated steel bars experienced pitting corrosion around damaged coating areas. Due to the combined effect of ion diffusion and capillary suction, wet–dry cyclic immersion caused more severe corrosion than continuous immersion. Both exposure conditions affected the corrosion rate more significantly than the water–cement ratio in mortar design.

1. Introduction

Reinforced concrete (RC) structures are often exposed to a variety of environmental conditions that lead to structural deterioration and service life reduction. For example, corrosion in reinforcing steel bars is one of the most severe forms of deterioration in transportation infrastructure. In general, the life span of corrosion-affected concrete structures with uncoated reinforcing steel bars can be divided into three stages [1]. Stage I represents the healthy state of RC structures from the completion time of new construction to the initiation of corrosion. This stage is controlled by the diffusion of carbon dioxide or aggressive ions such as chloride through the concrete cover, which mainly depends on thickness of the concrete cover, concrete permeability, and the concentration of aggressive ions on the concrete surface [2–4]. Stage II represents the damage state of the structures from the initiation of corrosion to the end of serviceability. The end of serviceability can be defined to correspond to the code-specified critical concrete crack width or delamination or the predetermined deflection design criterion associated with corrosion-induced reduction in stiffness. Stage II is controlled by the corrosion rate of reinforcement steel, which largely depends on environmental factors (temperature, moisture, and oxygen) and the characteristics of concrete materials (thickness and permeability) [5–7]. Stage III represents the safety state of the structures from the end of serviceability to the ultimate failure [8–11]. The ultimate failure due to corrosion can occur in several modes, including losses of flexural and shear strengths as a result of a cross sectional reduction of reinforcing steel. This stage is primarily controlled by environmental factors since the reinforcing steel is directly exposed to the environment through corrosion-induced cracks in the concrete cover.

Despite imperfections due to intrinsic defects and extrinsic damage induced during transportation and handling, protective coating is still one of the most effective and economic techniques to prevent steel from corrosion in RC structures. In our previous study [12], the corrosion mechanisms of deformed steel bars coated with three types of enamel and fusion-bonded epoxy (FBE) were investigated after immersion in 3.5 wt.% NaCl solution. The enamel coatings improved the corrosion resistance of the steel bars to various degrees, depending on their damage and uniformity. Electrochemical tests were also conducted to study the effect of enamel coatings on the corrosion resistance of smooth steel bars embedded in mortar cylinders [13] and indicated that the corrosion performance of enamel-coated smooth bars was significantly better than that of enamel-coated deformed bars. However, deformed instead of smooth steel bars are widely used in RC structures, and the influence of water–cement (w/c) ratio, exposure condition, the coating damage induced during transportation, and the types of corrosion attack related to different coatings is of great interest to engineering applications. More importantly, the influence of enamel coatings on the service life of RC structures especially in the first and second stages has not yet been investigated.

The aim of this study is to investigate the short- and long-term corrosion performance of uncoated, enamel-coated, and FBE-coated

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* Corresponding author at: Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology, 328 Butler-Carlton Hall, 1401 N. Pine Street, Rolla, MO 65409-0030, United States.
E-mail address: gchen@mst.edu (G. Chen).

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Table 1
Chemical composition of alkali borosilicate glass frits.

Element	SiO_2	B_2O_3	Na_2O	K_2O	CaO	CaF_2	Al_2O_3	ZrO_2	MnO_2	NiO	CoO
wt.%	44.0	19.3	15.8	2.8	0.1	4.7	4.6	5.3	1.5	1.0	0.9

deformed steel bars embedded in mortar specimens immersed in 3.5 wt.% NaCl solution. In particular, the effect of coatings on the initiation of steel corrosion is quantified. Open circuit potential and electrochemical impedance spectroscopy (EIS) were conducted approximately every month up to 244 days to monitor the evolution of corrosion especially during the transition from the passive to active state. At the end of immersion tests, potentiodynamic polarization test and visual inspection were performed to further characterize the type and rate of corrosion attack related to different coatings. Effects of w/c ratio and exposure condition on the chloride penetration in mortar, open circuit potential, and impedance over time were assessed.

2. Material and methods

2.1. Preparation of enamel coatings and cylindrical specimens

Enamel is a silicate-based material that can be deposited on steel bars by firing at high temperature after dipping in enamel slurry. The enamel slurry is made by milling glass frits, clay, and certain electrolytes, and then mixing them with water to provide a stable suspension. In this study, three types of enamel are investigated: pure enamel (PE), mixed enamel (ME), and double enamel (DE). The PE is a commercially-available alkali borosilicate glass frit from PEMCO (Product No. PO2025), and its chemical composition is given in Table 1. The ME is a mixture of 50% PE and 50% calcium silicate directly taken from the Type I Portland cement by weight, which is designed to enhance its bond strength with surrounding concrete by increased surface roughness and chemical adherence. The DE has an inner PE layer and an outer ME layer, which is designed to increase the corrosion resistance of coated steel bars through the inner PE layer and enhance its bond strength with concrete through the outer ME layer. The PE slurry was prepared by mixing water, alkali borosilicate glass frits, clay and borax in a proportion of 1.00:2.40:0.17:0.01 by weight. Alkali borosilicate glass frits was first added to water and mixed for 20 min. Clay and borax as suspension agents were then added and mixed again for 3.5 h. The ME slurry was made following the same procedure as the PE slurry except that calcium silicate was added to the glass frits.

