Electrochemical behavior of enamel-coated carbon steel in simulated concrete pore water solution with various chloride concentrations

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ABSTRACT

The electrochemical behavior of enamel coated carbon steel in simulated concrete pore water solution with various chloride concentrations was investigated by open circuit potential, linear polarization resistance, and electrochemical impedance spectroscopy tests. The phase composition, microstructure, and tensile strength of enamels were characterized by X-ray diffraction, scanning electron microscopy, and pull-off tests. Three types of coatings with pure, mixed, and double enamels were studied and compared for their corrosion behavior. Test results indicated that all three types of enamel coatings can reduce the corrosion current density of carbon steel in an alkaline environment with chloride; the pure and double coatings are superior to the mixed enamel coating. Cohesive failures were observed within the three coatings while their interface with the steel substrate remained intact. In comparison with the pure enamel, the mixed enamel was stronger with smaller open channels formed due to the addition of calcium silicate and the double enamel was weaker with larger air bubbles trapped in the inner pure enamel layer by the outer mixed enamel layer.

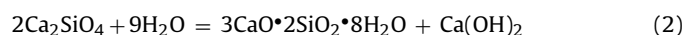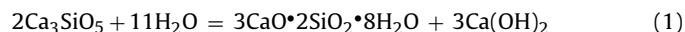© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Enamel coatings have been widely used to protect metals or alloys from corrosion due to their strong adherence to the substrate and chemical stability in various environments, including acid, alkaline, high temperature, and harsh working conditions [1,2]. Enamel-coated carbon steel has long been used for chemical reactors, heat exchangers, and food-processing vessels in industry as well as cookware in domestic applications. Commercial enamel is a silica-based glass-forming material containing various oxides to obtain optimum properties for specified applications. The enamel is typically fused to the substrate metal at temperatures between 750 °C and 850 °C. The properties of an enamel can be controlled either by adjusting its composition [3]. For example, acid resistance is improved by increasing the SiO_2 content and reducing B_2O_3 and BaO; water resistance is increased by adding TiO_2; alkaline resistance is improved by adding ZrO_2 [4]; adherence to substrate metals is increased by adding CoO and NiO [5]; and the hardness of coating is improved by crystallization treatment [6].

Recently, a number of studies have been performed at Missouri University of Science and Technology to investigate the performance of enamel as a coating material applied on reinforcement steel to (i) reduce the corrosion rate [7,8] and (ii) enhance the bond strength with steel and surrounding concrete [9,10]. Three types of enamel coatings were investigated including pure enamel (PE), mixed enamel (ME) and double enamel (DE). The PE is a commercially available product (PEMCO International) and used as a benchmark in this study. This enamel formulation was selected because it contains ZrO_2 for improved durability in alkaline environments, and NiO and CoO for increased adherence with steel substrates. The ME is a mixture of 50% PE with 50% calcium silicate by weight. Calcium silicate was added to improve the adherence of enamel-coated steel to concrete. The inter facial transition zone between the concrete and steel rebar has traditionally been a weak link due to bleed water and lack of small cement particles in the shadow of the concrete aggregates [11]. Our previous studies showed that an average increase of approximately 15% in bond strength was observed for deformed steel rebar in concrete and as much as a seven times increase in bond strength for smooth steel rods in mortar in comparison with uncoated rods [9,10]. The DE has an inner PE layer and an outer ME layer; it was developed to enhance the corrosion resistance of steel rebar by the inner layer and increase the bond strength of steel rebar with surrounding concrete by the outer layer.

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For deformed steel rebar tested in 3.5 wt.% NaCl solution, all three enamel coatings can reduce the corrosion rate of the steel by 12–20 times [7] even though the coating thickness on the surface of deformed rebar was non-uniform due to the rebar deformations and limitations in the chosen fabrication process. For smooth steel rebar in mortar cylinders tested in 3.5 wt.% NaCl solution, the PE and DE coatings can reduce the corrosion current density of the steel rebar by 50 and 360 times, respectively; the ME coating only reduced the current density by three times [8]. However, due to the influence of mortar cover, particularly with its non-homogeneity and diffusion behavior, both the coating properties and the coating/steel interface properties could not be accurately evaluated particularly for DE-coated samples. Moreover, the thickness of enamels applied on the smooth steel rebar was relatively thin due to curvature effects, making it difficult to compare the properties of the three enamel coatings.

