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Hot-dip galvanized steel dip-coated with ureasilicate hybrid in simulated concrete pore solution: Assessment of coating morphology and corrosion protection efficiency

Rita B. Figueira[a,b,*], Carlos J.R. Silva[b], Elsa V. Pereira[a]

[a] LNEC, Laboratório Nacional de Engenharia Civil, Av. Brasil 101, 1700-066 Lisboa, Portugal
[b] Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

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ABSTRACT

The barrier effect and the performance of an organic–inorganic hybrid (OIH) sol–gel coating are highly dependent on the coating deposition method as well as processing conditions. In this work, studies on the influence of experimental parameters using the dip coating method were performed. Factors such as residence time (Rt), a curing step between each dip step and the number of layers of sol–gel OIH films deposited on HDGS to prevent corrosion in highly alkaline environments were studied. These OIH coatings were obtained using a functionalized siloxane, 3-isociantepropyltriethoxysilane that reacted with a diamino-functionalized oligopolymer (Jeffamine® D-230). The barrier efficiency of OIH coatings in simulated concrete pore solutions (SCPS) was assessed in the first moments of contact, by electrochemical impedance spectroscopy and potentiodynamic methods. The durability and stability of the OIH coatings in SCPS was monitored during eight days by macrocell current density. The morphological characterization of the surface was performed by scanning electronic microscopy before and after exposure to SCPS. Glow discharge optical emission spectroscopy was used to obtain quantitative composition profiles to investigate the thickness of the OIH coatings as a function of the number of layers deposited and the influence of the Rt in the coating thickness.

1. Introduction

The use of hot dip galvanized steel (HDGS) in reinforced concrete (RC) structures to improve corrosion resistance of steel has been widely studied [1,2]. The galvanized coating acts as a physical barrier that hinders the contact of aggressive agents with the steel substrate. Additionally, the zinc layer acts as a sacrificial anode, protecting the steel against corrosion. Nowadays, this method has been recognized as an effective protection measure to increase service life of RC structures [3–10]. Nevertheless, HDGS shows a temporary instability in the first instants of contact with highly alkaline environments such as fresh concrete, which typically has a pH between 12.5 and 13.5. In this pH range the Zn layer is oxidized and hydrogen evolution takes place on the galvanized surface [2,8,11]. Common procedures such as the application of chromate based chemical conversion coatings (CCCs) on HDGS or increasing the chromate content of the cement have been implemented to minimize the initial zinc reaction, thus improving the corrosion resistance of the HDGS. However, due to the toxicity of Cr(VI) ions, actual commercialized Portland cements have limited the content of Cr(VI) in their composition and the use of CCCs are currently being avoided. Severe restrictions have been imposed due to health and environmental concerns on the use of hazardous compounds, e.g. VOCs (volatile organic compounds), HAPs (hazardous air pollutants) and Cr(VI). The lack of materials capable of accomplishing all technological needs for new applications, have led to an intense research for new ones in the last few decades. The development of low-VOC, low-HAP and non-toxic surface treatments, capable of providing effective corrosion protection, is necessary and the sol–gel method has been shown to be an adequate alternative to produce environmentally friendly surface treatments [12–16].

In the past three decades, organic-inorganic hybrid (OIH) materials produced by sol–gel methods have shown to be of high technological importance. Many material scientists and chemists, such as Schmidt and Wilkes, started to synthesize OIH materials by sol–gel process and published a series of pioneering research articles [17–19]. OIH materials can combine advantages of the coexistence of organic and inorganic components within the gel matrix. The organic component contributes to gel flexibility,

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* Corresponding author at: LNEC, Laboratório Nacional de Engenharia Civil, Av. Brasil 101, 1700-066 Lisboa, Portugal.
E-mail addresses: rmfigueira@lnec.pt, rita@figueira.pt (R.B. Figueira).

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lightness, resistance to impact and processability, whilst the inorganic network gives high mechanical strength, excellent chemical resistance and thermal stability. Despite the advantages of combining different properties, constraints are present. One of the major limitations of sol–gel processing for coating metals is the difficulty of coating complex shapes with a minimal thickness and assuring a uniform, crack-free film distribution on the substrate. Additionally, the gel has to be submitted to thermal treatment during the curing steps, which may also influence the final material [20]. Latella et al. in 2003 synthesized and assessed the mechanical properties and adhesion behaviour of coatings based on organically modified silanes. The authors observed a strong correlation between the film structure and its mechanical response indicating that the mechanical properties of the coatings are influenced by the organic substituent. Additionally, the authors also observed that the presence of an oxide layer, thermally grown on the substrate material prior to deposition, plays an important role on the film/substrate adhesion behaviour [21]. Therefore, the barrier effect and the performance of an OIH sol–gel coating are dependent on processing conditions and coating deposition method.

