



Hybrid sol–gel coatings for corrosion protection of hot-dip galvanized steel in alkaline medium



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ARTICLE INFO

Article history:

Received 25 October 2014

Accepted in revised form 14 January 2015

Available online 23 January 2015

Keywords:

Galvanized steel

Sol–gel

Organic–inorganic hybrid

Corrosion

Coatings

ABSTRACT

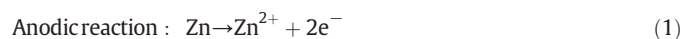
Two distinct organic–inorganic hybrid (OIH) matrices were synthesised using the sol–gel method and deposited on hot-dip galvanized steel (HDGS) by dip-coating. These OIHs, called ureasilicates, U(X), and amino-alcohol-silicates, A(X), were obtained using a functionalised siloxane and five oligopolymers with different molecular weights (MWs). Besides pure OIH coatings, HDGS samples were coated with OIHs doped with Cr³⁺, which was tested as a corrosion inhibitor. The OIH coatings deposited by one and three dip steps were assessed by electrochemical studies (polarisation resistance and macrocell current) in mortar in order to compare their performance. The SEM results were consistent with the data obtained by GD-OES and with the electrochemical analyses. The results indicated that the HDGS samples coated with OIHs show enhanced corrosion resistance in highly alkaline environment when compared to uncoated samples. The coatings involving the use of OIH matrices based on U(X) gels show superior corrosion behaviour when compared to the matrices based on A(X). The lowest and the highest corrosion rates were found for HDGS samples coated by one dip step of U(X) and for three dip steps of A(X) doped with Cr³⁺, using oligopolymers with MWs of 400 and 900, respectively.

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1. Introduction

One of the major causes of structural degradation is the corrosion of steel in concrete, which requires expensive restoration. To minimise the risk of reinforced concrete (RC) corrosion, the cover of the metallic reinforcement sections must be of an adequate thickness and possess a high concrete quality, with a proper mixing ratio, good compaction and curing. To increase the service life of RC structures, the use of hot-dip galvanized steel (HDGS) has been recognised as an effective measure [1,2]. The main cause for the widespread use of galvanized steel is the dual nature coating. The layer formed by the galvanizing process offers a resistant and metallurgically bonded zinc coating that covers the steel surface, protecting it from corrosive action. Moreover, the zinc's sacrificial (cathodic) action protects the steel even when damage occurs in the concrete [1,2] and the corrosion products of zinc occupy a smaller volume than those produced from iron. Yeomans [2] confirmed that zinc corrosion products are powdery, non-adherent and capable of migrating from the surface of the galvanized reinforcement into the concrete matrix, reducing the likelihood of zinc corrosion-induced spalling of the concrete [1,2]. Galvanized reinforced steel can withstand exposure to chloride ion concentrations several times higher (at least 4 to 5 times) than the chloride level that causes corrosion in steel

reinforcement. Additionally, while steel in concrete typically depassivates below a pH of 11.5, galvanized reinforcement can remain passivated at a lower pH, thereby offering substantial protection against the effects of concrete carbonation [1]. The combination of these two factors, carbonation resistance and chloride tolerance, are commonly accepted as the basis for superior performance of galvanized reinforcement compared to steel reinforcement [2]. However, when HDGS is in contact with highly alkaline environments, such as fresh concrete (pH ≥ 12.5), the zinc is oxidised and the cathodic reaction leading to hydrogen evolution takes place on the galvanized surface [3–10].



The global process can be described as:



This initial corrosion process, extensively studied by several authors [11–13], may lead to zinc consumption until either a passivation layer is formed (which passivates the steel reinforcement) or until all the zinc layer is consumed [11]. Increasing the chromate content of the cement, adding water-soluble chromates and using chromate conversion layers are procedures that have been widely employed to minimise this corrosion process. However, chromate and similar hexavalent chromium

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compounds are carcinogenic and their use is heavily regulated by most environmental legislation. As such, research is being performed to replace chromates with more ecological compounds.

Organic–inorganic hybrid (OIH) sol–gel films are considered potential alternatives to replace Cr^{6+} based pre-treatments. By using the sol–gel method, OIH materials are produced with good homogeneity at low temperatures, thus saving energy and reducing air pollution [14]. Moreover, these materials can be easily deposited on metallic substrates by spraying, dipping and spinning techniques. This improves the substrate's resistance to oxidation and corrosion. They may also modify their surface properties [15].

The OIHs represent a new class of materials characterised by a biphasic morphology consisting of distinct organic and inorganic domains at a nanometric level [16–20]. The inorganic and organic components may be partially or totally linked through covalent or Lewis acid–base bonds. OIHs based on siloxanes can be easily obtained from organo-substituted silicic acid esters ($\text{R}'_n\text{Si}(\text{OR})_{4-n}$) [21]. The conversion of the precursors into OIH materials proceeds via formation of siloxane (Si–O–Si) bonds. Additionally, sol–gel technology allows for the synthesis of functionalised materials by incorporating corrosion inhibitors within the OIH network. The presence of these types of species leads to the production of coatings with dual protection (physical barrier and corrosion inhibition), which can minimise/delay the corrosion process of the metallic substrates.

