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SMART COATING FOR DETECTION OF EARLY-STAGE CORROSION OF STEEL

A. Sushkova [1]*, M. Wilhelm [1], R. Montes [1]; C. Neves [1], M. C. Quevedo [1], A. C. Bastos [1], M. G. S. Ferreira [1], J. Tedim [1]

[1] CICECO – Aveiro Institute of Materials, DEMaC, Building N. 9, University of Aveiro, 3810-193 Aveiro, Portugal, alesia@ua.pt
* Corresponding author

ABSTRACT

The work describes the investigation of LDH-based nanoadditives for early-stage corrosion detection of steel, and subsequent development of a multi-layer functional protection coating. A systematic study on the level of degradation and the detected colorimetric signal was performed using electrochemical characterisation. The protection properties and detection functionality were also studied in conditions relevant to exploitation of metallic structures.

Keywords: Corrosion, Coating, Nanoadditives, Detection, LDH nanomaterials

1.   INTRODUCTION

The detection of corrosion at an early stage can contribute for reduction of maintenance costs and extend the service life of metallic structures. In this context, the development of protective coatings with "smart" functionality recently attracted considerable attention of researchers [1]. The published works available so far mainly describe the use of pH indicators and dyes [1,2] as 'sensing' species. In our work we showed that the intercalation of hexacyanoferrate, able to react with Fe^{2+} cations forming a blue precipitate, renders additional properties with respect to the free hexacyanoferrate [3]. The present work, developed in the frame of two international projects [4,5], aims at the study of LDH intercalated with hexacyanoferrate in organic-based coatings for detection of corrosion in carbon steel via colorimetric response of released Fe^{2+}.

2.   DESCRIPTION

Investigation of active nanomaterials

LDH intercalated with hexacyanoferrate ions were investigated as 'sensing' nanomaterials for detection of early-stage corrosion on steel. The anions were intercalated in Mg-Al and Zn-Al LDHs via simple ion-exchange procedure. Structural characterization via X-ray diffraction (XRD) confirmed replacement of the precursor nitrate anions by hexacyanoferrate. Fourier-transform infrared spectroscopy (FTIR) supported XRD data, additionally revealing presence of two forms of hexacyanoferrate anion (both are able to react with Fe cations giving a blue precipitate). The morphology of the nanomaterials was studied by scanning (SEM) and transmission (TEM) electron microscopies. The particles showed plate-like shape with average diameter around 500 nm for Zn-Al LDHs and 150 nm for Mg-Al LDHs (Fig.1a). The loading content of the active ions (17.6 wt% in Zn-Al and 17.2 wt% in Mg–Al LDH), estimated by UV-Vis spectroscopy and supported by gravimetric analysis, agreed with theoretical calculations from chemical composition taking in account FTIR data. The release of the active agent from the nanocarriers was studied in various aqueous media. The LDHs provided controlled release of the active ions under relevant corrosion conditions. The detection functionality of the nanomaterials was confirmed in model solutions in the presence of Fe^{2+} cations and verified by drop tests on

carbon steel plates following the visual changes as a function of time. Hexacyanoferrate-loaded Mg-Al LDH induced appearance of blue coloration on steel surface with the progress of corrosion process, while Zn-AL LDH showed more fade grey-violet colour, which can be explained by competitive reaction of the active anion with the Zn^{2+} from the LDH, forming $Zn_3[Fe(CN)_6]_2$. Potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS) were used to investigate the effect of the developed nanomaterials and free hexacyanoferrate ions on the corrosion reaction. Intercalation of the 'sensing' ion in the LDHs minimized the negative effect of hexacyanoferrate on steel stability in comparison to the salt directly dispersed in solution (Fig. 1b). After anodic polarization of steel plates, with the presence of $Mg-Al/[Fe(CN)_6]^{3-}$ LDH an intense blue colour was observed, while with Zn-Al LDH, a brown precipitate associated with $Zn_3[Fe(CN)_6]_2$ disguise the corrosion detection. Overall, results showed hexacyanoferrate-intercalated Mg-Al LDH as a perspective material to be used for steel corrosion detection. Details on the synthesis and characterization of the nanoadditives and their environmental behaviour could be found in our recently published papers [3,6].