To avoid the complexity involved in mortar or concrete, saturated $Ca(OH)_2$ solutions often have been used to simulate the alkaline environment of concrete pore water [12–14] because $Ca(OH)_2$ is the main product from the hydration process of cement as follows [11]:

$$2Ca_3SiO_5 + 11H_2O = 3CaO \bullet 2SiO_2 \bullet 8H_2O + 3Ca(OH)_2 \qquad (1)$$

$$2Ca_2SiO_4 + 9H_2O = 3CaO \bullet 2SiO_2 \bullet 8H_2O + Ca(OH)_2 \qquad (2)$$

Therefore, in the present study, the electrochemical properties of enamel coatings applied on structural steel plates (instead of reinforcing bars tested previously) are studied in saturated $Ca(OH)_2$ solution with different chloride concentrations. First, the phase compositions of the three different enamel coatings and the morphologies of the coatings and the coating-steel interfaces were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Second, the tensile strength of each enamel coating was determined with direct pull-off tests. Third, the effects of enamel coating uniformity and thickness on the corrosion behavior of steel are investigated by comparing the electrochemical tests of steel plates in this study with those of deformed steel rebar [7]. Fourth and last, the influence of corrosion environments on the electrochemical properties of three enamel coatings is studied by comparing the tests of steel plates in simulated concrete pore water solution in this study with those of smooth steel rebar in mortar [8].

2. Experimental

2.1. Preparation of enamel coatings and test samples

Carbon steel plates, 76.2 mm × 38.1 mm in size and 3.18 mm in thickness, were used in this study. The chemical composition by weight is: 0.27% C, 0.28% Si, 1.03% Mn, 0.05% S, 0.03% P, and the balance Fe. The plates were coated by Pro-Perma Engineered Coatings with three types of enamel (PE, ME, and DE). Prior to coating, all steel plates were sand-blasted and cleansed with a commercially available cleansing solvent.

The commercially available alkali borosilicate glass frit (PEMCO International) was used to prepare the PE coating [15], and its chemical composition is given in Table 1. The PE slurry was made by first adding 454 kg of glass frit into 189.3 liters of water and mixing them for 20 min, and then adding 31.8 kg of clay and 2.3 kg of borax as suspension agents and mixing again for 3.5 h. The ME coating was obtained by adding 50% calcium silicate to 50% of the alkaline
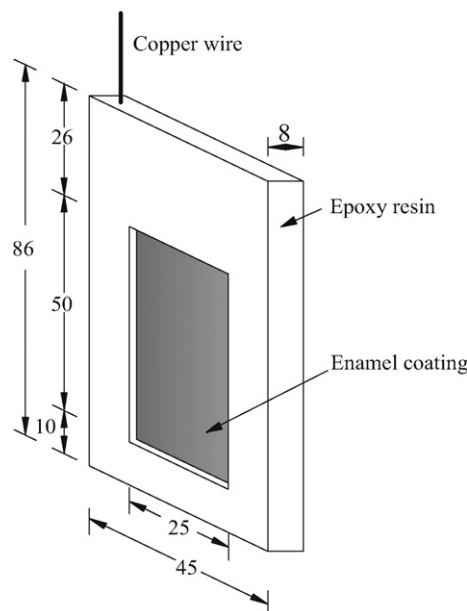

Fig. 1. Schematic view of the steel plate sample used in the electrochemical experiments (unit: mm).

borosilicate glass frit by weight, and then following the same procedure to produce a slurry. Calcium silicate was directly taken from Portland cement as specified in ASTM C150-07 [16]. The DE coating consists of two layers: an inner PE layer and an outer ME layer.

For PE and ME coatings, the steel plate samples were dipped into their corresponding slurries, heated at 150 °C for 2 min to drive off moisture, then fired at 810 °C for 10 min, and finally cooled to room temperature. For the DE coating, the steel plates were first dipped into the PE slurry, heated at 150 °C for 2 min to drive off moisture, and fired at 810 °C for 10 min. They were then dipped into the ME slurry, heated at 150 °C for 2 min again to drive off moisture, and finally fired at 810 °C for 10 min. The firing treatment melted the glass frit and chemically bonded the enamel to the steel substrate.

For each enamel-coated steel plate, schematically illustrated in Fig. 1, one corner was ground off to expose the steel for a soldering connection with a copper wire for electrochemical measurements. All four side edges and the back face of the steel plate were covered with EpoxyMount (ALLIED). Therefore, only the center portion on the front face of all steel plates, approximately 12.5 cm^2, was potentially exposed to the test solution. For comparison, uncoated steel plates were also prepared and characterized. Three steel plate samples were prepared and tested in each condition to ensure the repeatability of the test data.

2.2. Characterization of enamel coating

The morphologies of enamel-coated samples were investigated by SEM (Hitachi S4700). A small piece of an enamel-coated steel plate, 20 mm × 5 mm in size, was sectioned with a diamond blade, and directly used for the surface SEM imaging. Another small piece of the sample was cut across the cross-section and cold-mounted with EpoxyMount. The cross-section was then ground with silicon carbide papers to 1200 grit. The ground sample was rinsed with deionized water, cleansed with acetone, and finally dried in an oven preset at 60 °C prior to SEM imaging. The phase composition was

Table 1
Chemical composition of alkali borosilicate glass frits.

Composition	SiO$_2$	B$_2$O$_3$	Na$_2$O	K$_2$O	CaO	CaF$_2$	Al$_2$O$_3$	ZrO$_2$	MnO$_2$	NiO	CoO	Total
Amount (wt.%)	44.0	19.3	15.8	2.8	0.0	4.7	4.6	5.3	1.5	1.0	0.9	100