Numerous studies have been published [22–27] showing that the mechanical, thermal and electrical properties of the OIH materials based on siloxanes are attractive. As such, these materials can be used as pre-treatments to improve the corrosion resistance of several metals and alloys. In the last few decades, the synthesis, characterisation and application of OIH materials have developed rapidly. The major driving forces behind the intense activities in this area are the new and different properties of nanocomposites, which traditional macroscale composites and conventional materials do not have. By combining inorganic and organic components, using the appropriate processing methods, several types of primary bonding and secondary bonding within the matrix network can be developed. This can lead to the synthesis of OIH materials with proper technical features for electrical, optical and enhanced properties of adhesion and corrosion protection [23,28].

In this study, two distinct OIH matrices were synthesised using the sol–gel process. These OIHs, generally called ureasilicates [29] U(X) and amino-alcohol-silicates [30] A(X) were obtained using two different functionalised siloxanes: 3-Isocyanatopropyltriethoxysilane and 3-Glycidoxypropyltrimethoxysilane. Each functionalised siloxane was made to react with five oligopolymers (referred to as Jeffamine) with different molecular weights (MWs): 230, 400, 600, 900 and 2000. For coating deposition, a dip-coating method was used, since it has been considered an optimal method to prepare thin layers from chemical solutions [31] such as a sol obtained by the reaction of sol-gel precursors. It is a low-cost, waste-free method, which is easily reproduced on a large scale, creating coatings of controlled thickness [31]. In order to determine the optimal coating thickness when taking into account both corrosion behaviour and economic aspects, the

HDGS was covered with either one or three layers of the OIH coatings doped and undoped with Cr^{3+} as a corrosion inhibitor. This allowed for assessment of the anticorrosion behaviour of coatings dependent on the thickness. Cr^{3+} was chosen as a corrosion inhibitor since it is much less toxic than Cr^{6+} and some studies have shown that the performance (adhesion and corrosion protection) of Cr^{3+} based pre-treatments can be similar to the results obtained with industrial Cr^{6+} pre-treatments [32].

The OIH coatings based on siloxanes, obtained by sol–gel process, were assessed as possible eco-friendly alternatives to replace the use of Cr^{6+} based pre-treatments. Developed coatings aim to mitigate the reactions that occur in the first instances of contact of HDGS with fresh concrete. The behaviour of the HDGS samples coated with the different OIHs, U(X) and A(X), were evaluated when in contact with cementitious media for a period of 137 days. The barrier efficiency of pure OIH U(X) and A(X) coatings with similar Cr^{3+} doped gels were compared by using electrochemical techniques, namely macrocell current density and polarisation resistance. Scanning Electronic Microscopy/Energy Dispersive Spectrometry analyses of the coatings were performed before and after exposure to the mortar. The chemical composition depth profiling of the OIH coatings applied on HDGS was determined by Glow Discharge Optical Emission Spectroscopy.

2. Experimental

2.1. Reagents

Five di-amino functionalised polyethers (hereafter referred to generically as Jeffamine) with different molecular weights (MWs) provided by Fluka were used. All the precursor reagents used, namely: Jeffamine® with different MWs (Fluka), 3-isocyanate propyltriethoxysilane ($\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$, 95%, Aldrich) and 3-glycidoxypropyltrimethoxysilane ($\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$, 97%, Aldrich), were stored protected from light and used as supplied. The specifications of the gel precursors used are shown in Table 1. Absolute ethanol (EtOH, absolute 98%, Riedel-de-Haën), citric acid monohydrate (Merck) and chromium (III) nitrate nonahydrate (Aldrich) were also used as received. Ultra-pure water (0.055–0.060 $\mu\text{S}/\text{cm}$) obtained from a PURELAB Ultra System (Elga) was used.

2.2. Synthesis procedure of OIH sol–gel materials

Two different types of precursors were used for the production of coatings on HDGS samples. These were ICPTES and GPTMS, hereafter referred to as Precursors. Each was combined with Jeffamine® respectively forming ureasilicate and amino-alcohol-silicate hybrids. Jeffamine® was available with five different MWs, which when combined with the Precursors formed five ureasilicate and five amino-alcohol-silicate matrices. These were named U(X) and A(X) according to the MW of Jeffamine. As well as using different MWs, two different sets of materials were prepared, creating matrices that were either doped with Cr^{3+} ions or where no Cr^{3+} ions were present. This led to each matrix type having 10 sets of samples each. Each set of samples was prepared from a single

Table 1
Structural and physical details of reagents used in OIH synthesised samples.

Chemical name Molecular formula	Abbreviation	M (g mol^{-1})	Purity grade (%)	Company
3-Isocyanatopropyltriethoxysilane $\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$	ICPTES	247.37	95%	Aldrich
3-Glycidoxypropyltrimethoxysilane $\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$	GPTMS	236.34	97%	Aldrich
O,O'-bis(2-aminopropyl)-Poly propyleneglycol 130	Jeffamine D-230®	230 ^{a)}	–	Fluka
O,O'-bis(2-aminopropyl) Poly propyleneglycol 300	Jeffamine D-400®	400 ^{a)}	–	Fluka
Poly(propyleneglycol)-block-poly(ethyleneglycol)-block-poly(propyleneglycol)-bis-(2-amino propylether)-600	Jeffamine ED-600®	600 ^{a)}	–	Fluka
Poly(propyleneglycol)-block-poly(ethyleneglycol)-block-poly(propyleneglycol)-bis-(2-aminopropylether)-900	Jeffamine ED-900®	900 ^{a)}	–	Fluka
Poly(propyleneglycol)-block-poly(ethyleneglycol)-block-poly(propyleneglycol)-bis-(2-aminopropylether)-2000	Jeffamine ED-2000®	2000 ^{a)}	–	Fluka

^{a)} Molecular weight approximate value.

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