Development of 'sensing' layer

The above selected nanomaterial was incorporated into polymeric coating. Commercially available water-soluble acrylic urethane emulsion, characterized by environmental friendliness and high performance of the resulting coatings, was chosen for preparation of formulations, which were investigated considering different parameters to obtain well-dispersed, stable solution. Rheological studies of the developed formulation did not show any significant influence of the nanoadditive on viscosity and viscoelastic behaviour in the range of studied concentrations (0-10 wt%). Cured coating, applied on carbon steel plates, had thickness around 15 µm and showed excellent adhesion to the substrate. Structural characterisation via FTIR confirmed presence of the hexacyanoferrate ions. The morphology was observed by optical microscopy and SEM, showing homogeneous smooth surface of the coatings. The hardness was evaluated by Vickers method and showed positive effect of the nanoadditive to the coating mechanical properties. Corrosion detection functionality of the 'sensing' layer was investigated by visual observation of steel plates immersed in 0.6 M NaCl. A systematic study on the level of degradation and the detected colorimetric signal was performed using EIS, monitoring the evolution of corrosion of the coated plates without and with 'sensing' nanoadditive (10 wt%). It was found that the additive decreased barrier properties of the polyurethane coating. Nevertheless, the early-stage corrosion functionality was successfully confirmed: a blue colorimetric signal was detected on the plates coated with the 'sensing' layer, after 17 h of immersion, correlated with EIS results showing a decrease in the impedance magnitude, while steel degradation was still not visible for a naked eye. Hexacyanoferrate salt incorporated directly to the coating didn't show corrosion detection functionality.

Characterization of multi-layer protection system

To improve barrier properties of the coating for field tests, a system with an additional protective layer was developed. After testing of several commercial coatings, a transparent epoxy varnish was selected as the most promising system with a high barrier property and a good adhesion to the developed 'sensing' layer. Corrosion protection performance and the detection functionally of the developed multi-layer coating (dry thickness ~ 70 µm) was investigated using EIS (Fig. 1d, c). The colorimetric signal was detected after 1 week of immersion, although the initiation of corrosion was not yet detected electrochemically (coatings maintained a capacitive behaviour with high impedance values), the observation by optical microscopy confirmed the presence of the micro spots of corrosion invisible to the naked eye. Finally, the functionality of the developed coating was validated by salt spray test (ISO 9227) and in field tests in the harbour of Malta.
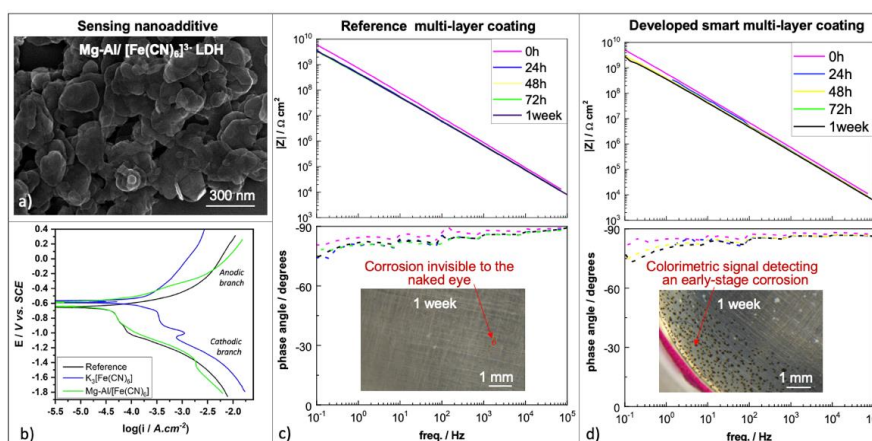
Fig. 1 – SEM observation of the nanoadditive (a); Potentiodynamic polarization of uncoated steel immersed in solutions with and without nanoadditives (b); Monitoring of corrosion (EIS) of steel with reference multi-layer coating (c) and with developed smart multi-layer coating (d)

3. CONCLUSIONS

LDHs intercalated with hexacyanoferrate ions were investigated as 'sensing' nanomaterials for colorimetric detection of early-stage corrosion of steel. A 'sensing' coating was developed by incorporation of the selected nanoadditive in commercial polymeric coating. Study on the level of degradation of coated steel and the detected colorimetric signal confirmed the detection functionally. The decrease in the barrier properties induced by the additive was overcome by elaboration of multi-layer system with an additional protective layer. The protection properties and detection functionality were confirmed in tests relevant to exploitation conditions.

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