Following the promising electrochemical results obtained for OIH coatings prepared by the sol–gel method to prevent the corrosion of HDGS in concrete [22], it became necessary to study the influence of factors on coating performance in the short term. In this work, the impact of three factors, on OIH coating performance, was studied namely residence time (Rt), cures between each deposition and the presence of more than one layer of coating. In order to assess the impact on the barrier properties of OIH coatings, as well to get coatings with a uniform distribution, an OIH sol–gel matrix was synthesized. This OIH, hereafter called U(230), was obtained using a functionalized siloxane 3-isociantepropyltriethoxysilane that reacted with an oligopolymer [22] (Jeffamine® D-230). HDGS dip-coated with an OIH sol–gel placed in a simulated concrete pore solution (SCPS) was assessed by electrochemical techniques. Coating methodology was studied in order to determine the influence of the Rt and the implementation of curing processes between each deposition when taking into account both corrosion behaviour and economic aspects. Two approaches were considered. In the first one, the assessment of U(230) was conducted using electrochemical impedance spectroscopy and potentiodynamic methods in the first instants of contact in SCPS. In the second approach, the macrocell current density was used to monitor the coating durability and stability during eight days of contact with SCPS. The surface morphology of HDGS coated samples before and after exposure to the SCPS was studied by scanning electronic microscopy/energy dispersive spectrometry analysis. Furthermore, glow discharge optical emission spectroscopy (GD-OES) was used to obtain quantitative composition profiles to investigate the OIH coatings thickness as a function of the number of deposited layers and the influence of the Rt on the coating thickness.

2. Experimental

2.1. Samples preparation

2.1.1. Reagents

The experimental steps involved in the synthesis of ureasilicate matrices, hereafter referred to as U(230), to produce coated HDGS samples are described schematically in Fig. 1. The code attributed to the coating is due to the type of bond established between the precursors (urea bond) and to the molecular weight of Jeffamine used (≈230). OIH sol–gel coating was prepared by a reaction between isocyanate groups of the derived siloxane (ICPTES) with one di-amino functionalized polyether (Jeffamine® D-230). All the reagents used (Jeffamine and 3-isocyanate propyltriethoxysilane) were stored protected from light and used as supplied. Ethanol (EtOH, absolute 98%, Riedel-de-Haën), citric acid monohydrate (Merck) were also used as received. Ultra-pure water (0.055–0.060 μS/cm) obtained from a Purelab Ultra System (Elga) was used.

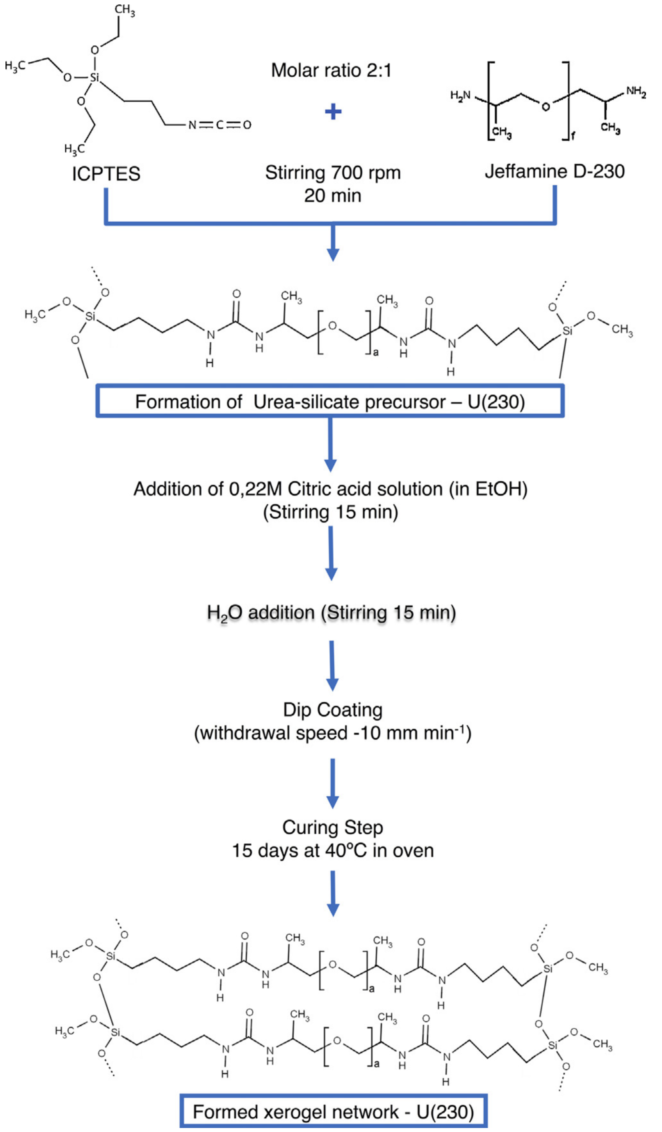

Fig. 1. Schematic representation of the main steps involved in the production of U(230) coatings.

2.1.2. Coating deposition

Coatings were applied on HDGS metal plates (5.0 cm × 1.0 cm × 0.1 cm) with an average Zn thickness of 16 μm on both sides cut from commercially available sheets. The curing of the coated HDGS samples was performed in an incubator-compressor (ICP-400, Memmert) kept at 40 °C for 15 days. HDGS coated samples were prepared by dipping HDGS metal plates on the prepared mixture (sol) at a withdrawal speed of 10 mm min^{-1} without residence time (Rt = 0 s) and with a residence time of 100 s (Rt = 100 s) using a dip coater (Nima, model DC Small). Coated samples were prepared with one, two and three dipping steps using always the same conditions for curing (15 days at 40 °C between each dipping step). Samples coated with three consecutive dip steps, without residence time and only one curing step, were also prepared.