In this study, deformed steel bars (12.7 mm in diameter) were used. Their chemical composition was analyzed and presented in Table 2. Before coating, all steel bars were sand-blasted and cleaned with commercially available cleansing solvent. For the PE and ME coatings, the cleaned bars were dipped into their corresponding slurry and heated for 2 min. at 150 °C to drive off moisture, then fired at 810 °C for 10 min., and finally cooled to room temperature. For the DE coating, the steel bar was first dipped into the PE slurry and heated for 2 min. at 150 °C to drive off moisture, then dipped into the ME slurry and heated to 150 °C again to drive off moisture, finally moved into a furnace to fire at 810 °C for 10 min. The firing treatment at high temperature was used to melt the glass frits and chemically bond the enamel to the steel. For comparison, both uncoated (as-received) and commercial FBE-coated steel bars were also prepared and tested.

Mortar was prepared using a mixture of cement, fine aggregate and water. Type I Portland cement as specified in Table 3 and Missouri River sands with a maximum size of 6.35 mm and a fineness modulus of 2.80 were used in this study. Two w/c ratios were considered in the batch design as given in Table 4.

Cylindrical mortar specimens were prepared as shown in Fig. 1. Each specimen was 114.3 mm tall and 38.1 mm in diameter with one concentrically embedded 88.9 mm long steel bar that is uncoated, enamel-coated, or FBE-coated. A copper wire was welded to the top end of the bar to provide an electrical connection. To force the corrosion activity in the middle portion of the steel bar and avoid any potential crevice corrosion at the two ends, each end of the bar was encased in a PVC tube filled with epoxy resins. Therefore, the actual length of steel bar potentially exposed to the corrosive environment was approximately 50.8 mm with a surface area of approximately 20.3 cm^2. The clear cover of mortar around the exposed portion of the steel bar was 12.7 mm.

To cast each specimen, a PVC pipe with a nominal inside diameter of 38.1 mm was used as a mold. The PVC mold and the steel bar were held in place by pre-cut grooves on a bottom plywood sheet. To ensure a proper consolidation, each mortar specimen was cast in three layers, each compacted 25 times with a 6.35-mm-diameter steel rod and tapped 15 times with a small rubber mallet on the PVC mold to close potential voids generated during each rodding/compaction. All specimens were de-molded after 24 h., moved to the curing room, and cured at 20 °C and 100% relative humidity for 28 days prior to testing. Three specimens were prepared for each condition to understand the variability of test results.

To investigate chloride penetration through mortar over time, additional mortar cylinders without steel bars were prepared at the same time when the cylinders with one steel bar each were cast. All the cylinder specimens were cured under the same condition.

2.2. Thickness, porosity and surface damage of coatings

The coating microstructure such as thickness, porosity, and surface damage are directly related to the corrosion protection of coating, and thus must be characterized for a better understanding of their effects on the corrosion of steel bars. The coating microstructure was investigated by scanning electron microscopy (SEM, Hitachi S4700). After 28 day curing, one mortar specimen of each type was cross-sectioned using a diamond saw, and then abraded using a series of silicon carbide papers to 1200 grit. After abrading, the sample was rinsed with deionized water and dried for SEM study. The surface damage of coated steel bars induced during transportation was quantified using the image analysis software “ImageJ” prior to mortar casting.

Fig. 2 shows cross-sectional SEM images of the mortar-steel interface of a representative specimen with uncoated steel bar, and the mortar-coating-steel interfaces of specimens with enamel- and FBE-coated steel bars. These images were taken between two ribs on the deformed bars where the enamel coatings are relatively uniform and thick in comparison with those areas over the ribs. Fig. 2a clearly indicates a thin porous oxide layer approximately 30 μm thick between the mortar and the uncoated steel bar, which is the mill scale formed on the steel surface. As shown in Fig. 2b, the PE coating is approximately 150 μm thick and has many small air bubbles (25 μm in diameter) and few large air bubbles (100 μm in diameter), which are generated from the oxidation–reduction reaction of enamel with the steel during the enameling process such as [14,15]:

$$Fe + H_2O\uparrow = H_2\uparrow + FeO \tag{1a}$$

Table 2
Chemical composition of steel bars.

Element	C	Si	Mn	P	S	Cr	Mo	Ni	Co	Cu	V	Sn	Fe
wt.%	0.38	0.18	1.00	0.12	0.06	0.10	0.07	0.20	0.01	0.37	0.02	0.03	97.40